have also been done on the simple assumption $\beta_1 = \beta_2 = \ldots = \beta$ (Gevers, 1953*c*).

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References

GEVERS, R. (1952). *Acta Cryst.* **5**, 518.
GEVERS, R. (1953*a*). *Natuurwet. Tijdschr.* **35**, 25.
GEVERS, R. (1953*b*). *C. R. Acad. Sci., Paris*, **237**, 463.
GEVERS, R. (1953*c*). *Natuurwet. Tijdschr.* **35**, 76.
GEVERS, R. (1954*a*). *Acta Cryst.* **7**, 337.
GEVERS, R. (1954*b*). *Acta Cryst.* **7**, 492.
HENDRICKS, S. B. & TELLER, E. (1942). *J. Chem. Phys.* **10**, 147.
JAGODZINSKI, H. (1949). *Acta Cryst.* **2**, 208.
KAKINOKI, J. & KOMURA, Y. (1952). *J. Inst. Polyt. Osaka*, **32**, 35.
PATERSON, M. C. (1952). *J. Appl. Phys.* **23**, 805.
WILSON, A. J. C. (1942). *Proc. Roy. Soc.* A, **180**, 277.

Acta Cryst. (1954). **7**, 744

Some Calculations of Atomic Form Factors[*]

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X-ray atomic form factors for carbon, nitrogen and oxygen have been computed from Hartree–Fock radial wave functions, and compared with the values previously obtained by James & Brindley, and McWeeny.

The X-ray form factor for coherent radiation is given by

$$f(\mathbf{s}) = \int \varrho(\mathbf{r}) \exp\,[i\mathbf{s}\cdot\mathbf{r}]dv_{\mathbf{r}}\,, \tag{1}$$

where $\varrho(\mathbf{r})$ is the electronic density of the isolated atom and $s = 4\pi\lambda^{-1}\sin\theta$ is the magnitude of the vector **s** in reciprocal space. If the electronic density is spherically symmetric (1) reduces to

$$f(s) = \int_0^\infty U(r)\frac{\sin sr}{sr}\,dr\,, \tag{2}$$

where $U(r)$ is the total radial charge density. James & Brindley (1931) (J & B) evaluated (2) for a number of atoms, using the Hartree values of $U(r)$ (self-consistent field, without exchange). For other atoms, for which the Hartree field was not available, they resorted to an interpolation. These calculations have been extended to higher values of s by Viervoll & Ögrim (1949).

If the electronic density is aspherical, it is convenient to decompose (1) into the separate electronic contributions. Filled or half-filled sub-shells are spherically symmetric and can be treated as in (2), but odd p electrons, d electrons, etc. require special handling: For a p electron defined by

$$\varrho_p = \left|\sqrt{\left(\frac{3}{4\pi}\right)}\frac{P(r)}{r}\cos\theta\right|^2 \tag{3}$$

(where θ is the polar angle relative to the axis of the orbital and $\int_0^\infty P^2(r)dr = 1$), McWeeny (1951) (McW) has shown that the transform of (3) by (1) gives

$$f_p = f_p^{\parallel}\cos^2\Theta + f_p^{\perp}\sin^2\Theta\,, \tag{4}$$

where Θ is the angle between **s** and the axis of the orbital and

$$f_p^{\parallel} = \frac{3}{4\pi}\iiint P^2(r)\cos^2\theta\sin\theta\exp\,[isr\cos\theta]\,dr\,d\theta\,d\varphi\,, \tag{5}$$

$$f_p^{\perp} = \frac{3}{4\pi}\iiint P^2(r)\sin^3\theta\exp\,[isr\cos\theta]\sin^2\varphi\,dr\,d\theta\,d\varphi\,. \tag{6}$$

McWeeny also obtains a 'mean contribution' by averaging (4) over all directions:

$$\bar{f_p} = \tfrac{1}{3}f_p^{\parallel} + \tfrac{2}{3}f_p^{\perp}\,. \tag{7}$$

Similar quantities $f^{\parallel}, f^{\perp}$ and $\bar{f}$ are defined for the whole atom by addition of the respective contributions of the individual electrons. McWeeny has applied these results to atoms from hydrogen to neon, using the approximate variational wave functions obtained in analytic form for the ground states by Duncanson & Coulson (1944).

Self-consistent fields, many of which even include exchange (the Hartree–Fock calculation), are now

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available for atoms for which there was no information when James & Brindley made their calculations. Thus it is now possible to compute f for most of the lighter atoms directly, without recourse to interpolations. It is of interest to do this for at least a few important atoms for comparison with the J & B and McW values.

We have computed $\bar{f}$ for C, N, and O from the ground-state Hartree–Fock radial wave functions $P(r)$ (Jucys, 1939; Hartree & Hartree, 1948; Hartree, Hartree & Swirles, 1939) without recourse to $f^{\parallel}$ and $f^{\perp}$. This is possible even for aspherical atoms because $f(\mathbf{s})$ is a linear function of $\varrho(\mathbf{r})$, so that averaging $f(\mathbf{s})$ over all orientations is equivalent to first averaging $\varrho(\mathbf{r})$ over all orientations and eventually applying (2)[*]:

$$\bar{f}(s) = \int_0^\infty \sum_{\text{all electrons}} P^2(r)\,\frac{\sin sr}{sr}\,dr\,. \tag{8}$$

This form is convenient for numerical integration by I.B.M. methods which were available to us (Shaffer, Schomaker & Pauling, 1946). The 1s, 2s, and 2p functions for each atom were transformed separately, and the interval of summation was in each case so small that the complete $\bar{f}$ values were unchanged (to within 0·002 electrons) when the interval was doubled in width. In Table 1 we give our numerical results and in Fig. 1 these results are plotted up to the copper limit, i.e. up to the maximum value of s obtainable with Cu $K\alpha$ radiation, together with the $\bar{f}$ of McWeeny and the values of James & Brindley.

Table 1. *Values of f*

$s/0{\cdot}5937$[*] (Å^{-1})	$\sin\theta/\lambda$	$f_{\text{C, valence}}$	$\bar{f}_{\text{C}}$	$\bar{f}_{\text{N}}$	$\bar{f}_{\text{O}}$
0	0·0000	6·000	6·000	7·000	8·000
1	0·0472	5·766	5·776	6·782	7·797
2	0·0945	5·181	5·212	6·269	7·322
3	0·1417	4·426	4·471	5·545	6·622
4	0·1890	3·696	3·738	4·768	5·824
5	0·2362	3·092	3·117	4·020	5·035
6	0·2835	2·634	2·638	3·428	4·320
7	0·3307	2·300	2·288	2·925	3·711
8	0·3780	2·061	2·038	2·542	3·208
10	0·4724	1·768	1·740	2·039	2·487
12	0·5669	1·597	1·577	1·761	2·051
16	0·7559	1·364	1·367	1·486	1·623
20	0·9449	1·155	1·171	1·311	1·420
24	1·1339	0·959	0·978	1·145	1·269
28	1·3228	0·783	0·801	0·988	1·126
32	1·5118	0·633	0·649	0·835	0·985

[*] $0{\cdot}5937 = \pi/10a_0$, where $a_0 = 0{\cdot}52917$ is the ratio of the atomic unit of length to the Ångström unit.

Between the copper and molybdenum limits we are in good agreement with Viervoll & Ögrim except for oxygen, where they appear to have made a slight error. In this range only the 1s electrons contribute to f, so that the good agreement which we also find with the McW curves is a measure of the reliability of the Duncanson–Coulson 1s wave functions.

In the copper range it can be seen from Fig. 1 that the J & B curves are inaccurate.[*] Such inadequacies of the J & B curves have already been cited experimentally (Brill, 1950; Bacon, 1952). Since the J & B curve for oxygen was computed directly from the Hartree wave functions without exchange, the departure from our values is a measure of the effect of exchange.[†] Exchange modifies primarily the density of the outer electrons, in this case the 2s and 2p electrons. This effect is approximately the same for C, N, and O, as can be seen from comparison of exchange and non-exchange wave functions. The increasing errors in the sequence O to C are therefore due to a failure of the J & B interpolation, in which the 2s contribution was obtained for C and N by interpolation between O and Li and the 2p contribution essentially by a guess. It is therefore not surprising that the J & B curves are unreliable in the s range where the 2s and 2p contributions are appreciable.

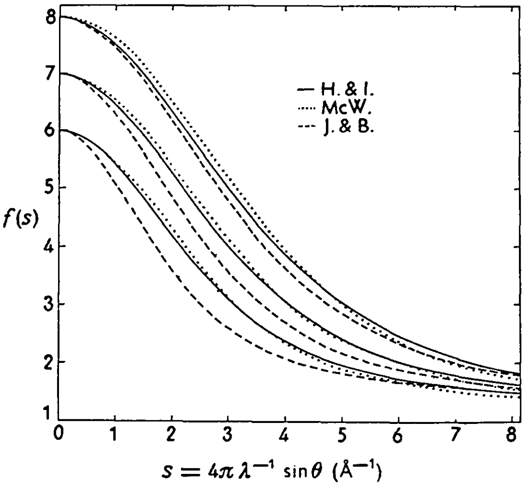

Fig. 1.

Fig. 1 also shows small differences between our curves and those of McWeeny. These differences are due to the approximate nature of the Duncanson–Coulson 2s and 2p wave functions. For C, McWeeny has shown how to calculate an approximate form factor for the valence state from ground-state wave functions. We have made a similar calculation with results as shown in Table 1. The differences which arise between $\bar{f}$ and f_{valence} are small in our work as they are in McWeeny's.[‡]

The usual procedure in structural investigations is

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[*] The J & B non-interpolated values for aspherical atoms are presumably $\bar{f}$ values calculated in this way.

[*] We note that the f values given by Pauling & Sherman (1932) are in closer agreement with our values for C, N, and O within the copper range than are the J & B values.

[†] We have recomputed $\bar{f}$ for oxygen from the $U(r)$ presumably used by J & B (Hartree & Black, 1933) and have found substantial agreement.

[‡] The McW values of $\bar{f}-f_{\text{valence}}$ are not quite smooth.

to employ isotropic form factors. Then any asymmetry in the electronic distribution, the anisotropy of thermal vibrations, and all other sundry effects are lumped together into asymmetric temperature factors. In this case, the use of $\bar{f}$ is a reasonable approximation and the $\bar{f}$ values deduced from the Hartree–Fock radial distributions are surely superior to McWeeny's. However, the differences do not exceed 0·2 electrons and are hardly significant in most crystal-structure work. If, on the other hand, the comparatively large effects of atomic asymmetry are to be taken into account in an elaborate structure refinement, we would write:

$$f^{\parallel} = \bar{f} + \tfrac{2}{3}\Delta\ , \tag{9}$$

$$f^{\perp} = \bar{f} - \tfrac{1}{3}\Delta\ , \tag{10}$$

where $\Delta = f^{\parallel} - f^{\perp}$ can be computed from McWeeny's values. This is a sufficient approximation, since Δ is small relative to the f value for the whole atom.

In agreement with McWeeny's work, the present work has shown that the interpolation technique of James & Brindley is unreliable. It is not unlikely that their interpolated values for other atoms as well are faulty, so that new calculations are desirable, based when possible on Hartree–Fock radial wave functions. If non-spherical effects are considered, it should be noted that, whereas (8) holds for any orbital, (4) and (7) apply only to p electrons. Corresponding expressions for d electrons, for example, can be worked out in a similar way, provided that the shape of orbital has been previously deduced from an estimate of the bonds in which the atom is engaged.

We wish to thank Prof. Verner Schomaker for suggesting this problem and for his continued interest in the work.

References

Bacon, G. E. (1952). *Acta Cryst.* **5**, 492.

Brill, R. (1950). *Acta Cryst.* **3**, 333.

Duncanson, W. E. & Coulson, C. A. (1944). *Proc. Roy. Soc. Edinb.* A, **62**, 37.

Hartree, D. R. & Black, M. M. (1933). *Proc. Roy. Soc.* A, **139**, 311.

Hartree, D. R. & Hartree, W. (1948). *Proc. Roy. Soc.* A, **193**, 299.

Hartree, D. R., Hartree, W. & Swirles, B. (1939). *Philos. Trans.* A, **238**, 229.

James, R. W. & Brindley, G. W. (1931). *Phil. Mag.* (7), **12**, 81.

Jucys, A. (1939). *Proc. Roy. Soc.* A, **173**, 59.

McWeeny, R. (1951). *Acta Cryst.* **4**, 513.

Pauling, L. & Sherman, J. (1932). *Z. Kristallogr.* **81**, 1.

Shaffer, P. A., Schomaker, V. & Pauling, L. (1946). *J. Chem. Phys.* **14**, 659.

Viervoll, H. & Ögrim, O. (1949). *Acta Cryst.* **2**, 277.

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On the Visual Estimation of X-ray Reflexion Intensities from Upper-Level Weissenberg Photographs

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Formulae are derived which govern the variations in reflexion spot area observed on upper-level Weissenberg photographs. It is shown that they can be used in a routine correction of intensities visually estimated from such photographs.

1. Introduction

The increasing use of three-dimensional methods in X-ray crystal structure analysis has stimulated interest in the measurement of reflected X-ray intensities, and it has been established that the visual estimation of intensities from photographic records is sufficiently accurate for many purposes. There are objections, however, to the general use of this simple and convenient method since the measurements do not give directly the required integrated intensities but rather the mean or peak intensities. The use of visually estimated intensities depends, therefore, on the absence of variations in area or density distribution in the reflexion spots or on the use of proper corrections for variations which do occur. Unfortunately, quite large variations in reflexion spot area do occur in upper-level Weissenberg photographs, those on which general X-ray reflexions from single crystals are recorded most conveniently. In these photographs corresponding reflexions are extended on one side of the film and contracted on the other, the degree of distortion varying from reflexion to reflexion in a way which depends on the experimental arrangement. The effect and its general explanation are well known (Buerger, 1942); many workers, for example,