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New Calculations of Atomic Scattering Factors

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Scattering factors for twenty-three atoms have been calculated from Hartree and Hartree-Fock radial wave functions. The results are compared with James & Brindley's values and with those recently obtained by other authors.

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Since the calculations of scattering factors by James & Brindley (1931) many new data on electron distributions in atoms, computed by the self-consistent field method, have become available. The work of James & Brindley (quoted as JB in the following) was some years ago extended by Viervoll & Ögrim (1949), who included electron distribution-data on Na⁺, K⁺, and Cu⁺ and extended the $\sin \theta/\lambda$ range. Viervoll & Ögrim were primarily interested in the f values at higher $\sin \theta/\lambda$; they therefore applied only wave functions calculated without exchange, as the corrections for exchange would presumably have only small effects on the scattering factors in this region.

Recently, new values for scattering factors have been calculated by: (a) McWeeny (1951) (McW), for all atoms lighter than Na, from wave functions given by Duncanson and Coulson; (b) Hoerni & Ibers (1954) (HI) for C, N and O from newer available self-consistent field data with exchange; (c) Henry (1954), for Au⁺ and Hg⁺⁺, from self-consistent field data without exchange.

It is evident from comparison of the results of HI and JB that the taking into account of exchange gives effects which make the corresponding effects on calculated structure factors outside the error limit for

structure determination by accurate modern methods. Also, the interval in $\sin \theta/\lambda$ chosen by JB is rather too large for suitable interpolation in the low $\sin \theta/\lambda$ region.

In view of the preparation of Volume 3 of the new edition of the *International Tables for X-ray Crystallography*, it was decided to recalculate atomic scattering factors from all the newest available self-consistent field data. This decision had, in fact, been taken before we were aware of the work being done by HI. We therefore included C, N and O in our computations, which has the advantage of giving the f values for these atoms at the same intervals as for the other atoms, and, moreover, affords the possibility of an extra check.

In this paper we give our results on all atoms, up to Rb⁺, for which the required electron distributions are available†. We omitted H and He, however, for which

† Besides the literature mentioned at the foot of Table 1, we found references to calculations on Sc and Ti (Hancock, 1934), and on Ni (Gray & Manning, 1941). We were unable to obtain the former; the latter is a short communication without numerical data.

Manning & Goldberg (1938) gave data on Fe. These, however, are on a logarithmic scale of r , whereas the data for the other atoms were on a linear r scale. It is therefore impossible to handle the Fe atom in the same mechanical way as the others. We are now computing the scattering factor of Fe separately and we intend to report on it in due time.

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Table 1. *Atomic scattering factors*

NS: Electron densities calculated for the normal state.

VS: Electron densities calculated for the valence state.

X: The electron distribution has been calculated with exchange.

$\sin \theta/\lambda$	Li NSX ¹	Be NSX ²	C VSX ³	N NSX ⁴	O NSX ⁵	F NS(X2p) ⁶	F ⁻ NS(X2p) ⁶	Ne NS(X2p) ⁶	Na NSX ⁷
0.00	3.000	4.000	6.000	7.000	8.000	9.000	10.000	10.000	11.00
0.05	2.710	3.706	5.764	6.781	7.796	8.790	9.630	9.812	10.56
0.10	2.215	3.065	5.141	6.203	7.250	8.208	8.733	9.295	9.76
0.15	1.904	2.462	4.362	5.420	6.482	7.396	7.656	8.546	9.02
0.20	1.741	2.059	3.612	4.600	5.634	6.501	6.597	7.665	8.34
0.25	1.627	1.827	3.003	3.856	4.814	5.625	5.643	6.768	7.62
0.30	1.512	1.693	2.538	3.241	4.094	4.837	4.820	5.905	6.89
0.35	1.394	1.600	2.212	2.760	3.492	4.160	4.129	5.128	6.16
0.40	1.269	1.520	1.983	2.397	3.010	3.598	3.566	4.454	5.47
0.50	1.032	1.362	1.707	1.944	2.338	2.769	2.751	3.403	4.29
0.60	0.823	1.195	1.548	1.698	1.944	2.252	2.237	2.692	3.40
0.70	0.650	1.030	1.423	1.550	1.714	1.926	1.921	2.234	2.76
0.80	0.513	0.877	1.313	1.444	1.566	1.725	1.723	1.934	2.31
0.90	0.404	0.739	1.202	1.350	1.462	1.587	1.583	1.737	2.00
1.00	0.320	0.621	1.096	1.263	1.374	1.484	1.485	1.601	1.78
1.10	0.255	0.521	0.992	1.175	1.296	1.404	1.406	1.496	1.63
1.20	0.205	0.438	0.896	1.083	1.220	1.333	1.334	1.418	1.52
1.30	0.164	0.369	0.802	1.005	1.144	1.263	1.264	1.345	1.44
$\sin \theta/\lambda$	Mg ²⁺ NSX ⁸	Al ³⁺ NS ⁹	Si ⁴⁺ NSX ¹⁰	Cl ⁻ NSX ¹¹	A NSX ¹²	K ⁺ NSX ¹²	Ca NSX ¹³	Cr ²⁺ NS ¹⁴	
0.00	10.00	10.00	10.00	18.00	18.00	18.00	20.00	22.00	
0.05	9.91	9.93	9.95	17.33	17.54	17.65	19.09	21.65	
0.10	9.66	9.72	9.79	15.68	16.30	16.68	17.33	20.67	
0.15	9.26	9.38	9.54	13.74	14.65	15.30	15.73	19.27	
0.20	8.75	8.94	9.20	11.97	12.93	13.76	14.32	17.67	
0.25	8.15	8.42	8.79	10.57	11.42	12.27	12.98	16.04	
0.30	7.51	7.85	8.33	9.51	10.20	10.96	11.71	14.50	
0.35	6.85	7.26	7.83	8.74	9.25	9.89	10.59	13.10	
0.40	6.20	6.65	7.31	8.15	8.54	9.04	9.64	11.87	
0.50	4.99	5.51	6.26	7.30	7.56	7.86	8.26	9.93	
0.60	4.03	4.53	5.28	6.60	6.86	7.11	7.38	8.60	
0.70	3.28	3.72	4.42	5.91	6.23	6.51	6.75	7.69	
0.80	2.71	3.10	3.71	5.24	5.61	5.94	6.21	7.06	
0.90	2.30	2.62	3.13	4.60	5.01	5.39	5.70	6.56	
1.00	2.01	2.27	2.68	4.01	4.43	4.84	5.19	6.13	
1.10	1.81	2.01	2.33	3.49	3.90	4.32	4.69	5.72	
1.20	1.65	1.82	2.06	3.06	3.43	3.83	4.21	5.31	
1.30	1.54	1.68	1.86	2.69	3.03	3.40	3.77	4.91	
$\sin \theta/\lambda$	Cu ⁺ NSX ¹⁵	Zn NS ¹⁶	Ga NS ¹⁶	Ge NS ¹⁷	As NS ¹⁶	Rb ⁺ NS ⁹			
0.00	28.00	30.00	31.00	32.00	33.00	36.00			
0.05	27.67	29.30	30.12	30.98	32.11	35.35			
0.10	26.71	27.63	28.29	28.91	30.06	33.61			
0.15	25.30	25.67	26.35	26.95	27.81	31.28			
0.20	23.59	23.74	24.48	25.09	25.76	28.85			
0.25	21.76	21.88	22.67	23.31	23.96	26.61			
0.30	19.92	20.11	20.94	21.67	22.30	24.68			
0.35	18.14	18.41	19.28	20.08	20.75	23.02			
0.40	16.50	16.83	17.70	18.53	19.27	21.57			
0.50	13.66	14.05	14.88	15.71	16.50	19.07			
0.60	11.45	11.84	12.54	13.29	14.06	16.82			
0.70	9.80	10.15	10.72	11.34	12.03	14.75			
0.80	8.61	8.90	9.35	9.85	10.40	12.88			
0.90	7.75	7.99	8.34	8.71	9.15	11.28			
1.00	7.12	7.32	7.59	7.86	8.21	9.96			
1.10	6.64	6.81	7.02	7.24	7.50	8.89			
1.20	6.24	6.40	6.57	6.74	6.95	8.05			
1.30	5.89	6.04	6.20	6.35	6.51	7.40			

1: Fock & Petrashen, 1935.

2: Hartree & Hartree, 1935.

3: Jucys, 1947.

4: Hartree & Hartree, 1948.

5: Hartree, Hartree & Swirles, 1939.

6: Brown, 1933.

7: Hartree & Hartree, 1948.

8: Yost, 1940.

9: Hartree, 1935.

10: Hartree, Hartree & Manning, 1941c.

11: Hartree & Hartree, 1936a.

12: Hartree & Hartree, 1938b.

13: Hartree & Hartree, 1938a.

14: Mooney, 1939.

15: Hartree & Hartree, 1936b.

16: Hartree, Hartree & Manning, 1941a.

17: Hartree, Hartree & Manning, 1941b.

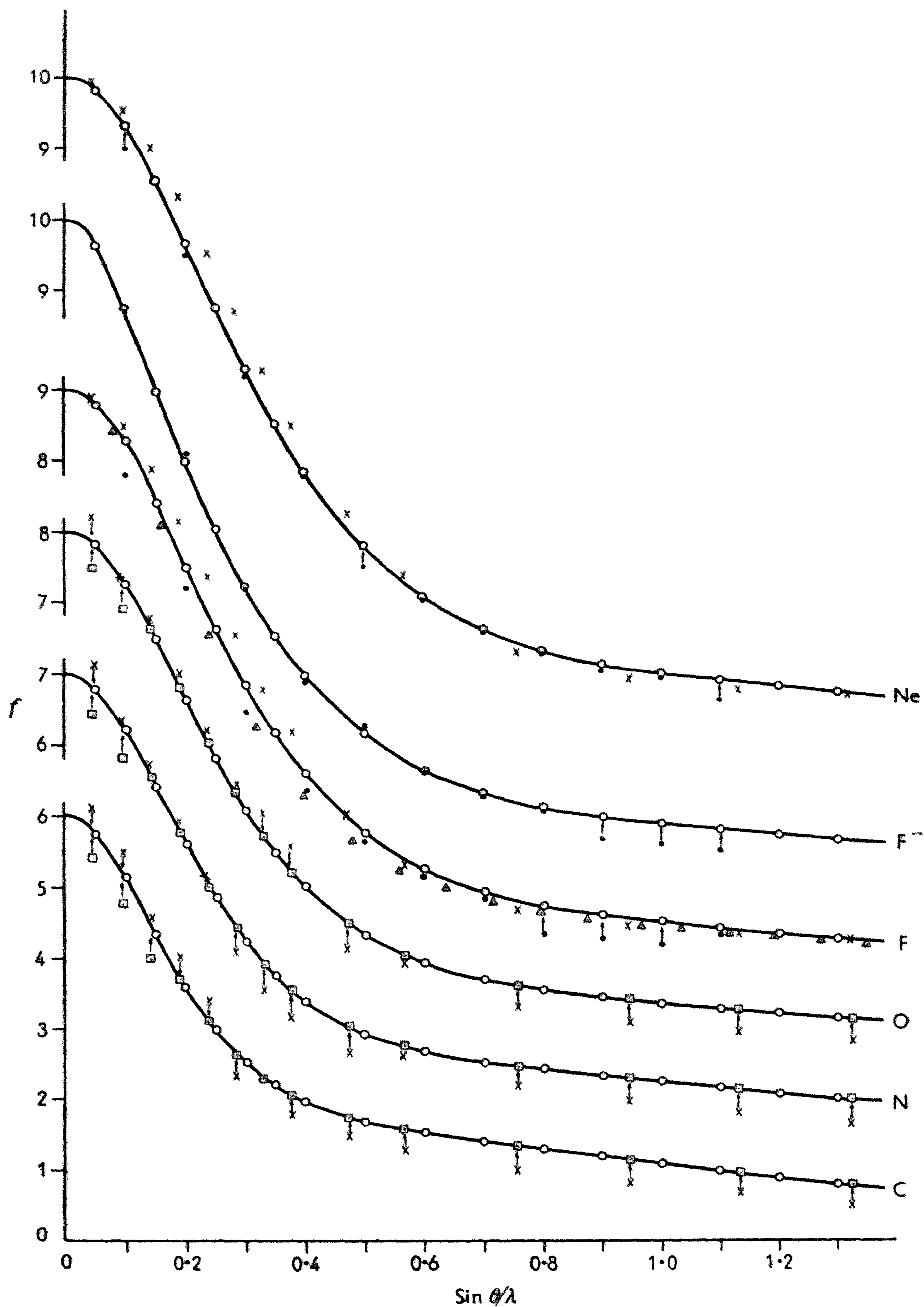


Fig. 1. Atomic scattering factors for Ne, F^- , F, O, N and C, calculated by different authors.

□: Hoerni & Ibers. ×: McWeeny. Δ: Viervoll & Ögrim. ●: James & Brindley. ○: Our calculations.

Arrows ↑, ↓ indicate that the symbol coincides with the curve, but has been drawn off the curve to avoid crowding.

atoms we consider that McWeeny's data are completely adequate. If necessary, the electron distributions were smoothed out spherically, as was also done by HI.

A point of consideration has been the computation for atoms in different states of ionization. The neces-

sary data are available only for Li and Li^+ (Fock & Petrashen, 1935); O^- , O, O^+ , O^{++} (Hartree, Hartree & Swirles, 1939); F and F^- (Brown, 1933); Na and Na^+ (Hartree & Hartree, 1948) and Ca and Ca^{++} (Hartree & Hartree, 1938a). These have all been calculated with exchange. It has been realized (James,

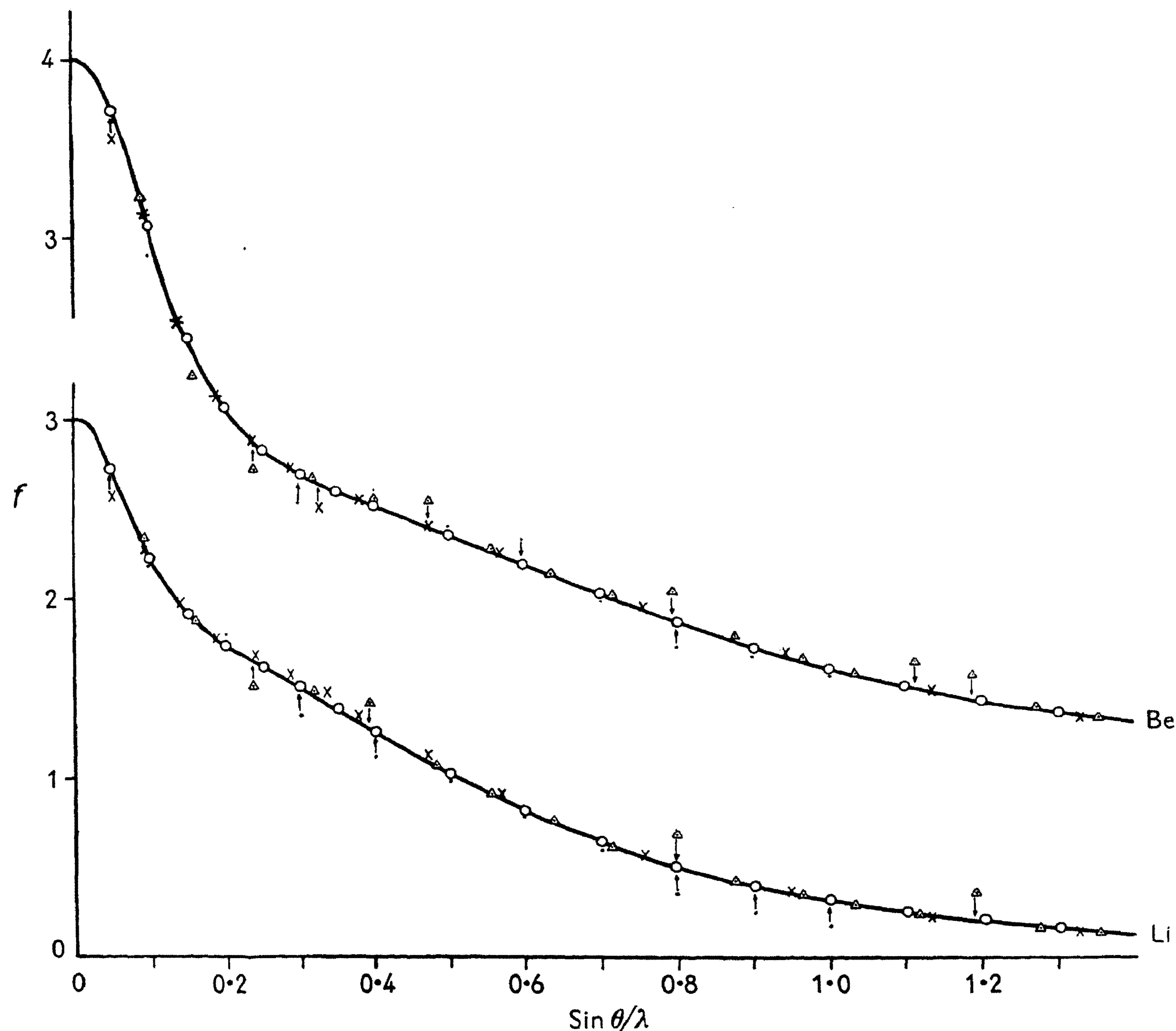


Fig. 2. Atomic scattering factors for Li and Be.

× : McWeeny. Δ : Viervoll & Ögrim. ● : James & Brindley. ○ : Our calculations.

1948; Bijvoet & Lonsdale, 1953), that the scattering factor changes very little with the state of ionization, except, of course, for very small values of $\sin \theta/\lambda$. We have checked and confirmed this for F and F⁻ (see Table 1). For the other atoms we have only computed f for the normal state, unless data for this state were not available.

2

The calculations have been performed on IBM machines in the Mathematical Centre, Amsterdam. Following JB, we have calculated the separate contributions of individual electron orbitals in order to be able to investigate the possibility of interpolation to the atoms omitted from our list. We will report on this later. As intervals in $\sin \theta/\lambda$ we have chosen:

$$0.00 \quad (0.05) \quad 0.40 \quad (0.1) \quad 1.30 \text{ \AA}^{-1},$$

that is, to the end of the Mo K diffraction region. Because of this choice of interval, our results are directly comparable with the JB values.

The integrals

$$\int_0^{r_l} P_k^2(r) \sin \mu r / \mu r dr$$

where $\mu = 4\pi \sin \theta/\lambda$, were uniformly calculated:

- (a) to the same upper limit $r_l = 13a_H$, where a_H is the 'atomic unit', 0.52917 Å,
- (b) in the same steps $r/a_H = 0 \quad (0.005) \quad 0.3 \quad (0.05) \quad 13.0$.

For the latter purpose, the data from the literature were interpolated to the required intervals.

The integrations were carried out according to Simpson, following a procedure described in the report MR 15 of the Mathematical Centre, Amsterdam.

The integrations were checked:

- (a) by the normalizing integral

$$\int_0^{r_l} P_k^2(r) dr;$$

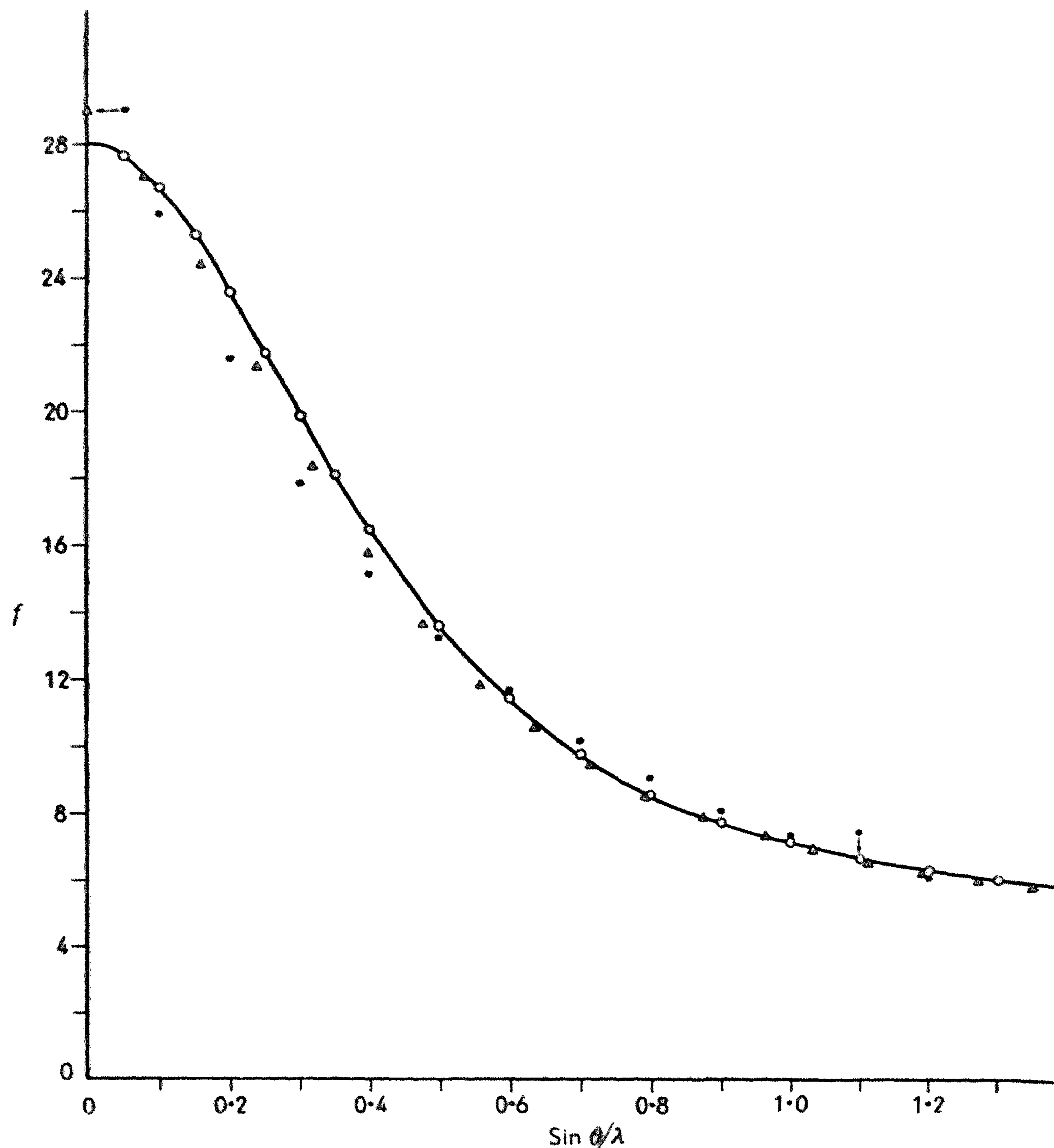
- (b) by the integral

$$\int_0^{r_l} P_k^2(r) \sum_i (\sin \mu_i r / \mu_i r) dr,$$

where the sum extends over all values of μ_i , i.e. of $\sin \theta/\lambda$;

- (c) by performing all 2033 integrations twice, using different counters and type-bars.

The data of Table 1 are given to three decimal places

Fig. 3. Scattering factor for Cu^+ .

○: Our calculations for Cu^+ with exchange. △: Viervoll & Ögrim for Cu without exchange.
 ●: James & Brindley for Cu from Thomas-Fermi field.

up to neon and to two decimal places for atoms of higher atomic number; the last place, of course, does not have any physical significance, but it facilitates interpolation.

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It is seen from Fig. 1 that our results agree completely with those of HI. The agreement with McWeeny's values, although calculated from different electron-distribution approximations, is in general very good (Figs. 1 and 2) except for F and Ne.

A comparison with James & Brindley's values shows the following points:

- (a) F^- , Al^{3+} and Rb^+ have evidently been computed from the same electron-distribution data. The deviations are in general smaller than 1%, and so are insignificant.
- (b) Li, O, F, Na, Si^{4+} , Cl^- and K^+ : Apparently,

different sets of electron-distribution data have been used. The ones we used were all computed taking exchange into account (in the case of F only for the 2p-electrons). Except for Li (Fig. 2), the fit is much worse than in the former group, differences going up to 10%; discrepancies are particularly large for F and for O. This shows the considerable influence of exchange on the scattering factors.

- (c) Be, N, Ne, Mg^{2+} and A have been computed by JB by interpolation. The discrepancies with our values are in general not larger than in the former group. Again, the agreement is good for Be, the lightest atom of the group (Fig. 2).
- (d) Ca, Cr^{2+} , Cu^+ , Zn, Ga, Ge and As: For these elements, JB gave only f values obtained from Thomas-Fermi electron distributions. The agreement of these values with ours is in general worse than in the cases (b) and (c). (Ca^{2+} , cal-

culated by JB from Hartree wave functions without exchange, fits our curve from $\sin \theta/\lambda = 0.5$ onwards.)

Finally, Fig. 3 gives a comparison between the scattering factor of Cu^+ , calculated by us from wave functions with exchange, and that for Cu calculated by Viervoll & Ögrim without exchange. The discrepancies are appreciable throughout the Cu K range. Likewise, Viervoll & Ögrim's values for Ca and Cr are considerably smaller than ours at low $\sin \theta/\lambda$ values. It appears, therefore, that more calculations for moderately heavy elements are very desirable.

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