

SIR88 (Burla, Camalli, Cascarano, Giacovazzo, Polidori, Spagna & Viterbo, 1989) of the SIR program.

Financial support for this work was provided by the CNR project *Metodologie Cristallografiche Avanzate*.

APPENDIX

If in the distribution (II.A1) only terms up to order $1/q^0$ are retained the result is

$$P(\varphi_1, \varphi_2, \varphi_3 | R'_i, R'_{pi}, \varphi_{pi}, i = 1, 2, 3) \approx L^{-1} \exp \left\{ \sum_{i=1}^3 G_i \cos(\varphi_i - \varphi_{pi}) \right\}. \quad (A1)$$

In this case $\varphi_1, \varphi_2, \varphi_3$ act as mutually independent variables, each φ_i being distributed according to the von Mises distribution

$$M(\varphi_i; \theta_i, G_i) = [2\pi I_0(G_i)]^{-1} \exp[G_i \cos(\varphi_i - \theta_i)],$$

where $\theta_i = \varphi_{pi}$. The following general theorem may then be applied to (A1) (Giacovazzo, 1979): let $\varphi_1, \varphi_2, \dots, \varphi_n$ be n mutually independent variables and let any φ_i be distributed according to $M(\varphi_i; \theta_i, G_i)$. Then the variable sum $\Phi = \varphi_1 + \varphi_2 + \dots + \varphi_n$ can be approximated by the von Mises distribution $M(\Phi; \theta_1 + \theta_2 + \dots + \theta_n, S)$ where S satisfies

$$D_1(S) = D_1(G_1)D_1(G_2) \dots D_1(G_n).$$

Acta Cryst. (1989). **A45**, 786–793

Relativistic Hartree–Fock X-ray and Electron Atomic Scattering Factors at High Angles

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(Received 12 December 1988; accepted 21 June 1989)

Abstract

An enlarged set (atomic number $Z=2$ to 98) of free-atom X-ray atomic scattering (form) factors for

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For $n=3$ this theorem gives the result provided by distribution (3).

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high angles [$2 \leq (\sin \theta)/\lambda \leq 6 \text{ \AA}^{-1}$] has been calculated based on those of Doyle & Turner [*Acta Cryst.* (1968). **A24**, 390–397]. Four-parameter 'exponential polynomial' fits for these are presented which give far more accurate estimates of the scattering factors at high angles than the Gaussian fits normally used.

The use of the Mott formula in conjunction with these new high-angle X-ray form factors allows the calculation of improved-accuracy high-angle electron scattering factors. The use of these high-accuracy high-angle scattering factors for important applications such as Fourier charge-density analysis and computer simulation of high-resolution electron microscope (HREM) images is discussed.

Introduction

In 1968 Doyle & Turner produced a classic paper tabulating the relativistic Hartree-Fock (RHF) X-ray and electron atomic scattering (form) factors for 76 atoms and ions from $(\sin \theta)/\lambda$ (s) = 0 to 6 \AA^{-1} . In addition Doyle & Turner produced nine-parameter Gaussian fits for the X-ray form factors for the angular range $s = 0$ to 2 \AA^{-1} based on the formula

$$f^x(s) = \sum_{i=1}^4 a_i \exp(-b_i s^2) + c \quad (1)$$

where the a_i , b_i and c are constants for a given element or ion, and $f^x(s)$ is the X-ray form factor. Subsequently Cromer & Waber (1968) 'filled in the gaps'

in Doyle & Turner's work, and so a complete set of X-ray form factors from $Z = 1$ to 98 for $s = 0$ to 2 \AA^{-1} with nine-parameter Gaussian fits was available. These results are shown in full in *International Tables for X-ray Crystallography* (1974) and have formed the basis for many computer and other applications requiring X-ray or electron scattering factors. For recent examples see O'Keefe, Buseck & Iijima (1978), Tabbernor, Fox & Fisher (1990) and Peng & Cowley (1988). As well as these RHF calculations, Hubbell, Veigele, Briggs, Brown & Cromer (1975) have made non-relativistic form-factor estimates for $Z = 1$ to 100 for $0.005 \leq x \leq 10^9 \text{ \AA}^{-1}$ [$x = \sin(\theta/2)/\lambda$] and this approximation led to form factors which are somewhat lower than the RHF values.

Unfortunately, (1) is only applicable to the angular range $s = 0$ to 2 \AA^{-1} and attempts to extend it to higher angles can lead to large errors. For example Fig. 1(a) shows the Doyle & Turner Gaussian fit to the calculated $f^x(s)$ for nitrogen ($Z = 7$) extrapolated to $s = 6 \text{ \AA}^{-1}$; it can be seen that the curve based on (1) drops well below the true values calculated by Doyle & Turner (1968), and in fact goes negative for $s > 3 \text{ \AA}^{-1}$. Another example, uranium ($Z = 92$), is shown in Fig. 1(b), and in this case the extrapolated Gaussian values are far too high. It is clear from this discussion that an accurate set of high-angle form factors for all elements from $s = 2$ to 6 \AA^{-1} is necessary, and that an n -parameter curve-fitting routine for this angular range is highly desirable; this is the object of the present work.

Calculations

High-angle form factors

As mentioned previously, Doyle & Turner (1968) calculated form factors for 76 atoms and ions up to $s = 6 \text{ \AA}^{-1}$. The elements they omitted to consider were those with atomic number $Z = 1, 39-41, 43-46, 52, 57-62, 64-79, 81, 84-85, 87-91$ and $93-98$. It is therefore necessary to calculate the high-angle form factors for all these elements; this could be done from first principles in the manner of Doyle & Turner or Cromer & Waber (1968). This, however, is very time consuming and tedious, and in this work a simpler alternative is discussed.

For hydrogen at angles for which $s \geq 1.5 \text{ \AA}^{-1}$, the X-ray form factor is less than 2×10^{-3} (e.g. Stewart, Davidson & Simpson, 1965) and can therefore be considered to be virtually zero for these high angles.

For elements in the range $Z = 35-92$, the variation of f^x with Z for the Doyle & Turner (1968) values was investigated, and it was found that they fell on a slowly varying smooth curve which is very close to linear for high Z . A simple polynomial curve-fitting routine available in the Cricket GraphTM software (Rafferty & Norling, 1986) for an Apple Macintosh

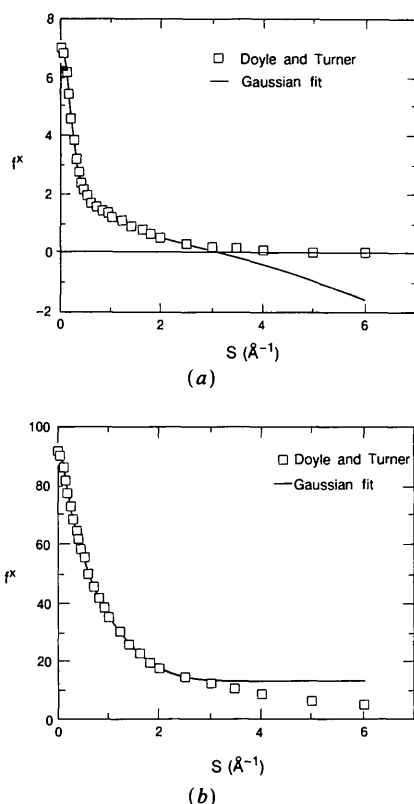


Fig. 1. (a) Graph of X-ray scattering factor, f^x , versus $(\sin \theta)/\lambda$ for nitrogen ($Z = 7$) showing the Gaussian fit going negative at high angles. (b) Graph of f^x versus $(\sin \theta)/\lambda$ for uranium ($Z = 92$) showing the Gaussian fit to be too high for high angles.

Table 1. High-angle X-ray atomic scattering factors $f^x(s)$ ($2 \leq s \leq 6 \text{ \AA}^{-1}$)

Z	Symbol	s=2.0	s=2.5	s=3.0	s=3.5	s=4.0	s=5.0	s=6.0
2	He	0.010	0.004	0.002	0.001	0.001	0.000	0.000
3	Li	0.044	0.021	0.011	0.006	0.004	0.002	0.001
4	Be	0.120	0.060	0.033	0.019	0.012	0.005	0.003
5	B	0.233	0.126	0.072	0.043	0.027	0.012	0.006
6	C	0.373	0.216	0.130	0.081	0.053	0.025	0.013
7	N	0.525	0.324	0.204	0.132	0.088	0.043	0.023
8	O	0.674	0.443	0.292	0.196	0.134	0.067	0.037
9	F	0.810	0.564	0.389	0.270	0.190	0.099	0.055
10	Ne	0.929	0.680	0.489	0.331	0.254	0.137	0.079
11	Na	1.032	0.791	0.591	0.438	0.325	0.183	0.107
12	Mg	1.120	0.892	0.691	0.527	0.401	0.234	0.141
13	Al	1.195	0.979	0.783	0.615	0.478	0.290	0.179
14	Si	1.264	1.056	0.867	0.699	0.556	0.349	0.222
15	P	1.333	1.122	0.942	0.777	0.632	0.411	0.268
16	S	1.411	1.182	1.009	0.849	0.705	0.474	0.316
17	Cl	1.502	1.240	1.069	0.915	0.773	0.536	0.367
18	Ar	1.614	1.301	1.123	0.974	0.836	0.597	0.419
19	K	1.748	1.367	1.174	1.028	0.895	0.657	0.472
20	Ca	1.908	1.444	1.225	1.078	0.949	0.715	0.524
21	Sc	2.090	1.533	1.279	1.125	0.998	0.770	0.577
22	Ti	2.290	1.637	1.338	1.171	1.044	0.821	0.627
23	V	2.506	1.756	1.404	1.217	1.087	0.869	0.677
24	Cr	2.727	1.888	1.479	1.266	1.129	0.914	0.724
25	Mn	2.963	2.037	1.563	1.319	1.171	0.956	0.769
26	Fe	3.195	2.197	1.658	1.377	1.213	0.995	0.813
27	Co	3.424	2.366	1.763	1.441	1.258	1.033	0.853
28	Ni	3.647	2.543	1.878	1.512	1.306	1.069	0.892
29	Cu	3.855	2.721	2.001	1.590	1.358	1.105	0.929
30	Zn	4.063	2.908	2.135	1.677	1.414	1.140	0.964
31	Ga	4.260	3.097	2.277	1.772	1.477	1.176	0.998
32	Ge	4.447	3.287	2.428	1.876	1.545	1.213	1.030
33	As	4.621	3.475	2.584	1.988	1.621	1.251	1.061
34	Se	4.782	3.658	2.745	2.108	1.703	1.292	1.092
35	Br	4.932	3.836	2.909	2.235	1.793	1.337	1.123
36	Kr	5.071	4.007	3.074	2.369	1.890	1.384	1.154
37	Rb	5.200	4.168	3.239	2.507	1.993	1.436	1.186
38	Sr	5.323	4.320	3.401	2.649	2.103	1.493	1.219
39	Y	5.440	4.460	3.560	2.780	2.215	1.550	1.250
40	Zr	5.558	4.590	3.720	2.920	2.335	1.620	1.285
41	Nb	5.680	4.710	3.860	3.065	2.405	1.690	1.327
42	Mo	5.813	4.827	3.988	3.217	2.581	1.766	1.373
43	Tc	5.946	4.930	4.110	3.350	2.690	1.840	1.420
44	Ru	6.097	5.040	4.230	3.485	2.820	1.925	1.470
45	Rh	6.262	5.140	4.350	3.620	2.940	2.012	1.520
46	Pd	6.443	5.240	4.460	3.740	3.080	2.100	1.575
47	Ag	6.651	5.351	4.566	3.862	3.207	2.206	1.635
48	Cd	6.871	5.461	4.665	3.977	3.330	2.304	1.698
49	In	7.110	5.577	4.761	4.087	3.449	2.406	1.746
50	Sn	7.367	5.702	4.853	4.192	3.565	2.509	1.835

personal computer was used to fit the f^x versus Z data for the appropriate values of s in order to 'fill in the gaps' in Doyle & Turner's values, and a correlation coefficient of 0.999 or better was obtained in each case with appropriate choice of polynomial coefficients; an example for $s = 3 \text{ \AA}^{-1}$ is shown in Fig. 2. Interpolation using these curve fits allowed the evaluation of the high-angle X-ray form factors for the atomic numbers not considered by Doyle & Turner up to $Z = 91$.

For the elements with $Z = 93-98$, a simple linear extrapolation from the f^x versus Z variation ($Z = 63-92$) of the values of Doyle & Turner (1968) for $2 \leq s \leq 6 \text{ \AA}^{-1}$ was used. This is likely to be a little less accurate than the interpolative method described previously, but still good (and certainly much better than the Gaussian fits) as the form of f^x versus Z is close to linear in the range $Z = 63-92$, as shown in Fig. 3 for $s = 3 \text{ \AA}^{-1}$.

The foregoing calculations together with the values of Doyle & Turner (1968) allowed a tabulation of the

X-ray form factors for $s = 2.5, 3.0, 3.5, 4.0, 5.0, 6.0 \text{ \AA}^{-1}$ for all elements ($Z = 2-98$) and these are shown in Table 1. It is also satisfactory to use these

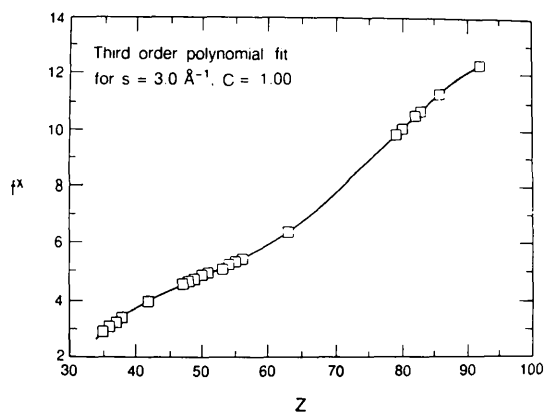


Fig. 2. Graph of X-ray scattering factor, f^x , versus atomic number, Z , for $(\sin \theta)/\lambda = 3 \text{ \AA}^{-1}$ showing the polynomial fit to the values of Doyle & Turner (1968).

Table 1 (cont.)

Z	Symbol	s=2.0	s=2.5	s=3.0	s=3.5	s=4.0	s=5.0	s=6.0
51	Sb	7.642	5.836	4.945	4.292	3.678	2.615	1.909
52	Te	7.921	5.980	5.040	4.390	3.780	2.722	1.990
53	I	8.239	6.142	5.132	4.478	3.891	2.828	2.067
54	Xe	8.556	6.315	5.229	4.566	3.991	2.935	2.150
55	Cs	8.881	6.502	5.332	4.651	4.087	3.041	2.237
56	Ba	9.213	6.704	5.440	4.735	4.178	3.146	2.325
57	La	9.550	6.917	5.550	4.820	4.270	3.240	2.410
58	Ce	9.868	7.117	5.663	4.910	4.360	3.340	2.490
59	Pr	10.166	7.333	5.800	5.000	4.445	3.435	2.580
60	Nd	10.473	7.567	5.930	5.090	4.525	3.530	2.670
61	Pm	10.773	7.817	6.088	5.180	4.600	3.625	2.770
62	Sm	11.064	8.083	6.250	5.280	4.675	3.720	2.865
63	Eu	11.345	8.348	6.435	5.378	4.750	3.812	2.965
64	Gd	11.631	8.683	6.588	5.490	4.830	3.905	3.070
65	Tb	11.886	8.983	6.775	5.610	4.915	3.990	3.170
66	Dy	12.141	9.267	6.963	5.720	5.000	4.075	3.270
67	Ho	12.392	9.533	7.163	5.850	5.090	4.155	3.355
68	Er	12.621	9.783	7.375	5.980	5.180	4.235	3.440
69	Tm	12.847	10.033	7.588	6.110	5.280	4.310	3.520
70	Yb	13.064	10.267	7.788	6.250	5.380	4.380	3.600
71	Lu	13.277	10.500	8.013	6.400	5.490	4.450	3.680
72	Hf	13.481	10.733	8.238	6.560	5.600	4.520	3.755
73	Ta	13.679	10.950	8.480	6.740	5.710	4.585	3.825
74	W	13.871	11.167	8.706	6.900	5.840	4.650	3.900
75	Re	14.057	11.383	8.938	7.080	5.960	4.715	3.970
76	Os	14.239	11.583	9.163	7.270	6.080	4.788	4.035
77	Ir	14.418	11.783	9.400	7.460	6.210	4.860	4.105
78	Pt	14.595	11.983	9.620	7.650	6.340	4.935	4.175
79	Au	14.770	12.168	9.826	7.878	6.489	5.010	4.244
80	Hg	14.949	12.360	10.049	8.081	6.644	5.090	4.310
81	Tl	15.131	12.530	10.270	8.290	6.800	5.175	4.374
82	Pb	15.317	12.724	10.482	8.495	6.973	5.260	4.441
83	Bi	15.510	12.896	10.690	8.704	7.145	5.351	4.505
84	Po	15.711	13.060	10.900	8.910	7.320	5.440	4.567
85	At	15.922	13.230	11.090	9.120	7.500	5.540	4.630
86	Rn	16.143	13.386	11.282	9.329	7.686	5.650	4.702
87	Fr	16.377	13.550	11.460	9.530	7.878	5.755	4.768
88	Ra	16.623	13.700	11.640	9.730	8.070	5.870	4.840
89	Ac	16.880	13.860	11.815	9.930	8.255	5.933	4.910
90	Th	17.149	14.020	11.980	10.130	8.440	6.118	4.982
91	Pa	17.423	14.180	12.150	10.320	8.630	6.250	5.055
92	U	17.713	14.341	12.294	10.495	8.823	6.378	5.136
93	Np	18.012	14.503	12.475	10.695	9.008	6.489	5.206
94	Pu	18.319	14.664	12.656	10.895	9.193	6.602	5.275
95	Am	18.640	14.826	12.838	11.095	9.378	6.713	5.345
96	Cm	18.975	14.988	13.019	11.295	9.563	6.825	5.414
97	Bk	19.315	15.150	13.200	11.495	9.748	6.937	5.484
98	Cf	19.665	15.311	13.381	11.695	9.933	7.049	5.553

for ions, as the ionic form factors of Cromer & Waber (1968) and Doyle & Turner for 2 \AA^{-1} are very close to the free-atom values for most elements; this is of course not surprising, as ionicity only significantly affects low-angle scattering factors which reflect the behaviour of valence electrons.

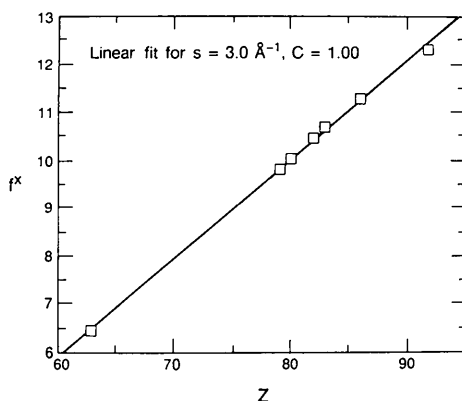


Fig. 3. As Fig. 2 but showing the linear variation of f^x with atomic number $Z = 63$ to 92 .

Parametric curve-fitting routines

Initially an attempt was made to fit accurately the full range of $f^x(s)$ values for $s = 0$ to 6 \AA^{-1} . It soon became apparent that this would be an impossible task with any conventional curve-fitting routines such as polynomial or Gaussian, and so to obtain accurate high-angle form factors for arbitrary values of s in the range $2 \leq s \leq 6 \text{ \AA}^{-1}$ the values of Table 1 only were considered. A simple, yet seemingly quite reasonable, approach to the fit is linear interpolation between the values shown in Table 1, although it is difficult to estimate the errors at the midpoints between the tabulated values. For computer applications it is more convenient to have an n -parameter function to fit the $f^x(s)$ versus s variation, and initially a conventional Tchebyshev polynomial curve fit was tried; it soon became clear from the shape of the $f^x(s)$ versus s curves for $2 \leq s \leq 6 \text{ \AA}^{-1}$ that an exponential or logarithmic expression would provide a better fit. Accordingly, expressions of the form

$$f^x(s) = as^{-b} \quad (2a)$$

Table 2. Parameters for the fit of $\ln[f^x(s)]$ in equation (4) within the range $2 \leq s \leq 6 \text{ \AA}^{-1}$

Z	Symbol	a_0	a_1	$a_2(\times 10)$	$a_3(\times 100)$	C
2	He	0.52543	-3.43300	4.80070	-2.54760	1.0000
3	Li	0.89463	-2.43660	2.32500	-0.71949	1.0000
4	Be	1.25840	-1.94590	1.30460	-0.04297	1.0000
5	B	1.66720	-1.85560	1.60440	-0.65981	1.0000
6	C	1.70560	-1.56760	1.18930	-0.42715	1.0000
7	N	1.54940	-1.20190	0.51064	0.02472	1.0000
8	O	1.30530	-0.83742	-0.16738	0.47500	1.0000
9	F	1.16710	-0.63203	-0.40207	0.54352	1.0000
10	Ne	1.09310	-0.50221	-0.53648	0.60957	0.9995
11	Na	0.84558	-0.26294	-0.87884	0.76974	1.0000
12	Mg	0.71877	-0.13144	-1.20900	0.82738	1.0000
13	Al	0.67975	-0.08756	-0.95431	0.72294	1.0000
14	Si	0.70683	-0.09888	-0.98356	0.55631	1.0000
15	P	0.85532	-0.21262	-0.37390	0.20731	1.0000
16	S	1.10400	-0.40325	0.20094	-0.26058	1.0000
17	Cl	1.42320	-0.63936	0.84722	-0.76135	0.9995
18	Ar	1.82020	-0.92776	1.59220	-1.32510	0.9995
19	K	2.26550	-1.24530	2.38330	-1.91290	0.9990
20	Ca	2.71740	-1.55670	3.13170	-2.45670	0.9990
21	Sc	3.11730	-1.81380	3.71390	-2.85330	0.9990
22	Ti	3.45360	-2.01150	4.13170	-3.11710	0.9995
23	V	3.71270	-2.13920	4.35610	-3.22040	0.9995
24	Cr	3.87870	-2.19000	4.38670	-3.17520	1.0000
25	Mn	3.98550	-2.18850	4.27960	-3.02150	1.0000
26	Fe	3.99790	-2.11080	3.98170	-2.71990	1.0000
27	Co	3.95900	-1.99650	3.60630	-2.37050	1.0000
28	Ni	3.86070	-1.88690	3.12390	-1.94290	1.0000
29	Cu	3.72510	-1.65500	2.60290	-1.49760	0.9995
30	Zn	3.55950	-1.45100	2.03390	-1.02160	0.9995
31	Ga	3.37560	-1.23910	1.46160	-0.55471	0.9995
32	Ge	3.17800	-1.02230	0.89119	-0.09984	0.9995
33	As	2.97740	-0.81038	0.34861	0.32231	0.9995
34	Se	2.78340	-0.61110	-0.14731	0.69837	0.9995
35	Br	2.60610	-0.43308	-0.57381	1.00950	0.9995
36	Kr	2.44280	-0.27244	-0.95570	1.27070	0.9995
37	Rb	2.30990	-0.14328	-1.22600	1.45320	1.0000
38	Sr	2.21070	-0.04770	-1.41100	1.55410	1.0000
39	Y	2.14220	0.01935	-1.52240	1.59630	1.0000
40	Zr	2.12690	0.08618	-1.49190	1.51820	1.0000
41	Nb	2.12120	0.05381	-1.50070	1.50150	1.0000
42	Mo	2.18870	-0.00655	-1.25340	1.24010	1.0000
43	Tc	2.25730	-0.05737	-1.07450	1.06630	1.0000
44	Ru	2.37300	-0.15040	-0.77694	0.79060	0.9995
45	Rh	2.50990	-0.25906	-0.44719	0.49443	0.9995
46	Pd	2.67520	-0.39137	-0.05894	0.15404	0.9995
47	Ag	2.88690	-0.56119	0.42189	-0.25659	0.9990
48	Cd	3.08430	-0.71450	0.84482	-0.60990	0.9990
49	In	3.31400	-0.89697	1.35030	-1.03910	0.9990
50	Sn	3.49840	-1.02990	1.68990	-1.29860	0.9990

and

$$f^x(s) = a \exp(-bs) \quad (2b)$$

(where a and b are constants which depend on atomic number, Z) were fitted using the Cricket GraphTM software on the Apple Macintosh personal computer. This resulted in an improvement over the polynomial fits, but the correlation coefficients C for these fits could still drop below 0.99. For example, for (2a) for silicon ($Z = 14$), $a = 3.7856$, $b = 1.4668$ and $C = 0.976$ which gave errors of up to 13% in the interpolated values of $f^x(s)$.

In order to improve the accuracy of fit, a three-parameter polynomial fit based on (2b) in the following form was tried:

$$\ln[f^x(s)] = a_0 + a_1s + a_2s^2. \quad (3)$$

This expression resulted in a minimum C value of 0.993 at $Z = 22$, corresponding to a maximum error of 8.8% in $f^x(s)$ at $s = 2.5 \text{ \AA}^{-1}$ for titanium.

To improve matters still further a four-parameter

fit of the form

$$\ln[f^x(s)] = a_0 + a_1s + a_2s^2 + a_3s^3 \quad (4)$$

was adopted and the correlation coefficient C remained at 0.999 or above, except for $Z = 95-97$ where it dropped to 0.9985 and for $Z = 98$ for which C was found to be 0.998. The values of a_0 , a_1 , a_2 , a_3 and C for all Z derived in this way from (4) are shown in Table 2. This use of equation (4) resulted in a maximum error in $f^x(s)$ of 5.0% which occurred for californium ($Z = 98$) at $s = 2.5 \text{ \AA}^{-1}$. For most other elements the maximum errors in $f^x(s)$ are below 3%, which is much better than the errors given by the Gaussian fits. As discussed by Doyle & Turner (1968) the percentage error in $f^x(s)$ is perhaps better expressed as a function of $f^x(0)$. For $Z = 98$ at $s = 2.5 \text{ \AA}^{-1}$ we find that $\delta f^x(s)/f^x(0) \times 100$ [where $\delta f^x(s)$ is the error on $f^x(s)$] is equal to 0.008; this error is about the same as the best equivalent average error values quoted by Doyle & Turner for their Gaussian fits in the range $s = 0$ to 2 \AA^{-1} . All other fitted values

Table 2 (cont.)

Z	Symbol	a_0	a_1	a_2 (x10)	a_3 (x100)	C
51	Sb	3.70410	-1.18270	2.08920	-1.61640	0.9990
52	Te	3.88240	-1.30980	2.41170	-1.86420	0.9990
53	I	4.08010	-1.45080	2.76730	-2.13920	0.9990
54	Xe	4.24610	-1.56330	3.04200	-2.34290	0.9990
55	Cs	4.38910	-1.65420	3.25450	-2.49220	0.9995
56	Ba	4.51070	-1.72570	3.41320	-2.59590	0.9995
57	La	4.60250	-1.77070	3.49970	-2.64050	0.9995
58	Ce	4.69060	-1.81790	3.60280	-2.70670	0.9995
59	Pr	4.72150	-1.81390	3.56480	-2.65180	0.9995
60	Nd	4.75090	-1.80800	3.51970	-2.59010	1.0000
61	Pm	4.74070	-1.76600	3.37430	-2.44210	1.0000
62	Sm	4.71700	-1.71410	3.20800	-2.28170	1.0000
63	Eu	4.66940	-1.64140	2.98580	-2.07460	1.0000
64	Gd	4.61010	-1.55750	2.73190	-1.84040	0.9995
65	Tb	4.52550	-1.45520	2.43770	-1.57950	0.9995
66	Dy	4.45230	-1.36440	2.17540	-1.34550	0.9990
67	Ho	4.37660	-1.27460	1.92540	-1.13090	0.9990
68	Er	4.29460	-1.18170	1.67060	-0.91467	0.9990
69	Tm	4.21330	-1.09060	1.42390	-0.70804	0.9990
70	Yb	4.13430	-1.00310	1.18810	-0.51120	0.9990
71	Lu	4.04230	-0.90518	0.92889	-0.29820	0.9990
72	Hf	3.95160	-0.80978	0.67951	-0.09620	0.9990
73	Ta	3.85000	-0.70599	0.41103	0.11842	0.9990
74	W	3.76510	-0.61807	0.18568	0.29787	0.9990
75	Re	3.67600	-0.52688	-0.04706	0.48180	0.9995
76	Os	3.60530	-0.45420	-0.22529	0.61700	0.9995
77	Ir	3.53130	-0.37856	-0.41174	0.75967	0.9995
78	Pt	3.47070	-0.31534	-0.56487	0.87492	0.9995
79	Au	3.41630	-0.25987	-0.69030	0.96224	0.9995
80	Hg	3.37350	-0.21428	-0.79013	1.02850	1.0000
81	Tl	3.34590	-0.18322	-0.84911	1.05970	1.0000
82	Pb	3.32330	-0.15596	-0.89878	1.08380	1.0000
83	Bi	3.31880	-0.14554	-0.90198	1.06850	1.0000
84	Po	3.32030	-0.13999	-0.89333	1.04380	1.0000
85	At	3.34250	-0.15317	-0.83350	0.97641	1.0000
86	Rn	3.37780	-0.17800	-0.74320	0.88510	1.0000
87	Fr	3.41990	-0.20823	-0.64000	0.78354	0.9995
88	Ra	3.47530	-0.25005	-0.50660	0.65836	0.9995
89	Ac	3.49020	-0.25109	-0.49651	0.64340	0.9995
90	Th	3.61060	-0.35409	-0.18926	0.36849	0.9995
91	Pa	3.68630	-0.41329	-0.01192	0.20878	0.9995
92	U	3.76650	-0.47542	0.16850	0.05060	0.9990
93	Np	3.82870	-0.51955	0.29804	-0.06566	0.9990
94	Pu	3.88970	-0.56296	0.42597	-0.18080	0.9990
95	Am	3.95060	-0.60554	0.54967	-0.29112	0.9985
96	Cm	4.01470	-0.65062	0.67922	-0.40588	0.9985
97	Bk	4.07780	-0.69476	0.80547	-0.51729	0.9985
98	Cf	4.14210	-0.73977	0.93342	-0.62981	0.9980

of the present work give values of $\delta f^x(s)/f^x(0) \times 100$ smaller than 0.008.

To check the accuracy of the curve fitting on the personal computer, equation (4) was used to fit the $\ln[f^x(s)]$ versus s data on a mainframe computer with polynomial curve-fitting NAG routines E02ADF and E02AEF (NAG Fortran Library Manual, 1987), and the interpolated values of $f^x(s)$ obtained using the NAG routines agreed to within 1 part in 10^4 with those generated by the personal computer.

Electron scattering factors

The electron scattering factor, $f^e(s)$, is related to the X-ray scattering factor by the usual Mott formula

$$f^e(s) = (me^2/2h^2)(\lambda/\sin \theta)^2[Z - f^x(s)] \quad (5)$$

which reduces to

$$f^e(s) = 0.023934(1/s)^2[Z - f^x(s)] \quad (6)$$

where $f^e(s)$ is a scattering length expressed in \AA . Hence a complete set of high-angle electron scattering

factors can be obtained by the use of (6) and Table 2 except for hydrogen where the simple use of (6) with $f^x = 0$ is very satisfactory. If δf^x is the error on f^x and δf^e the error on f^e , then differentiation of (6) gives

$$\delta f^e/f^e = \delta f^x/(Z - f^x), \quad (7)$$

which means that the larger s , the smaller f^x and the smaller the error in f^e . For higher angles f^x is smaller, and so the error in f^e is even smaller. As for f^x , the greatest error in f^e occurred for $Z = 98$ at $s = 2.5 \text{\AA}^{-1}$ and was 0.93%. All errors in f^e calculated by this method are therefore less than 1.0%, which is more than adequate for most applications.

It is worth noting that the use of the nine-parameter Gaussian-fitted X-ray form factors of Doyle & Turner (1968) for $0 \leq s \leq 2 \text{\AA}^{-1}$ and the four-parameter fits of the present work for $2 \leq s \leq 6 \text{\AA}^{-1}$ together with the Mott formula generally gives better interpolated electron scattering-factor values than the eight-parameter Gaussian fit for $f^e(s)$ quoted by Doyle & Turner. This is true except for very low angles ($s \leq 0.04 \text{\AA}^{-1}$) when $Z - f^x$ is small, and in this case the

procedure adopted by O'Keefe *et al.* (1978) and described in detail by Peng & Cowley (1988) should be used so that large errors in f^e are avoided for small s .

Examples of applications for high-angle form factors

Electron charge-density calculations

These are important for determining the distribution of electrons around atoms in crystalline solids. The electron charge-density, $\rho(x, y, z)$, at position vector $\mathbf{r}(x, y, z)$ in a unit cell is given by

$$\rho(x, y, z) = \Omega^{-1} \sum_h \sum_k \sum_l F_{hkl} \exp[-2\pi i(hx + ky + lz)] \quad (8)$$

where Ω is the volume of the unit cell and F_{hkl} are the X-ray structure factors for planes with Miller indices (hkl). For copper, Smart & Humphreys (1978) have shown that the Fourier sum in (8) requires well over 1200 terms for convergence. This has been confirmed by Tabbernor (1988) who also found that similar numbers of structure factors are needed for convergence of the charge-density sums of other elements. This means that many high-angle structure factors which occur in the range $2 \leq s \leq 6 \text{ \AA}^{-1}$ are needed for such calculations, and this is an important application for the high-angle form factors presented here.

Simulation of HREM images

The dynamical electron scattering calculation for the simulation of high-resolution electron microscope images requires a numerical evaluation of the crystal potential. This evaluation is normally carried out by Fourier transformation of the structure factors (for electrons), F_{hkl} , for the structure being simulated. In the case of the commonly used 'multislice' dynamical scattering algorithm (Goodman & Moodie, 1974), the structure-factor calculation requires accurately known scattering factors out to twice the scattering angle of the highest-order diffracted beam included in the computation (O'Keefe & Kilaas, 1988). In order to maintain sufficient precision, diffracted beams out to values of h, k, l corresponding to reciprocal-lattice vectors of 3 or 4 \AA^{-1} should be included in the computation; thus scattering factors are required for values out to $s = 3$ or 4 \AA^{-1} , equivalent to lattice vectors of 6 to 8 \AA^{-1} . Computations for structures that include heavy atoms, or for higher-voltage microscopes, increase the requirement for form factors accurate at higher angles, owing to the heavier scattering and larger-radii Ewald spheres involved.

For image simulations, it is convenient to be able to store scattering factors in the form of parameterized fits to the scattering curves. Lack of suitable complete

tables of parameterized fits of electron form factors has led to the widespread use of the Gaussian fits of *International Tables for X-ray Crystallography* for the X-ray form factors followed by conversion to the electron values by the Mott formula [equation (5)]. As discussed previously this can lead to form factors of very poor accuracy for $s \geq 2 \text{ \AA}^{-1}$ and the procedures recommended in the present work improve matters considerably.

Summary and concluding remarks

The effect of extending the Gaussian fits for X-ray form factors, f^x , presented in *International Tables for X-ray Crystallography* (1974), to high angles ($2 \leq s \leq 6 \text{ \AA}^{-1}$) has been carefully investigated, and it has been found that errors as high as 100% in f^x can occur, and that in some cases f^x can even go negative [see for example Fig. 1(a) for nitrogen] if this approach is adopted. For the electron scattering factors, f^e , derived by the Mott formula from these high-angle X-ray form factors, the situation is not as catastrophic, but errors in f^e as high as 10% can often be encountered.

It is clear that such inaccuracies are not acceptable when performing the Fourier analyses necessary for charge density studies or HREM image simulations, and in the present work an alternative method of producing high-angle X-ray and electron form factors has been discussed. This has involved curve fitting the f^x versus Z variation of the RHF values of Doyle & Turner (1968), so that a complete set of form factors from 2 to 6 \AA^{-1} is available for all elements from $Z = 1$ through 98. From these form factors, a four-parameter 'exponential polynomial' curve fitting of the variation of f^x with s has been made. Accurate values of the electron scattering factors were then calculated with the Mott formula in the usual way.

This procedure would appear to generate a maximum error of only about 5.0% in the X-ray scattering factors [for $Z = 98$ (californium) with $s = 2.5 \text{ \AA}^{-1}$] which is far more satisfactory than the Gaussian approach. If these best X-ray form factors are converted to electron scattering factors by the Mott formula, the maximum error encountered in f^e is less than 1.0%, which is more than adequate for most applications.

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Science Division of the US Department of Energy under Contract DEAC03-76SF00098. MAT would also like to thank the Science and Engineering Research Council (UK) for a research studentship and financial support while he was a visiting scientist at the Lawrence Berkeley Laboratory, University of California.

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