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Analytical Representation of Atomic Scattering Factors*

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Atomic scattering factors can be expressed analytically by an expansion of Gaussian functions. A two-term expansion is sufficiently accurate to cover the Cu $K\alpha$ range of scattering angles occurring in crystallographic calculations. For the Mo $K\alpha$ range, one extra constant is to be added.

The constants of the two-term expansion are evaluated for all the elements. The function fits the tabulated atomic scattering factors to better than 1% of $f(0)$ in most cases.

Introduction

The increasing availability of high-speed computers for crystallographic work creates need for analytical expression of atomic scattering factors. We have considered several possible functions for this purpose, and have decided upon a Gaussian expansion

$$f(x) = \sum_j A_j \exp(-a_j x^2), \qquad (1)$$

where $x = \sin\theta$.

This expansion has the advantage of very rapid convergence. If only two terms of the above series are taken, we obtain

$$f(x) = A \exp(-ax^2) + B \exp(-bx^2). \qquad (2)$$

This expression contains only four constants A, B, a, b, which depend on the range to be fitted; two of these are connected by the relation

$$A + B = N, \qquad (3)$$

where N is the number of electrons in the atom or ion. Thus (2) is essentially a three-constant formula. For atoms, $N = Z$, the atomic number; for ions, N differs from Z.

The two-term expansion proved to be sufficiently accurate for all the elements over the whole Cu $K\alpha$ range of angles θ, the error rarely exceeding 1% of $f(0)$. The additional practical advantage is that a subprogram for a Gaussian function is usually already available in the computing routine for the calculation of the temperature factor. A further advantage is that the function has a simple transform, so that computations of electron density and its derivatives are greatly facilitated whenever needed.

Over the Mo $K\alpha$ angular range, the two-term formula gives a poor fit for large angles, and addition of one more term is necessary. It is then sufficient to use a three-term formula:

$$f(x) = A \exp(-ax^2) + B \exp(-bx^2) + C, \qquad (4)$$

with the condition

$$A + B + C = N. \qquad (5)$$

The values of the constants A, B, a, b, are different from the values for the two-term formula.

The only serious disadvantage of the above formulae is that evaluation of the best values of the formula constants is not straightforward. It is a laborious procedure, and least-squares fitting must be done by successive approximations. For this reason only the constants of the two-term expansion have been calculated to date; an IBM 704 program has been designated to evaluate the constants of the three-term expansion.

It should be noted that the use of the Gaussian

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series for representation of atomic scattering factors is not new. Costain (1941), Booth (1945), and others suggested and applied one-term formulae for the electron-density distribution. Witte & Wölfel (1955), at the suggestion of R. Hoseman, used a two-term formula for the representation of scattering factors in NaCl. Our contribution consists of systematic calculation of the constants for all the elements, to render them available for practical applications.

It should also be noted that such a representation should be regarded as empirical rather than having any theoretical basis. The scattering curve of hydrogen can be expressed accurately by

$$f(x) = \frac{1}{[1+(ax)^2]^2}\,, \tag{6}$$

where $a = 2{\cdot}155$ for Cu $K\alpha$ radiation of wavelength 1·54 Å. In general, all atomic scattering factors can be expressed with good approximation by a finite series of fractions of the type

$$f(x) = \sum_n \frac{P_n}{[1+(a_n x)^2]^n}\,, \tag{7}$$

where P_n are polynomials, as has been shown by McWeeny (1951). These formulae, however, involve many more constants than our expansion; and although they are necessary for the first evaluation, they are unsuitable for repeated routine computations of scattering factors, especially for the heavier elements.

Method of fitting of constants

The first approximation was obtained graphically by plotting $\log f(x)$ against x^2. It was usually possible to fit two straight lines, one through the high-angle and one through the low-angle region. Further refinement was obtained by expanding $f(x)$ into a Taylor series. Assuming $\Delta A, \Delta a, \Delta b$ to be small, we have

$$f(x) = A\exp(-ax^2)+(N-A)\exp(-bx^2) \tag{8}$$

and

$$\Delta f = (\partial f/\partial A)\Delta A+(\partial f/\partial a)\Delta a+(\partial f/\partial b)\Delta b\,, \tag{9}$$

where

$$\partial f/\partial A = \exp(-ax^2)-\exp(-bx^2)\,, \tag{10}$$

$$\partial f/\partial a = -Ax^2\exp(-ax^2)\,, \tag{11}$$

$$\partial f/\partial b = -(N-A)x^2\exp(-bx^2)\,. \tag{12}$$

If the table in the required interval to be fitted has m entries, we have m equations for three unknowns $\Delta A, \Delta a, \Delta b$; these can be solved using a standard least-squares method. The process is repeated until no further improvement in fit is obtained, the fit being judged by the standard deviation σ given by

$$\sigma = \sqrt{\frac{\Sigma\Delta f^2}{m}}\,. \tag{13}$$

Description of the results

The constants A, B, a, b, of the two-term Gaussian expansion have been evaluated for all the elements, using the method of successive application of least squares. The formula was fitted to tabulated values of atomic scattering factors as reported in the literature. All the points within the selected interval have been taken with equal weight.

It is well known that, when calculating wave functions, exchange has an important effect. Its inclusion tends to shrink appreciably the electron-density distribution. If exchange is not taken into account, its neglect is partially compensated in practice by assuming an incorrect temperature factor. In tabulating our results, it appeared advisable to separate the computations with exchange from those without. The constants are therefore presented in four tables. Table 1 contains elements for which wave functions calculated with exchange were available. Table 2 contains some extrapolated values from Table 1, and Table 3 con-

Table 1. *Light elements with exchange*

	Z	N	A	A/Z	B	a	b	σ	σ/N (%)
H	1	1	0·3796	0·3796	0·6204	2·810	12·58	0·003	0·30
He	2	2	1·111	0·5555	0·889	1·39	5·49	0·001	0·07
Li	3	3	1·860	0·6200	1·140	0·954	42·69	0·020	0·66
Be	4	4	1·880	0·4700	2·120	0·530	22·7	0·016	0·40
C	6	6	2·240	0·3733	3·760	0·413	9·91	0·032	0·53
N	7	7	2·528	0·3611	4·472	0·444	7·47	0·033	0·47
O	8	8	3·093	0·3866	4·907	0·529	6·22	0·033	0·41
F	9	9	3·940	0·4378	5·060	0·640	6·14	0·039	0·43
F^-	9	10	4·726	0·5251	5·274	0·838	9·04	0·096	1·07
Ne	10	10	4·672	0·4672	5·328	0·653	5·00	0·032	0·32
Na	11	11	8·150	0·7409	2·850	0·999	13·03	0·16	1·46
Mg^{2+}	12	10	5·596	0·4663	4·404	0·519	2·64	0·015	0·15
Si^{4+}	14	10	8·000	0·5714	2·000	0·540	2·42	0·017	0·17
Cl^-	17	18	9·579	0·5635	8·421	0·429	11·78	0·092	0·51
A	18	18	9·140	0·5077	8·860	0·330	8·02	0·060	0·33
K^+	19	18	9·237	0·4862	8·763	0·310	6·29	0·036	0·20
Ca	20	20	11·864	0·5932	8·136	0·520	10·90	0·33	1·65
Cu^+	29	28	17·20	0·5931	10·80	0·496	4·19	0·059	0·21

tains some calculations without exchange. For heavier elements, Table 4 contains constants based on the Thomas–Fermi atomic scattering factors. These are without exchange.

For the data of Table 1, values were taken from Berghuis *et al.* (1955) with the exception of H and He. For these, McWeeny's (1951) values were taken. The

Table 2. *Some extrapolated constants (with exchange)*

	Z	*N*	*A*	*A/Z*	*B*	*a*	*b*
B	5	5	2·01	0·403	2·99	0·430	14·75
Na^+	11	10	5·14	0·467	4·86	0·575	3·54
Al^{3+}	13	10	6·75	0·519	3·25	0·530	2·53
Zn^{2+}	30	28	18·00	0·600	10·00	0·490	4·00

Table 3. *Light elements without exchange, from miscellaneous sources*

	Z	*N*	*A*	*B*	*a*	*b*	*σ*	Reference
C	6	6	1·97	4·03	0·278	8·83	0·018	*
C	6	6	2·08	3·92	0·304	13·5	—	†
N	7	7	2·016	4·984	0·201	6·14	0·038	*
O	8	8	2·205	5·795	0·267	4·66	0·019	*
O^{2-}	8	10	3·84	6·16	0·877	12·4	—	†
Al^{3+}	13	10	7·50	2·50	0·630	3·20	0·028	‡
P^{5+}	15	10	7·99	2·01	0·448	2·40	—	†
Cl	17	17	9·42	7·58	0·427	12·61	—	†
Ca^{2+}	20	18	9·244	8·756	0·280	5·63	0·052	‡
Cr^{2+}	24	22	12·04	9·96	0·40	5·09	0·078	‡
Zn	30	30	21·52	8·48	0·676	9·09	0·25	‡
Ga	31	31	23·08	7·92	0·69	10·95	0·30	‡
Ge	32	32	24·31	7·69	0·69	13·21	0·32	‡
As	33	33	24·79	8·21	0·65	13·06	0·24	‡
Rb^+	37	36	25·41	10·59	0·47	8·78	0·10	‡

* McWeeny (1951).
† James & Brindley (1931), interpolated value.
‡ Berghuis *et al.* (1955).

Table 4. *Thomas–Fermi atomic scattering factor curves, without exchange, for heavy elements*

	Z	*A*	*B*	*a*	*b*
Ne	10	5·636	4·364	0·7146	16·16
Na	11	6·261	4·739	0·6936	15·15
Mg	12	6·892	5·108	0·6750	15·01
Al	13	7·527	5·473	0·6583	14·53
Si	14	8·169	5·831	0·6432	14·10
P	15	8·816	6·184	0·6295	13·72
S	16	9·466	6·534	0·6169	13·36
Cl	17	10·12	6·880	0·6053	13·04
A	18	10·78	7·22	0·5946	12·74
K	19	11·44	7·56	0·5846	12·47
Ca	20	12·11	7·89	0·5753	12·21
Sc	21	12·78	8·22	0·5666	11·97
Ti	22	13·45	8·55	0·5584	11·75
V	23	14·13	8·87	0·5507	11·54
Cr	24	14·81	9·19	0·5434	11·34
Mn	25	15·49	9·51	0·5366	11·16
Fe	26	16·18	9·82	0·5300	10·98
Co	27	16·87	10·13	0·5238	10·82
Ni	28	17·56	10·44	0·5179	10·66
Cu	29	18·25	10·75	0·5122	10·51
Zn	30	18·94	11·06	0·5068	10·36
Ga	31	19·64	11·36	0·5016	10·23
Ge	32	20·34	11·66	0·4967	10·10
As	33	21·04	11·96	0·4919	9·973
Se	34	21·65	12·35	0·4874	9·853
Br	35	22·46	12·54	0·4830	9·738
Kr	36	23·17	12·83	0·4787	9·628
Rb	37	23·88	13·12	0·4746	9·522
Sr	38	24·59	13·41	0·4707	9·420
Y	39	25·31	13·69	0·4669	9·321
Zr	40	26·02	13·98	0·4632	9·226
Nb	41	26·74	14·26	0·4597	9·135
Mo	42	27·46	14·54	0·4562	9·046
Ma	43	28·19	14·81	0·4528	8·961
Ru	44	28·91	15·09	0·4496	8·877
Rh	45	29·63	15·37	0·4465	8·798
Pd	46	30·36	15·64	0·4434	8·719
Ag	47	31·09	15·91	0·4404	8·644
Cd	48	31·82	16·18	0·4376	8·571
In	49	32·55	16·45	0·4348	8·500
Sn	50	33·29	16·71	0·4320	8·430
Sb	51	34·03	16·97	0·4293	8·363
Te	52	34·76	17·24	0·4267	8·298
I	53	35·50	17·50	0·4242	8·234
Xe	54	36·24	17·76	0·4217	8·172
Cs	55	36·98	18·02	0·4193	8·112
Ba	56	37·72	18·28	0·4170	8·053
La	57	38·47	18·53	0·4146	7·996
Ce	58	39·21	18·79	0·4124	7·940
Pr	59	39·96	19·04	0·4102	7·885
Nd	60	40·71	19·29	0·4080	7·831
Il	61	41·45	19·55	0·4060	7·780
Sm	62	42·21	19·79	0·4039	7·728
Eu	63	42·95	20·05	0·4019	7·679
Gd	64	43·71	20·29	0·3999	7·630
Tb	65	44·46	20·54	0·3980	7·582
Dy	66	45·22	20·78	0·3961	7·536
Ho	67	45·98	21·02	0·3942	7·490
Er	68	46·73	21·27	0·3924	7·445
Tu	69	47·50	21·50	0·3906	7·401
Yb	70	48·25	21·75	0·3889	7·358
Lu	71	49·02	21·98	0·3871	7·316
Hf	72	49·77	22·23	0·3855	7·275
Ta	73	50·54	22·46	0·3838	7·235
W	74	51·30	22·70	0·3822	7·195
Re	75	52·08	22·92	0·3806	7·156
Os	76	52·84	23·16	0·3790	7·118
Ir	77	53·61	23·39	0·3774	7·080
Pt	78	54·37	23·63	0·3759	7·043
Au	79	55·14	23·86	0·3744	7·007
Hg	80	55·92	24·08	0·3730	6·972
Tl	81	56·69	24·31	0·3715	6·937
Pb	82	57·46	24·54	0·3701	6·903
Bi	83	58·24	24·76	0·3687	6·869
Po	84	59·01	24·99	0·3673	6·835
At	85	59·78	25·22	0·3660	6·803
Rn	86	60·56	25·44	0·3646	6·771
Fr	87	61·34	25·66	0·3633	6·739
Ra	88	62·12	25·88	0·3620	6·708
Ac	89	62·90	26·10	0·3607	6·678
Th	90	63·67	26·33	0·3595	6·648
Pa	91	64·45	26·55	0·3582	6·618
U	92	65·24	26·76	0·3570	6·589
Np	93	66·02	26·98	0·3558	6·560
Pu	94	66·80	27·20	0·3546	6·532
Am	95	67·59	27·41	0·3535	6·504
Cm	96	68·38	27·62	0·3523	6·476
Bk	97	69·17	27·83	0·3511	6·449
Cf	98	69·94	28·06	0·3500	6·423
	99	70·73	28·27	0·3489	6·396
	100	71·53	28·47	0·3478	6·370

atoms are assumed to be in their normal states. Exceptions are: C is calculated for the valence state; F, F^- and Ne data take only the exchange for $2p$ electrons into account. In the tables, Z refers to the atomic number, N is the number of electrons, and σ is the standard deviation. The formula refers to angle θ for Cu $K\alpha$ radiation, $\lambda = 1{\cdot}54$ Å. The formula was fitted in the interval $0 \le \sin\theta/\lambda \le 0{\cdot}7\times 10^8$, which actually covers slightly more than the Cu $K\alpha$ range.

The data of Table 1 are to be regarded as the best available at present. Wherever possible, they should be used in preference to the data without exchange.

In the heavy-element range, the constants can be expressed as a function of atomic number Z by means of the following equations:

$$\left.\begin{aligned} \log_{10} A &= -0{\cdot}35255+1{\cdot}10351 \log_{10} Z\,, \\ B &= Z-A\,, \\ \log_{10} a &= 0{\cdot}16672-0{\cdot}31268 \log_{10} Z\,, \\ \log_{10} b &= 1{\cdot}61276-0{\cdot}40430 \log_{10} Z\,. \end{aligned}\right\} \quad (14)$$

These values fit most of the tabulated functions with a standard deviation better than 1 %, over the Cu $K\alpha$ range, for elements with $Z > 20$. Since the Thomas–Fermi functions themselves may differ from true electron distributions by as much as 4% or more, this is ample accuracy of presentation.

Table 5. *Tabulated and calculated values of $f(\theta)$ for carbon*

$\sin\theta/\lambda$	f tabulated	f calculated	Δf
0·00	6·000	6·000	0·000
0·05	5·781	5·764	−0·017
0·10	5·188	5·141	−0·047
0·15	4·403	4·362	−0·041
0·20	3·618	3·612	−0·006
0·25	2·969	3·003	0·034
0·30	2·501	2·538	0·037
0·35	2·196	2·212	0·016
0·40	2·002	1·983	−0·019
0·50	1·762	1·707	−0·055
0·60	1·574	1·548	−0·026
0·70	1·384	1·423	0·039

The degree of fit is demonstrated in Table 5 for carbon. The variation of deviations with the angle shown in this table is typical of the other elements.

Discussion of the results

It is interesting to study the dependence of the formula constants on Z and degree of ionization. For this purpose, it is useful to plot $\log a$ and $\log b$ against $\log Z$, and also $\log A/Z$ against $\log Z$. Although there are indications of regularities with position in the periodic table, the results are disappointing. The probable reason lies in the present low accuracy of available calculations of atomic scattering factors and wave functions. This can be seen in the large differences between constants fitted to different calculations for the same element. In spite of such differences, the constants themselves must be calculated and used with a sufficient number of digits in order to obtain good fit with the tabulated values. This is the reason why some of our values were carried to four digits.

Suggested method of computation of the exponential functions on digital computers

The terms of the Gaussian expansion, as well as the expression for the temperature factor, are functions of $\sin^2\theta$. Let $y = \sin^2\theta$. Then it is comparatively easy to rearrange all the data, for example by sorting punched cards in order of increasing y. If any function of the form $f(y) = A \exp(ay)$ is to be evaluated, use can be made of the property

$$f(y+\Delta y) = f(y).\exp(a.\Delta y)\,, \qquad (15)$$

where $f(y)$ is read from the preceding card. Then Δy is, as a rule, small throughout the calculation; and if it is not small, it can be effectively reduced by bridging larger gaps with dummy cards. Expansion of the exponential part into a series can then be made, and all but the first two or at most three terms neglected. If all Δy are smaller than 0·05, let us say, one can use

$$f(y+\Delta y) = f(y)+f(y).a.\Delta y \qquad (16)$$

with very little error.

The case is especially simple when it is required to tabulate $f(y)$ over equal intervals of y, even when Δy is large. Then we can write

$$\exp(a.\Delta y) = 1+\alpha\,, \qquad (17)$$

where α is a numerical constant which can be accurately calculated from

$$\alpha = 1-\exp(a.\Delta y)\,. \qquad (18)$$

Then

$$f(y+\Delta y) = f(y)+\alpha.f(y)\,, \qquad (19)$$

which is a recurrence formula involving one multiplication and one addition only, with great saving of machine time compared to the time required for a full series calculation. Care is to be taken to avoid accumulation of rounding-off errors, especially when Δy is small.

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