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Analytic Approximations for the Incoherent X-ray Intensities of the Atoms from Ca to Am

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Two analogue analytic functions containing three parameters and valid for the atoms $Z \geq 20$ have been found, for accurately approximating both the well-known universal Bewilogua function and the atomic incoherent intensities computed by Cromer. The errors of the fits are not greater than the corresponding ones for the coherent intensities.

During the last decade, calculated form factors and incoherent intensities of atoms have been published in dozens of papers. The calculations are based on different atomic models (Thomas & Umeda, 1957; Cromer, Larson & Waber, 1964; Hanson, Herman, Lee & Skilman, 1964; Cromer & Waber, 1965; Tavard, Nicolas & Rouault, 1967; Cromer & Mann, 1968; Doyle & Turner, 1968; Freeman, 1959, 1960, 1962; Cromer, 1967, 1969; Pohler & Hanson, 1965; Moore, 1963; Pakes & Lee, 1969). All form factors have been approximated by an analytic function $s = \sin\theta/\lambda$.

The functions used for this purpose are superimpositions of Gaussians usually containing 9 parameters:

$$f(s) = \sum_{i=1}^{4} A_i \exp(-B_i s^2) + C\,. \tag{1}$$

On the other hand, the incoherent scattered intensities have been analytically approximated only for a minor proportion of the atoms. The Heisenberg–Bewilogua function (Bewilogua, 1931) which is based on the Thomas–Fermi statistical model of the atom has been well approximated analytically by Tietz (1959).

The incoherent intensities calculated by Tavard, Nicholas & Rouault (1967) with HF-SCF wave functions based on the complete Waller–Hartree theory have been fitted analytically by Hajdu (1971, 1972) for the atoms of atomic numbers 2 to 36 and for the H_2O molecule. The analytic function of Hajdu has the form

$$I_{\text{inc}}(s) = \left[Z - \frac{I_{\text{coh}}(s)}{Z}\right] \times \{1 - M[\exp(-Ks) - \exp(-Ls)]\}\,. \tag{2}$$

This function contains 12 parameters, parameters of equation (1) being included through $f(s)$. The values of the M, K, L parameters are not independent of the form factors used in the first factor of the expression. Earlier attempts at approximating the incoherent intensities are of a relatively low accuracy.

The present author endeavoured to find an analytic approximation for the atoms of higher atomic numbers, based on the tables of Cromer (1967, 1969) which for the time being can be regarded as the most accurate ones. As a first step the Bewilogua function was approximated by the following simple expression containing three parameters:

$$S_0^2 = 1 - \frac{a}{(1 + b^* w)^c} \tag{3}$$

where w is the universal scattering variable,

$$w = \frac{0.176}{Z^{2/3}} (4\pi/\lambda) \sin\theta,$$

and Z the atomic number.

The universal parameters calculated by the least squares method are the following:

$$a = 0.9200$$
$$b^* = 2.7769$$
$$c = 2.3266\,.$$

In Table 1 the S_0^2 values calculated by (3) are compared with those of Bewilogua and of Tietz. The standard deviation of this fit is

$$\sigma = \sqrt{\frac{\sum_i^n \delta_i^2}{n-1}} = 0.003$$

where the δ_i's are the deviations and index i refers to the points where tabulated values of Bewilogua's S_0^2 function were found.

Table 1. *Comparison of Bewilogua's numerical values for the incoherent scattering function S_0^2, the analytical values of Tietz and those calculated from the present analytical fit*

w	Bewilogua	Tietz	Present
0·0	0·0	0·0	0·134
0·025	0·199	0·198	0·206
0·05	0·319	0·308	0·320
0·10	0·486	0·459	0·480
0·20	0·674	0·646	0·672
0·30	0·776	0·761	0·776
0·40	0·839	0·839	0·838
0·50	0·880	0·893	0·884
0·60	0·904	0·931	0·906
0·80	0·944	0·977	0·950

Instead of the universal scattering variable w, we can choose s as independent variable for expression (3). We obtain then

$$I_{\text{inc}}(s) = Z\left(1 - \frac{a}{(1 + bs/Z^{2/3})^c}\right) \tag{4}$$

with

$$b = 0{\cdot}176\,.\,4\pi\,.\,b^*.$$

Since in the case of atoms of higher atomic number, the values of $Z.S_0^2$ are not far from the incoherent intensities calculated by the complete Waller–Hartree theory, Cromer's tables have been approximated by the similar expression,

$$I_{\text{inc}}(s) = Z\left[1 - \frac{a}{(1 + bs)^c}\right], \tag{5}$$

with individual atomic parameters a, b and c. The values of a, b and c are found by minimizing the expression

$$\sum_i s_i \delta_i^2$$

in the range $0 \le s \le 1{\cdot}5$.

The percentage errors of the fits are computed as

$$\varepsilon = \frac{100}{I_{\text{inc}}(1{\cdot}5)} \sqrt{\frac{\sum_i s_i \delta_i^2}{\sum_i s_i}} \tag{6}$$

The numerical values of the atomic parameters and the percentage errors for the atoms with $Z = 20$ to 95 are presented in Table 3. In Table 2 we give a comparison between calculated and tabulated data for the atoms Mn($Z = 25$) and U($Z = 92$) as examples with low and high atomic numbers.

Table 2. *Comparison of calculated and tabulated incoherent scattered X-ray intensities*

	Mn		U	
s	I_{cal}	I_{tab}	I_{cal}	I_{tab}
0·05	0·775	1·100	2·116	2·484
0·10	2·725	2·950	5·704	5·888
0·15	4·450	4·425	9·108	9·108
0·20	6·000	5·800	12·236	12·328
0·30	8·625	8·375	17·940	18·216
0·40	10·750	10·600	23·000	23·184
0·50	12·525	12·475	27·508	27·324
0·60	13·975	14·050	31·556	31·188
0·70	15·200	15·360	35·144	34·868
0·80	16·250	16·375	38·364	38·272
0·90	17·150	17·200	41·400	41·400
1·00	17·900	17·900	44·068	44·252
1·50	20·500	20·400	54·556	54·556

Discussion

Two alternatives are given for approximating the incoherent intensities of the atoms from $Z = 20$ through $Z = 95$. If the accuracy of Bewilogua's S_0^2 function (*i.e.* the TF model) is satisfactory, expression (4) can be

Table 3. *Parameters of the analytic fit for incoherent scattered X-ray intensities*

	Z	a	b	c	ε (%)
Ca	20	1·0236	0·9920	2·0323	0·7359
Sc	21	1·0341	1·0296	1·9649	0·6509
Ti	22	1·0442	1·0353	1·9409	0·5256
V	23	1·0521	0·9853	1·9886	0·5089
Cr	24	1·0734	0·8718	2·1680	0·6360
Mn	25	1·0573	0·7681	2·3091	0·6080
Fe	26	1·0651	0·7266	2·3802	0·6496
Co	27	1·0616	0·6362	2·5858	0·6956
Ni	28	1·0611	0·5531	2·8291	0·7491
Cu	29	1·0725	0·4717	3·1712	0·8343
Zn	30	1·0645	0·4452	3·2257	0·7814
Ga	31	1·0519	0·3973	3·4367	0·6881
Ge	32	1·0433	0·3688	3·5689	0·5162
As	33	1·0347	0·3415	3·7012	0·3443
Se	34	1·0283	0·3363	3·6680	0·2933
Br	35	1·0194	0·3097	3·8499	0·9539
Kr	36	1·0260	0·3607	3·3364	0·8083
Rb	37	1·0181	0·4202	2·8793	0·4546
Sr	38	1·0049	0·4189	2·8152	0·4523
Y	39	1·0050	0·4680	2·5423	0·4748
Zr	40	1·0084	0·5275	2·2926	0·4667
Nb	41	1·0267	0·6247	2·0235	0·4389
Mo	42	1·0340	0·6650	1·9265	0·4220
Tc	43	1·0283	0·6626	1·9069	0·3510
Ru	44	1·0431	0·7297	1·7839	0·4046
Rh	45	1·0470	0·7262	1·7848	0·4350
Pd	46	1·0592	0·7298	1·7869	0·5942
Ag	47	1·0549	0·6874	1·8487	0·6466
Cd	48	1·0487	0·6463	1·9123	0·6926
In	49	1·0412	0·5995	1·9979	0·6524
Sn	50	1·0367	0·5778	2·0339	0·5848
Sb	51	1·0343	0·5814	2·0016	0·5300
Te	52	1·0311	0·5793	1·9881	0·4999
I	53	1·0339	0·6365	1·8413	0·5035
Xe	54	1·0281	0·5886	1·9339	0·4667
Cs	55	1·0188	0·5679	1·9573	0·4290
Ba	56	1·0107	0·5510	1·9746	0·4361
La	57	1·0186	0·6951	1·6480	0·5863
Ce	58	1·0093	0·5537	1·9453	0·5024
Pr	59	1·0093	0·4739	2·1660	0·4445
Nd	60	1·0062	0·4132	2·3996	0·4714
Pm	61	1·0088	0·4082	2·4005	0·4568
Sm	62	1·0093	0·4013	2·4015	0·4613
Eu	63	1·0096	0·3945	2·4022	0·5264
Gd	64	1·0095	0·3913	2·4021	0·5461
Tb	65	1·0099	0·3858	2·4023	0·4928
Dy	66	1·0108	0·3792	2·4020	0·5107
Ho	67	1·0179	0·3791	2·4024	0·5215
Er	68	1·0116	0·3681	2·4020	0·5686
Tm	69	1·0124	0·3608	2·4147	0·5232
Yb	70	1·0146	0·3582	2·3999	0·5828
Lu	71	1·0120	0·3532	2·3993	0·4951
Hf	72	1·0126	0·3512	2·3990	0·4468
Ta	73	1·0131	0·3488	2·3987	0·4336
W	74	1·0131	0·3453	2·3983	0·4591
Re	75	1·0237	0·4417	1·9654	0·4015
Os	76	1·0249	0·4568	1·9049	0·4174
Ir	77	1·0273	0·4772	1·8335	0·3849
Pt	78	1·0354	0·5168	1·7275	0·4680
Au	79	1·0431	0·5814	1·5789	0·5306
Hg	80	1·0361	0·5293	1·6803	0·5130
Tl	81	1·0339	0·5341	1·6544	0·5149
Pb	82	1·0315	0·5297	1·6537	0·4979
Bi	83	1·0298	0·5477	1·6001	0·4606
Po	84	1·0287	0·5567	1·5709	0·4396
At	85	1·0298	0·5963	1·4861	0·4243
Rn	86	1·0275	0·5923	1·4856	0·3928
Fr	87	1·0216	0·5679	1·5185	0·3876
Ra	88	1·0146	0·5454	1·5502	0·3646

Table 3 (*cont.*)

	Z	a	b	c	ε (%)
Ac	89	1·0137	0·5648	1·5024	0·3088
Th	90	1·0110	0·5655	1·4917	0·3069
Pa	91	1·0135	0·5479	1·5279	0·3102
U	92	1·0184	0·5884	1·4479	0·3423
Np	93	1·0161	0·5407	1·5358	0·2950
Pu	94	1·0150	0·4812	1·6715	0·3230
Am	95	1·0162	0·4605	1·7288	0·3042

used with universal parameters, independently of the atomic species. The accurate values of Cromer (calculated from HF–SCF wave functions, based on the complete W–H theory) can be approximated by the analogue expression (5) with the individual parameters tabulated in Table 3. Neither of the fits depends on the atomic form factors.

As to the mean errors of the latter fits, they are of the same order of magnitude as those of the squares of the published analytic fits for the form factors. Thus both the coherent and the incoherent terms contribute equally to the error of the total scattered intensities. Weighting of the deviations by s was meant to enhance the accuracy of the fit with growing s in order to keep the error of the approximated total scattered intensities on a standard level.

The limiting value of the analytic expression for $s=0$ is $1-a$. It is seen from Table 3 that the parameter a is by 0·5–6% over unity. Although fixing it as $\equiv 1$ would result in zero for $I_{\rm inc}(0)$, the remaining two parameters would yield a poorer fit. From Table 2, it is seen that the fit is not very good below $s=0·1$. This inaccuracy is not significant for total scattered X-ray intensities, the contribution of the incoherent part being negligible in this range. However, the same cannot be stated of electron scattering, and therefore the use of our formula for deriving differential inelastic electron scattering factors in this range would lead to insufficient results.

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X-Ray Diffraction Profiles of Defective Layered Lattices Showing Preferred Orientation

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In layered lattices the layers tend to stratify and the stratified layer domains often exhibit preferred orientation in bulk samples. Using the Laplace and Hankel transform techniques, equations have been developed for the profiles of the two-dimensional (hk) reflections from defective layered lattices in different orientation modes. Two different approaches have been used in the derivation, the inter-atomic distance sum method and the lattice sum method, and the results have been compared.

Introduction

In explaining the linewidths of diffraction patterns, the concept of coherently scattering crystallites as domains has been found to be convenient. The particle size concept has been well entrenched in spite of recognition (Warren, 1959) that the materials studied in most instances are not fragmented into small separate par-