$b \simeq c \simeq 5{\cdot}7$ Å) (Landolt–Börnstein, 1969). Neither space group is a subgroup of the other, however, both are subgroups of $Pm3m$-O_h^1 which is also the space group of $BaTiO_3$ at high temperature. Thus the relevant group–subgroup relationships are $Pm3m \rightarrow R3m$ and $Pm3m \rightarrow Amm2$. Both, $R3m$ and $Amm2$ are translationengleiche (though not maximal) subgroups of $Pm3m$ and therefore only twin domains and no antiphase domains are allowed in the $R3m$ and $Amm2$ forms of $BaTiO_3$.

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Analytic Approximations for the Incoherent X-ray and Electron Intensities of Light Atoms and Ions

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It has been found that the incoherent scattered X-ray and electron intensities of light atoms, with 2 to 18 electrons, and of light ions, with 2 to 28 electrons, can be accurately approximated by an analytical formula containing six parameters.

The incoherent intensities of the first 36 atoms calculated by Tavard, Nicolas & Rouault (1967) have been fitted analytically by Hajdu (1971, 1972), those of the atoms of higher atomic numbers (from Ca to Am) were approximated by Pálinkás (1973) with the numerical values of Cromer (1967, 1969).

In these works, the validity of the approximations had been tested in the scattering-variable range available for X-ray diffraction, $0 \le s = \sin\theta/\lambda \le 1{\cdot}5$ Å^{-1}.

In the present paper, a new analytical expression with six parameters is proposed for similar purposes. Its applicability is demonstrated in two somewhat different domains:

(1) for light atoms of atomic numbers 2 to 18 over a wide range of the scattering variable: $0 \le s \le 4{\cdot}0$ Å^{-1},

(2) for all the ions ($2 < Z \le 30$) for which numerical incoherent-intensity tables were available. The scattering-variable range of these published tables extends to $s = 1{\cdot}1$ Å^{-1}, so the fit could not be checked beyond this limit in the case of the ions.

We endeavoured to find an approximating formula with good analytic behaviour. By the use of such a function, physical quantities determined by the incoherent scattering function, *e.g.* the exchange energy, and the contribution to the electron–electron correlation function (Bartell & Gavin, 1964), can also be expressed analytically.

We have found that an expression meeting these conditions and yielding a good approximation can be composed of terms similar to the function describing the incoherent scattering of the hydrogen atom:

$$I_i^x(S)/I_T \equiv S(s) = N\left[1 - \sum_{l=1}^{3} \frac{\gamma_l}{(1+\lambda_l s^2)^n}\right] \tag{1}$$

where $I_i^x(s)$ is the X-ray incoherent intensity, I_T is the Thomson formula, N is the number of electrons of the atom or the ion, γ_l and λ_l are independent parameters, and the power n of the denominator is 4 in the case of atoms and ions with $2 < Z \leq 20$, and $n=1$ for the ions with $21 \leq Z \leq 29$.*

The parameters γ_l and λ_l have been determined by a least-squares program, fitting the formula to the tabulated numerical intensities, *i.e.* the expression

$$\sum_{i=1}^{M} \delta_i^2 = \sum_{i=1}^{M} [S_{\text{fit}}(s_i) - S_{\text{tab}}(s_i)]^2$$

was minimized where i refers to the discrete $\sin\theta/\lambda$ points and M is the number of tabulated values.

The goodness of the fits is characterized in our tables by the percentage error defined as

$$\varepsilon = \frac{100}{S(s_M)} \sqrt{\frac{\sum_{i=1}^{M} \delta_i^2}{M-1}}. \tag{2}$$

Since the incoherent scattered electron intensities can be expressed – within the validity range of the first Born approximation – in terms of the corresponding X-ray intensity function (Morse, 1932), incoherent scattered electron intensities can also be expressed from (1) as

$$I_i^e = \frac{4}{a_0^2} \frac{S(s)}{(4\pi s)^4} \tag{3}$$

where a_0 is the Bohr radius.

Light neutral atoms with atomic number 2 to 18

Incoherent scattering functions of the atoms have been determined by Cromer (1967, 1969), based on the Waller–Hartree theory with the use of the numerical HF SCF wave functions of Mann (1967). On the basis of Cromer's tables we have obtained a good analytic fit for the atoms with 2 to 18 electrons by applying equation (1) with $n=4$. Table 1 contains the parameter values and the errors.

The accuracy of the calculations has been checked by a sum-rule procedure. It is known that the exchange-energy term of the two-particle potential energy of the scatterer is related to the incoherent scattering function in the following way (Bartell & Gavin, 1964);

$$\frac{1}{\pi}\int_0^\infty [S(s) - N]\,\mathrm{d}s = \left\langle \frac{1}{r_{12}} \right\rangle_{\text{exch}}. \tag{4}$$

Table 1. *Parameters* ($\times 10^4$) *of the analytic fits of* $S(s)$ *for atoms with electrons* 2 *to* 18

$n=4$, $s_{\max}=4$.

	N	γ_1	γ_2	γ_3	λ_1	λ_2	λ_3	ε
He	2	3	7675	2321	940858	49201	24780	170
Li	3	3506	901	5603	683877	15197	15196	2066
Be	4	5180	0	4846	327829	104297	7693	2331
B	5	4755	1304	3949	157768	157767	4762	902
C	6	6437	198	3366	88239	375057	3258	289
N	7	5756	1287	2958	47646	145022	2380	229
O	8	6274	1106	2622	34741	120632	1799	323
F	9	6532	1106	2362	25790	98417	1407	377
Ne	10	6421	1401	2179	18597	74088	1142	642
Na	11	6734	1146	2113	15725	586116	988	1510
Mg	12	6204	1869	1930	11669	433911	805	1061
Al	13	5745	2462	1788	9041	275293	675	615
Si	14	5351	2953	1686	7281	187721	580	818
P	15	5022	3320	1630	6118	130332	516	2056
S	16	4711	3726	1529	5049	98381	447	2203
Cl	17	4441	4078	1443	4242	76636	391	2336
Ar	18	4215	4339	1400	3703	60187	352	2975

Since (1) is analytically integrable we obtain simply

$$\left\langle \frac{1}{r_{12}} \right\rangle_{\text{exch}} = N\tfrac{5}{8}\pi a_0 \sum_{l=1}^{3} \frac{\gamma_l}{\sqrt{\lambda_l}}. \tag{5}$$

The exchange energies determined by the expression (5), and the corresponding HF SCF values (Kim & Gordon, 1974) are compared for a few atoms in Table 2.

Table 2. *Exchange energy values* (a.u.) *determined by the sum-rule procedure* (*SR*) *and calculated on the basis of the HF SCF atomic model*

	Z	SR	HF SCF
He	2	1·0256	1·0387
B	5	3·7961	3·822
N	7	6·6743	6·742
Ne	10	12·125	12·60
Ar	18	30·21	30·09

Ions with atomic numbers 3 to 30

It has been found that better fits could be attained by separating the ions in two groups for which power n in (1) was fixed differently. For the ions with $2 < Z \leq 20$, $n=4$, for those with $21 \leq Z \leq 29$, $n=1$ proved to be optimal.

Numerical values of the incoherent intensities of ions with $2 < Z \leq 20$ have been taken from the *International Tables for X-ray Crystallography* (1962) and those for $Z > 20$ from the paper of Freeman & Watson (1961).

Tables 3 and 4 show the best parameters found for the two groups of ions and the percentage errors of the fits. The exchange energies as calculated from the analytic expression, contain a certain error especially in the case of heavy ions, probably because the fit is poorer in the range above $s > 1{\cdot}1$ Å^{-1}.

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* For Zn^{2+} ($Z=30$) the better fit was obtained with $n=4$.

Table 3. *Parameters* ($\times 10^4$) *of the analytic fits of* $S(s)$ *for ions with atomic numbers* 3 *to* 20

$n=4$, $s_{\max}=1\cdot1$.

	N	γ_1	γ_2	γ_3	λ_1	λ_2	λ_3	ε
Li^+	2	55	7881	2066	2522	14692	23912	216
N^-	8	2396	3790	3801	2161	141843	37312	3231
O^-	9	2275	1777	5948	1714	189366	36593	97
O^+	7	2815	0	7201	1624	71049	34317	1921
F^-	10	2340	1440	6226	1643	168860	29172	2587
Na^+	10	2144	1189	6667	877	46793	13597	303
Al^+	12	2016	1868	6115	771	244040	9016	752
Al^{3+}	10	2176	887	6939	619	24640	8341	163
Si^{3+}	11	2027	1148	6827	526	125242	7047	575
Si^{4+}	10	2360	428	7217	608	23663	7248	460
Cl^-	18	4794	1956	3249	2152	186392	37255	2404
K^+	18	4831	1515	3654	1629	93534	25374	812
Ca^+	19	4677	1025	4298	1472	308314	25169	623
Ca^{2+}	18	4866	1236	3889	1444	78304	22023	295
Zn^{2+}	28	3291	1728	4981	540	43480	6047	123

Table 4. *Parameters* ($\times 10^4$) *of the analytic fits of* $S(s)$ *for ions with atomic numbers* 21 *to* 29

$n=1$, $s_{\max}=1\cdot1$.

	N	γ_1	γ_2	γ_3	λ_1	λ_2	λ_3	ε
Sc^+	20	3299	862	5842	5255	752363	90092	1664
Sc^{2+}	19	3653	251	6097	5632	646734	98386	1625
Sc^{3+}	18	3836	595	5578	5467	95597	95603	1864
Ti^+	21	2778	1346	5880	3892	500096	65939	1473
Ti^{2+}	20	3051	689	6266	4105	499864	71796	1296
Ti^{3+}	19	3458	754	5787	4593	169794	75246	1093
V^+	22	2265	1809	5931	2656	365028	48736	954
V^{2+}	21	2536	1727	5740	3037	229996	49774	1085
V^{3+}	20	2962	1239	5801	3592	172320	56594	862
Cr^+	23	1898	1940	6166	1875	322099	39741	839
Cr^{2+}	22	2112	2144	5748	2184	194745	38349	699
Cr^{3+}	21	2429	2058	5516	2553	141207	40721	626
Mn^+	24	1433	2259	6312	682	271435	31573	899
Mn^{2+}	23	1651	2340	6012	1245	175694	30415	592
Mn^{3+}	22	1850	2724	5428	1468	119970	30747	541
Fe^+	25	1160	2360	6484	0	246356	37247	683
Fe^{2+}	24	1242	2663	6096	264	152252	24820	467
Fe^{3+}	23	1271	3390	5340	382	98740	20773	478
Co^+	26	1080	2341	6583	0	233854	25106	776
Co^{2+}	25	1116	2588	6299	55	147509	23001	509
Co^{3+}	24	1273	3040	5688	495	99993	21071	262
Ni^+	27	989	2366	6641	0	216858	22660	875
Ni^{2+}	26	2794	2624	4558	4781	124559	29215	2046
Ni^{3+}	25	1893	2960	5147	2587	93298	22446	1130
Cu^+	28	862	2481	6660	23	193041	19928	1080
Cu^{2+}	27	3053	619	6342	4678	668242	40843	2830
Cu^{3+}	26	3001	717	6289	4284	207931	37378	1719

Discussion

We have given an expression of good analytic behaviour for the approximation of incoherent X-ray and electron intensities of light atoms and ions. For the first 18 atoms this approximation is more accurate than the previous ones, and fits the numerical values uniformly over a wide range of the scattering variable.

For the ions, accurate approximations of the incoherent X-ray intensities have not been published up to the present. The present work is primarily intended for use in X-ray and electron diffraction studies on ionic solutions.

In both cases the mean errors are of the same order of magnitude, or even smaller than those of the fits of the corresponding coherent intensities.

Note: Two papers have been published meanwhile on the analytic approximation for the incoherent scattering function of atoms (Smith, Thakkar & Chapman, 1975; Balyuzi, 1975). The merit of the first one is to give an analytic formula of correct asymptotic behaviour, approximating the incoherent scattering functions of atoms over a wide s range. It is easy to show, that our analytic expression (1) has also a correct asymptotic behaviour at both high and low values of s. It can be verified, by comparing the corresponding percentage errors (ε) pertaining to atoms common in both papers, that the present approximation is a better fit. The approximating formula, however, referred to in the second paper is valid only up to $s=1\cdot5$, and its asymptotic behaviour is not correct. Standard deviations given by the author have to be treated with criticism because they relate to the function $Z-I_{\text{inc}}(s)$ instead of the incoherent intensities themselves. Having converted them to the suitable form, we could establish that the percentage errors (ε) in the range $0 \le s \le 1\cdot5$ were similar to ours.

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