Revised Parameters of the Analytic Fits for Coherent and Incoherent Scattered X-Ray Intensities of the First 36 Atoms

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Analytical parameters have been recalculated for atomic scattering factors and incoherent scattered intensities of the elements of atomic numbers 2 to 36, based on the tables of Tavard, Nicolas & Rouault [*J. Chim. Phys.* (1967), **64**, 540]. The fit has also been checked with the total scattered intensities.

It has been shown in a previous paper (Hajdu, 1971) that the incoherent scattered intensity functions of the atoms can be approximated with high accuracy by an analytic function of s ($=\sin\theta/\lambda$) containing three individual 'atomic' parameters, assuming that the coherent scattered intensities are already known as functions of s. The coherent intensities, on their part, can also be obtained by the use of one of the known analytic fits, *e.g.* the nine-parameter fit of Cromer & Waber (1965) for the atomic scattering factors. Combining both approximating functions, we obtain a twelve-parameter fit for the incoherent intensities.

In calculating the approximations published in the previous paper, the three new parameters for the atoms 2 to 35 have been fitted to the *Incoherent Intensity Tables* of Tavard, Nicolas & Rouault (1967); the nine parameters for the coherent atomic scattering factors, however, had been taken over unchanged from the work of Cromer & Waber (1965).

In the work reported here, all parameters of both sets of approximating functions have been recalculated for the atoms 2 to 36 and the water molecule, fitting them uniformly to the coherent scattering factors and the incoherent intensities tabulated in the quoted work of Tavard *et al.* (1967), and in an unpublished table of Tavard on the molecular scattering functions of the H$_2$O molecule respectively (Tavard, 1970). [The data of this table have been used in graphical form by Tavard in his monograph (1966).]

There were at least two reasons for carrying out these calculations: firstly, there are considerable deviations between the tabulated atomic scattering factors of Tavard *et al.* on one hand and Cromer & Waber on the other; secondly, Tavard's tabulated atomic scattering factors and incoherent intensities were calculated on a uniform basis with the method of Waller & Hartree, and Clementi's wave functions. This ensures certain homogeneity of the data, which may be expected to lead to the most reliable values for the total scattered intensities.

The values of the parameters, together with standard deviations of the fits, are given in Tables 1 and 2, both of which include the atoms from He to Kr and

the H$_2$O molecule. (The hydrogen atom has not been included because of the existence of simple and theoretically exact expressions for its scattered intensities.) Table 2 contains, in addition, the mean errors of the total scattered intensities calculated by suitably summing up the two approximating functions.

With the aid of the parameters given in Tables 1 and 2, the respective scattering values of the atoms at any value of s can be calculated according to the following equations:
the coherent scattering factor

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

the coherent scattered intensity

$$I_{coh}(s) = [f(s)]^2; \tag{2}$$

the incoherent scattered intensity

$$I_{inc}(s) = \left[Z - \frac{I_{coh}(s)}{Z}\right]$$
$$\times \{1 - M[\exp(-Ks) - \exp(-Ls)]\}^* \tag{3}$$

where Z is the atomic number;
the total scattered intensity

$$I_{tot}(s) = I_{coh}(s) + I_{inc}(s). \tag{4}$$

In determining the parameters, functions (1) and (2) were fitted to the corresponding tabulated data at the same 21 s values in the range $0 \le s \le 1\cdot20$ for all atoms involved using the weighting factors

$$w(s) = \exp[-(s-0\cdot5)^2] \tag{5}$$

and

$$w'(s) = s \tag{6}$$

in the cases of coherent and incoherent scattering respectively. The same weighting factors were used in defining the mean errors as

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* In order to obtain relativistically corrected values for I_{inc}, expression (3) must be multiplied by the Breit-Dirac factor $R^{-3}(s)$ which is independent of the atomic species.

$$\varepsilon_1 = \frac{100}{f(0)} \left[\frac{\sum w_j \delta_j^2}{\sum w_j} \right]^{1/2} \qquad (7)$$

for the coherent scattering factor, and

$$\varepsilon_2 = \frac{100}{I_{inc}(1\cdot 2)} \left[\frac{\sum s_j \delta_j^2}{\sum s_j} \right]^{1/2} \qquad (8)$$

for the incoherent scattered intensity, the latter being slightly different from that in the previous paper. In equations (7) and (8), δ_j denotes the difference between the tabulated and calculated values for s_j, and $j = 1, 2, \ldots, 21$. Both ε_1 and ε_2 are given as percentages of the maximum value of the respective function.

The total intensities as calculated by the expression (4) have been compared with those computed from Tavard's Tables. Here, the mean error is defined as

$$\sigma = \left[\frac{\sum \delta_j^2}{21} \right]^{1/2} \qquad (9)$$

for division by $I_{tot}(0) = Z^2$ would lead to misleadingly low values. Table 3 is given as an illustration of the accuracy of the fits in the example of the oxygen atom.

Discussion of the results

(a) The mean errors ε_1 of the coherent scattering factors are in most cases somewhat higher than the ε values of Cromer & Waber (1965). This is probably owing to a lower efficiency of our least-squares algorithm. Our mean errors are nevertheless lower by one or two

orders of magnitude than the significant deviations between the original Tables of Tavard and those of Cromer.

(b) The ε_2 errors of the incoherent intensities are

Table 2. *Parameters of the analytic fit for incoherent scattered X-ray intensities*

	Z	M	K	L	EPS2	SIGMA
HE	2	0.0000	0.0000	0.0000	0.0541	0.0017
LI	3	1.7499	6.0432	9.5111	0.5448	0.0203
BE	4	1.6731	4.0244	6.0303	0.8082	0.0567
B	5	1.5147	3.1522	4.7893	0.1983	0.0312
C	6	0.4972	1.8438	7.8917	0.5367	0.0942
N	7	0.4098	1.4312	16.1978	0.3333	0.0316
O	8	0.3933	1.2843	32.6820	0.2592	0.0351
F	9	0.4174	1.2724	100.0000	0.5003	0.0562
NE	10	0.4634	1.3013	22.8010	0.5575	0.0516
NA	11	0.4934	1.2928	22.5601	0.5182	0.2858
MG	12	0.5189	1.2756	15.3134	0.5021	0.1130
AL	13	0.5268	1.2263	13.9320	0.3155	0.0880
SI	14	0.5254	1.1646	14.3259	0.1944	0.1399
P	15	0.5247	1.1132	17.0741	0.1249	0.2292
S	16	0.5222	1.0651	16.2889	0.1308	0.1533
CL	17	0.5206	1.0239	17.4444	0.1326	0.1798
AR	18	0.5302	1.0091	19.3321	0.2733	0.2656
K	19	0.5265	0.9717	19.6124	0.2298	0.7782
CA	20	0.5207	0.9320	18.1120	0.2620	0.4416
SC	21	0.5344	0.9346	16.8772	0.2929	0.3903
TI	22	0.5537	0.9452	15.6860	0.3508	0.3159
V	23	0.5759	0.9562	14.1234	0.3380	0.2065
CR	24	0.6000	0.9660	12.6326	0.3436	0.4653
MN	25	0.6272	0.9745	11.4062	0.3179	0.2427
FE	26	0.6414	0.9673	10.4405	0.3010	0.2649
CO	27	0.6154	0.8554	11.2260	0.3673	0.3650
NI	28	0.6738	0.9568	9.1335	0.2586	0.3302
CU	29	0.7122	0.9754	7.9780	0.3050	0.7623
ZN	30	0.7089	0.9377	7.9938	0.2772	0.5142
GA	31	0.6962	0.8898	8.1258	0.3916	0.4554
GE	32	0.6722	0.8278	8.6616	0.5438	0.4329
AS	33	0.6440	0.7624	9.9541	0.6583	0.4606
SE	34	0.6243	0.7117	10.6790	0.6478	0.5203
BR	35	0.6054	0.6640	12.1270	0.6123	0.5303
KR	36	0.5914	0.6269	14.8986	0.5079	0.4518
H2O	10	0.4296	1.6246	35.6472	0.9311	0.0914

Table 1. *Parameters of the analytic fit for atomic scattering factors*

	Z	A1	B1	A2	B2	A3	B3	A4	B4	C	EPS1
HE	2	0.1440	1.0083	0.7428	3.4564	0.7326	9.6977	0.3616	20.1280	0.0176	0.0670
LI	3	0.8488	1.1522	1.0590	4.3791	-0.2016	50.0710	1.2398	100.2600	0.0408	0.2089
BE	4	0.6514	0.6613	1.1166	1.9686	1.7812	49.3580	0.3164	100.0200	0.1294	0.1568
B	5	0.4131	0.6535	1.2097	0.9048	1.6086	20.1680	1.5661	50.5530	0.1987	0.0685
C	6	1.8563	0.4124	1.5280	10.0750	0.3173	20.3260	2.3965	30.7790	-0.1096	0.1461
N	7	1.0911	0.4770	0.2427	0.9099	2.4053	8.3907	2.7634	23.1130	0.4843	0.1301
O	8	1.3721	0.3870	2.0624	5.5416	3.0566	12.3320	1.0743	29.8800	0.4348	0.0400
F	9	1.3631	0.3012	2.6891	4.3402	3.3944	10.2547	1.1184	25.0341	0.4350	0.0310
NE	10	1.3212	1.1983	2.4951	4.4092	3.3219	7.3281	1.6841	18.7040	1.1773	0.0256
NA	11	1.9290	0.8307	4.1307	4.3690	2.7662	7.5375	1.2304	99.9568	0.9093	0.1704
MG	12	1.7214	0.5091	6.1695	3.4069	1.1777	9.9868	2.1435	80.4922	0.7801	0.0533
AL	13	2.3913	0.9131	5.9946	3.2803	2.1082	40.1807	1.3645	99.5953	1.1433	0.0317
SI	14	3.7464	1.3104	4.2959	2.8652	3.5786	36.3701	0.9544	97.9643	1.4345	0.0482
P	15	5.6374	1.4781	2.2092	2.4033	4.3964	28.6581	1.2380	67.9750	1.6249	0.0952
S	16	1.5484	0.5962	6.3527	1.5137	5.4342	22.8347	1.3629	59.5705	1.3096	0.0415
CL	17	2.6986	0.5643	5.3371	1.3294	6.3451	18.6911	1.5618	49.8626	1.0660	0.0451
AR	18	5.9435	0.7504	1.8388	0.9840	4.7067	11.9723	4.5353	27.3922	0.9665	0.0688
K	19	7.2013	0.8858	8.9378	14.1870	-1.4157	50.7998	2.3835	101.6003	1.8417	0.1369
CA	20	7.1869	0.7073	8.7943	10.7679	-0.7680	50.2482	3.1336	100.6352	1.6283	0.0800
SC	21	6.9762	0.6476	9.2947	9.3204	0.4098	49.8866	2.4814	100.8591	1.8101	0.0644
TI	22	6.6289	0.6365	9.9142	8.2781	1.0215	39.7076	2.2186	100.4239	2.2032	0.0521
V	23	7.0016	0.4781	10.2130	6.8858	2.0230	24.3886	2.1696	100.0569	1.5907	0.0248
CR	24	6.2129	0.5502	10.4380	6.2040	2.6521	19.1178	2.1659	99.6437	2.5393	0.0548
MN	25	6.3256	0.4707	11.2801	5.5442	2.7367	17.0717	2.3197	82.4396	2.3300	0.0264
FE	26	6.7127	0.3756	12.0760	4.9535	3.2058	16.7354	2.1868	81.5166	1.8157	0.0316
CO	27	5.7126	0.4535	12.1740	4.4345	3.7866	13.3870	2.3940	70.7430	2.9223	0.0354
NI	28	6.9130	0.3326	13.5648	4.2322	3.5796	14.7259	2.1748	72.0905	1.7611	0.0325
CU	29	6.0244	0.3595	13.2935	3.7182	5.3316	11.2861	1.7341	61.2610	2.5887	0.0540
ZN	30	5.1852	0.6660	14.1138	3.7186	4.0454	12.0170	2.2929	62.0659	4.3554	0.0393
GA	31	6.7774	0.3606	15.9690	3.4914	3.2526	15.6230	2.5491	70.0800	2.4428	0.0327
GE	32	7.5912	0.2894	16.5260	3.1670	3.0401	16.5730	3.2485	59.3150	1.5919	0.0279
AS	33	6.6686	0.4026	16.5330	2.9581	3.9291	21.9020	2.8578	56.6500	3.0168	0.0250
SE	34	6.7334	0.2214	17.4080	2.4704	5.4759	20.8740	2.5404	58.1690	1.8541	0.0319
BR	35	5.3834	0.3777	16.8990	2.2710	5.9395	19.3540	3.0412	46.4140	3.7390	0.0287
KR	36	6.9119	0.2395	17.0830	2.0460	7.9482	19.4860	2.0509	48.9320	2.0129	0.0226
H2O	10	1.6607	0.3042	1.6277	5.1864	3.7734	12.7450	2.7903	30.7880	0.1444	0.0434

Table 3. *Analytic fits for the oxygen atom, illustrating the accuracy of the method*

$\frac{\sin \Theta}{\lambda}$	$f(s)$			$I_{inc}(s)$			$I_{tot}(s)$		
	tab.	calc.	δ_j^2	tab.	calc.	δ_j^2	tab.	calc.	δ_j^2
0.000	8.000	8.000	0.000000	0.000	-0.000	0.000000	64.000	64.003	0.000008
0.032	7.917	7.917	0.000000	0.111	0.125	0.000203	62.790	62.808	0.000336
0.064	7.679	7.677	0.000002	0.426	0.434	0.000061	59.393	59.377	0.000267
0.096	7.310	7.306	0.000019	0.893	0.889	0.000014	54.329	54.262	0.004519
0.127	6.846	6.853	0.000051	1.453	1.431	0.000482	48.321	48.397	0.005828
0.159	6.326	6.329	0.000009	2.047	2.040	0.000052	42.065	42.096	0.000919
0.191	5.784	5.783	0.000001	2.633	2.647	0.000199	36.088	36.090	0.000004
0.223	5.249	5.245	0.000017	3.183	3.215	0.001049	30.735	30.724	0.000114
0.255	4.743	4.736	0.000050	3.683	3.724	0.001671	26.179	26.153	0.000673
0.286	4.277	4.283	0.000034	4.126	4.153	0.000715	22.419	22.496	0.005901
0.318	3.859	3.862	0.000012	4.512	4.531	0.000373	19.404	19.450	0.002144
0.382	3.169	3.169	0.000000	5.125	5.120	0.000022	15.168	15.166	0.000003
0.446	2.659	2.656	0.000009	5.563	5.539	0.000556	12.633	12.593	0.001584
0.509	2.292	2.292	0.000000	5.874	5.841	0.001089	11.127	11.096	0.000966
0.573	2.031	2.031	0.000000	6.101	6.074	0.000717	10.226	10.199	0.000742
0.637	1.846	1.846	0.000000	6.274	6.260	0.000205	9.682	9.666	0.000239
0.700	1.712	1.714	0.000003	6.415	6.411	0.000015	9.346	9.348	0.000003
0.764	1.613	1.613	0.000000	6.535	6.543	0.000069	9.137	9.145	0.000067
0.875	1.485	1.485	0.000000	6.719	6.737	0.000319	8.924	8.942	0.000311
1.035	1.348	1.347	0.000002	6.949	6.964	0.000229	8.766	8.778	0.000135
1.194	1.225	1.226	0.000001	7.151	7.149	0.000003	8.652	8.652	0.000000

EPS1=0.0400 %   EPS2=0.2588 %   SIGMA=0.0352 e.u.

higher than the corresponding ε_1's. This fact does not mean, however, that the fits for the incoherent intensities are necessarily poorer than those for the coherent ones. ε_1 being the error of the fit for the scattering factor (amplitude), it follows from the quadratic relationship (2) that the error in I_{coh} is $2f(s)\varepsilon_1$. For this reason both constituents contribute nearly equally to the errors of I_{tot}.

(c) In Table 2, all the parameters M, K and L for the helium atom are taken as zero whereas in the previous paper they had finite values, although M was very small [=0·00449, which determines the value of the term subtracted from 1 in equation (3)].

(d) Regarding the M, K and L columns of Table 2 we see that, from $Z=3$, these parameters arc fairly smooth functions of Z. It does not seem, therefore, impossible to find a physical interpretation for the empirical parameters, *i.e.* for the approximating formula. This suggestion may be supported by the fact that the first factor in equation (3) corresponds to a simplified physical picture of equal and non-interacting scattering electrons (Furukawa, Orton, Hamor & Williams, 1963). Consequently, the second factor, containing the empirical parameters, must be a correction for the in-fluence of the different bounding forces and interactions, and as such it certainly could be expressed in terms of quantum mechanics.

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