HIRTH, J. P. & LOTHE, J. (1968). *Theory of Dislocations*, pp. 398–440. New York: McGraw-Hill.
KAMBE, K. (1963). *Z. Naturforsch.* **18a**, 1010–1011.
KATO, N. (1963). *J. Phys. Soc. Japan*, **18**, 1785–1791.
KATO, N. (1974). *X-Ray Diffraction*, pp. 350–436. New York: McGraw-Hill.
LITZMANN, O. & JANAČEK, Z. (1974). *Phys. Stat. Sol.* (*a*), **25**, 663–666.
PENNING, P. & POLDER, D. (1961). *Philips Res. Rep.* **16**, 419–440.
STROH, A. N. (1958). *Phil. Mag.* **3**, 625–646.
TAKAGI, S. (1962). *Acta Cryst.* **15**, 1311–1312.
TAKAGI, S. (1969). *J. Phys. Soc. Japan*, **26**, 1239–1253.
TAUPIN, D. (1964). *Bull. Soc. Fr. Minér. Crist.* **87**, 469–511.
TAUPIN, D. (1967). *Acta Cryst.* **23**, 25–35.

Acta Cryst. (1975). A**31**, 600

Analytic Approximations to Incoherently Scattered X-Ray Intensities

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The theoretically calculated incoherently scattered X-ray intensities of Cromer & Mann [*J. Chem. Phys.* (1967). **47**, 1892–1893] and Cromer [*J. Chem. Phys.* (1969). **50**, 4857–4859] for the elements 2 to 95 and 102 have been fitted to an analytic function. The coefficients of fit are tabulated and the accuracy of the fitting is discussed. The accuracy is very good for $\sin\theta/\lambda \le 1{\cdot}5$ Å^{-1}.

In studies of liquids and amorphous solids by X-ray diffraction it is often necessary to remove the incoherently scattered contribution to the measured intensities. This contribution may be calculated using data taken from published tables of theoretically calculated atomic incoherent X-ray intensities [$I_{\text{inc}}(s)$, $s = \sin\theta/\lambda$], *e.g. International Tables for X-ray Crystallography* (1962), Cromer & Mann (1967), Cromer (1969), Tavard, Nicolas & Rouault (1967). These published intensities are however only tabulated for certain fixed values of s whereas in practice they may be needed for values of s other than these. It is convenient therefore to fit the tabulated data to an analytic function of s which may then be evaluated as required for any intermediate values of s. This has been done by Hajdu (1972) for the incoherent intensities calculated using Clementi wave functions by Tavard *et al.* (1967) for the elements from 2 to 36 inclusive. An almost complete set of incoherent intensities has been calculated by Cromer & Mann (1967) for spherically symmetric free atoms and by Cromer (1969) for aspherical free atoms using SCF Hartree–Fock wave functions; only the intensities for elements from 95 to 101 inclusive are missing from the set. In this paper the coefficients of an analytic function which has been fitted to this set of incoherent intensities are presented.

In the tables of Cromer & Mann (1967) and Cromer (1969) the incoherent intensities are listed for each element at s values 0·0, 0·005, 0·01, 0·05, 0·10, 0·15, 0·2, 0·3, 0·4, 0·5, 0·6, 0·7, 0·8, 0·9, 1·0, 1·5, 2·0, 3·0, 4·0, 5·0, 8·0 Å^{-1}. In X-ray diffraction experiments intensity measurements are not usually made at values of s greater than 1·5 Å^{-1} (the maximum possible value of s attainable when using Mo $K\alpha$ X-rays in 1·41 Å^{-1}) so it was decided to choose an analytic function which would fit the tabulated intensities well for s between 0·0 and 1·5 Å^{-1}. Traditionally X-ray scattering factors have been fitted to a function which is the sum of a number of Gaussians and a constant; Cromer & Waber (1965) used four Gaussians and a constant and hence obtained a nine-coefficient fit. On the other hand electron scattering factors have been fitted to the sum of a number of Gaussians without any constant term, *e.g.* Smith & Burge (1962). It was therefore decided to try fitting $F(s) = Z - I_{\text{inc}}(s)$ (Z is the atomic number), which is a smoothly decreasing function of s of the same general form as X-ray and electron scattering factors, to the sum of either four Gaussians and a constant or of five Gaussians. Preliminary investigation showed that the latter gave a better overall fit and used less computer time in doing so. Hence the analytic function chosen was

$$F_{\text{fit}}(s) = \sum_{i=1}^{5} a_i \exp(-b_i s^2),$$

where the a_i and b_i are the ten coefficients of fit. A non-linear least-squares fitting procedure (Pennington, 1970), in which the sum of the squares of the absolute differences between the fitted and tabulated values of $F(s)$ was minimized, was used to calculate the coefficients of fit. No weighting of the data was applied prior to the fitting procedure and hence no one region of s was emphasized relative to another.

In Table 1 the coefficients of fit are listed for each of the elements together with two indications of the quality of fit. The column headed MPD gives the mean percentage difference between the fitted and tabulated values of $F(s)$ for the 16 values of s less than or equal to 1·5 Å^{-1}, *i.e.* $\mathrm{MPD}=100\sum_{j=1}^{16} r_j$, where $r_j=|F_{\mathrm{fit}}(s_j)-F_{\mathrm{tab}}(s_j)|/|F_{\mathrm{tab}}(s_j)|$. The column headed WPD gives the worst percentage difference at any of the values of s less than or equal to 1·5 Å^{-1}, *i.e.* $\mathrm{WPD}=100\ \mathrm{Max}\ (r_j)$. The final column of the table which is headed S gives the source of the tabulated incoherent intensities for each of the elements; CM denotes Cromer & Mann (1967) and C denotes Cromer (1969).

The only element whose incoherent intensities caused problems in the fitting procedure was He. This was because the intensities tabulated for s greater than

Table 1. *Analytic coefficients for* $Z-I_{\mathrm{inc}}(s)$

ELEMENT	Z	A1	B1	A2	B2	A3	B3	A4	B4	A5	B5	MPD	WPD	S
HE	2	.5246	32.3717	1.0188	14.7084	.4068	6.6884	.0498	2.4843	0	0	*	*	CM
LI	3	.0518	533.9220	.9578	245.8450	.7348	10.1831	1.0817	4.4364	.1740	1.5031	.177	1.048	CM
BE	4	.4634	185.8560	1.5592	104.6010	.7685	4.8589	1.0623	2.1932	.1470	.7641	.026	.107	CM
B	5	.9046	104.9610	1.9822	46.0191	.2279	8.9873	1.4873	1.9674	.3979	.6778	.067	.355	C
C	6	.7568	82.2385	2.5511	31.7282	.7051	11.9471	1.4605	1.4637	.5263	.5150	.044	.264	C
N	7	.9070	64.1555	2.8972	20.8507	1.1659	7.7576	1.5526	1.0335	.4769	.3516	.078	.554	CM
O	8	.8847	52.0063	3.2189	16.4487	1.7990	6.5958	1.5538	.8143	.5434	.2815	.043	.165	C
F	9	.9756	41.7194	3.5101	12.7747	2.3561	5.2945	1.5896	.6470	.5683	.2254	.031	.144	C
NE	10	1.1544	34.2567	3.8033	9.7672	2.8085	4.0375	1.6647	.5256	.5687	.1800	.043	.309	CM
NA	11	1.0243	293.4110	2.0704	15.2373	5.3197	4.4697	1.5214	.6246	1.0637	.1922	.094	.304	CM
MG	12	2.0049	178.9830	1.9449	11.2433	5.4291	3.4272	1.6315	.4907	.9888	.1542	.092	.672	CM
AL	13	2.6790	121.3630	1.2336	16.0728	5.9358	3.2632	1.6622	.6616	1.4835	.1586	.145	.650	C
SI	14	2.1006	116.9570	2.2025	34.7760	5.3063	3.3215	2.5162	.9833	1.8716	.1553	.110	.438	C
P	15	1.8936	108.0330	3.3782	26.6586	5.3752	2.6865	2.4942	.7973	1.8564	.1333	.113	.667	CM
S	16	2.0717	86.7211	4.2023	21.4574	5.6883	2.1255	2.2623	.5882	1.7735	.1128	.124	.787	C
CL	17	2.1221	73.8395	5.0905	17.9756	5.6885	1.8037	2.2809	.5162	1.8164	.1008	.095	.447	C
AR	18	2.1778	65.6187	5.9791	14.4380	5.6104	1.5611	2.3442	.4716	1.8873	.0914	.057	.185	CM
K	19	1.0863	425.4740	2.8562	35.7249	5.6616	9.3261	6.7809	1.0206	2.6145	.1036	.190	1.247	CM
CA	20	2.0554	289.8620	2.7251	28.7190	5.9104	7.4788	6.7171	.8644	2.5916	.0920	.129	.527	CM
SC	21	2.1608	251.3870	2.9545	26.8528	6.5125	6.4238	6.7745	.7616	2.5969	.0831	.091	.234	C
TI	22	2.1983	226.9680	3.2282	24.9306	7.0649	5.6213	6.8832	.6865	2.6243	.0758	.091	.423	C
V	23	2.2399	206.3990	3.4348	22.9026	7.6412	4.9366	7.0270	.6256	2.6558	.0697	.093	.568	C
CR	24	1.5893	196.5840	3.6692	25.2663	8.7249	4.5848	7.2913	.5876	2.7226	.0650	.113	.606	CM
MN	25	2.3156	174.6560	3.7420	19.5879	8.8241	3.8896	7.3811	.5326	2.7355	.0597	.083	.669	CM
FE	26	2.3141	164.1040	3.9729	18.2898	9.2624	3.5861	7.5083	.5155	2.9404	.0597	.067	.504	C
CO	27	2.3636	151.3370	4.4188	16.0770	9.7350	3.1445	7.6872	.4553	2.7927	.0514	.094	.629	C
NI	28	2.4174	139.9630	4.7076	14.5797	10.2289	2.8142	7.8357	.4203	2.8071	.0476	.097	.520	C
CU	29	1.7532	127.2510	4.8167	16.9194	11.2836	2.7458	8.2460	.4076	2.8943	.0454	.127	.669	CM
ZN	30	2.4474	125.0830	5.1080	12.8443	11.4407	2.3122	8.1791	.3605	2.8211	.0410	.090	.299	CM
GA	31	3.0360	104.5770	5.1760	11.2803	11.6692	2.0663	8.2940	.3314	2.8148	.0380	.084	.260	C
GE	32	3.4795	87.5304	5.2306	10.8491	11.9324	1.9060	8.5063	.3107	2.8388	.0356	.101	.257	C
AS	33	3.3385	82.4879	5.6229	12.0723	12.2449	1.8317	8.8668	.2996	2.9138	.0341	.130	.347	CM
SE	34	3.5333	73.4400	5.9644	12.2369	12.4403	1.7151	9.1212	.2824	2.9289	.0318	.137	.367	C
BR	35	3.4898	68.5438	6.5641	12.5940	12.5318	1.6235	9.3877	.2712	3.0170	.0308	.133	.370	C
KR	36	3.0598	70.8068	7.6671	12.6448	12.5852	1.5230	9.6168	.2577	3.0647	.0294	.114	.330	CM
RB	37	2.3770	178.8670	8.6605	13.9200	12.5729	1.5224	10.1507	.2567	3.2083	.0289	.205	.482	CM
SR	38	3.0740	210.8030	8.8344	12.3784	12.5145	1.4148	10.3129	.2424	3.2433	.0275	.195	.420	CM
Y	39	3.5086	177.4230	9.2574	11.0509	12.4297	1.3242	10.4962	.2300	3.2840	.0263	.198	.464	C
ZR	40	3.8436	152.2740	9.6980	10.0161	12.3352	1.2610	10.7459	.2206	3.3493	.0254	.211	.534	C
NB	41	3.7519	117.4490	10.5738	8.9975	12.2251	1.2044	10.9745	.2127	3.4425	.0248	.195	.575	C
MO	42	3.9567	105.1800	11.1228	8.0754	12.1674	1.1551	11.2328	.2038	3.4857	.0237	.192	.608	CM
TC	43	4.3317	115.9390	10.7065	7.9151	12.1316	1.2769	12.0687	.2105	3.7296	.0240	.280	.799	CM
RU	44	4.7308	77.6118	12.0616	6.4667	11.9367	1.0431	11.6021	.1877	3.6225	.0223	.197	.557	C
RH	45	4.8745	71.5772	12.2804	6.1701	12.0133	1.0589	12.0245	.1853	3.7592	.0220	.210	.625	C
PD	46	5.4847	53.2508	13.7150	4.9329	11.6608	.8575	11.4709	.1655	3.6545	.0206	.076	.193	CM
AG	47	5.3490	58.9663	13.4127	5.0548	11.9402	.9684	12.3201	.1715	3.9205	.0210	.222	.502	CM
CD	48	4.5224	87.3897	9.6282	7.7119	14.9509	1.5820	14.2066	.2036	4.6563	.0234	.276	.898	CM
IN	49	4.7031	89.2096	8.2361	8.9965	16.4206	1.7229	14.6608	.2062	4.9493	.0238	.245	.810	C
SN	50	4.9677	83.2133	7.4873	10.1130	17.4268	1.7605	14.9229	.2042	5.1678	.0237	.218	.787	C
SB	51	4.6001	82.5070	7.4399	12.5902	18.3475	1.7906	15.1777	.2029	5.4096	.0238	.199	.712	CM
TE	52	4.5671	79.7245	7.7178	13.8028	18.8338	1.7411	15.2844	.1976	5.5769	.0235	.181	.740	C
I	53	4.3147	78.6996	8.3728	14.9421	19.1861	1.6795	15.3645	.1921	5.7365	.0232	.165	.755	C
XE	54	3.4467	88.3050	19.4724	1.6131	9.7473	16.1669	15.4210	.1869	5.9034	.0229	.147	.751	CM
CS	55	2.5751	224.5980	19.7181	1.5722	11.0138	17.7908	15.5312	.1845	6.1374	.0229	.181	.661	CM
BA	56	3.2477	266.5930	19.7824	1.4758	11.2142	16.2710	15.4790	.1775	6.2602	.0225	.165	.678	CM
LA	57	3.6683	224.7260	11.7149	14.7472	19.8077	1.3823	15.4015	.1708	6.3860	.0222	.151	.662	C
CE	58	3.7218	212.5660	12.0076	14.0417	20.1925	1.3272	15.4540	.1681	6.5996	.0221	.154	.632	C
PR	59	3.6287	208.1030	11.9193	13.8486	20.8823	1.3025	15.6425	.1690	6.8971	.0222	.178	.619	C
ND	60	3.7229	194.9980	12.0836	13.2282	21.2664	1.2573	15.7405	.1677	7.1521	.0222	.182	.609	C
PM	61	3.8009	184.3400	12.2546	12.6793	21.6281	1.2139	15.8659	.1669	7.4126	.0222	.190	.607	C
SM	62	3.8533	176.3920	12.3520	12.2878	22.0136	1.1810	16.0323	.1672	7.7082	.0223	.192	.627	C
EU	63	3.9234	167.8160	12.4961	11.8294	22.3133	1.1433	16.2152	.1676	8.0085	.0224	.204	.626	CM
GD	64	4.1100	160.8590	13.0008	11.0492	22.2962	1.0914	16.2937	.1659	8.2594	.0223	.189	.622	C
TB	65	4.1589	155.1860	13.2197	10.6407	22.4627	1.0667	16.5329	.1674	8.5842	.0224	.195	.649	C
DY	66	4.0415	150.0580	13.1038	10.6511	22.8132	1.0708	17.0066	.1723	8.9849	.0227	.220	.704	C
HO	67	4.0620	145.9760	13.2132	10.3972	22.9351	1.0569	17.3999	.1752	9.3388	.0228	.224	.740	C
ER	68	4.0815	142.0720	13.3282	10.1525	22.9865	1.0438	17.8548	.1785	9.6967	.0229	.227	.773	C
TM	69	4.7416	100.1700	13.2875	9.0676	23.1429	.9833	17.9215	.1753	9.8935	.0227	.169	.732	C
YB	70	4.1014	135.8330	13.4586	9.8125	22.9675	1.0290	18.9998	.1860	10.4188	.0231	.228	.832	CM
LU	71	4.3261	133.3600	13.8638	9.1664	22.6992	.9951	19.3649	.1861	10.6986	.0230	.207	.820	C
HF	72	4.5759	124.5010	14.3292	8.5195	22.3741	.9599	19.7027	.1857	10.9720	.0229	.192	.794	C
TA	73	4.7416	117.6480	14.9284	7.9070	22.0214	.9250	20.0290	.1850	11.2347	.0227	.180	.749	C
W	74	4.8423	112.6940	15.6421	7.3551	21.6701	.8892	20.3207	.1837	11.4817	.0226	.169	.689	C
RE	75	5.0015	106.0010	16.3874	6.7592	21.3263	.8491	20.5247	.1817	11.7163	.0224	.160	.604	CM
OS	76	5.3630	93.6155	17.5066	6.0569	23.3197	.7156	20.9425	.1373	8.8158	.0127	.179	.458	C
IR	77	5.0953	98.2594	15.4321	6.9463	15.5924	1.2550	26.5617	.2600	14.2784	.0242	.123	.352	C
PT	78	5.6451	69.2677	18.8015	5.3127	20.6881	.7107	20.5266	.1702	12.2868	.0216	.125	.239	C
AU	79	5.8170	65.4079	19.5635	4.9469	20.3716	.6809	20.6837	.1680	12.5114	.0214	.114	.192	CM
HG	80	5.9389	74.0107	19.4946	4.9118	19.0547	.7375	22.4442	.1779	13.0069	.0216	.156	.253	CM
TL	81	6.5803	69.9997	19.6010	4.6032	18.3955	.7312	23.0433	.1787	13.3134	.0216	.158	.292	C
PB	82	7.3754	62.4634	19.7974	4.2561	18.0002	.7021	23.2605	.1757	13.4943	.0213	.151	.246	C
BI	83	8.2324	53.0479	20.0183	3.9249	17.6603	.6675	23.3246	.1722	13.6777	.0210	.147	.280	CM
PO	84	9.0662	48.3272	20.1395	3.6624	23.6273	.1701	17.1872	.6471	13.8913	.0208	.141	.304	C
AT	85	9.9223	43.7514	20.2544	3.4229	23.9015	.1680	16.7271	.6271	14.1028	.0206	.138	.330	C
RN	86	10.7789	38.6121	20.3926	3.2050	16.3720	.6037	24.0637	.1650	14.2879	.0203	.141	.381	CM
FR	87	2.5332	269.8780	11.5319	21.9610	24.7459	2.0716	31.9247	.2243	16.2475	.0223	.105	.379	CM
RA	88	3.2249	321.6630	11.6694	20.3846	24.8687	1.9730	31.8957	.2166	16.3306	.0219	.094	.303	CM
AC	89	3.6207	270.7740	12.1269	18.9025	24.9363	1.8811	31.8798	.2095	16.4227	.0215	.091	.257	C
TH	90	4.0181	232.3710	12.6119	17.3825	24.9621	1.7950	31.8646	.2030	16.5249	.0211	.086	.301	C
PA	91	3.7926	236.8030	12.6626	17.5908	25.8795	1.7607	31.9403	.1984	16.7045	.0209	.094	.272	C
U	92	3.9051	221.1780	12.8415	16.8737	26.4298	1.7008	31.9514	.1932	16.8475	.0205	.098	.268	C
NP	93	4.0333	207.7270	12.9014	16.3175	26.7571	1.6677	31.4732	.1954	17.8065	.0220	.095	.208	C
PU	94	4.2695	185.9550	12.5662	15.5936	28.0362	1.5914	31.9382	.1834	17.1487	.0200	.113	.241	C
AM	95	4.3981	174.3590	12.6808	14.9676	28.6781	1.5304	31.9085	.1786	17.2883	.0197	.118	.231	CM
NO	102	4.7363	135.6760	14.1419	12.0550	32.9866	1.1972	31.6913	.1510	18.3800	.0180	.141	.272	CM

or equal to 1·5 Å^{-1} were all 2·0, which meant that all the corresponding values of $F_{\text{tab}}(s)$ were zero. It was only possible to obtain a fit to the sum of four Gaussians (an eight coefficient fit) and hence a_5 and b_5 are listed as zero. The relative errors for s less than or equal to 0·8 Å^{-1} are all less than 1% while the remainder are rather large or could not be calculated because of division by the zero $F_{\text{tab}}(s)$. However, because the actual values of $F_{\text{tab}}(s)$ are very small for s greater then 0·8 Å^{-1}, the fit is in fact quite acceptable.

For the other elements the mean percentage differences are all less than 0·3% while the worst percentage differences are all less than 1% except for Li, where the problems were similar to those encountered with He, and K. The rather large value of 1·25% at $s=1·5$ Å^{-1} obtained in the latter case is not readily explicable but if the calculated and fitted values of $Z-I_{\text{inc}}(s)$ are plotted it is obvious that the overall fit is very good. The quality of the overall fit for the other elements is as good as or better than that for K.

The computations were performed using the CDC 6600 and 7600 computers at the University of London Computer Centre.

References

CROMER, D. T. (1969). *J. Chem. Phys.* **50**, 4857–4859.
CROMER, D. T. & MANN, J. B. (1967). *J. Chem. Phys.* **47**, 1892–1893.
CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* **18**, 104–109.
HAJDU, F. (1972). *Acta Cryst.* A**28**, 250–252.
International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.
PENNINGTON, R. H. (1970). *Introductory Computer Methods and Numerical Analysis*, 2nd ed., pp. 417–427. New York: Macmillan.
SMITH, G. H. & BURGE, R. E. (1962). *Acta Cryst.* **15**, 182–186.
TAVARD, C., NICOLAS, D. & ROUAULT, M. (1967). *J. Chem. Phys.* **64**, 540–554.

Acta Cryst. (1975). A**31**, 602

Strengthening of the $\sum_1$ Relationship: a Quartet Method

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A probabilistic theory of special quartets is described which is able to fix the sign of reflexions with even indices. The method proves suitable for removing a large percentage of the $\sum_1$ formula failures.

Statement of the problem

Direct methods are today the most powerful crystallographic tool for solving equal-atom structures. Although various types of phase-determining formulae have been proposed, the most effective is the sign relationship

$$\varphi_{\mathbf{h}}+\varphi_{\mathbf{k}}+\varphi_{-\mathbf{h}-\mathbf{k}}\simeq 0 .$$

It has long been recognized, however, that this formula may not lead to a physically correct solution without the introduction of auxiliary phase information. Several procedures, therefore, have been proposed (*i.e.* symbolic addition procedures or multisolution methods) which are able to give routine solutions even to complicated structures. As the choice of starting reflexions constitutes a very critical element influencing success or failure of a direct solution of the phase problem, much effort has been devoted to improving the selection of the starting set (Germain, Main & Woolfson, 1970).

It is a matter of experience that the phase-determining process is more effective if one has a large starting set: unfortunately the size of the set is limited by the number of phase combinations it is practical to explore. Thus it is useful to be able to enlarge the starting set by knowing in advance a number of phases.

In order to achieve this, several additional formulae have been exploited by different authors. In this paper we shall devote our attention to some auxiliary formulae which are able to fix the phase of the $E_{2\mathbf{h}}$ reflexions. We shall discuss their limits and shall try to improve their effectiveness. We treat here only the centrosymmetric case: formulae useful in non-centrosymmetric cases will be described in a subsequent paper.

The mathematical approach

A variety of conditional probability distributions will be described. We denote by $P(E_1,E_2,\ldots,E_n)$ the joint probability distribution function of n normalized structure factors. The characteristic function of the distribution (Giacovazzo, 1975*a*) is

$$C(u_1,u_2,\ldots,u_n)=\exp\left[-\tfrac{1}{2}(u_1^2+u_2^2+\ldots+u_n^2)\right] \times\left\{1+\frac{S_3}{t^{3/2}}+\frac{S_4}{t^2}+\frac{S_3^2}{2t^3}+\ldots\right\}, \quad (1)$$