ANNALES ACADEMIAE SCIENTIARUM FENNICAE

Series A

VI. PHYSICA

198

GAUSSIAN REPRESENTATION OF ATOMIC SCATTERING FACTORS FOR X-RAYS

BY

K. KURKI-SUONIO, V. MEISALO, M. MERISALO and E. PELTOLA

Department of Physics
University of Helsinki
Helsinki, Finland

HELSINKI 1966
SUOMALAINEN TIEDEAKATEMIA

Abstract

Analytic approximations of theoretical atomic factors are discussed. For a number of atoms ($8 \leq Z \leq 37$) a Gaussian representation is given, fitted to the basic numerical values up to the last significant decimal place.

In detailed studies of electron distributions in crystals it has proved advantageous to employ analytic representations for the theoretical atomic factors, especially when electronic computers are used. Such a representation must, of course, coincide with the theoretical atomic factors accurately enough. When the representation is needed only in a limited $\varkappa$ ($= \sin\theta/\lambda$) range, any reasonable functional form will do if it can be fitted to the tabulated values. However, when actually used in place of the theoretical values in a complete analysis, for instance with convolution methods [1], the function must also have the correct behaviour at infinity and near the origin.

In most cases the theoretical atomic factor $f(\boldsymbol{h})$ is spherically symmetric. Therefore only even functions $f(\varkappa)$ can be used for its description. Any odd components would make the atomic factor or some of its derivatives discontinuous at the origin causing errors at small $\varkappa$ values. (This limitation is generally valid for the real part of the scattering amplitude of any real electron distribution in any direction.) On the other hand, we know that asymptotically $f(\varkappa) \sim e^{-a\varkappa^2}$.

The Gaussian representation

$$f(\varkappa) = \sum a_i e^{-b_i \varkappa^2} \, , \, b_i > 0 \, ,$$

has all these properties. In addition, it has another remarkable advantage. The Fourier transform is easy to perform and gives directly an analytic representation for the corresponding density function.

First attempts to apply the Gaussian method evidently suffered from limited computing facilities. The fit with two or three Gaussians was not satisfactory for a detailed analysis. Therefore one turned to other approximations hoping to find simple forms with few parameters. During recent years many different propositions have been made [2—10]. Often they give good fits to the tabulated theoretical values, but do not fulfill the other conditions. Therefore they have limited applicability. One of the best fits

and most complete lists of atomic factors is given by CROMER and WABER [10], who represent their relativistic HFS scattering factors with a sum of four Gaussians and a constant. However, the constant term, or in some cases even a positive exponent spoils the behaviour at infinity and makes the corresponding density function singular. On the other hand, for the lighter elements ($Z \lesssim 36$) the older HF scattering factors with exchange are evidently more reliable [11]. In connection with our earlier works [12—16] we have been compelled to pay special attention to the possibilities of detailed analysis, and we have several times met with the need for more accurate analytic representations.

In most cases we can evidently make the fit as good as needed with a sufficient number of Gaussians. Also, in the use of present-day computers it is no appreciable disadvantage to have, say, 50 parameters instead of 5. Moreover, due to the general trend of the Gaussians, there is no danger of getting wrong values between standard points even with a great number of terms, as is the case with e.g. polynomial methods. Therefore we have found the pure Gaussian representation the most convenient. We have calculated the corresponding parameters a_i, b_i for the HF atomic factors of a number of common atoms ($8 \leq Z \leq 37$). The basic numerical values were taken from International Tables [17] except for F^- and O^{-2} for which the values of refs. [18] and [19, 20], respectively, were used. In some cases also the value at $\varkappa = 6$ Å^{-1} from the tables of HANSON et al. [21] was taken into account. We needed 6 to 12 terms, depending on the case, to reach a fit up to the last significant decimal place of the theoretical values. The addition of the point $\varkappa = 6$ Å^{-1} had only a slight tendency to increase this number.

There are some practical difficulties in finding what is the sufficient number of terms and in evaluating the parameters, especially because the parameters giving the desired fit need not be unique [22]. The calculations were performed on ELLIOTT 503 and 803 computers. The program was written in ALGOL. It was based on an iterative process sketched below.

As starting values one gives a set of b_i values. In the first stage the factors a_i are calculated for the given b_i values by the method of least squares, but with the limitation $a_i \geq 0$. This is done by using a special procedure written by PAATERO [23] and designed originally for the determination of lifetimes in radioactive decay. This procedure itself is iterative and its main feature is the use of gradients in a gradual evaluation of the a_i factors. Then, as a second stage, the number of a_i's different from zero is decreased, if possible, combining adjacent b_i's. The resulting b_i values form then the starting point of the next iteration cycle. The iteration is stopped when the sum of the squares of the residuals and the number of a_i's do not change any more.

Another run of the calculation may give different parameters and even a different number of terms. The fit, however, is always the same. The accuracy of the resulting representations does not change regularly with Z, which was the case reported earlier for polynomial approximations [8]. The method accidentally failed to give any satisfactory representation for two ions (Cl^-, S^{-2}). This is certainly due to the fact that the Gaussians do not form a complete set of functions. Moreover, from a general point of view, we must admit that the good fits found for most atoms are exceptional.

The reliability of the representation was tested in some cases by new calculations leaving off a few standard points. Only a negligible effect on the fit was observed, unless the last points were missing, in which case the fit became less accurate at these points. If our results are compared with the values of HANSON et al. [21] for large values of $\varkappa$, in the cases where these were not included in the calculation, we observe similarly that the fit is not so good at the ultimate values. In the worst cases the values at $\varkappa = 6$ Å^{-1} differ by a factor of 3. In general, however, it is sufficient to have the correct asymptotic behaviour, which is Gaussian. Numerical differences at large values of $\varkappa$ have no great significance. They could be corrected with some additional Gaussians with small a and large b, the effect of which is less important and well controlled [1].

Acknowledgements

We are indebted to the National Research Council for Sciences, to the Finnish Atomic Energy Commission and to Emil Aaltonen Foundation for financial support.

Table

Parameters for the Gaussian representations $f = \Sigma a_i \exp(-b_i \varkappa^2)$ of some HF atomic factors. The number in brackets refers to the source of the basic numerical values if they are not taken from International Tables [17]. The asterisk indicates that the representation is fitted at $\varkappa = 6$ Å^{-1} to the values of Hanson et. al. [21].

Element	a_i	b_i
O^{-2}	0.20453	0.00050
[19]	1.55062	0.30000
	0.08506	2.00000
	3.05979	7.00000
	3.35961	17.00000
	0.97949	35.00000
	0.75679	50.00000
	0.00413	200.00000
O^{-2}	0.20013	0.00100
[20]	0.13926	0.25000
	1.38808	0.30000
	0.12951	1.25000
	1.67653	5.50000
	1.37229	10.46827
	2.07430	15.00000
	0.27728	26.99502
	2.35692	34.59520
	0.38143	105.00000
F^-	0.76875	0.10000
	0.96778	0.30000
	0.09167	1.00000
	2.13390	4.00000
	2.27098	8.00000
	1.43582	13.02203
	1.12298	17.00000
	1.15689	25.41793
	0.05112	45.00000
F^-	0.08143	0.10000
[18]	1.67319	0.20718
	0.96358	3.18682
	2.48382	5.83983
	2.40192	11.00000
	1.31628	20.00000
	0.53276	29.26554
	0.54742	55.00000

Element	a_i	b_i
Na^+	0.09678	0.00500
	1.54636	0.12860
	0.23579	0.75000
	3.07795	2.72163
	3.28779	5.36484
	1.40801	10.00000
	0.09262	15.00000
	0.25474	19.22734
Mg^{+2}	0.45642	0.00100
	1.42610	0.20000
	4.75005	2.51596
	3.33842	6.50000
	0.00643	7.00000
	0.02086	45.00000
Al	0.83846	0.00050
	0.98780	0.25000
	0.31253	1.00000
	3.47904	1.92011
	3.69604	3.70307
	0.28580	6.00000
	0.68803	34.99805
	0.16829	45.15373
	1.27641	49.45225
	0.91376	81.62434
	0.33396	147.84744
	0.01993	200.00000
Si	1.22577	0.00050
	1.61095	0.75000
	0.93818	1.25000
	4.95028	2.50000
	0.71967	3.00000
	0.69155	25.00000
	2.58771	40.00000
	0.64003	50.00000
	0.63665	105.00000

Table (continued)

Element	a_i	b_i
Si^{+4}	1.21831	0.00050
	0.71084	0.50000
	4.11611	1.50000
	3.69942	3.50000
	0.25449	7.00000
	0.00213	40.00000
K^{+}	1.37554	0.00050
	6.81505	0.75000
	0.65133	1.00000
	2.21178	12.00000
	5.81686	13.00000
	0.73405	30.00000
	0.39734	35.00000
Ca^{+2}	1.33169	0.00100
	3.05284	0.60000
	4.37381	0.70000
	8.53855	10.52150
	0.53324	27.00000
	0.17106	31.00000
Cr	0.72253	0.00050
*	5.08048	0.30000
	2.69159	0.50000
	2.16405	5.00000
	8.45148	6.50000
	2.01638	15.00000
	1.47932	25.00000
	1.32661	80.00000
	0.06759	300.00000
Cr^{+2}	0.72256	0.00050
*	5.22037	0.30000
	2.50586	0.50000
	5.79508	5.50000
	4.29081	6.50000
	1.80522	13.00118
	1.06078	15.00000
	0.59659	30.00000
	0.00199	500.00000

Element	a_i	b_i
Mn	0.77362	0.00050
*	6.53870	0.30000
	1.06898	0.50000
	0.03077	3.00000
	10.88315	5.27008
	3.14224	14.19669
	0.13352	40.00000
	2.09520	70.37231
	0.02214	169.82470
	0.31087	200.00000
Mn^{+2}	0.77363	0.00050
*	6.54018	0.30000
	1.07007	0.50000
	8.74776	5.00000
	2.01057	7.00000
	2.28022	11.00000
	1.55365	19.00000
	0.01763	80.00000
	0.00637	300.00000
Fe	0.81400	0.00050
*	0.42082	0.20000
	7.08495	0.30000
	8.91578	4.50000
	2.32304	5.50000
	3.15091	11.00000
	0.82901	25.00000
	0.63724	35.00000
	1.09188	80.00000
	0.71853	105.00000
	0.01372	500.00000
Fe^{+2}	0.81423	0.00050
*	0.80580	0.25000
	6.69693	0.30000
	9.88854	4.50000
	0.53398	6.00000
	4.12232	10.00000
	0.61148	19.00000
	0.52019	25.00000
	0.00662	500.00000

Table (continued)

Element	a_i	b_i
Co	0.85465	0.00050
*	4.29654	0.25000
	3.13831	0.30000
	0.23172	3.00000
	11.49973	4.23431
	4.17324	11.00000
	0.55434	30.00000
	0.78374	50.00000
	1.17554	80.00000
	0.29310	140.00000
Co^{+2}	0.85439	0.00050
*	6.82574	0.25000
	0.78676	0.75000
	0.51046	3.00000
	6.40382	4.00000
	6.05618	5.50000
	3.11735	13.00000
	0.30823	19.00000
	0.13862	40.00000
Ni	0.88474	0.00050
*	0.02954	0.15000
	7.33975	0.25000
	0.53856	2.50000
	11.14379	3.85286
	2.10810	7.00000
	2.99759	11.00000
	0.99639	26.45838
	1.71335	70.98541
	0.06691	105.00000
	0.18164	162.32611
Ni^{+2}	0.88488	0.00050
*	7.35430	0.25000
	0.05019	1.50000
	0.05583	1.75000
	10.20649	3.61442
	5.82664	7.50000
	1.37100	17.04543
	0.24744	23.00000
	0.00281	500.00000

Element	a_i	b_i
Cu	0.09859	0.00050
*	0.79023	0.00100
	1.85939	0.10000
	5.64360	0.30000
	5.80408	3.00000
	8.29916	4.50000
	4.19229	11.00000
	0.94277	21.00000
	1.19802	56.51347
	0.94701	80.00000
	0.07739	222.08623
Cu^{+}	5.18697	0.10000
	3.44572	0.50000
	10.93042	3.50000
	0.77955	5.00000
	3.86671	7.00000
	1.17649	11.00000
	2.34025	17.00000
	0.18298	45.00000
	0.09360	50.00000
Cu^{+2}	1.24509	0.00050
	7.03399	0.25000
	5.99841	3.00000
	5.82549	4.00000
	4.41133	7.00000
	1.43773	11.00000
	1.04952	19.00000
Zn	0.93770	0.00050
*	0.14174	0.10000
	3.33422	0.15000
	3.90570	0.30000
	9.92243	3.00000
	4.44998	4.50000
	4.42064	9.00000
	1.34828	30.00000
	0.09316	50.00000
	1.42132	80.00000
	0.02440	500.00000

Table (continued)

Element	a_i	b_i
Zn^{+2}	4.53316	0.05000
	4.27930	0.50000
	0.92567	2.50000
	12.50135	3.50000
	3.58286	8.00000
	1.44638	11.00000
	0.73116	21.00000
Ge	0.49070	0.00500
	7.19160	0.15000
	2.13527	1.50000
	8.10773	2.50000
	7.79201	4.00000
	1.48207	11.00000
	0.76386	21.00000
	1.44338	35.00000
	1.88758	50.00000
	0.68981	105.00000
	0.01772	140.00000
Ge^{+4}	3.45118	0.00500
	3.05246	0.25000
	3.05962	0.75000
	13.39202	3.00000
	1.87172	4.00000
	2.05435	8.00000
	1.12008	9.00000

Element	a_i	b_i
Br^-	0.94236	0.00050
*	6.01893	0.10000
	6.04228	1.25000
	12.92151	2.50000
	0.29038	5.00000
	0.83833	15.00000
	5.61768	23.00000
	2.12955	50.00000
	1.17997	80.00000
	0.01932	200.00000
Rb^+	2.60561	0.00100
	4.81933	0.15000
	10.95218	1.50000
	7.24559	2.00000
	7.09768	15.00000
	1.89459	25.00000
	1.38563	35.00000