

- BURZLAFF, H., ZIMMERMANN, H. & DE WOLFF, P. M. (1983). In *International Tables for Crystallography*, Vol. A, edited by T. HAHN. Dordrecht: Kluwer Academic Publishers.
- ENGEL, P. (1989). *Geometric Crystallography*. Dordrecht: Reidel.
- GRUBER, B. (1978). *Acta Cryst.* **A34**, S2.
- HUREWICZ, W. & WALLMAN, H. (1948). *Dimension Theory*. Princeton Univ. Press.
- HYDE, S.T. (1989). *Z. Kristallogr.* **187**, 165–185.
- PACIOREK, W. A. & BONIN, M. (1992). *J. Appl. Cryst.* **25**, 632–637.
- PATTERSON, A. L. & LOVE, W. E. (1957). *Acta Cryst.* **10**, 111–116.
- RODGERS, J. R. & LE PAGE, Y. (1992). Proc. Am. Crystallogr. Assoc. Meet. Abstr. PA106.
- SEEBER, L. A. (1831). *Über die Eigenschaften der positiven ternären quadratischen Formen*. Freiburg.
- STOUT, G. H. & JENSEN, L. H. (1989). *X-ray Structure Determination*. New York: Wiley.

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New Analytical Scattering-Factor Functions for Free Atoms and Ions

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Abstract

New analytical X-ray scattering-factor representations valid for the full range of $\sin \Theta/\lambda$ from 0.0 to 6.0 \AA^{-1} have been developed from fits of a linear combination of five Gaussians to the values of the scattering factors tabulated in *International Tables for Crystallography* (1992) [Vol. C. Dordrecht: Kluwer Academic Publishers]. The resulting functions for both neutral atoms and ions are compared with the existing parametrizations, which are applicable for $0.0\text{--}2.0 \text{ \AA}^{-1}$ and $2.0\text{--}6.0 \text{ \AA}^{-1}$, respectively. The quality of the new parametrization involving 11 parameters per atom (ion) compares well with the previous work or is even superior. Examples are discussed, some errors in *International Tables for Crystallography*, Vol. C are indicated and a warning is given that most of the previously published four Gaussian expansions for ions are inadequate for calculations involving $\sin \Theta/\lambda \geq 2.0 \text{ \AA}^{-1}$.

Introduction

Isotropic X-ray scattering factors for free atoms and/or ions are required in numerous crystallographic calculations, in particular in structure least-squares refinements. Results for distinct values of $s = \sin \Theta/\lambda$ obtained from atomic wavefunctions are compiled in *International Tables for Crystallography*, Vol. C (Maslen, Fox & O'Keefe, 1992), Tables 6.1.1.1 and 6.1.1.3. With the exception of hydrogen, all scattering-factor values are either derived from the calculations of Doyle & Turner (1968) using the wavefunctions of Coulthard (1967) or from those of Cromer & Waber (1968) using the wavefunctions of Mann (1968). The latter calculations are designated by an asterisk indicating a more exact treatment with respect to the finite size of the nucleus. Scattering factors for ions are either based on non-relativistic or relativistic Hartree–Fock calculations

(Cromer & Mann, 1968) using the wavefunctions of Mann (1968) or on relativistic Dirac–Slater wavefunctions (Cromer & Waber, 1968).

While the calculations of Doyle & Turner were made for 76 elements up to $s = 6.0 \text{ \AA}^{-1}$, Cromer & Waber filled in the missing elements, though only for $0 < s < 2.0 \text{ \AA}^{-1}$, which is sufficient for most applications. Owing to an increasing number of applications requiring high-angle X-ray or electron scattering factors, e.g. high-resolution electron microscopy or experiments with γ -radiation or synchrotron radiation, extended scattering-factor calculations for the range $2.0 < s < 6.0 \text{ \AA}^{-1}$ were provided by Fox, O'Keefe & Tabbernor (1989) and have been included into Table 6.1.1.1, which is the basis for the interpretation of almost any X-ray or electron scattering experiment.

For a given atom and scattering-vector length, the corresponding scattering-factor value $f(s)$ must be calculated from the nearest entries of the appropriate table. In order to circumvent interpolation and to facilitate computational handling, several authors have presented analytical scattering-factor functions for the data available, e.g. Onken & Fischer (1968) who also reviewed earlier studies. The most frequently used representations to date are those developed by Doyle & Turner (1968) who used linear combinations of four Gaussians:

$$f(s) = \sum_{i=1}^4 a_i \exp(-b_i s^2) + c. \quad (1)$$

These have been found to give close fits to the tabulated values up to $s_{\max} = 2.0 \text{ \AA}^{-1}$. Equation (1) and the parameters a_i , b_i and c compiled in Table 6.1.1.4 of *International Tables for Crystallography* (1992), Vol. C can be easily implemented in programs, e.g. the recently released *SHELXL-93*. One interesting application of the analytical scattering functions is given by Sasaki, Fujino,

Takeuchi & Sadanaga (1980) using (1) for the calculation of series-termination errors in spherical charge integrations around atomic sites. These corrections involve $f(s)$ values from (1) calculated for $\sin \Theta/\lambda$ between the experimental limit and $5.0\text{--}7.0 \text{ \AA}^{-1}$. Possible errors introduced by these extrapolations of (1) were considered negligible. Meanwhile, however, Fox, O'Keefe & Tabernor (1989) have shown that (1) can be highly inaccurate beyond $s = 2.0 \text{ \AA}^{-1}$ and they produced a 'logarithmic polynomial' fit (LP) based on

$$\ln\{f(s)\} = \sum_{i=0}^3 a_i s^i. \quad (2)$$

The four parameters a_i given in Table 6.1.1.5 [*International Tables for Crystallography* (1992), Vol. C] provide satisfactory fits to the slowly varying scattering factors in the range $2.0 < s < 6.0 \text{ \AA}^{-1}$.

The implementation of (2) into programs is straightforward. However, dealing with data exceeding $s = 2.0 \text{ \AA}^{-1}$ requires both the input of 13 parameters per atom and a program switch to the appropriate analytical expression. Furthermore, (2) cannot be easily included in the algorithm given by Sasaki, Fujino, Takeuchi & Sadanaga (1980). Therefore, it seemed worthwhile to look for analytical scattering-factor functions of the form (1) which simultaneously cover the whole s range up to 6.0 \AA^{-1} and provide satisfactory approximations of the tabulated values.

In the course of this work, new scattering-factor values following from Dirac-Fock calculations were reported in a recent contribution by Rez, Rez & Grant (1994). Since the differences between these results and those of *International Tables for Crystallography* (1992), Vol. C can be considered negligible, these new values were not considered in the present study. To be consistent with previous work, Rez, Rez & Grant (1994) also prepared new parametrizations on the basis of four Gaussians; for every atom, a 'high-accuracy fit' for the range 0.0 to 2.0 \AA^{-1} and a 'lower-accuracy fit' for the whole range from 0.0 to 6.0 \AA^{-1} . Both kinds of fit were carried out omitting the constant term (equation 1), which the authors considered unphysical. This is certainly a valid argument, but in our opinion it is not a helpful one. The primary aim of a parametrization is to obtain a 'best possible' analytical expression for $f(s)$ rather than to account for the underlying physics. (Besides, a couple of their fits resulted in such 'unphysical' representations involving a constant term, *i.e.* $a_4 \neq 0$, $b_4 = 0$.) Thus, in the present contribution, we do not adopt the view of Rez, Rez & Grant (1994) but propose to fit all tabulated values with (1), extended to five Gaussians, *i.e.* only two more parameters are needed for a unified representation of $f(s)$. Contrary to the statement of Fox, O'Keefe & Tabernor (1989), this is not an impossible task, although it is a tedious one. New parameters a_i , b_i and c ($i = 1$ to 5) are given along with mean and maximum

deviations from the tabulated $f(s)$ values. This information is augmented by including agreement indices [rather than χ^2 values (Rez, Rez & Grant, 1994)] seeming most appropriate to convey an impression of the fit quality (Onken & Fischer, 1968). Examples of the fits serve to illustrate the properties of the new scattering-factor representations and to reveal a few inconsistencies in the tabulated data.

Method

With $a_5 \simeq 0.3$ and $b_5 \simeq 1.0$ along with the neutral atom or ion parameters a_i , b_i and c ($i = 1$ to 4) of Table 6.1.1.4 [*International Tables for Crystallography* (1992), Vol. C] as starting values and all tabulated scattering-factor values as 'observations' $f(s)_o$, minimizations of

$$Q = \sum_j [\sigma_j^2]^{-1} \left\{ f(s)_o - \left[\sum_{i=1}^5 a_i \exp(-b_i s_i^2) + c \right] \right\}^2 \quad (3)$$

were carried out using *MINUIT* (James & Roos, 1987). In order to account for rounding effects, the $f(s)_o$ below $s = 2.0 \text{ \AA}^{-1}$ were assigned an uncertainty σ_j of 0.0005 , those above that limit 0.0008 . Depending on the range of the tabulated values, the $f(s)_o$ for ions above $s = 2.0$ or $s = 1.5 \text{ \AA}^{-1}$, respectively, were those of the neutral atoms because scattering from valence electrons can be neglected.

All refinements were carried out employing the *MINUIT* option *MINIMIZE* (a combination of the program options *MIGRAD* and *SIMPLEX*) and converged after about ten cycles, convergence being indicated by relative changes $\Delta Q/Q \leq 0.001$ in subsequent cycles. The resulting fit parameters were then checked for dependence on the starting values a_i , b_i . In agreement with Rez, Rez & Grant (1994), the fits do not always give unique values of the parameters, which can vary depending on the starting situation. Nevertheless, the final fit qualities were the best that could be reached within reasonable times.

Finally, the refined functions were analysed, both graphically and numerically, and compared with the corresponding results obtained from (1) and (2). In the following, these functions are denoted as $f^{IV}(s)$ and $f^{LP}(s)$, the new functions as $f^V(s)$. In order to obtain quantitative criteria, various agreement indices were calculated according to

$$R_{0,2}^X = \frac{\sum_{j=1}^{21} |f(s)_o - f^X(s)_{\text{calc}}|}{\sum_{j=1}^{21} f(s)_o} \quad (4)$$

with $X = IV$ or V and $s_j = (j-1)/10 \text{ \AA}^{-1}$. Similar R values are

$$R_{2,6}^X = \frac{\sum_{j=1}^5 |f(s)_o - f^X(s)_{\text{calc}}|}{\sum_{j=1}^5 f(s)_o} \quad (5)$$

with $X = IV$, V or LP and $s_j = (j+1) \text{ \AA}^{-1}$. In order to

Table 1. Parameters of analytical scattering-factor functions

(a) For neutral atoms

Atom	a_1	b_1	a_2	b_2	a_3	b_3	a_4	b_4	a_5	b_5	c
He RHF	0.732354	11.553918	0.753896	4.595831	0.283819	1.546299	0.190003	26.463964	0.039139	0.377523	0.000487
Li RHF	0.974637	4.334946	0.158472	0.342451	0.811855	97.102969	0.262416	201.363824	0.790108	1.409234	0.002542
Be RHF	1.533712	42.662078	0.638283	0.595420	0.601052	99.106501	0.106139	0.151340	1.118414	1.843093	0.002511
B RHF	2.085185	23.494069	1.064580	1.137894	1.062788	61.238975	0.140515	0.114886	0.641784	0.399036	0.003823
C RHF	2.657506	14.780758	1.078079	0.776775	1.490909	42.086843	-4.241070	-0.000294	0.713791	0.239535	4.297983
N RHF	11.893780	0.000158	3.277479	10.232723	1.858092	30.344690	0.858927	0.656065	0.912985	0.217287	-11.804902
O RHF	2.960427	14.182259	2.508818	5.936858	0.637853	0.112726	0.722838	34.958481	1.142756	0.390240	0.027014
F RHF	3.511943	10.687859	2.772244	4.380466	0.678385	0.093982	0.915159	27.255203	1.089261	0.313066	0.032557
Ne RHF	4.183749	8.175457	2.905726	3.252536	0.520513	0.063295	1.135641	21.813909	1.228065	0.224952	0.025576
Na RHF	4.910127	3.281434	3.081783	9.119178	1.262067	0.102763	1.098938	132.013942	0.560991	0.405878	0.079712
Mg RHF	4.708971	4.875207	1.194814	108.506079	1.558157	0.111516	1.170413	48.292407	3.239403	1.928171	0.126842
Al RHF	4.730796	3.628931	2.313951	43.051166	1.541980	0.095960	1.117564	108.932389	3.154754	1.555918	0.139509
Si RHF	5.275329	2.631338	3.191038	33.730728	1.511514	0.081119	1.356849	86.288640	2.519114	1.170087	0.145073
P RHF	1.950541	0.908139	4.146930	27.044953	1.494560	0.071280	1.522042	67.520190	5.729711	1.981173	0.155233
S RHF	6.372157	1.514347	5.154568	22.092528	1.473732	0.061373	1.635073	55.445176	1.089372	0.646925	0.154722
Cl RHF	1.446071	0.052357	6.870609	1.193165	6.151801	18.343416	1.750347	46.398394	0.634168	0.401005	0.146773
Ar RHF	7.188004	0.956221	6.638454	15.339877	0.454180	15.339862	1.929593	39.043824	1.523654	0.062409	0.265954
K RHF	8.163991	12.816323	7.146945	0.808945	1.070140	210.327009	0.877316	39.597651	1.486434	0.052821	0.253614
Ca RHF	8.593655	10.460644	1.477324	0.041891	1.436254	81.390382	1.182839	169.847839	7.113258	0.688098	0.196255
Sc RHF	1.476566	53.131022	1.487278	0.035325	1.600187	137.319495	9.177463	9.098031	7.099750	0.602102	0.157765
Ti RHF	9.818524	8.001879	1.522646	0.029763	1.703101	39.885423	1.768774	120.158000	7.082555	0.532405	0.102473
V RHF	10.473575	7.081940	1.547881	0.026040	1.986381	31.909672	1.865616	108.022844	7.056250	0.474882	0.067744
Cr RHF	11.007069	6.366281	1.555477	0.023987	2.985293	23.244838	1.347855	105.774500	7.034779	0.429369	0.065510
Mn RHF	11.709542	5.597120	1.733414	0.017800	2.673141	21.788419	2.023368	89.517915	7.003180	0.383054	-0.147293
Fe RHF	12.311098	5.009415	1.876623	0.014461	3.066177	18.743041	2.070451	82.767874	6.975185	0.346506	-0.304931
Co RHF	12.914510	4.507138	2.481908	0.009126	3.466894	16.438130	2.106351	76.987317	6.960892	0.314418	-0.936572
Ni RHF	13.521865	4.077277	6.947285	0.286763	3.866028	14.622634	2.135900	71.966078	4.284731	0.004437	-2.762697
Cu RHF	14.014192	3.738280	4.784577	0.003744	5.056806	13.034982	1.457971	72.554793	6.932996	0.265666	-3.254477
Zn RHF	14.741002	3.389232	6.907748	0.243315	4.642337	31.903689	2.191766	63.312130	38.424042	0.000397	-36.915828
Ga RHF	15.758946	3.121754	6.841123	0.226057	4.121016	12.482196	2.714681	66.203622	2.395246	0.007238	-0.847395
Ge RHF	16.540614	2.866618	1.567900	0.012198	3.727829	13.432163	3.345098	58.866046	6.785079	0.210974	0.018726
As RHF	17.025643	2.597739	4.503441	0.003012	3.715904	14.272119	3.937200	50.437997	6.790175	0.193015	-2.984117
Se RHF	17.354071	2.349787	4.653248	0.002550	4.259489	15.579460	4.136455	45.181201	6.749163	0.177432	-3.160982
Br RHF	17.550570	2.119226	5.411882	16.557185	3.937180	0.002481	3.880645	42.164009	6.707793	0.162121	-2.492088
Kr RHF	17.655279	1.908231	6.848105	16.606235	4.171004	0.001598	3.446760	39.917471	6.685200	0.146896	-2.810592
Rb RHF	8.123134	15.142385	2.138042	33.542666	6.761702	0.129372	1.156051	224.132506	17.679547	1.713368	1.139548
Sr RHF	17.730219	1.563060	9.795867	14.310868	6.099763	0.120574	2.620025	135.771318	0.600053	0.120574	1.140251
Y RHF*	17.792040	1.429691	10.253252	13.132816	5.714949	0.112173	3.170516	108.197029	0.918251	0.112173	1.131787
Zr RHF*	17.859771	1.310692	10.911038	12.319285	5.821115	0.104353	3.512513	91.777544	0.746965	0.104353	1.124859
Nb RHF*	17.958398	1.211590	12.063054	12.246687	5.007015	0.098615	3.287667	75.011944	1.531019	0.098615	1.123452
Mo RHF	6.236218	0.090780	17.987711	1.108310	12.973127	11.468720	3.451426	66.684153	0.210899	0.090780	1.108770
Tc RHF*	17.840964	1.005729	3.428236	41.901383	1.373012	119.320541	12.947364	9.781542	6.335469	0.083391	1.074784
Ru RHF*	6.271624	0.077040	17.906739	0.928222	14.123269	9.555345	3.746008	35.860678	0.908235	123.552247	1.043992
Rh RHF*	6.216648	0.070789	17.919738	0.856121	3.854252	33.889484	0.840326	121.686688	15.173498	9.029517	0.995452
Pd RHF*	6.121511	0.062549	4.784063	0.784031	16.631683	8.751391	4.318258	34.489983	13.246773	0.784031	0.883099
Ag RHF	6.073874	0.055333	17.155437	7.896512	4.173344	28.443739	0.852238	110.376108	17.986685	0.716809	0.756663
Cd RHF	6.080986	0.048990	18.019468	7.273646	4.018197	29.119283	1.303510	95.831208	17.974669	0.661231	0.603504
In RHF	6.196477	0.042072	18.816183	6.695665	4.050479	31.009791	1.638929	103.284350	17.962912	0.610714	0.333097
Sn RHF	19.325171	6.118104	6.281571	0.036915	4.498866	32.529047	1.856934	95.037182	17.917318	0.565651	0.119024

account for the density of $f(s_j)_o$ values varying over the whole range from 0.0 to 6.0 \AA^{-1} , the overall R values $R_{0,6}^V$ for the new expansions were calculated including a space weighting scheme. All differences $\Delta f(s) = |f(s_j)_o - f^V(s_j)_{\text{calc}}|$ were weighted with the Δs

distances from adjacent points. This measure precludes the dominance of the much denser 'observations' in the low- s regime.

Though all these agreement indices cannot reveal local deviations from the tabulated scattering-factor values,

Table 1(a) (cont.)

Atom	a_1	b_1	a_2	b_2	a_3	b_3	a_4	b_4	a_5	b_5	c
Sb RHF	5.394956	33.326523	6.549570	0.030974	19.650681	5.564929	1.827820	87.130965	17.867833	0.523992	-0.290506
Te RHF*	6.660302	33.031656	6.940756	0.025750	19.847015	5.065547	1.557175	84.101613	17.802427	0.487660	-0.806668
I RHF	19.884502	4.628591	6.736593	0.027754	8.110516	31.849096	1.170953	84.406391	17.548715	0.463550	-0.448811
Xe RHF	19.978920	4.143356	11.774945	0.010142	9.332182	28.796199	1.244749	75.280688	17.737501	0.413616	-6.065902
Cs RHF	17.418675	0.399828	8.314444	0.016872	10.323193	25.605828	1.383834	233.339674	19.876252	3.826915	-2.322802
Ba RHF	19.747344	3.481823	17.368476	0.371224	10.465718	21.226641	2.592602	173.834271	11.003653	0.010719	-5.183497
La RHF*	19.966018	3.197408	27.329654	0.003446	11.018425	19.955492	3.086696	141.381979	17.335454	0.341817	-21.745489
Ce RHF*	17.355121	0.328369	43.988498	0.002047	20.546650	3.088196	3.130670	134.907661	11.353665	18.832961	-38.386017
Pr RHF*	21.551311	2.995675	17.161729	0.312491	11.903859	17.716705	2.679103	152.192827	9.564197	0.010468	-3.871068
Nd RHF*	17.331244	0.300269	62.783923	0.001320	12.160097	17.026001	2.663483	148.748986	22.239951	2.910268	-57.189844
Pm RHF*	17.286388	0.286620	51.560161	0.001550	12.478557	16.223755	2.675515	143.984513	22.960947	2.796480	-45.973681
Sm RHF*	23.700364	2.689539	23.072215	0.003491	12.777782	15.495437	2.684217	139.862475	17.204366	0.274536	-17.452166
Eu RHF	17.186195	0.261678	37.156839	0.001995	13.103387	14.787360	2.707246	134.816293	24.419271	2.581883	-31.586687
Gd RHF*	24.898118	2.435028	17.104951	0.246961	13.222581	13.996325	3.266152	110.863093	48.995214	0.001383	-43.505684
Tb RHF*	25.910013	2.373912	32.344139	0.002034	13.765117	13.481969	2.751404	125.836511	17.064405	0.236916	-26.851970
Dy RHF*	26.671785	2.282593	88.687577	0.000665	14.065445	12.920230	2.768497	121.937188	17.067782	0.225531	-83.279831
Ho RHF*	27.150190	2.169660	16.999819	0.215414	14.059334	12.213148	3.386979	100.506781	46.546471	0.001211	-41.165253
Er RHF*	28.174886	2.120995	82.493269	0.000640	14.624002	11.915256	2.802756	114.529936	17.018515	0.207519	-77.135221
Tm RHF*	28.925894	2.046203	76.173796	0.000656	14.904704	11.465375	2.814812	111.411979	16.998117	0.195376	-70.839813
Yb RHF*	29.676760	1.977630	65.624068	0.000720	15.160854	11.044622	2.830288	108.139150	16.997850	0.192110	-60.313812
Lu RHF*	30.122865	1.883090	15.099346	10.342764	56.314899	0.000780	3.540980	89.559248	16.943730	0.183849	-51.049417
Hf RHF*	30.617033	1.795613	15.145351	9.934469	54.933548	0.000739	4.096253	76.189707	16.896157	0.175914	-49.719838
Ta RHF*	31.066358	1.708732	15.341823	9.618455	49.278296	0.000760	4.577665	66.346202	16.828321	0.168002	-44.119025
W RHF*	31.507901	1.629485	15.682498	9.446448	37.960127	0.000898	4.885509	59.980675	16.792113	0.160798	-32.864576
Re RHF*	31.888456	1.549238	16.117103	9.233474	42.390296	0.000689	5.211669	54.516371	16.767591	0.152815	-37.412681
Os RHF*	32.210298	1.473531	16.678440	9.049695	48.559907	0.000519	5.455839	50.210201	16.735532	0.145771	-43.677954
Ir RHF*	32.004437	1.353767	1.975454	81.014172	17.071014	0.128093	15.939454	7.661196	5.990003	26.659403	4.018893
Pt RHF*	31.273891	1.316992	18.445441	8.797154	17.063745	0.124741	5.555933	40.177994	1.575270	1.316997	4.050394
Au RHF	16.777389	0.122737	19.317156	8.621570	32.979682	1.256902	5.595453	38.008821	10.576854	0.000601	-6.279078
Hg RHF	16.839889	0.115905	20.023823	8.256927	28.428565	1.195250	5.881564	39.247226	4.714706	1.195250	4.076478
Tl RHF*	16.630795	0.110704	19.386615	7.181401	32.808570	1.119730	1.747191	90.660262	6.356862	26.014978	4.066939
Pb RHF	16.419567	0.105499	32.738592	1.055049	6.530247	25.025890	2.342742	80.906596	19.916475	6.664449	4.049824
Bi RHF	16.282274	0.101180	32.725137	1.002287	6.678302	25.714145	2.694750	77.057550	16.735559	6.291882	4.040914
Po RHF*	16.289164	0.098121	32.807170	0.966265	21.095164	6.046622	2.505901	76.598071	7.254589	28.096128	4.046556
At RHF*	16.011461	0.092639	32.615549	0.904416	8.113899	26.543256	2.884082	68.372961	21.377867	5.499512	3.995684
Rn RHF	16.070228	0.090437	32.641105	0.876409	21.489659	5.239687	2.299218	69.188477	9.480184	27.632640	4.020977
Fr RHF*	16.007386	0.087031	32.663830	0.840187	21.594351	4.954467	1.598497	199.805805	11.121192	26.905106	4.003472
Ra RHF*	32.563691	0.801980	21.396671	4.590666	11.298093	22.758973	2.834688	160.404392	15.914965	0.083544	3.981773
Ac RHF*	15.914053	0.080511	32.535042	0.770669	21.553976	4.352206	11.433394	21.381622	3.612409	130.500748	3.939212
Th RHF*	15.784024	0.077067	32.454898	0.735137	21.849222	4.097976	4.239077	109.464113	11.736191	20.512138	3.922533
Pa RHF*	32.740208	0.709545	21.973674	4.050881	12.957398	19.231542	3.683832	117.255006	15.744058	0.074040	3.886066
U RHF	15.679275	0.071206	32.824305	0.681177	13.660459	18.236157	3.687261	112.500040	22.279435	3.930325	3.854444
Np RHF*	32.999899	0.657086	22.638076	3.854918	14.219973	17.435474	3.672950	109.464485	15.683245	0.068033	3.769391
Pu RHF*	33.281176	0.634999	23.148545	3.856168	15.153755	16.849736	3.031492	121.292040	15.704215	0.064857	3.664200
Am RHF*	33.435163	0.612785	23.657259	3.792942	15.576339	16.195778	3.027023	117.757005	15.746100	0.061755	3.541160
Cm RHF*	15.804837	0.058619	33.480800	0.590160	24.150198	3.674720	3.655563	100.736192	15.499866	15.408296	3.390840
Bk RHF*	15.889072	0.055503	33.625285	0.569571	24.710380	3.615472	3.707139	97.694787	15.839268	14.754303	3.213169
Cf RHF*	33.794074	0.550447	25.467693	3.581973	16.048486	14.357388	3.657525	96.064975	16.008982	0.052450	3.005326

they are well suited to detect (possible) misprints in the published tables or systematic inconsistencies, examples of which are discussed below. Additionally, absolute maximum and mean deviations of $f^V(s)$ from the input $f(s_j)_0$ values were evaluated by inspection of the resulting $\Delta f(s)$ lists.

Results

Results are summarized in Tables 1 to 3. Tables 1(a) and (b) contain the new parameters to be used in the extended version of (1). The H atom is omitted because scattering is effectively zero for $s > 1.50 \text{ \AA}^{-1}$. Correspondingly,

Table 1 (cont.)

(b) For ions

Atom	a_1	b_1	a_2	b_2	a_3	b_3	a_4	b_4	a_5	b_5	c	
H ¹⁺	HF	0.702260	23.945605	0.763666	74.897918	0.248678	6.773289	0.261323	233.583447	0.023017	1.337531	0.000425
Li ¹⁺	RHF	0.432724	0.260367	0.549257	1.042836	0.376575	7.885294	-0.336481	0.260368	0.976060	3.042539	0.001764
Be ²⁺	RHF	3.055430	0.001226	-2.372617	0.001227	1.044914	1.542106	0.544233	0.456279	0.381737	4.047479	-0.653773
C ⁴⁺	HF	1.258489	10.683769	0.728215	0.208177	1.119856	0.836097	2.168133	24.603705	0.705239	58.954274	0.019722
O ¹⁻	HF	3.106934	19.868080	3.235142	6.960252	1.148886	0.170043	0.783981	65.693509	0.676953	0.630757	0.046136
F ¹⁻	HF	0.457649	0.917243	3.841561	5.507803	1.432771	0.164955	0.801876	51.076207	3.395041	15.821679	0.069525
Na ¹⁺	RHF	3.148690	2.594987	4.073989	6.046925	0.767888	0.070139	0.995612	14.122657	0.968249	0.217037	0.045300
Mg ²⁺	RHF	3.062918	2.015803	4.135106	4.417941	0.853742	0.065307	1.036792	9.669710	0.852520	0.187818	0.058851
Al ³⁺	HF	4.132015	3.528641	0.912049	7.378344	1.102425	0.133708	0.614876	0.039065	3.219136	1.644728	0.019397
Si ⁴⁺	HF	2.879033	1.239713	3.072960	38.706277	1.515981	0.081481	1.390030	93.616334	4.995051	2.770293	0.146030
Si ⁴⁺	HF	3.676722	1.446851	3.828496	3.013144	1.258033	0.064397	0.419024	0.206254	0.720421	5.970222	0.097266
Cl ¹⁻	RHF	1.061802	0.144727	7.139886	1.171795	6.524231	17.616756	2.355626	60.320301	35.829404	0.000436	-34.916604
K ¹⁺	RHF	-17.609339	18.840979	1.494873	0.053453	7.150305	0.812940	10.899569	22.264104	15.808228	14.351593	0.257164
Ca ²⁺	RHF	8.501441	10.525848	12.880483	-0.004033	9.765095	0.010692	7.156669	0.684443	0.711160	27.231772	-21.013188
Sc ³⁺	HF	7.104340	0.601957	1.511488	0.033386	-53.669773	12.572138	38.404815	10.859736	24.532240	14.125230	0.118642
Ti ²⁺	HF	7.040119	0.537072	1.496285	0.031914	9.857304	0.009958	0.006534	201.800290	0.006534	24.039483	0.015362
Ti ³⁺	HF	36.587932	0.000681	7.230255	0.522262	-9.086077	5.262317	2.084594	15.881716	17.294009	6.149805	-35.111284
Ti ⁴⁺	HF	45.355538	9.252186	7.092900	0.523046	7.483858	13.082852	-43.498818	10.193876	1.678915	0.023064	-0.110628
V ²⁺	RHF	7.754356	7.066315	2.064100	0.014993	2.576998	7.066308	2.011404	22.055786	7.126177	0.467568	-0.533379
V ³⁺	HF	9.958480	6.763041	1.596350	0.056895	1.843442	17.750029	-10.846044	0.328826	17.332868	0.888013	0.474921
V ⁵⁺	HF	15.575018	0.682708	8.448095	5.566640	1.612040	10.527077	-9.721855	0.907961	1.534029	0.066667	0.552676
Cr ²⁺	HF	10.598877	6.151846	1.565858	0.023519	2.728280	17.432815	0.098064	54.002388	6.959321	0.426301	0.049870
Cr ³⁺	HF	7.989310	0.608867	1.765079	0.018342	2.627125	6.068887	1.829380	16.309285	6.980908	0.420864	-0.192123
Mn ²⁺	RHF	11.287712	5.506225	26.042414	0.000774	3.058096	16.158576	0.090258	54.766353	7.088306	0.355800	-24.566131
Mn ³⁺	HF	6.926972	0.378315	2.081342	0.015054	11.128379	5.379957	2.375107	14.429586	-0.419287	0.004939	-0.093713
Mn ⁴⁺	HF	12.409131	0.300400	7.466993	0.112814	1.809947	12.520756	-12.138477	0.168653	10.780248	5.173237	0.672146
Fe ²⁺	RHF	11.776765	4.912232	11.165097	0.001748	3.533495	14.166556	0.165345	42.381959	7.036932	0.341324	-9.676919
Fe ³⁺	RHF	9.721638	4.869297	63.403845	0.002293	2.141347	4.867602	2.629274	13.539076	7.033846	0.338520	-61.930725
Co ²⁺	RHF	6.993840	0.310779	26.285812	0.000684	12.254289	4.400528	0.246114	35.741448	4.017407	12.536393	-24.796852
Co ³⁺	HF	6.861739	0.309794	2.678570	0.008142	12.281889	4.331703	3.501741	11.914167	-0.179384	11.914167	-1.147345
Ni ²⁺	RHF	12.519017	3.933053	37.832057	0.000442	4.387257	10.449184	0.661552	23.860999	6.949072	0.283723	-36.344472
Ni ³⁺	HF	13.579366	0.313140	1.902844	0.012621	12.859268	3.966407	3.811005	10.894311	-6.838595	0.344379	-0.317618
Cu ¹⁺	RHF	12.960763	3.576010	16.342150	0.000975	1.110102	29.523219	5.520682	10.114283	6.915452	0.261326	-14.849320
Cu ²⁺	HF	11.895569	3.378519	16.344979	0.000924	5.799817	8.133653	1.048804	20.526524	6.789088	0.254741	-14.878383
Zn ²⁺	RHF	13.340772	3.215913	10.428857	0.001413	5.544489	8.542680	0.762295	21.891757	6.869172	0.239215	-9.845248
Ga ³⁺	HF	13.123875	2.809960	35.288189	0.000323	6.126979	6.831534	0.611551	16.784312	6.724807	0.212002	-33.875121
Ge ⁴⁺	HF	6.876636	2.025174	6.779091	0.176650	9.969591	3.573822	3.135857	7.685848	0.152389	16.677575	1.086542
Br ¹⁻	RHF	17.714310	2.122554	6.466926	19.050767	6.947385	0.152708	4.402674	58.690361	-0.697279	58.690373	1.152674
Rb ¹⁺	RHF	17.684321	1.710209	7.761588	14.919863	6.680874	0.128542	2.668883	31.654478	0.070974	0.128543	1.133263
Sr ²⁺	RHF	17.694973	1.550888	1.275762	30.133042	6.154252	0.118774	9.234786	13.821799	0.515995	0.118774	1.125309
Y ³⁺	*DS	46.660366	-0.019971	10.369686	13.180257	4.623042	0.176398	-62.170835	-0.016727	17.471145	1.467348	19.023841
Zr ⁴⁺	*DS	6.802956	0.096228	17.699254	1.296127	10.650647	11.240715	-0.248108	-0.219259	0.250338	-0.219021	0.827902
Nb ⁵⁺	*DS	17.714323	1.172419	1.675213	30.102790	7.483963	0.080255	8.322464	-0.002983	11.143573	10.456687	-8.339573
Nb ⁵⁺	*DS	17.580206	1.165852	7.633277	0.078558	10.793497	9.507652	0.180884	31.621656	67.837924	-0.000438	-68.024780
Mo ³⁺	*DS	7.447050	0.072000	17.778122	1.073145	11.886068	9.834720	1.997905	28.221746	1.789626	-0.011674	-1.898764
Mo ⁵⁺	*DS	7.929879	0.688856	17.667670	1.068064	11.515987	9.046229	0.500402	26.558945	77.444084	-0.000473	-78.056896
Mo ⁶⁺	*DS	34.757684	1.301770	9.653037	7.123843	6.584769	0.094097	-18.628115	1.617443	2.490594	12.335434	1.141916
Ru ³⁺	*DS	17.894759	0.902827	13.579529	8.740579	10.729251	0.045125	2.474095	24.764953	48.227995	-0.001699	-51.905242
Ru ⁴⁺	*DS	17.845775	0.901070	13.455084	8.482392	10.229087	0.055972	1.653524	23.015273	14.059795	-0.004889	-17.241762
Rh ³⁺	*DS	17.758621	0.841779	14.569813	8.319533	5.298320	0.069050	2.533579	23.709131	0.879753	0.069050	0.960843
Rh ⁴⁺	*DS	17.716189	0.840572	14.446654	8.100647	5.185801	0.068995	1.703448	22.357308	0.989992	0.068995	0.959941
Pd ²⁺	*DS	6.122282	0.062424	15.651012	8.018296	3.513508	24.784276	9.060790	0.776457	8.771199	0.776457	0.879336
Pd ⁴⁺	*DS	6.125421	0.063951	-96.069025	11.090354	31.622140	13.466152	81.578258	9.758302	17.801403	0.783014	0.915874
Ag ¹⁺	*DS	6.091192	0.056305	4.019526	0.719340	16.948173	7.758938	4.258638	27.368350	13.889437	0.719340	0.785127
Ag ²⁺	*DS	6.401808	0.068167	48.699802	0.942270	4.799859	20.639496	-32.332524	1.100365	16.356710	6.883131	1.068247
Cd ²⁺	*DS	6.093711	0.050624	43.909690	8.654143	17.041305	15.621396	-39.675119	11.082067	17.958918	0.667591	0.664795
In ³⁺	*DS	6.206277	0.041357	18.497745	6.605563	3.078131	18.792249	10.524613	0.608082	7.401234	0.608082	0.293677
Sa ³⁺	RHF	6.353672	0.034720	4.770377	6.167891	14.672025	6.167879	4.235959	29.006456	18.002130	0.561774	-0.042519
Sa ⁴⁺	RHF	15.445732	6.280898	6.420892	0.033144	4.562980	6.280899	1.713385	17.983600	18.033536	0.557988	-0.172219
Sb ³⁺	*DS	10.189171	0.089485	57.461917	0.375256	19.356574	5.357987	4.862206	22.153737	-45.394095	0.297768	1.516108

Table 1(b) (cont.)

Atom	a_1	b_1	a_2	b_2	a_3	b_3	a_4	b_4	a_5	b_5	c	
Sb ³⁺	*DS	17.920621	0.522315	6.647932	0.029487	12.724075	5.718210	1.555545	16.433775	7.600591	5.718204	-0.445371
I ¹⁺	RHF	20.010331	4.565931	17.835523	0.444266	8.104130	32.430671	2.231118	95.149044	9.158548	0.014906	-3.341004
Cs ¹⁺	RHF	19.939057	3.770511	24.967620	0.004040	10.375884	25.311276	0.454243	76.537763	17.660247	0.384730	-19.394307
Ba ²⁺	*DS	19.750200	3.430748	17.513683	0.361590	10.884892	21.358307	0.321585	70.309404	65.149833	0.001418	-59.618171
La ³⁺	*DS	19.688887	3.146211	17.345704	0.339586	11.356296	18.753831	0.099418	90.345458	82.358127	0.001072	-76.846908
Ce ³⁺	*DS	26.593231	3.280381	85.866429	0.001012	-6.677695	4.313575	12.111847	17.868503	17.401904	0.326962	-80.313426
Ce ⁴⁺	*DS	17.457533	0.311812	25.659941	-0.003793	11.691037	16.568687	19.695251	2.886395	-16.994750	-0.008931	-3.515096
Pr ³⁺	*DS	20.879840	2.870897	36.035797	0.002364	12.135341	16.615237	0.283103	53.909360	17.167803	0.306993	-36.500784
Pr ⁴⁺	*DS	17.496082	0.294457	21.538509	-0.002742	20.403115	2.772886	12.062211	15.804613	-7.492403	-0.013556	-9.016722
Nd ³⁺	*DS	17.120078	0.291295	56.038141	0.001421	21.468307	2.743681	10.000671	14.581367	2.965866	22.480598	-56.5411992
Pm ³⁺	*DS	22.221066	2.635767	17.068141	0.277039	12.805423	14.927315	0.435687	45.768016	52.238770	0.001455	-46.767182
Sm ²⁺	*DS	15.618565	0.006001	19.538091	0.306379	13.398946	14.979594	-4.588111	0.748825	24.490462	2.454492	-9.714854
Eu ²⁺	*DS	23.899035	2.467332	31.657498	0.002230	12.955752	13.625002	1.700576	35.089480	16.992198	0.253136	-26.204316
Eu ³⁺	*DS	17.758327	0.244474	33.498665	-0.003901	24.067189	2.485752	13.436883	14.568011	-9.019134	-0.015628	-18.103626
Gd ³⁺	*DS	24.344999	2.333971	16.945311	0.239215	13.866931	12.982995	0.481674	43.876347	93.506377	0.000673	-88.147176
Tb ³⁺	*DS	24.878252	2.223301	16.856017	0.227290	13.663937	11.812528	1.279671	29.910064	39.271293	0.001527	-33.950316
Dy ³⁺	*DS	16.864344	0.216275	90.383461	0.000593	13.675473	11.121207	1.687078	26.250975	25.540652	2.135930	-85.150653
Ho ³⁺	*DS	16.837524	0.206873	63.221338	0.000796	13.703766	10.500283	2.601602	24.031883	26.202621	2.055060	-58.026503
Er ³⁺	*DS	16.810128	0.198293	22.681060	0.002126	13.864114	9.973341	2.294506	22.836387	26.864478	1.979442	-17.513461
Tm ³⁺	*DS	16.787501	0.190852	15.350905	0.003036	14.182357	9.602934	2.299111	22.526880	27.573770	1.912862	-10.192087
Yb ²⁺	*DS	28.443795	1.863896	16.849528	0.183811	14.165081	9.225469	3.445311	23.691354	28.308853	0.001463	-23.214936
Yb ³⁺	*DS	28.191629	1.842889	16.828086	0.182788	14.167848	9.045957	2.744962	20.799847	23.171773	0.001759	-18.103676
Lu ³⁺	*DS	28.828694	1.776641	16.823227	0.175560	14.247617	8.575531	3.079559	19.693701	25.647666	0.001453	-20.626528
Hf ⁴⁺	*DS	29.267378	1.697911	16.792544	0.168313	14.785310	8.190025	2.184128	18.277579	23.791996	0.001431	-18.820384
Ta ⁵⁺	*DS	29.539468	1.612934	16.741854	0.160460	15.182070	7.654408	1.642916	17.070733	16.437446	0.001858	-11.542459
W ⁶⁺	*DS	29.729357	1.501648	17.247808	0.140803	15.184488	6.880573	1.154652	14.299601	0.739335	14.299601	3.945157
Os ⁴⁺	*DS	17.113485	0.131850	15.792370	7.288542	23.342392	1.389307	4.090271	19.629425	7.671292	1.389307	3.983390
Ir ³⁺	*DS	31.537575	1.334144	16.363339	7.451918	15.597141	0.127514	5.051404	21.705648	1.436935	0.127515	4.009459
Ir ⁴⁺	*DS	30.391248	1.328519	16.146995	7.181766	17.019068	0.127337	4.458904	19.060147	0.975372	1.328519	4.006865
Pt ²⁺	*DS	31.986849	1.281143	17.249048	7.625512	15.269374	0.123571	5.760234	24.190826	1.694079	0.123571	4.032512
Pt ⁴⁺	*DS	41.932714	1.111409	16.339224	6.466086	17.653895	0.128917	6.012420	16.954155	-12.036877	0.778721	4.094551
Au ¹⁺	*DS	32.124307	1.216073	16.716476	7.165378	16.814101	0.118715	7.311565	20.442485	0.993064	53.095984	4.040792
Au ³⁺	*DS	31.704272	1.215561	17.545767	7.220506	16.819552	0.118812	5.522640	20.050970	0.361725	1.215562	4.042679
Hg ¹⁺	*DS	28.866837	1.173967	19.277541	7.583842	16.776051	0.115351	6.281459	29.055994	3.710289	1.173968	4.068430
Hg ²⁺	*DS	32.411081	1.162980	18.690371	7.329806	16.711773	0.114518	9.974835	22.009489	-3.847611	22.009493	4.052869
Tl ¹⁺	*DS	32.295045	1.101544	16.570049	0.110020	17.991013	6.528559	1.535355	52.495068	7.554591	20.338635	4.054030
Tl ³⁺	*DS	32.525638	1.094966	19.139185	6.900992	17.100320	0.103667	5.891115	18.489615	12.599463	-0.001401	-9.256075
Pb ²⁺	*DS	27.392647	1.058874	16.496823	0.106305	19.984500	6.708123	6.813923	24.395554	5.233910	1.058874	4.065623
Pb ⁴⁺	*DS	32.505656	1.047035	20.014240	6.670321	14.645661	0.105279	5.029499	16.525040	1.760138	0.105279	4.044678
Bi ³⁺	*DS	32.461438	0.997930	19.438682	6.038867	16.302487	0.101338	7.322662	18.371585	0.431704	46.361045	4.043703
Bi ⁵⁺	*DS	16.734028	0.105076	20.580493	4.773282	9.452623	11.762162	61.155835	1.211775	-34.041022	1.619408	4.113663
Ra ²⁺	*DS	4.986228	0.082597	32.474946	0.791468	21.947443	4.680034	11.800013	24.792431	10.807292	0.082597	3.956572
Ac ³⁺	*DS	15.584983	0.077438	32.022127	0.739963	21.456327	4.040735	0.757593	47.525000	12.341252	19.406846	3.839884
Th ⁴⁺	*DS	15.515445	0.074499	32.090691	0.711663	13.996399	3.871044	12.918157	18.596891	7.635514	3.871044	3.831122
U ³⁺	*DS	15.360309	0.067815	32.395655	0.654643	21.961291	3.643409	1.325894	39.604964	14.251453	16.330571	3.706622
U ⁴⁺	*DS	15.355091	0.067789	32.235305	0.652613	0.557745	42.354235	14.396367	15.908239	21.751173	3.553231	3.705863
U ⁶⁺	*DS	15.333844	0.067644	31.770849	0.646384	21.274415	3.317894	13.872636	14.650250	0.048519	75.339700	3.700591
Np ³⁺	*DS	15.378152	0.064613	32.572134	0.631420	22.206126	3.561936	1.413295	37.875511	14.828381	15.546129	3.603370
Np ⁴⁺	*DS	15.373926	0.064597	32.423018	0.629658	21.969994	3.476389	0.662078	39.438942	14.969350	15.135764	3.603039
Np ⁶⁺	*DS	15.359986	0.064528	31.992824	0.624505	21.412458	3.253441	0.066574	67.658315	14.568174	13.980832	3.600942
Pu ³⁺	*DS	15.356004	0.060590	32.769126	0.604663	22.680210	3.491509	1.351055	37.260635	15.416232	14.981921	3.428895
Pu ⁴⁺	*DS	15.416219	0.061456	32.610569	0.607938	22.256662	3.411848	0.719495	37.628793	15.518152	14.464360	3.480408
Pu ⁶⁺	*DS	15.436506	0.061815	32.289717	0.606541	14.726737	3.245363	15.012391	13.616438	7.024677	3.245364	3.502325

Tables 2(a) and (b) list the various agreement indices defined above that act as figures of merit for the different analytical representations. Both the mean and the absolute maximum deviations from the tabulated values, the latter along with the corresponding s values are finally given in Tables 3(a) and (b). These deviations allow a quick estimate of the error introduced by using $f^V(s)$.

Discussion

In addition to Tables 1–3, a detailed compilation of all relevant results (one page per atom or ion) has been prepared in the form of an 'atlas', which is available on request. An example is given in Fig. 1 for the Si atom. Si has been chosen because it is a frequently used element and shows one of the inconsistencies mentioned above.

The box in the upper half of Fig. 1 contains the new fit results, parameters and R values, followed by the 0.0–2.0 \AA^{-1} representations of *International Tables for Crystallography* (1992), Vol. C along with their agreement indices, and finally the 2.0–6.0 \AA^{-1} representa-

tions of Fox, O'Keefe & Tabbernor (1989), again with an R value. The plot below depicts the tabulated $f(s)$ values and all three functions. For clarity, the inset provides an enlargement of the range 1.5–6.0 \AA^{-1} , which is of special interest in the following.

Si

14

Parameters and results of 5 Gaussian fit (V)						
a1 =	5.275329	b1 =	2.631338	Maximum error	$\sin \theta/\lambda$	Mean error
a2 =	3.191038	b2 =	33.730728	0.008	4.00	0.001
a3 =	1.511514	b3 =	0.081119			
a4 =	1.356849	b4 =	86.288640		$R_{0.2}^V = 0.0003$	
a5 =	2.519114	b5 =	1.170087		$R_{2.6}^V = 0.0082$	
c =	0.145073				$R_{0.6}^V = 0.0021$	
Parameters and results of 4 Gaussian fit (IV)						
a1 =	6.291500	b1 =	2.438600	Maximum error	$\sin \theta/\lambda$	Mean error
a2 =	3.035300	b2 =	32.333698	0.009	2.00	0.002
a3 =	1.989100	b3 =	0.678500			
a4 =	1.541000	b4 =	81.693703		$R_{0.2}^{IV} = 0.0005$	
c =	1.140700				$R_{2.6}^{IV} = 0.7871$	
Parameters and results of logarithmic polynomial fit (LP)						
a0 =	0.7068300					
a1 =	-0.0988800					
a2 =	-0.0983560				$R_{2.6}^{LP} = 0.1982$	
a3 =	0.0055631					

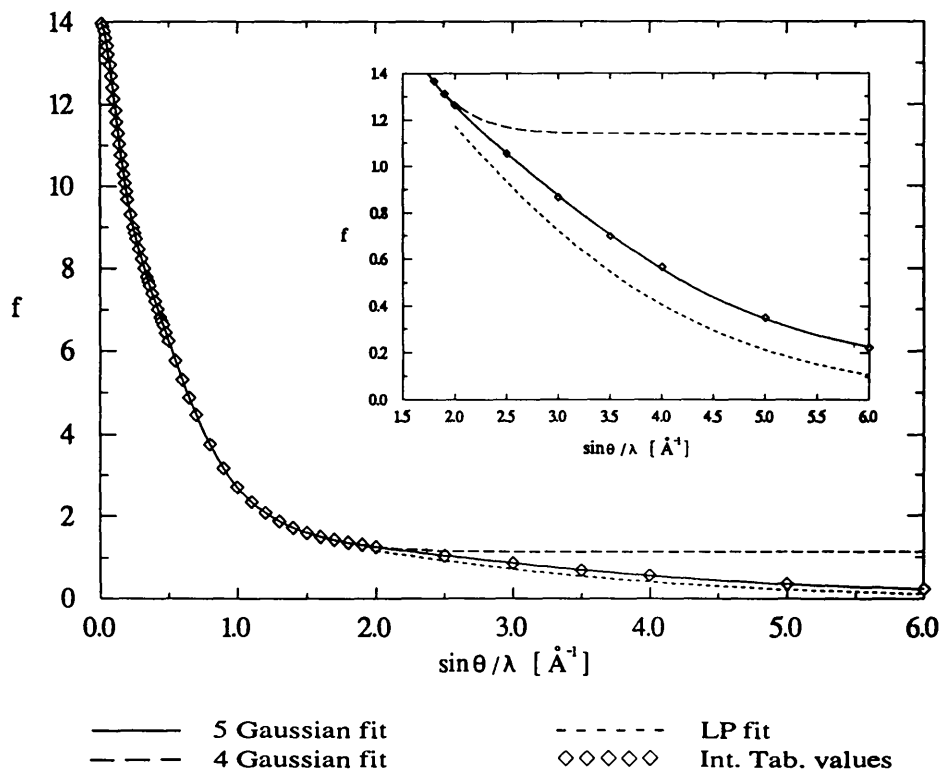


Fig. 1 Scattering-factor parametrizations for neutral Si, full excerpt from the scattering-factor 'atlas'. For details see text.

Table 2. Agreement indices of $f(s)$ fits

(a) For neutral atoms

Atom		$R_{0,2}^{IV}$	$R_{0,2}^V$	$R_{2,6}^{IV}$	$R_{2,6}^{LP}$	$R_{2,6}^V$	$R_{0,6}^V$
He	RHF	0.0007	0.0005	1.6664	0.0679	0.1104	0.0019
Li	RHF	0.0020	0.0007	2.2211	0.0229	0.0924	0.0037
Be	RHF	0.0007	0.0008	0.6179	0.0087	0.0032	0.0014
B	RHF	0.0005	0.0005	1.6847	0.0018	0.0054	0.0009
C	RHF	0.0008	0.0009	1.1061	0.0020	0.0096	0.0024
N	RHF	0.0011	0.0013	3.6053	0.0032	0.0080	0.0029
O	RHF	0.0001	0.0001	0.4703	0.0030	0.0035	0.0010
F	RHF	0.0002	0.0002	0.3549	0.0029	0.0019	0.0007
Ne	RHF	0.0002	0.0003	0.3557	0.0086	0.0068	0.0024
Na	RHF	0.0007	0.0011	0.7095	0.0021	0.0089	0.0030
Mg	RHF	0.0010	0.0007	0.7790	0.1740	0.0195	0.0054
Al	RHF	0.0013	0.0004	0.9403	0.0024	0.0116	0.0034
Si	RHF	0.0005	0.0003	0.7871	0.1982	0.0082	0.0021
P	RHF	0.0002	0.0002	0.6204	0.0056	0.0023	0.0011
S	RHF	0.0003	0.0004	0.2915	0.0081	0.0022	0.0081
Cl	RHF	0.0005	0.0005	0.9697	0.0108	0.0019	0.0010
Ar	RHF	0.0010	0.0008	0.6176	0.0126	0.0098	0.0033
K	RHF	0.0007	0.0010	0.5076	0.0136	0.0064	0.0020
Ca	RHF	0.0008	0.0011	0.3970	0.0131	0.0026	0.0017
Sc	RHF	0.0008	0.0011	0.3085	0.0121	0.0035	0.0021
Ti	RHF	0.0008	0.0011	0.2273	0.0107	0.0052	0.0023
V	RHF	0.0006	0.0011	0.1665	0.0123	0.0061	0.0021
Cr	RHF	0.0005	0.0009	0.1273	0.0084	0.0056	0.0017
Mn	RHF	0.0004	0.0009	0.0881	0.0086	0.0053	0.0018
Fe	RHF	0.0004	0.0008	0.0704	0.0078	0.0045	0.0018
Co	RHF	0.0004	0.0007	0.0586	0.0077	0.0036	0.0017
Ni	RHF	0.0004	0.0006	0.0497	0.1535	0.0029	0.0017
Cu	RHF	0.0005	0.0006	0.0467	0.0093	0.0023	0.0015
Zn	RHF	0.0005	0.0007	0.0640	0.0100	0.0029	0.0014
Ga	RHF	0.0008	0.0010	0.1848	0.0100	0.0035	0.0015
Ge	RHF	0.0008	0.0011	0.2919	0.0102	0.0037	0.0014
As	RHF	0.0007	0.0010	0.3843	0.0100	0.0034	0.0014
Se	RHF	0.0006	0.0009	0.4416	0.0095	0.0032	0.0015
Br	RHF	0.0004	0.0006	0.4388	0.0087	0.0034	0.0016
Kr	RHF	0.0002	0.0004	0.3739	0.0138	0.0039	0.0017
Rb	RHF	0.0006	0.0002	0.5064	0.0064	0.0054	0.0021
Sr	RHF	0.0003	0.0006	0.2588	0.0069	0.0043	0.0021
Y	RHF*	0.0004	0.0007	0.1429	0.0074	0.0045	0.0023
Zr	RHF*	0.0005	0.0008	0.1647	0.1813	0.0058	0.0028
Nb	RHF*	0.0008	0.0011	0.4392	0.0121	0.0099	0.0036
Mo	RHF	0.0008	0.0012	0.5288	0.0079	0.0065	0.0030
Tc	RHF*	0.0007	0.0008	0.7264	0.0090	0.0101	0.0037
Ru	RHF*	0.0004	0.0009	0.6725	0.0100	0.0105	0.0040
Rh	RHF*	0.0003	0.0010	0.6166	0.0112	0.0117	0.0046
Pd	RHF*	0.0003	0.0010	0.5601	0.0132	0.0142	0.0054
Ag	RHF	0.0004	0.0008	0.5020	0.0135	0.0149	0.0058
Cd	RHF	0.0004	0.0009	0.4448	0.0139	0.0158	0.0062
In	RHF	0.0005	0.0010	0.3884	0.0135	0.0164	0.0063
Sn	RHF	0.0005	0.0011	0.3284	0.0133	0.0173	0.0065

The broken curve $f^{IV}(s)$ is typical for most elements. Above $s = 2.0 \text{ \AA}^{-1}$, the function levels off and remains almost constant for Si at 1.17 e. Thus, the $f^{IV}(s)$ values between 2.0 and 6.0 \AA^{-1} are systematically too large. At 6.0 \AA^{-1} , the error amounts to several hundred percent. These findings are also expressed by $R_{2,6}^{IV} = 0.787$

compared with $R_{0,2}^{IV} = 0.0005$, the latter indicating an excellent fit. Exceptions from the above-mentioned behaviour are found for the elements between Ba ($Z = 56$) and Tb ($Z = 65$), for which the opposite occurs. $f^{IV}(s)$ becomes lower than the tabulated values, though approaches them as s increases. Also untypical

Table 2(a) (cont.)

Atom		$R_{0,2}^{IV}$	$R_{0,2}^V$	$R_{2,6}^{IV}$	$R_{2,6}^{LP}$	$R_{2,6}^V$	$R_{0,6}^V$
Sb	RHF	0.0005	0.0012	0.2728	0.0131	0.0174	0.0065
Te	RHF*	0.0004	0.0013	0.2276	0.0124	0.0173	0.0063
I	RHF	0.0004	0.0015	0.1785	0.0121	0.0128	0.0050
Xe	RHF	0.0004	0.0013	0.1416	0.0111	0.0174	0.0064
Cs	RHF	0.0005	0.0015	0.1223	0.0106	0.0117	0.0052
Ba	RHF	0.0004	0.0014	0.1257	0.0114	0.0107	0.0051
La	RHF*	0.0006	0.0014	0.1721	0.0128	0.0105	0.0052
Ce	RHF*	0.0004	0.0013	0.2046	0.0136	0.0098	0.0052
Pr	RHF*	0.0003	0.0010	0.1819	0.0166	0.0117	0.0055
Nd	RHF*	0.0003	0.0011	0.1836	0.0130	0.0088	0.0047
Pm	RHF*	0.0003	0.0011	0.1752	0.0116	0.0086	0.0042
Sm	RHF*	0.0003	0.0011	0.1525	0.0100	0.0096	0.0041
Eu	RHF	0.0003	0.0011	0.1136	0.0092	0.0096	0.0038
Gd	RHF*	0.0004	0.0010	0.1247	0.0101	0.0120	0.0039
Tb	RHF*	0.0004	0.0009	0.0433	0.0102	0.0118	0.0038
Dy	RHF*	0.0004	0.0009	0.0507	0.0107	0.0121	0.0043
Ho	RHF*	0.0005	0.0009	0.0717	0.0110	0.0125	0.0047
Er	RHF*	0.0005	0.0009	0.1887	0.0108	0.0114	0.0047
Tm	RHF*	0.0005	0.0008	0.2563	0.0103	0.0107	0.0048
Yb	RHF*	0.0005	0.0008	0.3202	0.0099	0.0102	0.0048
Lu	RHF*	0.0005	0.0009	0.3437	0.0092	0.0093	0.0047
Hf	RHF*	0.0006	0.0009	0.3844	0.0124	0.0083	0.0045
Ta	RHF*	0.0006	0.0009	0.4287	0.0093	0.0067	0.0040
W	RHF*	0.0006	0.0009	0.4699	0.0088	0.0057	0.0038
Re	RHF*	0.0006	0.0009	0.5052	0.0086	0.0049	0.0036
Os	RHF*	0.0006	0.0009	0.5347	0.0086	0.0048	0.0035
Ir	RHF*	0.0006	0.0003	0.5573	0.0095	0.0071	0.0039
Pt	RHF*	0.0005	0.0008	0.5566	0.0102	0.0065	0.0039
Au	RHF	0.0005	0.0008	0.5703	0.0097	0.0055	0.0032
Hg	RHF	0.0005	0.0008	0.5979	0.0099	0.0054	0.0031
Tl	RHF*	0.0007	0.0004	0.6278	0.0100	0.0056	0.0026
Pb	RHF	0.0007	0.0003	0.6266	0.0095	0.0063	0.0028
Bi	RHF	0.0006	0.0003	0.6191	0.0091	0.0065	0.0027
Po	RHF*	0.0005	0.0005	0.6056	0.0087	0.0069	0.0027
At	RHF*	0.0005	0.0004	0.5868	0.0084	0.0081	0.0032
Rn	RHF	0.0004	0.0006	0.5628	0.0086	0.0088	0.0031
Fr	RHF*	0.0005	0.0007	0.5450	0.0085	0.0091	0.0033
Ra	RHF*	0.0003	0.0007	0.5153	0.0092	0.0095	0.0033
Ac	RHF*	0.0002	0.0008	0.4896	0.0106	0.0108	0.0039
Th	RHF*	0.0002	0.0007	0.4613	0.0101	0.0097	0.0034
Pa	RHF*	0.0002	0.0007	0.4426	0.0104	0.0094	0.0033
U	RHF	0.0002	0.0007	0.4229	0.0106	0.0087	0.0033
Np	RHF*	0.0002	0.0007	0.4031	0.0112	0.0092	0.0037
Pu	RHF*	0.0003	0.0007	0.3888	0.0116	0.0096	0.0042
Am	RHF*	0.0003	0.0006	0.3717	0.0120	0.0100	0.0047
Cm	RHF*	0.0003	0.0006	0.3519	0.0122	0.0103	0.0052
Bk	RHF*	0.0003	0.0006	0.3367	0.0123	0.0106	0.0057
Cf	RHF*	0.0003	0.0006	0.3225	0.0124	0.0110	0.0063

are the commonly used elements B, N and Cl for which $f^{IV}(s)$ diverges and even becomes negative. As already noted by Fox, O'Keefe & Tabbemor (1989), the N atom shows the most remarkable inadequacy of $f^{IV}(s)$, expressed by $R_{2,6}^{IV} = 3.605$ (Table 2a).

Similarly detected from an agreement index is the error in the $f^{LP}(s)$ representation of Si (Fig. 1), $R_{2,6}^{LP} = 0.198$. The plot reveals that $f^{LP}(s)$ contains a systematic

error that seemed to be due to a misprint of a_0 on first sight. An erroneous a_0 value should introduce a constant offset from the tabulated values; however, Fig. 1 shows the deviation increasing with s . Other examples of such inconsistencies are Mg, Ni and Zr (see Table 2a). There are also two apparent misprints in Table 6.1.1.1 of *International Tables for Crystallography* (1992), Vol. C, which were corrected for the $f^V(s)$ fits. For P at

Table 2 (cont.)

(b) For ions

Atom	$R_{0,2}^{IV}$	$R_{0,2}^V$	$R_{2,6}^{IV}$	$R_{2,6}^V$	$R_{0,6}^V$	
H ¹⁻	HF	0.0048	0.0019	not defined	not defined	not defined
Li ¹⁺	RHF	0.0007	0.0006	0.8110	0.0300	0.0019
Be ²⁺	RHF	0.0003	0.0003	5.0402	0.0821	0.0084
C _{val}	HF	0.0021	0.0011	1.6130	0.0349	0.0070
O ¹⁻	HF	0.0129	0.0009	*****	0.0348	0.0076
F ¹⁻	HF	0.0029	0.0009	1.2726	0.0388	0.0092
Na ¹⁺	RHF	0.0001	0.0001	0.3170	0.0005	0.0003
Mg ²⁺	RHF	0.0001	0.0001	0.3131	0.0008	0.0004
Al ³⁺	HF	0.0003	0.0001	0.4412	0.0004	0.0001
Si _{val}	HF	0.0012	0.0004	0.9288	0.0088	0.0024
Si ⁴⁺	HF	0.0003	0.0001	0.3684	0.0025	0.0008
Cl ¹⁻	RHF	0.0005	0.0007	1.0904	0.0105	0.0036
K ¹⁺	RHF	0.0008	0.0009	0.6850	0.0066	0.0022
Ca ²⁺	RHF	0.0007	0.0011	2.0046	0.0057	0.0024
Sc ³⁺	HF	0.0067	0.0009	*****	0.0061	0.0025
Ti ²⁺	HF	0.0036	0.0007	0.1594	0.0035	0.0017
Ti ³⁺	HF	0.0031	0.0006	*****	0.0244	0.0075
Ti ⁴⁺	HF	0.0057	0.0012	*****	0.0084	0.0035
V ²⁺	RHF	0.0006	0.0008	0.1701	0.0096	0.0037
V ³⁺	HF	0.0033	0.0005	0.2027	0.0048	0.0023
V ⁵⁺	HF	0.0004	0.0004	0.4397	0.0137	0.0038
Cr ²⁺	HF	0.0027	0.0006	0.2223	0.0052	0.0014
Cr ³⁺	HF	0.0026	0.0007	0.2735	0.0074	0.0020
Mn ²⁺	RHF	0.0003	0.0007	0.0883	0.0097	0.0032
Mn ³⁺	HF	0.0024	0.0006	0.3227	0.0053	0.0017
Mn ⁴⁺	HF	0.0022	0.0005	0.3882	0.0077	0.0020
Fe ²⁺	RHF	0.0002	0.0006	0.0694	0.0074	0.0024
Fe ³⁺	RHF	0.0002	0.0006	0.0712	0.0076	0.0026
Co ²⁺	RHF	0.0001	0.0005	0.0726	0.0055	0.0020
Co ³⁺	HF	0.0018	0.0006	0.3300	0.0031	0.0018
Ni ²⁺	RHF	0.0001	0.0004	0.0821	0.0037	0.0017
Ni ³⁺	HF	0.0015	0.0008	0.2721	0.0021	0.0017
Cu ¹⁺	RHF	0.0001	0.0003	0.0716	0.0036	0.0014
Cu ²⁺	HF	0.0010	0.0006	0.0476	0.0041	0.0020
Zn ²⁺	RHF	0.0000	0.0002	0.1035	0.0039	0.0014
Ga ³⁺	HF	0.0011	0.0008	0.1282	0.0085	0.0030
Ge ⁴⁺	HF	0.0012	0.0008	0.0937	0.0211	0.0071
Br ¹⁻	RHF	0.0005	0.0009	0.5000	0.0109	0.0042
Rb ¹⁺	RHF	0.0001	0.0002	0.1864	0.0059	0.0021
Sr ²⁺	RHF	0.0001	0.0003	2.1009	0.0056	0.0021
Y ³⁺	*DS	0.0001	0.0012	1.7818	0.0109	0.0049
Zr ⁴⁺	*DS	0.0001	0.0007	9.1766	0.0019	0.0014
Nb ³⁺	*DS	0.0002	0.0004	0.4875	0.0106	0.0036
Nb ⁵⁺	*DS	0.0002	0.0005	0.3342	0.0109	0.0038
Mo ³⁺	*DS	0.0002	0.0004	0.3416	0.0063	0.0026
Mo ⁵⁺	*DS	0.0002	0.0005	0.3169	0.0064	0.0027
Mo ⁶⁺	*DS	0.0004	0.0001	0.575	0.0038	0.0011

Table 2(b) (cont.)

Atom	$R_{0,2}^{IV}$	$R_{0,2}^V$	$R_{2,6}^{IV}$	$R_{2,6}^V$	$R_{0,6}^V$	
Ru ³⁺	*DS	0.0002	0.0006	0.1655	0.0074	0.0029
Ru ⁴⁺	*DS	0.0778	0.0006	0.4539	0.0075	0.0029
Rh ³⁺	*DS	0.0002	0.0007	0.3232	0.0142	0.0048
Rh ⁴⁺	*DS	0.0002	0.0007	0.3531	0.0142	0.0049
Pd ²⁺	*DS	0.0003	0.0007	0.5656	0.0146	0.0051
Pd ⁴⁺	*DS	0.0002	0.0007	0.7011	0.0128	0.0047
Ag ¹⁺	*DS	0.0002	0.0008	0.5093	0.0144	0.0054
Ag ²⁺	*DS	0.0003	0.0003	0.5089	0.0045	0.0016
Cd ²⁺	*DS	0.0003	0.0007	0.4546	0.0141	0.0055
In ³⁺	*DS	0.0004	0.0008	0.3994	0.0162	0.0063
Sn ²⁺	RHF	0.0005	0.0011	0.3292	0.0183	0.0072
Sn ⁴⁺	RHF	0.0002	0.0010	*****	0.0193	0.0076
Sb ³⁺	*DS	0.0004	0.0005	0.2865	0.0048	0.0024
Sb ⁵⁺	*DS	0.0004	0.0010	0.2859	0.0175	0.0068
I ¹⁻	RHF	0.0004	0.0012	0.1786	0.0179	0.0068
Cs ¹⁺	RHF	0.0004	0.0013	0.1213	0.0167	0.0065
Ba ²⁺	*DS	0.0003	0.0011	0.1110	0.0140	0.0059
La ³⁺	*DS	0.0003	0.0011	0.1378	0.0113	0.0053
Ce ³⁺	*DS	0.0002	0.0010	0.1764	0.0099	0.0049
Ce ⁴⁺	*DS	0.0003	0.0011	0.2355	0.0123	0.0062
Pr ³⁺	*DS	0.0002	0.0009	0.2111	0.0110	0.0051
Pr ⁴⁺	*DS	0.0002	0.0009	0.2701	0.0125	0.0062
Nd ³⁺	*DS	0.0001	0.0009	0.2386	0.0119	0.0053
Pm ³⁺	*DS	0.0001	0.0007	0.2616	0.0112	0.0048
Sm ³⁺	*DS	0.0001	0.0009	0.2772	0.0054	0.0026
Eu ²⁺	*DS	0.0001	0.0005	0.2316	0.0117	0.0046
Eu ³⁺	*DS	0.0000	0.0010	0.2866	0.0084	0.0040
Gd ³⁺	*DS	0.0004	0.0008	0.2862	0.0132	0.0046
Tb ³⁺	*DS	0.0001	0.0004	0.2720	0.0139	0.0045
Dy ³⁺	*DS	0.0000	0.0004	0.2622	0.0144	0.0046
Ho ³⁺	*DS	0.0000	0.0004	0.2398	0.0145	0.0049
Er ³⁺	*DS	0.0000	0.0004	0.2071	0.0141	0.0051
Tm ³⁺	*DS	0.0001	0.0003	0.1663	0.0134	0.0052
Yb ²⁺	*DS	0.0001	0.0003	0.0273	0.0127	0.0051
Yb ³⁺	*DS	0.0001	0.0003	0.1165	0.0131	0.0053
Lu ³⁺	*DS	0.0001	0.0003	0.0634	0.0119	0.0050
Hf ⁴⁺	*DS	0.0000	0.0003	0.0978	0.0107	0.0049
Ta ⁵⁺	*DS	0.0000	0.0003	0.1285	0.0093	0.0044
W ⁶⁺	*DS	0.0000	0.0002	0.1623	0.0148	0.0061
Os ⁴⁺	*DS	0.0001	0.0002	0.1721	0.0094	0.0046
Ir ³⁺	*DS	0.0001	0.0003	0.2902	0.0072	0.0039
Ir ⁴⁺	*DS	0.0001	0.0002	0.1973	0.0073	0.0039
Pt ²⁺	*DS	0.0002	0.0003	0.3985	0.0066	0.0036
Pt ⁴⁺	*DS	0.0001	0.0001	0.2190	0.0059	0.0032
Au ¹⁺	*DS	0.0003	0.0003	0.4956	0.0060	0.0030
Au ³⁺	*DS	0.0001	0.0003	0.3272	0.0060	0.0030
Hg ¹⁺	*DS	0.0003	0.0005	0.5442	0.0057	0.0030

$s = 2.50 \text{ \AA}^{-1}$, f is very probably 1.122, and likewise for Am at $s = 3.50 \text{ \AA}^{-1}$, $f = 11.095$. While these six cases should be reviewed, the majority of the elements show $f^{LP}(s)$ and $f^V(s)$ graphs that can hardly be

distinguished, in agreement with the corresponding $R_{2,6}^{LP}$ and $R_{2,6}^V$ indices. An example is Ba, shown in Fig. 2.

Finally, the full curve of Fig. 1 depicts the new $f^V(s)$ representation with an overall $R_{0,6}^V = 0.0021$ and $R_{0,2}^V =$

Table 2(b) (cont.)

Atom	$R_{0,2}^{IV}$	$R_{0,2}^V$	$R_{2,6}^{IV}$	$R_{2,6}^V$	$R_{0,6}^V$	
Hg ²⁺	*DS	0.0002	0.0003	0.4278	0.0058	0.0028
Tl ¹⁺	*DS	0.0003	0.0002	0.5678	0.0061	0.0026
Tl ³⁺	*DS	0.0002	0.0002	0.3514	0.0067	0.0030
Pb ²⁺	*DS	0.0002	0.0004	0.5415	0.0058	0.0026
Pb ⁴⁺	*DS	0.0001	0.0003	0.2329	0.0065	0.0028
Bi ³⁺	*DS	0.0002	0.0003	0.5206	0.0064	0.0026
Bi ⁵⁺	*DS	0.1997	0.0002	1.6264	0.0048	0.0018
Ra ²⁺	*DS	0.0002	0.0006	0.5086	0.0094	0.0036
Ac ³⁺	*DS	0.0001	0.0004	0.4843	0.0118	0.0045
Th ⁴⁺	*DS	0.0001	0.0004	0.4567	0.0105	0.0039
U ³⁺	*DS	0.0001	0.0003	0.4160	0.0102	0.0038
U ⁴⁺	*DS	0.0000	0.0003	0.4128	0.0102	0.0038
U ⁶⁺	*DS	0.0000	0.0004	0.4052	0.0103	0.0039
Np ³⁺	*DS	0.0000	0.0003	0.3953	0.0108	0.0040
Np ⁴⁺	*DS	0.0000	0.0004	0.3922	0.0108	0.0040
Np ⁶⁺	*DS	0.0000	0.0004	0.3849	0.0108	0.0040
Pu ³⁺	*DS	0.0001	0.0004	0.3754	0.0118	0.0046
Pu ⁴⁺	*DS	0.0000	0.0004	0.3722	0.0112	0.0045
Pu ⁶⁺	*DS	0.0000	0.0004	0.3652	0.0109	0.0045

0.0003, which is even lower than $R_{0,2}^{IV} = 0.0005$. This result is, however, accidental. For most elements, $R_{0,2}^V$ is somewhat larger than $R_{0,2}^{IV}$. Simultaneously, however, $R_{2,6}^V$ is often lower than $R_{2,6}^{IV}$ so that in general $f^V(s)$ gives an equally valid or even better representation of the tabulated scattering-factor values than taking $f^{IV}(s)$ and $f^{LP}(s)$ together. Inspecting Table 2, the reader may easily convince himself that, using the unified and thus more convenient $f^V(s)$, neither unwanted nor unacceptable errors are introduced.

As to the scattering factors of the ions, the functions $f^{LP}(s)$ are the same as for the neutral atoms. Hence, the same remarks apply and only $f^{IV}(s)$ and $f^V(s)$ need to be compared. Again, for many of the ions, $f^{IV}(s)$ levels off

above $s = 2.0 \text{ \AA}^{-1}$ providing systematically too large or too small scattering-factor values. Occasionally, there are also $f^{IV}(s)$ curves showing more or less drastic increases above 2.0 \AA^{-1} , which compromise any application of them. These are in particular those of K^+ , Ca^{2+} , Sc^{3+} , Ti^{3+} , Ti^{4+} and Sn^{4+} , all ions that cannot be called exotic. Fig. 3 illustrates the situation for Ti^{4+} indicating that the use of $f^{IV}(s)$ beyond 2.0 \AA^{-1} is fatal. For such a case, the corresponding agreement index is so large that it has been denoted by '*****' in Table 2(b). In other cases, $f^{IV}(s)$ diverges to negative values: Be^{2+} , O^- , Cl^- , Sr^{2+} , Y^{3+} , Zr^{4+} , Nb^{3+} , Nb^{5+} , Mo^{3+} , Mo^{5+} and Bi^{5+} . The example, O^- in Fig. 4, is another warning not to use $f^{IV}(s)$ for ions at high resolution. This warning is emphasized by Table 2(b) showing only a rather limited

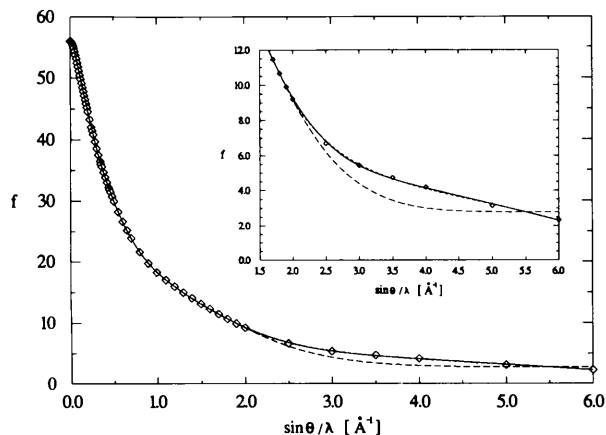


Fig. 2. Scattering factor of neutral Ba. Symbols: tabulated values; full line: $f^V(s)$; broken line: $f^{IV}(s)$; dashed line: $f^{LP}(s)$.

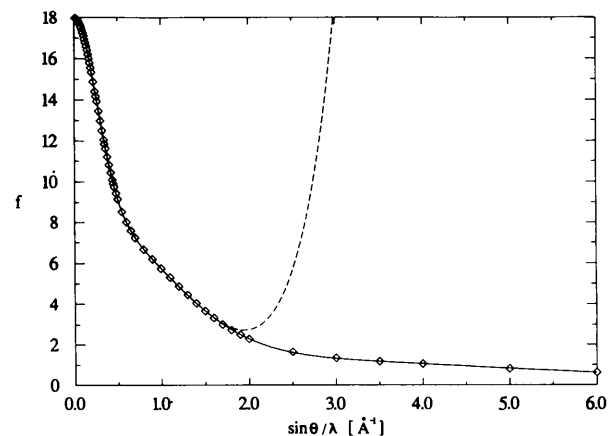


Fig. 3. As Fig. 2, scattering factor of the cation Ti^{4+} .

Table 3. Absolute maximum and mean errors (e) introduced by $f^V(s)$

(a) For neutral atoms

Atom	MAXIMUM ERROR	$\sin\theta/\lambda$	MEAN ERROR	Atom	MAXIMUM ERROR	$\sin\theta/\lambda$	MEAN ERROR		
He	RHF	0.001	1.90	0.000	Sb	RHF	0.119	3.00	0.017
Li	RHF	0.002	2.00	0.000	Te	RHF*	0.121	3.00	0.018
Be	RHF	0.003	0.80	0.001	I	RHF	0.089	5.00	0.019
B	RHF	0.002	0.50	0.001	Xe	RHF	0.138	5.00	0.019
C	RHF	0.004	0.65	0.002	Cs	RHF	0.090	5.00	0.022
N	RHF	0.006	0.80	0.002	Ba	RHF	0.110	2.50	0.021
O	RHF	0.002	5.00	0.000	La	RHF*	0.132	2.50	0.024
F	RHF	0.002	0.70	0.000	Ce	RHF*	0.155	2.50	0.024
Ne	RHF	0.012	3.50	0.001	Pr	RHF*	0.189	2.50	0.022
Na	RHF	0.007	0.06	0.004	Nd	RHF*	0.165	2.50	0.022
Mg	RHF	0.014	6.00	0.003	Pm	RHF*	0.155	2.50	0.022
Al	RHF	0.010	5.00	0.002	Sm	RHF*	0.133	2.50	0.022
Si	RHF	0.008	4.00	0.001	Eu	RHF	0.110	2.50	0.022
P	RHF	0.004	5.00	0.001	Gd	RHF*	0.148	3.00	0.023
S	RHF	0.006	1.00	0.001	Tb	RHF*	0.154	3.00	0.022
Cl	RHF	0.008	0.70	0.002	Dy	RHF*	0.158	3.00	0.023
Ar	RHF	0.015	2.50	0.003	Ho	RHF*	0.160	3.00	0.026
K	RHF	0.016	0.90	0.004	Er	RHF*	0.138	3.00	0.026
Ca	RHF	0.021	1.00	0.004	Tm	RHF*	0.123	3.00	0.027
Sc	RHF	0.021	1.10	0.004	Yb	RHF*	0.135	2.50	0.028
Ti	RHF	0.020	1.20	0.005	Lu	RHF*	0.138	2.50	0.029
V	RHF	0.019	1.20	0.005	Hf	RHF*	0.145	2.50	0.030
Cr	RHF	0.018	1.30	0.005	Ta	RHF*	0.135	2.50	0.031
Mn	RHF	0.017	2.00	0.005	W	RHF*	0.136	2.50	0.031
Fe	RHF	0.015	2.00	0.006	Re	RHF*	0.134	2.50	0.031
Co	RHF	0.017	2.50	0.006	Os	RHF*	0.126	2.50	0.031
Ni	RHF	0.019	2.50	0.006	Ir	RHF*	0.147	5.00	0.012
Cu	RHF	0.016	2.50	0.006	Pt	RHF*	0.130	5.00	0.029
Zn	RHF	0.016	0.90	0.007	Au	RHF	0.106	2.50	0.028
Ga	RHF	0.022	0.90	0.010	Hg	RHF	0.104	2.50	0.030
Ge	RHF	0.025	1.00	0.011	Tl	RHF*	0.107	2.50	0.013
As	RHF	0.024	1.00	0.010	Pb	RHF	0.138	2.50	0.013
Se	RHF	0.021	1.00	0.008	Bi	RHF	0.142	2.50	0.013
Br	RHF	0.016	2.50	0.006	Po	RHF*	0.116	4.00	0.015
Kr	RHF	0.019	2.50	0.004	At	RHF*	0.146	2.50	0.014
Rb	RHF	0.030	5.00	0.003	Rn	RHF	0.128	3.00	0.017
Sr	RHF	0.025	2.50	0.010	Fr	RHF*	0.126	3.00	0.022
Y	RHF*	0.035	2.50	0.013	Ra	RHF*	0.131	3.00	0.021
Zr	RHF*	0.039	2.50	0.016	Ac	RHF*	0.133	3.00	0.024
Nb	RHF*	0.068	4.00	0.021	Th	RHF*	0.126	3.00	0.024
Mo	RHF	0.045	2.50	0.021	Pa	RHF*	0.123	3.00	0.023
Tc	RHF*	0.060	2.50	0.010	U	RHF	0.120	5.00	0.023
Ru	RHF*	0.067	2.50	0.011	Np	RHF*	0.143	5.00	0.025
Rh	RHF*	0.065	2.50	0.012	Pu	RHF*	0.166	5.00	0.027
Pd	RHF*	0.082	2.50	0.017	Am	RHF*	0.191	5.00	0.029
Ag	RHF	0.092	2.50	0.013	Cm	RHF*	0.216	5.00	0.031
Cd	RHF	0.102	3.00	0.014	Bk	RHF*	0.251	2.50	0.033
In	RHF	0.111	3.00	0.015	Cf	RHF*	0.312	2.50	0.035
Sn	RHF	0.118	3.00	0.016					

number of ions with tolerable $R_{2,6}^{IV}$ indices, e.g. Cu^+ , Cu^{2+} , Fe^{2+} , Fe^{3+} and Co^{3+} . Inspecting $R_{0,6}^V$, on the other hand, shows that the scattering factors of the ions can be well represented by the functions $f^V(s)$. With $R_{0,2}^V$ frequently being even lower than $R_{0,2}^{IV}$, all $R_{0,6}^V$ indices are well below 0.01 so that the use of the new scattering functions is recommended for both ions and neutral atoms.

An application

In the course of a thorough structure analysis of natrolite, $\text{Na}_2(\text{Al}_2\text{Si}_3)\text{O}_{10} \cdot 2\text{H}_2\text{O}$, the accurate data of

Stuckenschmidt, Joswig & Baur (1993) were used to perform spherical charge integrations around the atoms according to Sasaki, Fujino, Takeuchi & Sadanaga (1980). These calculations were made using both neutral $f^{IV}(s)$ and $f^V(s)$ parametrizations for the series-termination corrections for all atoms in the structure. Results for the Si1 atom are depicted in Fig. 5. The number of electrons contained in a sphere of radius R , $Z(R)$, is not much affected, local deviations $|Z^{IV}(R) - Z^V(R)|$ being at most 0.06e. This does, however, not apply to the derivatives dZ/dR , the radial density distribution function, and to d^2Z/dR^2 . These curves can be used to assign a formal cation radius R_c .

Table 3 (cont.)

(b) For ions

Atom	MAXIMUM ERROR	$\sin\theta/\lambda$	MEAN ERROR	Atom	MAXIMUM ERROR	$\sin\theta/\lambda$	MEAN ERROR		
H ¹⁻	HF	0.001	0.38	0.000	Ru ³⁺	*DS	0.046	2.50	0.007
Li ¹⁺	RHF	0.001	0.65	0.000	Ru ⁴⁺	*DS	0.047	2.50	0.007
Be ²⁺	RHF	0.005	2.50	0.001	Rh ³⁺	*DS	0.074	2.50	0.010
C _{val}	HF	0.009	1.60	0.001	Rh ⁴⁺	*DS	0.075	2.50	0.011
O ¹⁻	HF	0.013	2.50	0.002	Pd ²⁺	*DS	0.077	2.50	0.011
F ¹⁻	HF	0.018	6.00	0.003	Pd ⁴⁺	*DS	0.069	3.00	0.010
Na ¹⁺	RHF	0.001	0.90	0.000	Ag ¹⁺	*DS	0.084	3.00	0.014
Mg ²⁺	RHF	0.002	2.50	0.000	Ag ²⁺	*DS	0.027	5.00	0.006
Al ³⁺	HF	0.001	1.60	0.000	Cd ²⁺	*DS	0.092	3.00	0.013
Si _{val}	HF	0.008	4.00	0.001	In ³⁺	*DS	0.115	3.00	0.014
Si ⁴⁺	HF	0.004	4.00	0.000	Sn ²⁺	RHF	0.132	3.00	0.019
Cl ¹⁻	RHF	0.017	5.00	0.004	Sn ⁴⁺	RHF	0.141	3.00	0.018
K ¹⁺	RHF	0.016	0.90	0.003	Sb ³⁺	*DS	0.049	2.50	0.010
Ca ²⁺	RHF	0.019	1.00	0.004	Sb ⁵⁺	*DS	0.129	3.00	0.016
Sc ³⁺	HF	0.022	2.50	0.004	I ¹⁻	RHF	0.141	5.00	0.019
Ti ²⁺	HF	0.020	1.50	0.003	Cs ¹⁺	RHF	0.135	5.00	0.021
Ti ³⁺	HF	0.039	2.50	0.005	Ba ²⁺	*DS	0.119	5.00	0.019
Ti ⁴⁺	HF	0.024	2.50	0.005	La ³⁺	*DS	0.121	2.50	0.018
V ²⁺	RHF	0.028	3.00	0.005	Ce ³⁺	*DS	0.150	2.50	0.023
V ³⁺	HF	0.018	2.50	0.003	Ce ⁴⁺	*DS	0.160	2.50	0.021
V ⁵⁺	HF	0.027	5.00	0.003	Pr ³⁺	*DS	0.194	2.50	0.018
Cr ²⁺	HF	0.013	1.60	0.002	Pr ⁴⁺	*DS	0.184	2.50	0.022
Cr ³⁺	HF	0.018	2.00	0.003	Nd ³⁺	*DS	0.206	2.50	0.021
Mn ²⁺	RHF	0.026	3.00	0.004	Pm ³⁺	*DS	0.203	2.50	0.017
Mn ³⁺	HF	0.019	1.60	0.003	Sm ³⁺	*DS	0.085	2.50	0.023
Mn ⁴⁺	HF	0.015	3.00	0.002	Eu ²⁺	*DS	0.160	2.50	0.014
Fe ²⁺	RHF	0.018	3.00	0.003	Eu ³⁺	*DS	0.118	2.50	0.026
Fe ³⁺	RHF	0.020	3.50	0.004	Gd ³⁺	*DS	0.179	0.20	0.020
Co ²⁺	RHF	0.016	3.50	0.003	Tb ³⁺	*DS	0.170	3.00	0.014
Co ³⁺	HF	0.032	1.60	0.004	Dy ³⁺	*DS	0.196	3.00	0.012
Ni ²⁺	RHF	0.075	0.09	0.005	Ho ³⁺	*DS	0.197	3.00	0.013
Ni ³⁺	HF	0.034	1.60	0.005	Er ³⁺	*DS	0.185	3.00	0.014
Cu ¹⁺	RHF	0.023	2.50	0.002	Tm ³⁺	*DS	0.170	3.00	0.014
Cu ²⁺	HF	0.038	1.60	0.003	Yb ²⁺	*DS	0.158	3.00	0.014
Zn ²⁺	RHF	0.024	2.50	0.002	Yb ³⁺	*DS	0.164	3.00	0.014
Ga ³⁺	HF	0.040	1.60	0.005	Lu ³⁺	*DS	0.140	3.00	0.014
Ge ⁴⁺	HF	0.068	6.00	0.008	Hf ⁴⁺	*DS	0.135	5.00	0.014
Br ¹⁻	RHF	0.058	6.00	0.012	Ta ⁵⁺	*DS	0.133	5.00	0.013
Rb ¹⁺	RHF	0.031	5.00	0.003	W ⁶⁺	*DS	0.194	5.00	0.014
Sr ²⁺	RHF	0.033	3.50	0.004	Os ⁴⁺	*DS	0.166	5.00	0.012
Y ³⁺	*DS	0.061	4.00	0.019	Ir ³⁺	*DS	0.148	5.00	0.013
Zr ⁴⁺	*DS	0.031	0.65	0.012	Ir ⁴⁺	*DS	0.148	5.00	0.011
Nb ³⁺	*DS	0.057	4.00	0.006	Pt ²⁺	*DS	0.130	5.00	0.015
Nb ⁵⁺	*DS	0.058	5.00	0.007	Pt ⁴⁺	*DS	0.137	5.00	0.009
Mo ³⁺	*DS	0.038	5.00	0.006	Au ¹⁺	*DS	0.105	5.00	0.010
Mo ⁵⁺	*DS	0.038	5.00	0.006	Au ³⁺	*DS	0.105	2.50	0.011
Mo ⁶⁺	*DS	0.023	3.00	0.002	Hg ¹⁺	*DS	0.112	2.50	0.020

and a formal cation charge $Q(R_o)$ (Sasaki, Fujino, Takeuchi & Sadanaga, 1980). Taking the absolute minimum of dZ/dR as indicated in Fig. 5, one obtains the radii 0.70 Å for $f^{IV}(s)$ and 0.665 Å for $f^V(s)$, corresponding to a change of -5%. The associated charge values are +3.72 and +3.92 e, respectively. Another possibility to partition the atoms is given by the relative minimum in d^2Z/dR^2 at about 1 Å. For this choice, one finds, for $f^{IV}(s)$, $R_o = 1.07$ Å (+1.51 e), for $f^V(s)$, $R_o = 1.02$ Å (+1.90 e). Table 4 shows the formal radii and associated

charges of all atoms in the structure based on the absolute minima of the radial distribution functions and using both $f^{IV}(s)$ and $f^V(s)$, respectively. It is obvious that the new scattering-factor functions can have a bearing on the results. This is particularly evident for the Si and Al atoms. Compared with using $f^{IV}(s)$, the cations are contracted, whereas the oxygen atoms become slightly larger and more charged. Without further discussion of these results in terms of crystal chemical implications, it should be noted that according to Table 2 the same

Table 3(b) (cont.)

Z Element		MAXIMUM ERROR	$\sin\theta/\lambda$	MEAN ERROR
Hg ²⁺	*DS	0.115	2.50	0.013
Tl ¹⁺	*DS	0.112	2.50	0.010
Tl ³⁺	*DS	0.102	5.00	0.011
Pb ²⁺	*DS	0.126	2.50	0.017
Pb ⁴⁺	*DS	0.136	2.50	0.011
Bi ³⁺	*DS	0.135	2.50	0.011
Bi ⁵⁺	*DS	0.084	4.00	0.009
Ra ²⁺	*DS	0.147	3.00	0.028
Ac ³⁺	*DS	0.172	3.00	0.017
Th ⁴⁺	*DS	0.160	3.00	0.022
U ³⁺	*DS	0.155	3.00	0.015
U ⁴⁺	*DS	0.155	3.00	0.016
U ⁶⁺	*DS	0.157	3.00	0.016
Np ³⁺	*DS	0.172	5.00	0.016
Np ⁴⁺	*DS	0.172	5.00	0.016
Np ⁶⁺	*DS	0.172	5.00	0.017
Pu ³⁺	*DS	0.203	5.00	0.019
Pu ⁴⁺	*DS	0.195	5.00	0.018
Pu ⁶⁺	*DS	0.192	5.00	0.021

results would have been obtained using $f^{LP}(s)$. Thus, the effects of inadequate scattering-factor functions on spherical charge integrations cannot be neglected in general.

Summary

Contrary to the approach favoured by Rez, Rez & Grant (1994), whose representations suffer from the omission of a constant term, and contrary to the doubts of Fox, O'Keefe & Tabborn (1989), we have developed accurate X-ray scattering-factor representations for neutral atoms and ions on the basis of a five-Gaussian expansion, *i.e.* an 11-parameter fit. The qualities of the fits are equal or frequently superior to those of the existing parametrizations. Programs using (1) can be

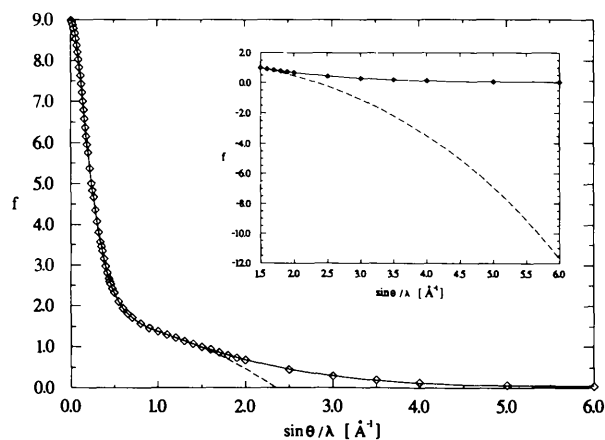


Fig. 4. As Fig. 2, scattering factor of the anion O⁻.

Table 4. Formal ionic radii R_o (Å) and associated charges Q (e) in natrolite, using $f^{IV}(s)$ and $f^V(s)$ for the calculations of series-termination corrections

	$f^{IV}(s)$		$f^V(s)$	
	R_o	Q	R_o	Q
Si1	0.700	+3.72	0.665	+3.92
Si2	0.700	+3.74	0.645	+4.02
Al	0.800	+2.80	0.730	+3.06
O1	1.045	-0.11	1.070	-0.22
O2	1.115	-0.67	1.120	-0.70
O3	1.105	-0.50	1.110	-0.53
O4	1.060	-0.22	1.070	-0.27
O5	1.045	-0.11	1.055	-0.17
OW	1.630	-1.86	1.630	-1.86
Na	1.100	+0.93	1.105	+0.92

easily changed to accommodate the new representations, which makes the use of two different scattering functions unnecessary. A warning must be given to employing the old parameter sets with respect to ions when high-resolution data are required. Extrapolations on the basis of these parameters are likely to compromise the results.

The implications of possessing a single satisfactory representation for every atom or ion over the full $\sin\theta/\lambda$ range from 0.0 to 6.0 \AA^{-1} are obvious. As discussed by Fox, O'Keefe & Tabborn (1989), whose arguments need not be repeated in detail, more accurate charge-density calculations can be carried out in structure analyses, and more accurate and convenient electron scattering factor functions can be derived from the Mott formula. This applies at least to the range beyond 2.0 \AA^{-1} for which the use of the new functions can only be recommended.

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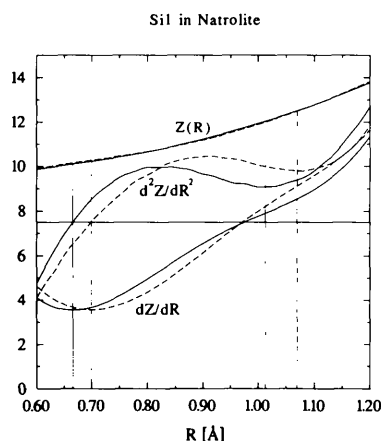


Fig. 5. Spherical charge integration results for Si1 in natrolite. Series-termination corrections calculated with $f^{IV}(s)$ (broken lines) and $f^V(s)$ (solid lines). $Z(R)$ and dZ/dR on absolute scale, d^2Z/dR^2 and the horizontal zero line on a relative scale.

References

- COULTHARD, M. A. (1967). *Proc. Phys. Soc.* **91**, 44–49.
- CROMER, D. T. & MANN, J. B. (1968). Report LA 3816. Los Alamos Scientific Laboratory, Los Alamos, NM, USA.
- CROMER, D. T. & WABER, J. T. (1968). Unpublished work in *International Tables for X-ray Crystallography* (1974), Vol. IV, p. 71. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
- DOYLE, P. A. & TURNER, P. S. (1968). *Acta Cryst.* **24**, 390–397.
- FOX, A. G., O'KEEFE, M. A. & TABBERNOR, M. A. (1989). *Acta Cryst.* **A45**, 786–793.
- International Tables for Crystallography* (1992). Vol. C, edited by A. J. C. WILSON. Dordrecht: Kluwer Academic Publishers.
- JAMES, F. & ROOS, M. (1987). *MINUIT* program. Program Library no. D506. CERN Computer Center, Geneva, Switzerland.
- MANN, J. B. (1968). In *International Tables for X-ray Crystallography* (1974), Vol. IV, p. 71. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
- MASLEN, E. N., FOX, A. G. & O'KEEFE, M. A. (1992). In *International Tables for Crystallography*, Vol. C, edited by A. J. C. WILSON. Dordrecht: Kluwer Academic Publishers.
- ONKEN, H. & FISCHER, K. F. (1968). *Z. Kristallogr.* **127**, 188–199.
- REZ, D., REZ, P. & GRANT, I. (1994). *Acta Cryst.* **A50**, 481–497.
- SASAKI, S., FUJINO, K., TAKEUCHI, Y. & SADANAGA, R. (1980). *Acta Cryst.* **A36**, 904–915.
- STUCKENSCHMIDT, E., JOSWIG, W. & BAUR, W. H. (1993). *Phys. Chem. Miner.* **19**, 562–570.

Acta Cryst. (1995). **A51**, 431–438

Enantiomorphism and Three-Beam X-ray Diffraction: Determination of the Absolute Structure

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Abstract

It is shown that three-beam X-ray diffraction provides a means of resolving the enantiomorphism problem. It is based on the fact that three-beam interference leads to significantly different ψ -scan profiles for triplet phases close to $+90^\circ$ or -90° , which are selectors between enantiomorphs. Since this method works without the need of anomalous scattering, it is particularly suitable for resolving the absolute structure of light-atom compounds. The application of this method is discussed in detail. Its capability of distinguishing between enantiomorphs has been rejected in a recent paper by Colella [*Acta Cryst.* (1994), **A50**, 55–57]. Detailed comments on the invalid arguments of Colella's analysis are presented.

I. Introduction

For each non-centrosymmetric space group, there are two enantiomorphic forms that can be mapped onto each other by a center of symmetry, *i.e.* the two forms differ in their handedness, which cannot be distinguished in an ordinary X-ray diffraction pattern if Friedel's law is valid. This ambiguity has different meanings for different point groups. For enantiomorphic merohedral point groups, its resolution means the determination of the absolute configuration for chiral species or the determination of the absolute conformation for achiral species. For polar point groups, it means fixing the structure with respect to the polar direction. For non-centrosymmetric roto-inversional point groups, with roto-inversions 4 or

$\bar{6}$, it means assignment of absolute axes (Burzlaff & Hümmel, 1988). Jones (1986) summarized the resolution of these ambiguities by the expression 'determination of the absolute structure'. It ultimately reduces to a determination of structure-factor phases.

One possible method is to exploit the violation of Friedel's law due to anomalous scattering and compare the intensities of suitable Bijvoet pairs (Bijvoet, Peerdemon & van Bommel, 1951). However, difficulties arise for light-atom structures.

A second, newer, method is the direct experimental determination of triplet phase relationships by means of X-ray three-beam diffraction, which works independently of anomalous scattering. This method is, therefore, particularly suited to the determination of the absolute structure of light-atom compounds. It has been shown both theoretically and experimentally in several papers (Hümmel & Billy, 1986; Hümmel, Weckert & Bondza, 1989; Burzlaff *et al.*, 1989; Weckert & Hümmel, 1990; Chang, King, Huang & Gao, 1991; Weckert, Hümmel, Addae-Mensah & Achenbach, 1992; Hümmel, Schwegle & Weckert, 1992; Weckert, Hümmel, Dominguez, Horn & Achenbach, 1993; Platzbecker *et al.*, 1993; Weckert, Schwegle & Hümmel, 1993; Spence, Zuo, O'Keefe, Marthinsen & Hoier, 1994) that three-beam diffraction using ψ -scan experiments does provide a means of distinguishing between the two enantiomorphic forms of a compound.

However, in a very recent paper by Colella (1994), this point is openly rejected. Therefore, we will present in the following a short review and new experimental results on