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Relativistic X-ray Elastic Scattering Factors for Neutral Atoms $Z = 1$–54 from Multiconfiguration Dirac–Fock Wavefunctions in the 0–12 $Å^{-1}$ $\sin\theta/\lambda$ Range, and Six-Gaussian Analytical Expressions in the 0–6 $Å^{-1}$ Range

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Abstract

X-ray elastic scattering factors for the ground-state atoms H to Xe have been calculated from the relativistic wavefunctions in the 0–12 $Å^{-1}$ $\sin\theta/\lambda$ range and fitted in the 0–6 $Å^{-1}$ $\sin\theta/\lambda$ range to a sum of six Gaussian functions for three different $\sin\theta/\lambda$ ranges. More than one configuration was included for elements with several electronic configurations having the same subshell occupancy. The resulting parameterized scattering factors are significantly more accurate than those previously published. Separate core- and valence-electron scattering values have also been obtained. The relativistic atomic energies, the atomic second moments and the limiting values of the electron scattering factor as $\sin\theta/\lambda$ approaches zero have been tabulated. The wavefunctions were calculated with the *GRASP*92 program package [Parpia, Froese Fischer & Grant (1996). *Comput. Phys. Commun.* **94**, 249–271] with the optimal level (OL) model rather than with the extended average level (EAL) model used in previous calculations [Rez, Rez & Grant (1994). *Acta Cryst.* A**50**, 481–497].

1. Introduction

Recently, Wang, Smith, Bunge & Jáuregui (1996) published relativistic X-ray scattering factors for He–Ar from multiconfiguration Dirac–Hartree–Fock calculations. The authors note that, in order to get reliable differences between relativistic and non-relativistic scattering factors, multiconfiguration calculations must be performed for some of the open-shell atoms. Although X-ray scattering factors for the elements H–Cf based on multiconfiguration wavefunctions from the average level model have been reported (Su & Coppens, 1994; Rez, Rez & Grant, 1994), they do not correspond to the optimized ground states of the atoms. We have therefore extended the work of Wang *et al.* to the elements beyond Ar, up to Xe, using atomic wavefunctions obtained with the optimal level (OL) model and the program *GRASP*92 (Parpia, Froese Fischer & Grant, 1996). We have used finite spherical nuclear charges, rather than point-charge nuclei, with the Fermi radial distribution for all elements, except for H and He. As the atomic number increases, the effect of the use of a finite nucleus increases, as pointed out by Grant (1970). The resulting scattering factors have been fitted in the 0–6 $Å^{-1}$ range by a sum of Gaussian functions. The fitting functions are highly accurate and suitable for advanced diffraction studies.

2. Calculations of atomic wavefunctions and scattering factors

The program package *GRASP*92 (Parpia, Froese Fischer & Grant, 1996) was kindly provided by Dr F. A. Parpia. It was slightly modified to run on a Sun Sparcstation with the Solaris 2 operating system.

The ground-state electron configurations and terms and the average atomic weights of the elements used for the nuclear size calculation were taken from the literature (Lide, 1996; Emsley, 1996). Only the J value corresponding to the ground-state term was used to generate the relativistic configuration state functions (CSF). 25 of the 54 elements included in this work required more than one CSF in representing the ground-state atomic state functions (ASF), they are the elements in the ranges C–O, Si–S, Ti–Ni, Ge–Se, Zr–Rh and Sn–Te. The use of the OL model is more computationally expensive than that of the EAL (extended average level) model, but has the advantage of giving the optimized wavefunctions for the ground-state atomic state functions and, therefore, more accurate results.

Subroutines were added to the program package that convert the wavefunctions into densities, calculate the X-ray elastic scattering factors $f(\sin\theta/\lambda)$ and the atomic second moments $\langle r^2\rangle$, using the expressions

$$f(\sin\theta/\lambda) = \int_0^\infty 4\pi r^2 \rho(r) \frac{\sin(4\pi r \sin\theta/\lambda)}{(4\pi r \sin\theta/\lambda)} \mathrm{d}r \quad (1)$$

Table 1. *Scattering factors for the elements C, P, Fe, Cu and I*

$\sin\theta/\lambda$ (Å^{-1})	C	P	Fe	Cu	I
0.00	6.00000	15.00000	26.00000	29.00000	53.00000
0.05	5.75587	14.47133	25.30369	28.44773	51.90948
0.10	5.12689	13.16987	23.68255	27.08423	49.13990
0.15	4.33726	11.65976	21.84282	25.36970	45.69992
0.20	3.58328	10.34214	20.06675	23.54022	42.33883
0.25	2.96531	9.33664	18.37640	21.68762	39.33329
0.30	2.50339	8.59519	16.76515	19.86933	36.67579
0.35	2.17634	8.02403	15.24966	18.13269	34.27941
0.40	1.95074	7.54342	13.85589	16.51337	32.07474
0.45	1.79516	7.10235	12.60447	15.03419	30.02990
0.50	1.68496	6.67471	11.50523	13.70644	28.13993
0.60	1.53634	5.83114	9.75219	11.50663	24.85037
0.70	1.42526	5.02101	8.50991	9.86027	22.22688
0.80	1.32184	4.28464	7.64307	8.66273	20.19215
0.90	1.21803	3.64910	7.02171	7.79894	18.59946
1.00	1.11383	3.12224	6.54444	7.16569	17.29381
1.20	0.91341	2.36390	5.77457	6.28544	15.09093
1.40	0.73605	1.90269	5.06992	5.61783	13.08185
1.60	0.58787	1.62597	4.38691	5.00455	11.21264
1.80	0.46817	1.45281	3.75185	4.41267	9.57471
2.00	0.37321	1.33363	3.19421	3.85485	8.23760
2.50	0.21569	1.12210	2.19625	2.72017	6.14167
3.00	0.12943	0.94229	1.65748	2.00051	5.13213
3.50	0.08089	0.77713	1.37682	1.59044	4.47827
4.00	0.05254	0.63209	1.21333	1.35770	3.89092
5.00	0.02450	0.41083	0.99553	1.10492	2.82746
6.00	0.01274	0.26763	0.81249	0.92887	2.06642

and

$$\langle r^2\rangle = \int_0^\infty 4\pi r^4 \rho(r)\mathrm{d}r, \qquad (2)$$

where θ is the Bragg angle and λ the wavelength of the incident radiation.

The electronic volume charge density $\rho(r)$ is given by

$$\rho(r) = (4\pi r^2)^{-1} \sum_a N_A[P_A^2(r) + Q_A^2(r)], \qquad (3)$$

the radial functions $P_A(r)$ and $Q_A(r)$ being, respectively, the major and minor components of the relativistic wavefunction and N_A the generalized occupation number of the electron shell A. The N_A values were derived from the mixing coefficients of the configurations, determined with the *GRASP*92 component programs *rscf*92 and *rci*92.

Equations (1) and (2) were evaluated numerically as follows: the numerical values $\rho(r)$ from (3), at the tabulation points used in solving the Dirac–Fock equations, were fitted by cubic spine interpolants (Burden & Faires, 1989). Subsequently, the integrals were evaluated by the composite-Simpson formula (Burden & Faires, 1989). The step size was reduced until the scattering factors were invariant to five digits after the decimal point and the second moments to six digits after the decimal point. Scattering factors were evaluated at $\sin\theta/\lambda$ intervals of 0.05 Å^{-1} in the 0 to 12.0 Å^{-1} range. Selected values for C, P, Fe, Cu and I are listed in Table 1. Separate scattering factors for the core and valence electrons, needed for charge-density analyses, have also been calculated. The complete data sets for all elements from H and Xe will be available on the Internet.

Table 2. *Atomic ground-state energies in a.u. for the elements H through Xe*

Z	Element	J	Energy (a.u.)
1	H	1/2	−5.00006692D+01
2	He	0	−2.86175031D+00
3	Li	1/2	−7.43327492D+00
4	Be	0	−1.45752035D+01
5	B	1/2	−2.45351462D+01
6	C	0	−3.77023952D+01
7	N	3/2	−5.44278947D+01
8	O	2	−7.48584245D+01
9	F	3/2	−9.94912468D+01
10	Ne	0	−1.28675897D+02
11	Na	1/2	−1.62055612D+02
12	Mg	0	−1.99794170D+02
13	Al	1/2	−2.42290643D+02
14	Si	0	−2.89429369D+02
15	P	3/2	−3.41497892D+02
16	S	2	−3.98541818D+02
17	Cl	3/2	−4.60836725D+02
18	Ar	0	−5.28558113D+02
19	K	1/2	−6.01374488D+02
20	Ca	0	−6.79529437D+02
21	Sc	3/2	−7.63165864D+02
22	Ti	2	−8.52606795D+02
23	V	3/2	−9.47980190D+02
24	Cr	3	−1.04947587D+03
25	Mn	5/2	−1.15717692D+03
26	Fe	4	−1.27110828D+03
27	Co	9/2	−1.39161448D+03
28	Ni	4	−1.51880389D+03
29	Cu	1/2	−1.65282457D+03
30	Zn	0	−1.79390605D+03
31	Ga	1/2	−1.94177656D+03
32	Ge	1/2	−2.09661536D+03
33	As	3/2	−2.25853337D+03
34	Se	2	−2.42753852D+03
35	Br	3/2	−2.60383849D+03
36	Kr	0	−2.78755091D+03
37	Rb	1/2	−2.97836794D+03
38	Sr	0	−3.17650748D+03
39	Y	3/2	−3.38206019D+03
40	Zr	0	−3.59520069D+03
41	Nb	1/2	−3.81622875D+03
42	Mo	3	−4.04512318D+03
43	Tc	5/2	−4.28191051D+03
44	Ru	5	−4.52678934D+03
45	Rh	9/2	−4.77992710D+03
46	Pd	0	−5.04141710D+03
47	Ag	1/2	−5.31123475D+03
48	Cd	0	−5.58987955D+03
49	In	1/2	−5.87675243D+03
50	Sn	0	−6.17221563D+03
51	Sb	3/2	−6.47636649D+03
52	Te	2	−6.78923971D+03
53	I	3/2	−7.11101605D+03
54	Xe	0	−7.44179817D+03

3. Ground-state energies of H–Xe

The ground-state energies are given in Table 2. They are the sums of the expectation values of the Dirac

Table 3. *Analytical parameters for scattering factors in the* $0 \leq \sin\theta/\lambda < 2.0\ \text{Å}^{-1}$ *range*

Z	Atom	a_1	a_2	a_3	a_4	a_5	a_6
		b_1	b_2	b_3	b_4	b_5	b_6
1	H	0.43028	0.28537	0.17134	0.09451	0.01725	0.00114
		23.02312	10.20138	51.25444	4.13511	1.35427	0.24269
2	He	0.69475	0.62068	0.38661	0.15223	0.12661	0.01907
		5.83366	12.87682	2.53296	28.16171	0.97507	0.25308
3	Li	0.84645	0.81146	0.81096	0.26115	0.26055	0.00930
		4.63253	1.71862	97.87364	0.50620	200.00000	0.00010
4	Be	1.59261	1.12768	0.70296	0.53815	0.03863	0.00010
		43.67397	1.86275	0.54243	103.44910	0.00010	0.34975
5	B	2.07418	1.20577	1.07592	0.52023	0.12280	0.00010
		23.39543	1.07672	60.93249	0.27132	0.27192	0.11361
6	C	2.09921	1.80832	1.26159	0.56775	0.26303	0.00010
		13.18997	30.37956	0.69255	0.16381	68.42774	0.44083
7	N	2.45424	2.15782	1.05782	0.57557	0.44959	0.30480
		18.66694	8.31271	0.46989	42.44646	0.08747	0.47126
8	O	2.34752	1.83006	1.61538	1.52402	0.41423	0.26867
		9.69710	18.59876	5.19879	0.32408	39.79099	0.01150
9	F	2.96981	2.04536	1.78123	1.52086	0.42253	0.26008
		7.52365	15.41441	3.79721	0.25209	33.76478	0.00488
10	Ne	3.56413	2.72559	1.67359	1.58884	0.25468	0.19320
		7.30559	3.34491	15.93226	0.13859	0.69111	35.26368
11	Na	4.16491	2.38097	1.70484	1.59622	0.66291	0.48971
		4.23096	9.48502	0.12559	1.98358	172.13327	82.23091
12	Mg	3.90882	2.62159	1.69157	1.52610	1.47907	0.77262
		3.06041	6.12146	0.10357	58.65022	1.56940	125.49980
13	Al	4.25474	3.58301	2.37351	1.72366	0.99400	0.07031
		3.76670	1.69151	45.27810	0.09238	113.96978	17.47922
14	Si	2.34752	1.83006	1.61538	1.52402	0.41423	0.26867
		9.69710	18.59876	5.19879	0.32408	39.79099	0.01150
15	P	6.48197	1.89537	4.31666	27.61455	1.73759	0.50991
		1.35793	66.28296	1.10559	0.00010	0.00010	12.05652
16	S	6.90565	5.24410	1.54516	1.42922	0.87564	0.00010
		1.46764	22.31576	56.06328	0.25588	0.00010	26.96892
17	Cl	7.13381	6.26972	1.82658	1.62579	0.14431	0.00010
		1.17455	18.57626	0.07869	48.08203	0.07871	23.23894
18	Ar	7.28551	7.24549	1.74775	1.72174	0.00010	0.00010
		15.63295	0.95562	0.04456	41.07550	0.00617	20.09628
19	K	8.13161	7.43972	1.42159	1.12030	0.88342	0.00010
		12.73675	0.77443	0.00010	200.00000	36.18711	82.98380
20	Ca	8.62965	7.38765	1.63044	1.37681	0.97538	0.00010
		10.45238	0.66036	87.06258	0.00010	181.27760	28.57890
21	Sc	9.18894	7.36727	1.60214	1.33655	0.78386	0.72047
		9.02948	0.57364	137.40503	0.00010	51.53615	53.74395
22	Ti	9.75861	7.35354	1.46842	1.40591	1.28669	0.72609
		7.86172	0.50107	32.75146	90.95131	0.00010	149.02872
23	V	10.25443	7.34699	1.84039	1.72148	1.22611	0.61000
		6.86177	0.43939	23.70259	79.72053	0.00010	149.36488
24	Cr	10.67225	4.62093	3.33159	2.72784	1.45281	1.19090
		6.12143	0.39293	20.15470	0.39293	92.01317	0.00010
25	Mn	10.98576	7.35617	2.92091	1.65707	1.08018	0.99906
		5.27951	0.34199	14.55791	54.87900	0.00010	118.26511
26	Fe	11.18858	7.37206	3.55141	1.68125	1.20893	0.99652
		4.64599	0.30327	12.07655	44.15316	104.11866	0.00010
27	Co	11.41624	7.38902	4.21351	1.80189	1.26103	0.91710
		4.12258	0.27069	10.36636	38.32442	97.14970	0.00010
28	Ni	11.76300	7.39888	4.85491	1.98079	1.14857	0.85325
		3.69729	0.24374	9.30593	36.58880	96.02875	0.00010
29	Cu	11.87211	7.37491	6.08548	1.94337	0.86475	0.85837
		3.34773	0.22522	8.46165	27.95010	98.02165	0.00012
30	Zn	12.53020	6.57092	5.84880	2.07610	1.65893	1.31388
		3.05828	0.14326	7.58930	28.50706	0.38369	82.22092
31	Ga	10.69865	7.89127	4.74778	3.83120	2.59218	1.23712
		3.44787	0.15426	2.07387	8.38441	34.93356	99.34732
32	Ge	9.56335	7.86994	7.64215	3.31296	2.13351	1.47704
		2.21494	0.14284	3.86490	32.69417	8.94286	82.15827

Table 3 (*cont.*)

Z	Atom	a_1	a_2	a_3	a_4	a_5	a_6
		b_1	b_2	b_3	b_4	b_5	b_6
33	As	10.86205	7.83248	5.48862	4.21250	2.56904	2.03413
		2.10046	0.13209	3.33631	26.38254	5.81992	63.74567
34	Se	12.63843	7.77316	5.80645	4.44296	1.82898	1.50938
		1.97006	0.12167	3.57609	28.84348	15.15766	64.03025
35	Br	12.56835	7.70669	5.76243	4.78093	2.48412	1.69674
		1.79826	0.11204	2.98848	25.62856	14.95420	55.44329
36	Kr	13.32373	7.64645	5.71351	4.95009	2.80427	1.56038
		1.67399	0.10346	17.43646	2.62566	42.87908	19.80281
37	Rb	17.73932	7.70415	5.33484	4.92829	1.28671	0.00010
		1.68298	0.09944	12.80739	23.59343	200.00000	77.16806
38	Sr	11.77920	9.53489	7.57120	6.03047	2.02653	1.05652
		1.52266	13.50271	0.08995	1.52251	162.86971	53.07068
39	Y	17.89478	9.91124	7.40424	2.14475	1.64266	0.00010
		1.37779	12.18084	0.08009	137.73235	49.81442	0.42187
40	Zr	18.00877	10.47108	7.22234	2.43263	1.86405	0.00010
		1.25042	11.25972	0.07050	49.09408	131.67513	1.76480
41	Nb	18.18722	11.07349	7.02786	3.35224	1.35250	0.00606
		1.13993	10.82683	0.06116	38.71734	115.18009	1.19550
42	Mo	18.36000	6.75320	6.25470	5.52972	3.76774	1.33338
		1.03291	0.05000	10.10135	10.12179	34.16693	104.10497
43	Tc	18.53113	12.72135	6.39681	2.88811	1.72002	0.74148
		0.93112	9.26800	0.03703	31.91681	110.11821	44.07274
44	Ru	18.82022	13.49636	6.01136	3.54102	1.19962	0.93207
		0.84363	8.84277	0.02355	27.02179	44.09284	113.68484
45	Rh	19.15093	14.43898	4.66972	4.66263	1.22522	0.85125
		0.75936	8.27523	26.67965	0.00694	97.04210	0.00695
46	Pd	19.32300	15.30162	5.26970	5.12338	0.98021	0.00010
		0.69750	7.93132	0.00010	23.54133	60.82499	1.28291
47	Ag	19.28330	16.71519	5.18450	4.77793	1.03807	0.00010
		0.64519	7.48785	0.00010	24.79225	100.31405	2.33951
48	Cd	19.22320	17.67107	5.07851	4.43017	1.59588	0.00010
		0.59542	6.92490	0.00010	24.85505	87.61222	31.90172
49	In	19.16300	18.59170	4.95237	4.27994	2.00969	0.00010
		0.54868	6.39500	0.00010	26.18224	93.70112	8.23922
50	Sn	19.22704	19.09869	4.79841	4.37320	2.50037	0.00010
		5.84698	0.50421	0.00010	27.22571	81.57248	31.56814
51	Sb	19.04077	13.05412	6.63670	4.95963	4.60941	2.69795
		0.46176	5.31900	5.31953	28.54198	0.00010	72.65174
52	Te	19.96327	18.99686	6.19148	4.38583	2.46194	0.00010
		4.81879	0.42169	28.79858	0.00010	70.63864	12.77096
53	I	18.97925	15.69578	7.06433	4.42489	4.10018	2.73271
		0.38267	4.34879	26.93604	4.35210	0.00010	61.59836
54	Xe	20.29787	19.00556	9.04165	3.76022	1.89561	0.00010
		3.93838	0.34588	26.70066	0.00010	65.34476	20.30305

Hamiltonian, the contributions of the Breit magnetic interaction and retardation energies and the vacuum polarization correction. Since the energies in Table 2 include Breit interactions, they cannot be compared directly with the single configuration energies published by Mohanty & Clementi (1990).

4. Parameterization of X-ray scattering factors

It is convenient to use the parameterized scattering factors in structure determination and refinement programs. The popular parameterization by Doyle & Turner (1968),

$$f(\sin\theta/\lambda) = \sum_{i=1}^{4} a_i \exp[-b_i(\sin\theta/\lambda)^2] + c, \qquad (4)$$

has been criticized by Rez, Rez & Grant (1994) because it contains a constant term c, which corresponds to an unphysical density component in the form of a δ function normalized to c. Rez *et al.* eliminated this term and used only four Gaussians as the fitting function, but a perusal of their published parameters (Tables 3–6 of Rez, Rez & Grant, 1994) reveals that, as a result of a zero b_i value, for a number of elements a constant term still occurs (for instance Pd was fitted by three Gaussians and a constant). Furthermore, the fits are not very accurate as evidenced by the large χ^2 values and significant deviations at $\sin\theta/\lambda = 0$ Å^{-1}.

As an alternative, we fit the scattering factors with six Gaussian functions:

$$f(\sin\theta/\lambda) = \sum_{i=1}^{6} a_i \exp[-b_i(\sin\theta/\lambda)^2]. \qquad (5)$$

Table 4. *Values of $\sum_{i=1}^{6} a_i$, maximum deviation of the fit, sin θ/λ for the maximum deviation and the mean deviation for the six-Gaussian analytical fit with the parameters in Table 3*

Z	Atom	$\sum a_i$	χ^2	Maximum deviation	At sin θ/λ (Å^{-1})	Mean deviation
1	H	0.99990	0.62037D−07	0.00014	0.10	0.00002
2	He	1.99996	0.20667D−07	0.00006	0.10	0.00002
3	Li	2.99987	0.51731D−05	0.00109	0.35	0.00026
4	Be	4.00013	0.32305D−04	0.00209	0.35	0.00069
5	B	4.99901	0.26407D−04	0.00148	0.75	0.00065
6	C	6.00000	0.67265D−05	0.00078	0.95	0.00033
7	N	6.99984	0.10825D−05	0.00029	2.00	0.00015
8	O	7.99987	0.20844D−06	0.00018	0.10	0.00006
9	F	8.99987	0.13641D−06	0.00019	0.10	0.00003
10	Ne	10.00003	0.15188D−06	0.00010	0.50	0.00005
11	Na	10.99955	0.48347D−05	0.00097	0.10	0.00027
12	Mg	11.99977	0.63966D−06	0.00045	0.05	0.00007
13	Al	12.99923	0.80577D−05	0.00138	0.50	0.00035
14	Si	13.99949	0.18438D−04	0.00153	0.55	0.00057
15	P	14.99985	0.66919D−04	0.00296	0.60	0.00100
16	S	15.99988	0.19397D−03	0.00479	0.70	0.00180
17	Cl	17.00031	0.47698D−03	0.00761	0.75	0.00274
18	Ar	18.00069	0.10445D−02	0.01011	0.85	0.00419
19	K	18.99673	0.12997D−02	0.01085	0.90	0.00476
20	Ca	20.00003	0.22852D−02	0.01525	1.00	0.00601
21	Sc	20.99923	0.23248D−02	0.01427	1.05	0.00620
22	Ti	21.99926	0.18980D−02	0.01339	2.00	0.00557
23	V	22.99940	0.13265D−02	0.01291	2.00	0.00455
24	Cr	23.99632	0.83521D−03	0.00980	2.00	0.00398
25	Mn	24.99915	0.44320D−03	0.00879	2.00	0.00260
26	Fe	25.99875	0.21890D−03	0.00647	2.00	0.00184
27	Co	26.99881	0.95838D−04	0.00435	2.00	0.00121
28	Ni	27.99940	0.38855D−04	0.00254	2.00	0.00083
29	Cu	28.99899	0.28399D−04	0.00168	0.05	0.00071
30	Zn	29.99882	0.26534D−04	0.00166	0.05	0.00069
31	Ga	30.99819	0.39247D−04	0.00281	0.50	0.00008
32	Ge	31.99895	0.15327D−04	0.00151	0.05	0.00048
33	As	32.99882	0.23988D−04	0.00201	0.15	0.00056
34	Se	33.99937	0.39963D−05	0.00092	0.15	0.00023
35	Br	34.99927	0.66159D−05	0.00094	0.15	0.00033
36	Kr	35.99844	0.35946D−04	0.00224	0.30	0.00063
37	Rb	36.99341	0.42115D−03	0.01253	0.05	0.00235
38	Sr	37.99881	0.88262D−04	0.00275	0.35	0.00112
39	Y	38.99777	0.26240D−03	0.00470	0.85	0.00220
40	Zr	39.99898	0.52002D−03	0.00667	2.00	0.00306
41	Nb	40.99938	0.75927D−03	0.00869	2.00	0.00356
42	Mo	41.99874	0.10059D−02	0.01071	2.00	0.00407
43	Tc	42.99890	0.11707D−02	0.01191	2.00	0.00448
44	Ru	44.00064	0.12879D−02	0.01262	2.00	0.00470
45	Rh	44.99873	0.12571D−02	0.01288	2.00	0.00461
46	Pd	45.99802	0.16296D−02	0.01243	1.10	0.00523
47	Ag	46.99909	0.28346D−02	0.01601	1.15	0.00684
48	Cd	47.99892	0.41692D−02	0.01865	1.15	0.00825
49	In	48.99680	0.52571D−02	0.02408	2.00	0.00925
50	Sn	49.99782	0.57351D−02	0.02822	2.00	0.00955
51	Sb	50.99858	0.58843D−02	0.03082	2.00	0.00938
52	Te	51.99947	0.56991D−02	0.03162	2.00	0.00913
53	I	52.99713	0.56033D−02	0.03219	2.00	0.00915
54	Xe	54.00101	0.54040D−02	0.03128	2.00	0.00913

To ensure that none of the b_i's go to zero, we use the bound constrained non-linear least-squares optimization program *L-BFGS-B* (Zhu, Byrd, Lu & Nocedal, 1994) for the fitting, with a_i and b_i bounds of 0.000 10 and 200.000 00. For each element, fits were performed in the sin θ/λ ranges of 0.0–2.0, 2.0–4.0 and 4.0–6.0 Å^{-1}, using points with a spacing of 0.05 Å^{-1}. The point sin $\theta/\lambda = 0$ was added to the last two ranges in order to prevent $\sum_{i=1}^{6} a_i$ from differing substantially from the total number of electrons in the element. As a result, for all fits in the 2–4 and 4–6 Å^{-1} ranges, $\sum_{i=1}^{6} a_i$ equals $f(0)$ within five digits after the decimal point.

Table 5. *Analytical parameters for scattering factors in the* $2.0 \leq \sin\theta/\lambda < 4.0\ \text{Å}^{-1}$ *range*

Z	Atom	a_1	a_2	a_3	a_4	a_5	a_6
		b_1	b_2	b_3	b_4	b_5	b_6
1	H	0.42530	0.28039	0.16636	0.08953	0.03757	0.00083
		23.02312	10.20138	51.25444	4.13511	1.35175	0.23103
2	He	0.68359	0.67135	0.47591	0.12155	0.04257	0.00503
		4.89722	11.93838	1.62563	27.69307	0.49948	0.12670
3	Li	0.88868	0.87199	0.79814	0.25226	0.16534	0.02359
		1.38272	4.54264	97.52985	200.00000	0.45756	0.11757
4	Be	1.57736	1.02906	0.59806	0.51785	0.23469	0.04299
		43.77112	1.90160	0.79719	103.50034	0.32228	0.08820
5	B	2.12478	1.12652	0.87309	0.62712	0.22679	0.02169
		23.39543	60.93249	1.10830	0.48299	0.17433	0.03083
6	C	2.13237	1.81267	0.91756	0.63134	0.34893	0.15713
		13.10945	28.50497	0.70652	0.28312	57.25664	0.07718
7	N	2.44708	2.15066	0.83014	0.77658	0.56841	0.22713
		18.66694	8.31271	0.61670	0.25330	42.44646	0.06960
8	O	2.93656	2.53291	0.83154	0.74837	0.67992	0.27071
		14.05516	5.98365	0.21109	0.49834	34.06486	0.05879
9	F	3.49248	2.70776	0.97709	0.85966	0.79896	0.16405
		10.47716	4.36556	26.58575	0.35906	0.13752	0.03166
10	Ne	4.03806	2.96652	1.19764	0.86778	0.68731	0.24269
		8.15631	3.34129	21.25595	0.27749	0.11527	0.03675
11	Na	4.24472	3.71726	1.11328	0.82041	0.65711	0.44721
		7.20138	2.72438	0.19890	165.16286	0.05364	51.92083
12	Mg	4.18615	3.71863	1.49918	1.13149	0.84254	0.62199
		5.16800	2.21629	55.52364	0.16026	124.77432	0.04281
13	Al	4.27074	3.57214	2.35612	1.20084	1.06755	0.53261
		3.78018	1.66194	43.73724	0.12735	111.35596	0.03146
14	Si	5.64317	3.98910	1.94080	1.17902	0.70291	0.54500
		1.49609	34.62069	84.56737	0.10894	56.34187	0.02770
15	P	5.24872	4.48644	2.46531	1.42177	1.10302	0.27474
		1.91681	28.32664	1.05214	0.08109	67.46291	0.00751
16	S	5.89928	5.40332	1.70107	1.47967	1.31771	0.19894
		1.46570	22.80051	0.82159	0.06706	57.85201	0.00010
17	Cl	7.14857	4.46380	2.86011	1.25833	0.81183	0.45737
		18.18337	0.89006	45.89666	0.03658	23.22369	0.11549
18	Ar	7.92591	5.25995	2.36214	1.53919	0.62494	0.28788
		15.63295	0.83571	41.07550	0.03859	20.09628	0.24316
19	K	8.23699	4.73597	2.04905	1.76848	1.62715	0.58237
		12.21015	0.65394	28.27004	200.00000	0.03751	82.98356
20	Ca	9.01729	5.46146	2.02815	1.63518	1.38385	0.47406
		10.44441	0.60776	86.31958	0.03417	181.45094	28.57932
21	Sc	9.44634	6.00180	1.88578	1.64709	1.03493	0.98405
		9.08162	0.56135	137.40234	0.03148	51.54073	53.74777
22	Ti	10.10530	6.42233	1.66273	1.50904	1.34169	0.95893
		8.05962	0.51793	0.02932	92.71004	31.20186	144.27502
23	V	11.27405	6.73892	1.74870	1.68174	0.79802	0.75857
		7.25373	0.47778	120.58589	0.02759	54.89369	22.00492
24	Cr	10.43232	4.76512	3.16411	2.74320	1.60301	1.29224
		6.21670	0.58872	0.34051	26.27260	0.02269	63.74598
25	Mn	12.24240	7.09766	1.76068	1.72482	1.68332	0.49114
		5.69636	0.40612	101.12197	0.02491	19.85275	37.71895
26	Fe	12.65956	7.16694	1.85845	1.74352	1.31499	1.25654
		4.94500	0.37376	17.18779	0.02370	43.20144	104.18386
27	Co	13.24880	7.17858	2.56710	1.75551	1.51306	0.73696
		4.57509	0.34333	15.27805	0.02238	90.17243	40.63471
28	Ni	13.34779	7.15137	3.24290	1.75559	1.33643	1.16593
		4.09346	0.31459	12.23973	0.02080	38.55532	95.83599
29	Cu	11.72086	7.09358	5.93423	1.79212	1.74571	0.71350
		3.34778	0.28828	8.46165	27.95010	0.01904	98.02165
30	Zn	14.24718	7.05271	4.33028	1.69647	1.41414	1.25920
		3.35970	0.26162	10.15307	0.01625	33.12649	79.99036
31	Ga	14.92001	7.02666	3.89771	2.35987	1.60865	1.18711
		6.79473	0.23591	9.22370	36.60456	0.01249	98.89710
32	Ge	15.56336	7.03637	3.16346	3.07508	1.69141	1.47032
		6.10774	0.21109	8.14629	31.23299	72.07498	0.00731

Table 5 (*cont.*)

Z	Atom	a_1	a_2	a_3	a_4	a_5	a_6
		b_1	b_2	b_3	b_4	b_5	b_6
33	As	14.08828	7.09546	4.04940	3.61977	2.87058	1.27650
		11.75137	0.18747	20.56814	4.20554	56.42794	0.00027
34	Se	8.83137	7.46814	7.05070	4.85416	4.53456	1.26108
		3.58242	28.84348	0.17285	15.15766	64.03025	0.00010
35	Br	17.35945	6.99543	4.96870	2.86161	1.57331	1.24150
		8.10872	0.15904	26.85549	12.56219	54.84699	0.00010
36	Kr	17.60004	6.94060	5.78653	2.96797	1.49195	1.21291
		6.56055	0.14599	16.69003	42.37337	19.93619	0.00010
37	Rb	17.65604	9.13615	6.89267	1.21527	1.17631	0.92355
		6.08626	16.42089	0.13390	200.00000	0.00010	44.98589
38	Sr	17.62206	7.37217	6.85650	2.68421	2.32985	1.13520
		6.26610	14.18503	0.12297	127.93172	14.22984	0.00010
39	Y	17.69130	9.86697	6.83236	2.22134	1.28763	1.10040
		2.41440	12.78677	0.11367	137.29778	50.49248	0.00010
40	Zr	32.15426	6.80271	1.04273	0.00010	0.00010	0.00010
		1.75623	0.10418	0.00010	11.94156	51.09940	129.29105
41	Nb	33.24233	6.78151	0.97587	0.00010	0.00010	0.00010
		1.52815	0.09545	0.00010	11.77344	42.92228	133.27890
42	Mo	34.32939	6.77336	0.89695	0.00010	0.00010	0.00010
		1.38491	0.08728	0.00010	10.78110	50.04189	81.05093
43	Tc	19.26166	16.15002	6.77863	0.80949	0.00010	0.00010
		1.27785	1.27770	0.07978	0.00010	10.85734	80.39102
44	Ru	36.46918	6.78339	0.74714	0.00010	0.00010	0.00010
		1.19294	0.07386	0.00010	9.60627	42.29401	64.57157
45	Rh	21.57643	10.71823	6.80000	4.78230	0.65832	0.46472
		1.07940	1.08194	0.06783	8.96262	0.00010	36.53622
46	Pd	27.27332	6.84304	5.59717	5.06602	0.69379	0.52666
		0.96326	0.06162	9.10948	9.12418	37.47312	0.00010
47	Ag	24.89885	13.88998	6.92293	0.54798	0.38987	0.35039
		0.87363	8.40420	0.05539	102.02171	34.93690	0.00010
48	Cd	23.52794	12.28950	6.29213	2.80914	2.19516	0.88614
		0.79965	7.82362	0.04527	7.82457	49.12746	0.07286
49	In	23.29033	16.81728	7.10981	1.57893	0.19952	0.00412
		0.74584	6.78516	0.04524	31.57445	8.21999	92.83768
50	Sn	23.29745	18.01043	7.07108	0.87824	0.65178	0.09101
		0.70091	6.26640	0.04279	34.38731	85.79001	33.82304
51	Sb	23.13106	11.62665	7.02596	5.17279	3.09210	0.95144
		0.65722	5.70303	0.04042	5.75197	34.19915	69.27843
52	Te	22.85443	17.96965	6.97377	4.14837	0.02689	0.02689
		0.61519	5.25956	0.03812	36.28090	65.30504	12.76925
53	I	22.53413	12.53981	6.91424	6.91423	4.09672	0.00086
		0.57543	4.84566	38.06353	0.03588	4.84561	14.22179
54	Xe	22.18869	17.90011	7.06493	6.84607	0.00010	0.00010
		0.53788	4.40596	32.27948	0.03368	64.94894	20.30429

The parameters are listed in Tables 3, 5 and 7, while the χ^2 and $\sum_{i=1}^{6} a_i$ values and maximum and mean deviations of the fitting for each of the elements are given in Tables 4, 6, 8 and 9. The quality of the fitting is illustrated by the χ^2 values relative to those obtained with the earlier expressions. For the 0–2 Å^{-1} range, the average ratio of the four-term χ^2 to the present six-term χ^2 is 1312. For the 0–6 Å^{-1} range, the average χ^2 ratio is 7580. The only elements for which improvements are small are B, S, Cl and Ar in the $\sin\theta/\lambda$ range of 0.0 to 2.0 Å^{-1}. The relative deviation at the point of maximum deviation (see Table 9) is very small for all the elements, ranging from 0.002% for F to 0.372% for Sr, the latter at $\sin\theta/\lambda = 3.95$ Å^{-1}. The fit obtained for iodine is illustrated in Fig. 1.

We note that for some elements the χ^2 in Table 9 is smaller than the sum of χ^2's in Tables 4, 6 and 8. The reason is that the points at 2.0 and 4.0 Å^{-1} contribute to two of the three individual χ^2's. By the same token, because Table 9 is based on using parameters in Tables 3, 5 and 7 in the ranges $0 \leq \sin\theta/\lambda < 2.0$ Å^{-1}, $2.0 \leq \sin\theta/\lambda < 4.0$ Å^{-1} and $4.0 \leq \sin\theta/\lambda \leq 6.0$ Å^{-1}, respectively, the maximum deviation in Table 9 is smaller than the largest of the maximum deviations in Tables 4, 6 and 8 for some elements. For comparison, the non-relativistic scattering factors were also obtained with the program *GRASP*92 by using an artificially large value for the speed of light. The differences between the relativistic and non-relativistic values in the $\sin\theta/\lambda$ range 0–12 Å^{-1} for the halogen atoms Cl, Br and I are shown in Fig. 2.

Table 6. *Values of* $\sum_{i=1}^{6} a_i$, *maximum deviation of the fit, sin* θ/λ *for the maximum deviation and the mean deviation for the six-Gaussian analytical fit with the parameters in Table 5*

Z	Atom	$\sum a_i$	χ^2	Maximum deviation	At sin θ/λ (Å^{-1})	Mean deviation
1	H	1.00000	0.19776D−08	0.00001	2.20	0.00001
2	He	2.00000	0.12631D−08	0.00001	4.00	0.00000
3	Li	3.00000	0.10281D−07	0.00003	4.00	0.00001
4	Be	4.00000	0.37507D−09	0.00001	3.65	0.00000
5	B	5.00000	0.92120D−09	0.00001	2.00	0.00000
6	C	6.00000	0.27818D−08	0.00002	4.00	0.00001
7	N	7.00000	0.18745D−08	0.00002	4.00	0.00001
8	O	8.00000	0.26617D−09	0.00001	2.65	0.00000
9	F	9.00000	0.19176D−08	0.00002	2.00	0.00001
10	Ne	10.00000	0.19151D−07	0.00006	2.00	0.00002
11	Na	11.00000	0.27237D−07	0.00007	2.00	0.00002
12	Mg	12.00000	0.42897D−07	0.00006	2.00	0.00003
13	Al	13.00000	0.36751D−07	0.00007	4.00	0.00003
14	Si	14.00000	0.88373D−07	0.00014	2.00	0.00003
15	P	15.00000	0.63188D−08	0.00003	4.00	0.00001
16	S	16.00000	0.75939D−07	0.00010	2.00	0.00004
17	Cl	17.00000	0.79467D−07	0.00010	2.00	0.00004
18	Ar	18.00000	0.13768D−06	0.00013	4.00	0.00005
19	K	19.00000	0.30834D−04	0.00200	2.00	0.00073
20	Ca	20.00000	0.36782D−04	0.00228	2.00	0.00080
21	Sc	21.00000	0.46348D−04	0.00259	2.00	0.00090
22	Ti	22.00000	0.55136D−04	0.00279	2.00	0.00099
23	V	23.00000	0.58697D−04	0.00280	2.00	0.00102
24	Cr	24.00000	0.12040D−06	0.00016	2.00	0.00004
25	Mn	25.00000	0.41557D−04	0.00226	4.00	0.00086
26	Fe	26.00000	0.24690D−04	0.00190	4.00	0.00066
27	Co	27.00000	0.10140D−04	0.00135	4.00	0.00042
28	Ni	28.00000	0.51221D−05	0.00094	2.00	0.00029
29	Cu	29.00000	0.12447D−04	0.00197	2.00	0.00040
30	Zn	30.00000	0.40362D−04	0.00329	2.00	0.00078
31	Ga	31.00000	0.87632D−04	0.00451	2.00	0.00118
32	Ge	32.00000	0.14904D−03	0.00553	2.00	0.00157
33	As	33.00000	0.21179D−03	0.00617	2.00	0.00190
34	Se	34.00000	0.39504D−03	0.00959	2.00	0.00243
35	Br	35.00000	0.73994D−03	0.01159	2.00	0.00352
36	Kr	36.00000	0.10667D−02	0.01162	2.00	0.00435
37	Rb	37.00000	0.11998D−02	0.00937	4.00	0.00471
38	Sr	38.00000	0.10796D−02	0.01025	4.00	0.00447
39	Y	39.00000	0.87919D−03	0.00933	4.00	0.00402
40	Zr	40.00000	0.80302D−03	0.00928	4.00	0.00382
41	Nb	41.00000	0.66912D−03	0.00899	4.00	0.00349
42	Mo	42.00000	0.50718D−03	0.00838	4.00	0.00302
43	Tc	43.00000	0.33980D−03	0.00738	4.00	0.00244
44	Ru	44.00000	0.19194D−03	0.00569	4.00	0.00182
45	Rh	45.00000	0.13707D−03	0.00447	4.00	0.00157
46	Pd	46.00000	0.10172D−03	0.00390	4.00	0.00135
47	Ag	47.00000	0.78258D−04	0.00344	4.00	0.00118
48	Cd	48.00000	0.63844D−04	0.00329	4.00	0.00105
49	In	49.00000	0.60428D−04	0.00276	2.00	0.00104
50	Sn	50.00000	0.11067D−03	0.00396	2.00	0.00140
51	Sb	51.00000	0.19079D−03	0.00511	2.00	0.00185
52	Te	52.00000	0.28794D−03	0.00629	2.00	0.00227
53	I	53.00000	0.40506D−03	0.00760	2.00	0.00268
54	Xe	54.00000	0.55236D−03	0.00913	2.00	0.00312

5. The atomic second moments $\langle r^2 \rangle$ and the electron scattering factors $f_{el}(0)$

The atomic second moments $\langle r^2 \rangle$ and the electron scattering factors $f_{el}(0)$ are listed in Table 10. $\langle r^2 \rangle$ is related to the mean inner potential (Becker & Coppens, 1990; O'Keeffe & Spence, 1994). The contribution to the mean inner potential from the IAM (independent-atom model) for a crystal is

$$(2\pi/3V)\sum_j \langle r^2 \rangle_j, \qquad (6)$$

where V is the unit-cell volume and the summation is

Table 7. *Analytical parameters for scattering factors in the* $4.0 \leq \sin\theta/\lambda < 6.0\ \text{Å}^{-1}$ *range*

Z	Atom	a_1	a_2	a_3	a_4	a_5	a_6
		b_1	b_2	b_3	b_4	b_5	b_6
1	H	0.43051	0.28560	0.17157	0.09474	0.01748	0.00010
		23.02312	10.20138	51.25444	4.13511	1.35427	0.07925
2	He	0.73151	0.71927	0.31319	0.16947	0.06400	0.00256
		4.89723	11.93838	1.83920	27.69307	0.58432	0.08598
3	Li	0.93538	0.86153	0.84472	0.31565	0.03826	0.00446
		4.54265	97.52985	1.63985	200.00000	0.19390	0.04957
4	Be	1.60945	1.05263	0.66608	0.54994	0.10771	0.01417
		43.77112	1.92769	0.69884	103.50034	0.18806	0.04866
5	B	2.20211	1.33369	1.20385	0.22689	0.03303	0.00043
		23.39543	1.07687	60.93249	0.18397	0.04745	0.21648
6	C	2.14806	1.82836	1.33723	0.36462	0.27457	0.04718
		13.10945	28.50497	0.42547	57.25664	0.14733	0.03953
7	N	2.47201	2.43548	1.11094	0.52080	0.38633	0.07444
		8.64871	19.61227	0.36713	43.58268	0.13620	0.03681
8	O	3.00590	2.60225	1.03232	0.74926	0.50166	0.10861
		14.05516	5.98365	0.32724	34.06486	0.12653	0.03445
9	F	3.52591	2.74119	1.01052	0.96212	0.61180	0.14848
		10.47716	4.36556	26.58575	0.29553	0.11775	0.03227
10	Ne	4.03969	2.96823	1.19927	0.81126	0.76534	0.21621
		8.15631	3.34037	21.25595	0.28588	0.11771	0.03229
11	Na	4.32848	3.80095	1.08229	0.90417	0.53097	0.35315
		7.20138	2.72535	0.13543	165.16286	51.92083	0.03532
12	Mg	4.23374	3.77114	1.54677	1.13333	0.89013	0.42487
		5.16800	2.13995	55.52364	0.12623	124.77432	0.03312
13	Al	4.29478	3.59215	2.38016	1.15060	1.09159	0.49073
		3.78023	1.69494	43.73724	0.11646	111.35596	0.03079
14	Si	4.66828	3.46099	3.08480	1.14364	1.09398	0.54830
		2.74920	35.52517	1.32385	0.10644	80.40524	0.02844
15	P	5.27722	4.51857	2.35454	1.13515	1.12441	0.59010
		2.03674	28.32664	1.01667	67.46291	0.09591	0.02593
16	S	5.94845	5.41744	1.58567	1.33183	1.10802	0.60860
		1.55852	22.80051	0.75525	57.85201	0.08492	0.02319
17	Cl	7.15746	6.17588	1.88742	1.11001	0.59643	0.07281
		1.16607	18.18337	45.89666	0.07381	0.02012	23.22369
18	Ar	7.29820	7.25818	1.73443	1.13745	0.55402	0.01773
		15.63295	0.95548	41.07550	0.06333	0.01682	20.09628
19	K	9.39735	3.20941	2.92884	1.78760	1.18962	0.48718
		12.21015	28.27004	200.00000	82.98356	0.05400	0.01335
20	Ca	10.39184	3.40270	2.75840	1.77909	1.20798	0.45999
		10.44441	86.31958	181.45094	28.57932	0.04749	0.01133
21	Sc	10.94006	3.37950	2.52865	2.47777	1.01943	0.65458
		9.08162	137.40234	51.54073	53.74777	0.04750	0.01424
22	Ti	11.69987	3.10361	2.93626	2.55350	1.16297	0.54378
		8.05962	92.71004	31.20186	144.27503	0.01964	0.06434
23	V	12.92694	3.40159	2.45091	2.41146	1.43062	0.37848
		7.25373	120.58589	54.89369	22.00492	0.02112	0.10869
24	Cr	12.83718	5.14806	3.69710	1.50701	0.59008	0.22058
		6.21670	26.27260	63.74598	0.02045	0.16482	68.88348
25	Mn	13.76643	3.28471	3.20735	2.01517	1.53658	1.18977
		5.69636	101.12197	19.85275	37.71895	0.01925	0.21023
26	Fe	13.98131	3.18020	2.63674	2.57829	2.07208	1.55137
		4.94500	17.18779	43.20144	104.18386	0.23306	0.01800
27	Co	14.34964	3.66794	2.96999	2.61390	1.83780	1.56075
		4.57509	15.27805	0.23907	90.17243	40.63471	0.01680
28	Ni	14.25237	4.14748	3.72080	2.24101	2.07051	1.56782
		4.09347	12.23973	0.23557	38.55532	95.83599	0.01569
29	Cu	12.46573	6.67910	4.28522	2.53699	1.57460	1.45837
		3.34773	8.46165	0.22725	27.95010	0.01470	98.02165
30	Zn	14.83864	4.92174	4.80275	2.00560	1.85066	1.58060
		3.35978	10.15307	0.21816	33.12649	79.99036	0.01379
31	Ga	15.42207	5.23057	4.33627	2.79843	1.62567	1.58699
		3.05376	0.20821	9.22370	36.60456	98.89710	0.01298
32	Ge	15.93149	5.60315	3.47718	3.38880	2.00513	1.59426
		2.77405	0.19829	8.14629	31.23299	72.07498	0.01227

Table 7 (*cont.*)

Z	Atom	a_1	a_2	a_3	a_4	a_5	a_6
		b_1	b_2	b_3	b_4	b_5	b_6
33	As	14.42406	5.93000	4.21720	3.78773	3.03838	1.60262
		2.42897	0.18865	20.56814	4.20318	56.42794	0.01164
34	Se	17.17400	6.21788	5.03680	2.43266	1.61251	1.52617
		2.32214	0.17942	28.93463	10.08637	0.01109	61.65971
35	Br	17.46143	6.46430	4.98441	2.87732	1.62354	1.58902
		2.11212	0.17054	26.85549	12.56219	0.01060	54.84699
36	Kr	17.61110	6.67129	5.73175	2.91319	1.63549	1.43717
		1.91784	0.16201	16.69003	42.37337	0.01018	19.93619
37	Rb	17.59789	9.01628	6.83910	1.64764	1.09540	0.80368
		1.73467	16.42089	0.15383	0.00978	200.00000	44.98589
38	Sr	17.51450	7.19723	6.965341	2.50927	2.15491	1.65877
		1.56850	14.18503	0.14588	127.93172	14.22984	0.00941
39	Y	17.50681	9.66836	7.04463	2.02273	1.66846	1.08902
		1.43461	12.78677	0.13816	137.29778	0.00904	50.49248
40	Zr	17.52682	10.24298	7.08400	1.77248	1.69936	1.67436
		1.31592	11.94156	0.13059	51.09940	129.29104	0.00864
41	Nb	17.61902	11.17550	7.08432	2.22654	1.67512	1.21952
		1.21391	11.77344	0.12319	42.92228	0.00820	133.27890
42	Mo	17.61629	11.69921	7.06320	3.67548	1.66629	0.27952
		1.11745	10.78110	0.11586	50.04189	0.00767	81.05093
43	Tc	14.13464	10.23625	7.12979	7.02850	2.82720	1.64360
		10.85734	1.02759	1.02766	0.10855	80.39102	0.00699
44	Ru	17.57992	13.46961	6.97474	4.36924	1.60607	0.00042
		0.95049	9.60627	0.10136	42.29401	0.00617	64.57157
45	Rh	14.11606	14.10591	6.92593	5.03053	3.27670	1.54486
		8.96262	0.87857	0.09416	36.53622	0.88015	0.00508
46	Pd	17.69188	8.46690	7.93575	6.88468	3.56352	1.45726
		0.81028	9.10948	9.12418	0.08705	37.47312	0.00369
47	Ag	17.65492	17.56029	6.87287	3.07323	1.33347	0.50523
		1.32570	8.40420	0.07993	34.93690	0.00183	102.02171
48	Cd	17.64118	13.94652	6.87610	4.46616	3.85218	1.21785
		1.50685	7.82362	0.07369	7.82457	49.12746	0.00010
49	In	23.05221	7.81386	6.83574	5.94952	4.13700	1.21167
		6.78516	31.57445	0.06968	92.83768	8.21999	0.00010
50	Sn	23.60743	6.78062	6.47524	6.24878	5.68801	1.19990
		6.26640	0.06568	34.38731	85.79001	33.82304	0.00010
51	Sb	17.19136	10.73750	8.65681	6.71660	6.51615	1.18157
		5.70303	5.75197	34.19915	0.06170	69.27843	0.00010
52	Te	24.06321	10.24194	6.64773	5.77451	4.11703	1.15558
		5.25957	36.28090	0.05776	65.30504	12.76925	0.00010
53	I	18.41511	12.78954	9.97202	6.58022	4.12222	1.12090
		4.84569	38.06353	4.84562	0.05390	14.22179	0.00010
54	Xe	22.47924	11.64406	9.06711	6.51865	3.21450	1.07642
		4.40617	32.27948	20.30429	0.05013	64.94894	0.00010

over all atoms in the unit cell. From the $\langle r^2 \rangle$ value for Si in Table 10, the IAM contribution to the mean inner potential for the silicon crystal at room temperature ($a_{cell} = 5.4310$ Å) is calculated as 13.57 V, which is very close to the calculated value of 13.61 V from the non-relativistic atomic wavefunction (O'Keeffe & Spence, 1994), but differs significantly from the observed value of 9.30 (12) V (O'Keeffe & Spence, 1994).

For neutral atoms, the electron scattering factors $f_{el}(0)$ are related to the atomic second moments $\langle r^2 \rangle$. Integration of the electrostatic potential due to the electrons over the atomic volume gives (Ibers, 1958)

$$f_{el}(0) = 0.529\,177\,249 \langle r^2 \rangle / 3, \qquad (7)$$

where $\langle r^2 \rangle$ is in a.u. and $f_{el}(0)$ is in Å. The values in Table 10 have been obtained with this equation.

6. Discussion

For elements He–Ar, our f values agree better with the results of Wang, Smith, Bunge & Jáuregui (1996) than those given by Rez, Rez & Grant (1994). We will not consider the results for the element Cu for which apparently an incorrect initial configuration was used in the earlier work.† Excluding Cu, the largest differences between the present scattering factors and those of Rez *et al.* are less than 0.5% but absolute discrepancies of about 0.07 electrons occur for transition metals. As an example, for Cr and Mo, respectively, the present values for f at $\sin\theta/\lambda = 0.15$ Å^{-1} are 20.0796 and 35.9458, as compared to Rez *et al.*'s results of 20.0093 and 35.8788.

† Private communication.

Table 8. *Values of* $\sum_{i=1}^{6} a_i$, *maximum deviation of the fit, sin* θ/λ *for the maximum deviation and the mean deviation for the six-Gaussian analytical fit with the parameters in Table 7*

Z	Atom	$\sum a_i$	χ^2	Maximum deviation	At sin θ/λ (Å^{-1})	Mean deviation
1	H	1.00000	0.34593D−09	0.00001	4.85	0.00000
2	He	2.00000	0.84839D−08	0.00004	4.00	0.00001
3	Li	3.00000	0.41850D−09	0.00001	6.00	0.00000
4	Be	4.00000	0.10261D−08	0.00001	5.95	0.00000
5	B	5.00000	0.46310D−08	0.00002	4.00	0.00001
6	C	6.00000	0.51150D−09	0.00001	5.15	0.00000
7	N	7.00000	0.70662D−09	0.00001	5.75	0.00000
8	O	8.00000	0.73482D−09	0.00001	4.00	0.00000
9	F	9.00000	0.61241D−09	0.00001	4.00	0.00000
10	Ne	10.00000	0.25978D−08	0.00002	6.00	0.00001
11	Na	11.00000	0.78168D−07	0.00010	4.00	0.00004
12	Mg	12.00000	0.73211D−07	0.00010	6.00	0.00004
13	Al	13.00000	0.56319D−07	0.00009	4.00	0.00003
14	Si	14.00000	0.30755D−07	0.00007	6.00	0.00002
15	P	15.00000	0.11341D−07	0.00004	6.00	0.00001
16	S	16.00000	0.12189D−08	0.00001	6.00	0.00000
17	Cl	17.00000	0.23845D−08	0.00002	4.00	0.00001
18	Ar	18.00000	0.74005D−08	0.00004	4.00	0.00001
19	K	19.00000	0.40968D−08	0.00002	6.00	0.00001
20	Ca	20.00000	0.63051D−08	0.00004	4.00	0.00001
21	Sc	21.00000	0.88740D−07	0.00016	4.00	0.00004
22	Ti	22.00000	0.41291D−06	0.00031	4.00	0.00008
23	V	23.00000	0.99249D−06	0.00043	4.00	0.00013
24	Cr	24.00000	0.13776D−05	0.00045	4.00	0.00015
25	Mn	25.00000	0.13149D−05	0.00043	6.00	0.00015
26	Fe	26.00000	0.10129D−05	0.00039	6.00	0.00013
27	Co	27.00000	0.74640D−06	0.00034	6.00	0.00011
28	Ni	28.00000	0.60109D−06	0.00029	6.00	0.00010
29	Cu	29.00000	0.53578D−06	0.00027	6.00	0.00010
30	Zn	30.00000	0.52892D−06	0.00026	4.00	0.00010
31	Ga	31.00000	0.56383D−06	0.00028	4.00	0.00010
32	Ge	32.00000	0.64716D−06	0.00030	4.00	0.00011
33	As	33.00000	0.71688D−06	0.00032	4.00	0.00011
34	Se	34.00000	0.79289D−06	0.00034	4.00	0.00012
35	Br	35.00000	0.81266D−06	0.00033	4.00	0.00012
36	Kr	36.00000	0.77800D−06	0.00032	4.00	0.00012
37	Rb	37.00000	0.67376D−06	0.00030	6.00	0.00011
38	S	38.00000	0.51206D−06	0.00027	6.00	0.00009
39	Y	39.00000	0.30708D−06	0.00022	6.00	0.00007
40	Zr	40.00000	0.12435D−06	0.00016	6.00	0.00005
41	Nb	41.00000	0.41329D−07	0.00008	6.00	0.00003
42	Mo	42.00000	0.13639D−06	0.00020	4.00	0.00004
43	Tc	43.00000	0.54106D−06	0.00037	4.00	0.00009
44	Ru	44.00000	0.12991D−05	0.00054	4.00	0.00015
45	Rh	45.00000	0.25304D−05	0.00072	4.00	0.00020
46	Pd	46.00000	0.42550D−05	0.00092	4.00	0.00027
47	Ag	47.00000	0.65060D−05	0.00111	4.00	0.00033
48	Cd	48.00000	0.10110D−04	0.00159	4.00	0.00040
49	In	49.00000	0.27590D−04	0.00271	4.00	0.00064
50	Sn	50.00000	0.62377D−04	0.00377	4.00	0.00100
51	Sb	51.00000	0.11159D−03	0.00474	4.00	0.00136
52	Te	52.00000	0.16936D−03	0.00556	4.00	0.00170
53	I	53.00000	0.22864D−03	0.00617	4.00	0.00198
54	Xe	54.00000	0.28037D−03	0.00653	4.00	0.00220

The largest relative difference in $f_{el}(0)$ is 5.5% in the case of Cr, our value being 6.589 697 Å and that of Rez *et al.* 6.9550 Å. The only other atoms for which the relative difference in $f_{el}(0)$ exceeds 3.0% are N (3.43%), Nb (4.35%), Mo (5.04%) and Sb (3.02%).

The fitting parameters given in Tables 3, 5 and 7 for the whole range $0.0 \leq \sin\theta/\lambda \leq 6.0$ Å^{-1} eliminate the need for different functional forms for different ranges of $\sin\theta/\lambda$, as used by Fox, O'Keeffe & Tabbernor (1989). The present parameterization has a minor discontinuity at $\sin\theta/\lambda$ values of 2.0 and 4.0 Å^{-1}. We recommend that parameters in Tables 5 and 7, respectively, be used to evaluate $f(\sin\theta/\lambda)$ and its derivatives at the boundary points with $\sin\theta/\lambda = 2.0$ and 4.0 Å^{-1}.

Table 9. *Summary of maximum deviation, $\sin\theta/\lambda$ for the maximum deviation and the mean deviation for $0.0 \leq \sin\theta/\lambda < 6.0$ Å^{-1}*

Z	Atom	χ^2	Maximum deviation	At $\sin\theta/\lambda$ (Å^{-1})	Mean deviation
1	H	0.64067D−07	0.00013	0.10	0.00001
2	He	0.30578D−07	0.00005	0.00	0.00001
3	Li	0.51638D−05	0.00109	0.35	0.00009
4	Be	0.32094D−04	0.00224	0.55	0.00023
5	B	0.26396D−04	0.00161	0.50	0.00023
6	C	0.62572D−05	0.00078	0.95	0.00011
7	N	0.10031D−05	0.00025	1.15	0.00005
8	O	0.19883D−06	0.00019	0.10	0.00002
9	F	0.14143D−06	0.00019	0.10	0.00002
10	Ne	0.16819D−06	0.00010	0.65	0.00003
11	Na	0.47128D−05	0.00096	0.10	0.00011
12	Mg	0.75839D−06	0.00045	0.05	0.00005
13	Al	0.78712D−05	0.00137	0.05	0.00014
14	Si	0.18283D−04	0.00153	0.55	0.00021
15	P	0.66260D−04	0.00297	0.60	0.00035
16	S	0.18860D−03	0.00479	0.70	0.00061
17	Cl	0.47507D−03	0.00760	0.75	0.00095
18	Ar	0.99372D−03	0.01010	0.85	0.00138
19	K	0.12595D−02	0.01084	0.90	0.00179
20	Ca	0.22798D−02	0.01524	1.00	0.00226
21	Sc	0.22318D−02	0.01427	1.05	0.00232
22	Ti	0.17697D−02	0.01231	1.15	0.00213
23	V	0.12143D−02	0.01004	1.20	0.00182
24	Cr	0.74086D−03	0.00700	1.25	0.00134
25	Mn	0.40450D−03	0.00579	1.75	0.00115
26	Fe	0.19888D−03	0.00420	1.75	0.00083
27	Co	0.85917D−04	0.00284	1.80	0.00055
28	Ni	0.37902D−04	0.00171	1.80	0.00040
29	Cu	0.40976D−04	0.00195	2.00	0.00042
30	Zn	0.66255D−04	0.00330	2.00	0.00053
31	Ga	0.12106D−03	0.00445	2.00	0.00069
32	Ge	0.15522D−03	0.00557	2.00	0.00072
33	As	0.22132D−03	0.00623	2.00	0.00085
34	Se	0.40025D−03	0.00962	2.00	0.00097
35	Br	0.73157D−03	0.01157	2.00	0.00135
36	Kr	0.10534D−02	0.01168	2.00	0.00171
37	Rb	0.15180D−02	0.01253	0.05	0.00237
38	Sr	0.10636D−02	0.00800	3.95	0.00189
39	Y	0.10413D−02	0.00699	3.95	0.00209
40	Zr	0.11920D−02	0.00675	2.00	0.00224
41	Nb	0.12698D−02	0.00759	0.95	0.00229
42	Mo	0.13261D−02	0.00864	0.95	0.00229
43	Tc	0.13147D−02	0.00905	1.00	0.00224
44	Ru	0.12905D−02	0.00928	1.00	0.00213
45	Rh	0.12153D−02	0.00925	1.05	0.00204
46	Pd	0.17079D−02	0.01242	1.10	0.00227
47	Ag	0.28322D−02	0.01600	1.15	0.00274
48	Cd	0.39114D−02	0.01870	1.15	0.00312
49	In	0.47633D−02	0.02003	1.20	0.00351
50	Sn	0.51092D−02	0.02014	1.25	0.00383
51	Sb	0.52337D−02	0.02087	1.70	0.00402
52	Te	0.51414D−02	0.02081	1.70	0.00418
53	I	0.51720D−02	0.02051	1.75	0.00441
54	Xe	0.52047D−02	0.02001	1.75	0.00462

Parameters in Tables 3, 5, and 7 are used for $\sin\theta/\lambda$ ranges of [0.0, 2.0 Å^{-1}], [2.0, 4.0 Å^{-1}] and [4.0, 6.0 Å^{-1}], respectively.

The accurate analytical expressions for X-ray scattering factors are also useful for electron diffraction studies, for the atomic scattering factors for the diffraction of electrons are related to the X-ray scattering factors by the Mott formula

$$f_{el}(s) = 0.023\,934\,\lambda^2[Z - f_X(s)]/\sin^2\theta, \qquad (8)$$

where λ is the wavelength of the incident electrons in Å, Z the atomic number, $f_{el}(s)$ the electron scattering factor in Å and $f_X(s)$ the X-ray scattering factors in electron

units. It should be interesting to compare the $f_{el}(s)$ calculated from (8) and (5) to the results obtained directly from the Fourier–Bessel transformation of the atomic potential, especially at low angles where the Mott formula may be numerically inaccurate (Peng & Cowley, 1988).

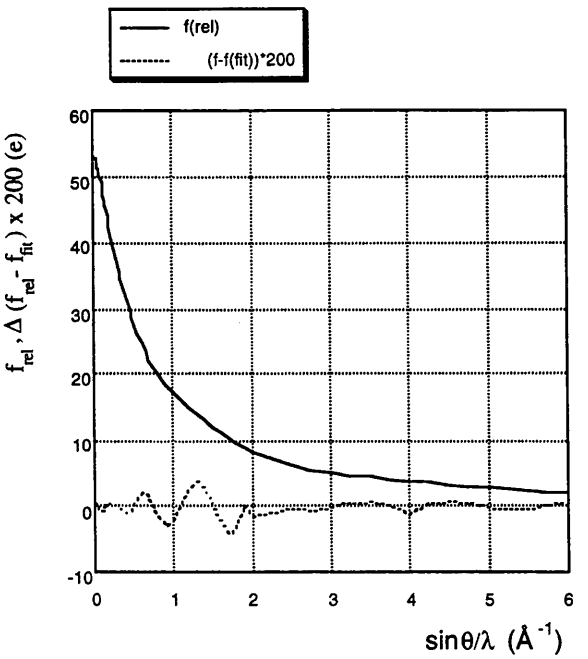

Fig. 1. The relativistic scattering factor for iodine, and the difference between f_{rel} and the fit, multiplied by a factor of 200.

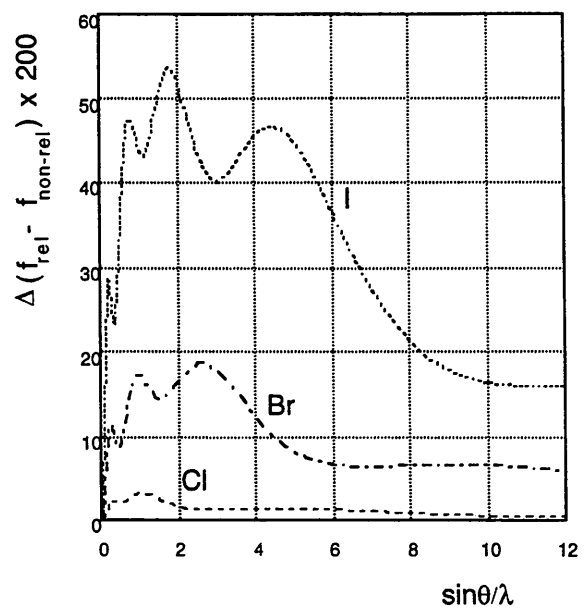

Fig. 2. The difference between the relativistic and non-relativistic form factors for I, Br and Cl, multiplied by a factor of 200.

Table 10. *Summary of* $\langle r^2 \rangle$ *and* $f_{el}(0)$ *for the elements H–Xe*

Z	Atom	$\langle r^2 \rangle$ (a.u.)	$f_{el}(0)$ (Å)
1	H	2.999906	0.529161
2	He	2.369438	0.417951
3	Li	18.628952	3.286006
4	Be	17.312983	3.053879
5	B	15.844575	2.794863
6	C	13.785530	2.431667
7	N	12.076709	2.130240
8	O	11.164123	1.969267
9	F	10.226818	1.803933
10	Ne	9.364624	1.651849
11	Na	27.095897	4.779511
12	Mg	29.531438	5.209122
13	Al	33.390525	5.889835
14	Si	32.187175	5.677574
15	P	30.223540	5.331203
16	S	29.103657	5.133664
17	Cl	27.569091	4.862979
18	Ar	25.973470	4.581523
19	K	50.944380	8.986202
20	Ca	56.203256	9.913828
21	Sc	52.791432	9.312008
22	Ti	49.755831	8.776551
23	V	47.091959	8.306664
24	Cr	37.358167	6.589697
25	Mn	42.596293	7.513663
26	Fe	40.642298	7.168993
27	Co	38.870290	6.856424
28	Ni	37.248708	6.570390
29	Cu	31.752800	5.600953
30	Zn	34.386584	6.065533
31	Ga	40.300987	7.108789
32	Ge	41.025939	7.236665
33	As	40.638097	7.168252
34	Se	40.698616	7.178927
35	Br	40.058859	7.066079
36	Kr	39.104753	6.897782
37	Rb	66.797111	11.782504
38	Sr	74.321817	13.109805
39	Y	71.818836	12.668298
40	Zr	69.051635	12.180185
41	Nb	58.126992	10.253161
42	Mo	55.430030	9.777437
43	Tc	61.389271	10.828602
44	Ru	52.886093	9.328706
45	Rh	51.590182	9.100117
46	Pd	42.981606	7.581629
47	Ag	49.157026	8.670927
48	Cd	52.351815	9.234463
49	In	59.156095	10.434687
50	Sn	60.907674	10.743652
51	Sb	61.505416	10.849089
52	Te	62.073578	10.949308
53	I	61.874783	10.914242
54	Xe	61.198713	10.794989

7. Concluding remarks

For the elements between H and Xe, we have obtained relativistic ground-state energies, atomic second moments $\langle r^2 \rangle$, electron scattering factors $f_{el}(0)$, total X-ray scattering factors in the range $0.0 \leq \sin\theta/\lambda \leq 12.0$ Å^{-1} and analytical expressions for the X-ray scattering factors

in the range $0.0 \leq \sin\theta/\lambda \leq 6.0$ Å^{-1}. Scattering factors in this extended range are required for diffraction studies with increasingly available high-energy synchrotron radiation. The wavefunctions from which the scattering factors are derived take into account part of the configuration interaction (CI) in the case of some open shell atoms but are not fully correlated. Meyer, Müller & Schweig (1995) have suggested that the relativistic correction and the correction due to electron correlation should be combined. However, this procedure assumes additivity of the two effects, which may not be valid.

The new analytical expressions give a much better fit than those employed previously and are suitable for accurate studies. The total scattering factors, the parameters for the fit to the total scattering factors, as well as separate core and valence scattering factors, are available in electronic form from the authors. Results on the elements Cs to Cf will be the subject of a future publication. Fitted linear combinations of Slater-type functions, describing the atomic orbitals of the relativistic atoms, are being calculated.

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