Acta Crystallographica Section A
Foundations of Crystallography
ISSN 0108-7673

Received 16 May 2001
Accepted 20 June 2001

Relativistic analytical wave functions and scattering factors for neutral atoms beyond Kr and for all chemically important ions up to I^-

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Relativistic wave functions for elements with $Z = 37–54$ [Su & Coppens (1998). *Acta Cryst.* A**54**, 646–652] have been fitted with a linear combination of Slater-type functions as defined by Bunge, Barrientos & Bunge [*At. Data Nucl. Data Tables* (1993), **53**, 113–162], for use in charge-density analysis and other applications. In addition, numerical relativistic wave functions have been calculated for all chemically relevant ions up to $Z = 54$, and corresponding analytical expressions have been derived. X-ray scattering factors calculated from the numerical wave functions are parameterized [in the $\sin(\theta)/\lambda$ ranges 0.0–2.0, 2.0–4.0 and 4.0–6.0 Å^{-1}] with six Gaussian functions, using the same method applied previously by Su & Coppens [*Acta Cryst.* (1997), A**53**, 749–762].

1. Introduction

Analytical expressions for atomic wave functions are widely used in X-ray charge-density analysis to evaluate the charge density and to calculate the electrostatic properties from models fitted to the X-ray intensities (Coppens, 1997). The well known functions by Clementi & Roetti (1974) have been commonly employed for this purpose and have similarly been applied in many other theoretical applications. However, with the increased accuracy of experimental charge densities due to recent technical developments, there is a need for more accurate analytical functions, especially for heavier atoms.

Analytical wave functions including relativistic effects have been determined for neutral ground-state atoms up to $Z = 36$ (Su & Coppens, 1998) by fitting a linear combination of Slater-type functions (from Bunge *et al.*, 1993) to the numerical solutions at multiconfiguration Dirac–Fock level, obtained with the program *GRASP92* (Parpia *et al.*, 1996).

We describe here an extension of this work to neutral atoms of the fifth period (Rb–Xe) using the same procedure, based on a non-linear least-squares fitting program [*L-BFGS-B*, Zhu *et al.* (1994)]. For the neutral atoms, the relativistic wave functions already calculated by Su & Coppens (1997) were used. In addition, numerical relativistic wave functions have been calculated for all chemically relevant ions up to $Z = 54$ and corresponding analytical expressions have been derived.

The X-ray scattering factors for the ions, calculated from the numerical wave functions, are parameterized [in the $\sin(\theta)/\lambda$ ranges 0.0–2.0, 2.0–4.0 and 4.0–6.0 Å^{-1}] with six Gaussian functions, using the same method previously adopted for neutral atoms (Su & Coppens, 1997). For the heavier ions, only the first range is included, as the higher-order scattering factors are almost identical to those of the neutral configurations.

2. Computational details

The program package *GRASP92* (Parpia *et al.*, 1996) was used to calculate multiconfigurational relativistic wave functions for chemically relevant ions, from Li^+ up to I^-. All the configurations reported in *International Tables for Crystallography* (Maslen *et al.*, 1992) were computed, with the exception of Mo^{5+}, for which convergence could not be achieved. The calculated energies are reported in the supporting material.[1]

For anions, there are well known problems in performing the calculations owing to the inherent lack of convergence. Wang *et al.* (1996) computed only those anions that are stable at the Dirac–Fock level of treatment (namely, the halides and O^-). On the other hand, Rez *et al.* (1994) adopted the procedure suggested by Watson (1958), *i.e.* surrounding the anion by a sphere of positive charges for stabilization. Consequently, the scattering factors reported in the literature differ significantly. Our calculations were performed for O^- and the halides, without applying Watson's (1958) method. Accordingly, the results are quite similar to those reported by Wang *et al.* (1996) and exclude the ions that are not stable in isolation.

[1] Supplementary data for this paper, including calculated energies and maximum and mean deviations for each fit, are available from the IUCr electronic archives (Reference: AU0256). Services for accessing these data are given at the back of the journal.

For cations with large charges (M^{n+}), false convergence was sometimes encountered. To avoid this problem, an initial guess was taken from the wave function converged for either $M^{(n-1)+}$ or the nearest isoelectronic cation in the Periodic Table.

As for the ground-state neutral atoms, multiconfiguration calculations were necessary for all the open-shell ions, for which several relativistic configuration state functions (CSF) were used. In the self-consistent field (SCF) procedure, we adopted the optimal level (OL) model, which is known to give more accurate results than the extended average level (EAL).

The radial functions of each relativistic subshell contain a major, $P(r)$, and a minor, $Q(r)$, component, which are evaluated at selected exponential grid points (typically less than 400). The radial density of a given shell A can be easily computed as

$$R_A(r) = [P_A^2(r) + Q_A^2(r)]. \tag{1}$$

In relativistic atomic structure theory, subshells nl with $l \neq 0$ are split: np is split into $np_{3/2}$ and $np_{1/2}$; while nd is split into $nd_{5/2}$ and $nd_{3/2}$. The radial density for the corresponding non-relativistic electron shell can be obtained by averaging the two relativistic radial densities (which are slightly different) using weights proportional to their generalized occupancies. The radial density of each orbital was then fitted by varying the coefficients and exponents of the analytical expressions for neutral atoms by Bunge *et al.* (1993). Other high-quality non-relativistic wave functions have been reported more recently [see for example Koga *et al.* (1999)], but for consistency we used the same functions previously adopted for the neutral atoms up to Kr (Su & Coppens, 1998). The Fortran routine *L-BFGS-B* (Zhu *et al.*, 1994) was used for the least-squares procedure. For each atomic orbital φ, the function χ^2 was minimized:

$$\chi^2 = \sum_{i=1}^{npts} w(r_i)\left(R(r_i) - r_i^2\left\{\sum_{j=1}^{m}[(2n_j)!]^{-1/2}(2\zeta_j)^{n_j+1/2}c_j r_i^{n_j-1} \times \exp(-\zeta_j r_i)\right\}\right)^2. \tag{2}$$

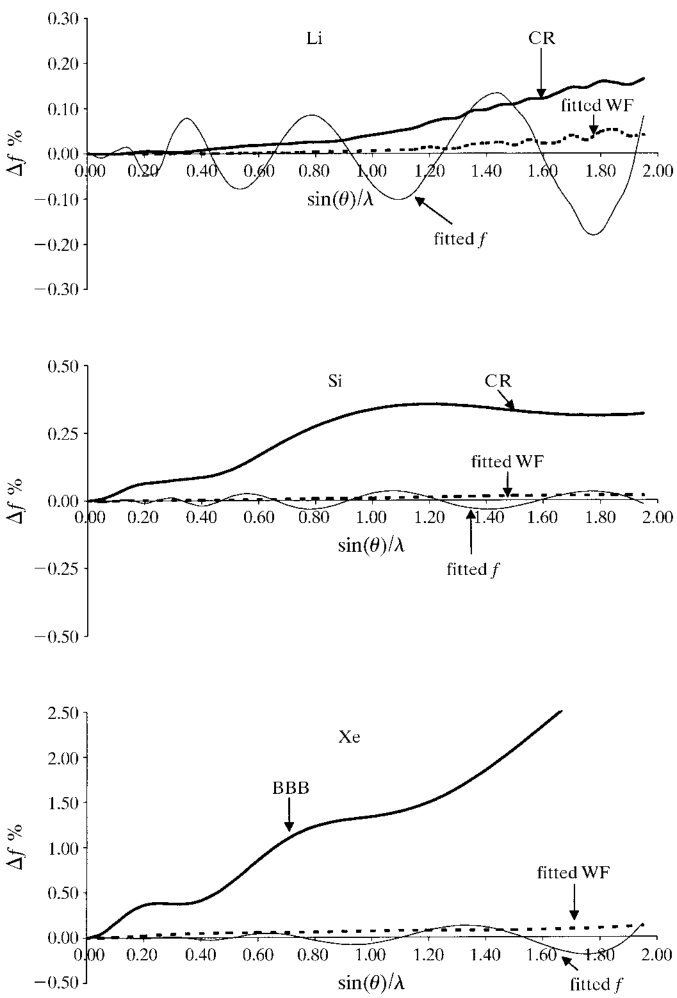

Figure 1
Δf% for neutral ground-state Li, Si and Xe, as a function of $\sin(\theta)/\lambda$ (Å^{-1}). The reference f is obtained with equation (4) from the numerical Dirac–Fock solution. The 'CR' curve is computed with $f^\dagger$ calculated for the Clementi & Roetti (1974) wave function [for Xe, the non-relativistic wave function is taken from Bunge *et al.* (1993), 'BBB']; 'fitted WF' refers to $f^\dagger$ calculated from Bunge *et al.* (1993) wave function after applying the fitting procedure (2) to the density of the relativistic numerical solution [Su & Coppens (1998) for Li and Si; this work for Xe]; 'fitted f' refers to the six-term Gaussian expansion (5) of the relativistic numerical scattering factor (Su & Coppens, 1998).

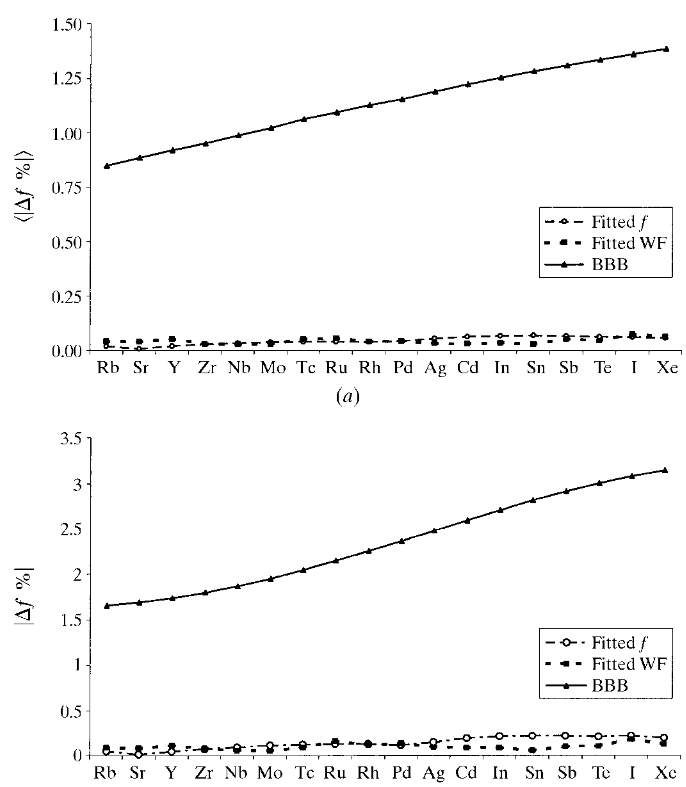

Figure 2
Average (*a*) and largest (*b*) absolute Δf% for neutral atoms of the fifth row. 'BBB', 'fitted WF' and 'fitted f' have the same meaning as in Fig. 1. The 'fitted WF' results come from this work, 'fitted f' from Su & Coppens (1997).

Table 1
Parameters of the six Gaussian expansion for ionic scattering factors (0–2.0 Å^{-1} range).

Atom	a_1 b_1	a_2 b_2	a_3 b_3	a_4 b_4	a_5 b_5	a_6 b_6
Li^{+}	0.79375	0.54736	0.46161	0.13918	0.05800	0.00010
	2.88678	1.16905	6.18250	0.31715	12.60983	28.15927
Be^{2+}	0.82577	0.73691	0.23557	0.20135	0.00034	0.00010
	2.04212	0.80252	4.60157	0.21162	43.68258	103.45510
C_{val}	2.03492	1.64286	0.68060	0.67022	0.51650	0.45488
	25.99675	11.77809	0.51013	0.97866	0.16915	57.91874
O^{-}	3.56378	2.14950	1.52760	1.47980	0.27065	0.00010
	14.10561	5.60491	0.32801	46.88862	0.00980	10.98084
F^{-}	3.22684	2.47111	1.59839	1.28490	1.11335	0.30182
	4.95997	14.45952	0.17267	11.39653	43.30817	0.96703
Na^{+}	3.69529	3.30459	1.68333	0.69149	0.62431	0.00088
	3.24183	7.07179	0.12279	15.45334	1.43664	35.26383
Mg^{2+}	4.30385	2.58390	1.71397	1.39368	0.00470	0.00010
	4.02045	1.85304	0.10693	8.78523	58.58712	125.50050
Al^{3+}	4.19367	3.00032	1.71590	1.08840	0.00167	0.00010
	3.37134	1.58637	0.09158	6.99679	45.26456	113.97270
Si_{val}	5.49488	3.33770	2.38765	1.59864	1.17986	0.00010
	2.60802	37.46289	1.09647	0.06439	80.52337	56.27056
Si^{4+}	3.98392	3.53675	1.72808	0.75103	0.00013	0.00010
	2.94648	1.39488	0.08069	5.91604	56.23176	79.76580
Cl^{-}	7.13932	6.34213	2.29801	1.97826	0.22854	0.00983
	1.18073	19.52901	61.04850	0.08057	23.18225	0.09759
K^{+}	8.00372	7.44077	1.42217	1.13491	0.00010	0.00010
	12.70476	0.77473	0.00010	32.44270	199.99900	82.98298
Ca^{2+}	8.66803	7.39747	1.38325	0.55348	0.00010	0.00010
	10.62955	0.66306	0.00010	30.98476	199.99880	82.97898
Sc^{3+}	9.01395	7.36477	1.32160	0.30179	0.00010	0.00010
	8.86658	0.56771	0.00010	29.98133	137.40030	53.69811
Ti^{2+}	9.67607	7.35874	1.66775	1.29681	0.00010	0.00010
	7.92858	0.50388	23.88214	0.00010	92.10388	145.58810
Ti^{3+}	9.56376	7.35320	1.26997	0.81496	0.00010	0.00010
	7.72729	0.49604	0.00010	22.37931	92.10560	145.58920
Ti^{4+}	9.22395	7.35117	1.23367	0.19305	0.00010	0.00010
	7.44634	0.48595	0.00010	28.20512	92.10930	145.59010
V^{2+}	10.14209	7.35015	2.25361	1.23887	0.01533	0.00010
	6.90615	0.44224	20.14575	0.00010	120.21700	55.09812
V^{3+}	10.05723	7.34875	1.38759	1.20752	0.00010	0.00010
	6.75290	0.43509	18.25122	0.00010	120.22150	55.11062
V^{5+}	9.37695	7.36389	1.11621	0.14450	0.00010	0.00010
	6.31625	0.41568	0.00010	25.36044	199.99870	82.97847
Cr^{2+}	10.54130	4.41457	2.93436	2.87024	1.17229	0.06743
	6.04009	0.38967	0.38966	16.94938	0.00010	59.98400
Cr^{3+}	10.45597	4.43683	2.92505	2.06149	1.11981	0.00120
	5.90641	0.38863	0.37041	15.34221	0.00010	59.68271
Mn^{2+}	10.86580	7.35401	3.49267	1.09987	0.18537	0.00249
	5.30450	0.34487	14.15718	0.00010	38.60730	100.13560
Mn^{3+}	11.04414	4.43611	4.06737	2.44502	0.00559	0.00189
	5.32462	0.15971	0.47488	13.90108	100.14020	38.59723
Mn^{4+}	10.80739	7.37819	1.80548	1.00948	0.00010	0.00010
	5.12031	0.33181	12.46589	0.00010	100.14660	38.60185
Fe^{2+}	11.32394	7.35828	4.08542	1.03934	0.19438	0.00010
	4.71611	0.30793	12.87900	0.00024	43.73118	103.91920
Fe^{3+}	11.27641	7.37595	3.32058	0.98461	0.04263	0.00010
	4.63894	0.30169	11.63908	0.00010	44.10289	103.92070
Co^{2+}	11.59539	7.37601	4.75131	0.95818	0.31843	0.00010
	4.18474	0.27510	11.19206	0.00010	36.27509	93.95933
Co^{3+}	11.58135	7.38964	4.01201	0.91419	0.10353	0.00010
	4.13155	0.27012	10.32693	0.00010	35.20369	93.95908
Ni^{2+}	11.83838	5.16446	4.59215	3.72826	0.67719	0.00010
	3.76040	9.57707	0.31557	0.11646	25.17286	96.76703
Ni^{3+}	12.08932	7.37051	4.53328	0.89389	0.11440	0.00010
	3.73486	0.24588	9.52524	0.00100	36.54998	96.77110
Cu^{+}	11.74994	6.77249	6.21229	1.75552	1.47560	0.03461
	3.34714	0.23831	8.32820	23.58346	0.04331	98.01738
Cu^{2+}	11.83187	5.78192	5.77531	2.46041	1.14698	0.00353
	3.33965	0.25530	8.03031	0.08201	19.99327	98.02090
Zn^{2+}	12.49609	7.88148	4.99190	2.05602	0.57505	0.00010
	3.52509	0.16619	9.20541	1.71372	24.20427	82.21923
Ga^{3+}	10.80193	7.89470	5.30620	3.91136	0.08693	0.00010
	3.67800	0.15468	2.08510	9.11568	34.76155	99.34953

Table 1 (continued)

Atom	a_1 / b_1	a_2 / b_2	a_3 / b_3	a_4 / b_4	a_5 / b_5	a_6 / b_6
Ge^{4+}	8.64238	8.44015	7.88210	2.99985	0.03590	0.00010
	3.75852	2.14595	0.14366	8.16207	30.93576	72.31449
Br^{-}	14.72809	7.73340	4.08153	3.89920	2.84995	2.70412
	1.87781	0.11285	23.45650	3.65207	21.50646	68.50430
Rb^{+}	17.72736	7.70846	6.22707	4.23320	0.10456	0.00010
	1.68258	0.09962	13.34713	25.64859	76.90928	199.99860
Sr^{2+}	13.56253	9.15282	7.57461	4.23621	1.47524	0.00010
	1.52639	13.37893	0.09009	1.50827	28.97999	162.86130
Y^{3+}	17.83594	10.00061	7.34299	0.76995	0.05161	0.00010
	1.37290	11.94201	0.07979	27.59179	0.08311	137.72530
Zr^{4+}	17.88797	10.57832	7.18725	0.34750	0.00010	0.00010
	1.24006	10.60035	0.06944	29.00543	131.45550	1.67829
Nb^{3+}	17.94269	11.64938	7.03542	1.17571	0.20353	0.00010
	1.13911	10.82291	0.06147	34.40293	1.15832	134.27490
Nb^{5+}	17.35713	10.99074	7.04050	0.57079	0.04542	0.00010
	1.13181	9.52278	0.06199	1.11378	134.27980	38.40765
Mo^{3+}	16.70847	11.98967	6.70451	1.98553	1.61267	0.00010
	1.02628	9.86398	0.04848	26.23584	1.02613	83.38388
Mo^{6+}	16.84671	11.18317	6.67150	1.21668	0.08306	0.00010
	1.01489	8.31776	0.04772	1.01511	36.37142	83.39908
Ru^{3+}	16.20121	13.68489	5.92693	2.62037	2.56751	0.00010
	0.83651	8.66621	0.02083	0.83653	22.32915	67.41669
Ru^{4+}	15.97671	13.58921	5.91839	2.79182	1.72564	0.00010
	0.83452	8.38679	0.02066	0.83387	21.20783	67.42265
Rh^{3+}	14.55243	14.36520	5.43109	3.60085	2.86567	1.18601
	8.09600	0.75250	0.00422	0.75381	21.00325	0.75895
Rh^{4+}	14.57165	14.10996	5.40851	3.65768	1.90013	1.35484
	7.90759	0.75012	0.00354	0.75338	19.97214	0.75124
Pd^{2+}	19.27390	15.67787	5.26036	3.78685	0.00010	0.00010
	0.69511	7.84482	0.00010	22.21775	60.82368	1.12994
Pd^{4+}	19.16608	15.58248	5.24991	1.97949	0.02452	0.00010
	0.69220	7.50980	0.00010	19.35021	0.69139	60.83056
Ag^{+}	19.29333	16.76786	5.18419	4.69146	0.06334	0.00010
	0.64534	7.54710	0.00010	23.16034	100.32570	2.35114
Ag^{2+}	19.26038	16.76118	5.17728	3.80102	0.00010	0.00010
	0.64383	7.44215	0.00010	21.24567	100.31430	2.43992
Cd^{2+}	19.24328	17.81622	5.07556	3.86538	0.00010	0.00010
	0.59548	7.03822	0.00010	20.12238	87.60555	31.88584
In^{3+}	19.15099	19.02664	5.11556	1.72846	1.00259	0.00010
	0.55860	6.79490	0.00370	25.60539	8.23095	93.69624
Sn^{2+}	19.14517	19.11002	4.80720	4.48861	0.25075	0.20103
	5.86776	0.50516	0.00010	24.33452	87.00222	31.41846
Sn^{4+}	19.71431	19.14550	4.79767	2.34645	0.00010	0.00010
	6.04052	0.50506	0.00010	16.17828	87.05909	31.49791
Sb^{3+}	19.06093	12.90928	6.64901	4.63278	4.60732	0.14140
	0.46390	5.35884	5.35853	0.00010	21.75129	70.66362
Sb^{5+}	19.55274	19.11016	4.62585	1.75378	0.96170	0.00010
	5.57560	0.46433	0.00010	15.08594	5.57571	70.66860
I^{-}	18.97534	15.68841	6.74714	4.42194	4.08431	4.06854
	0.38165	4.33217	26.51128	4.35007	0.00013	70.73529

$w(r)$ is a weighting function; c_j and ζ_j are the coefficient and exponent (variable parameters) of the basis function j in the expansion of orbital φ_A; n_j is the principal quantum number of the basis function j (it is kept fixed); r_i are the gridpoints where the numerical wave function is evaluated. As in the preceding work, we used $w(r) = 1.0$ for all orbitals, with few exceptions (applied for $r < 0.5$ a.u.): (a) for 1s orbitals of the fourth period ions $w(r) = 1.0 \times 10^{-3}$; ($b$) for 1$s$ orbitals of the fifth period atoms and ions, $w(r) = 1.0 \times 10^{-5}$; ($c$) for 2$s$ and 2p orbitals of the fifth period atoms and ions, $w(r) = 1.0 \times 10^{-3}$.

Note that the least-squares fittings produce wave functions that no longer have the same basis exponents for all the orbitals of a given l type. For example, in the energy-minimized wave functions (Clementi & Roetti, 1974; Bunge *et al.*, 1993), all the s orbitals of an atomic configuration are expanded in terms of the same m functions; thus, 1s, 2s *etc.* differ only for the c_j coefficients of the expansion. Instead, in the wave functions based on least-squares minimization of the error function (2), 1s, 2s *etc.* differ for the c_j coefficients as well as (slightly) for the ζ_j exponents of the basis functions. The principal quantum numbers n_j and the total number of basis functions m are the same for all the orbitals of a given l type and are identical to the values of the starting data set (Bunge *et al.*, 1993). However, four ions required a change in one of the basis functions in order to improve the fitting: (*a*) O^- and F^-: for the outermost function of the 2*p* orbital, we set $n_j = 3$ instead of $n_j = 2$; (*b*) Co^{2+} and Co^{3+}: for the eighth function of the 1*s* orbitals, we set $n_j = 3$ instead of $n_j = 4$.

The converged wave functions are slightly unnormalized (typically by less than 0.05%). Therefore, a rescaling of the c_j's was necessary in order to have perfectly normalized functions. In Figs. 1–6, the scattering factors calculated from these wave functions are labeled 'fitted WF'.

A parameterization of the relativistic scattering factors from the numerical solution was also performed for all the ions considered, applying the method proposed by Su & Coppens (1997). For each ion, the numerical radial wave function was first converted into the corresponding electron density

$$\rho(r) = (4\pi r^2)^{-1} \sum_A N_A [P_A^2(r) + Q_A^2(r)]. \quad (3)$$

N_A is the generalized occupation of the relativistic shell A, as determined from the multiconfiguration calculation. Then, the scattering factor was computed, evaluating numerically

$$f(\sin\theta/\lambda) = \int_0^\infty 4\pi r^2 \rho(r)[\sin(4\pi r \sin\theta/\lambda)/4\pi r \sin\theta/\lambda]\,\mathrm{d}r. \quad (4)$$

Finally, a non-linear least-squares fit to the six Gaussian expansion [equation (5)] was performed:

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

The starting a_i and b_i coefficients were those refined for neutral configurations (Su & Coppens, 1997). The optimization was performed using a modified routine of the non-linear optimization program *L-BFGS-B* (Zhu *et al.*, 1994). In the range $0.0 < \sin(\theta)/\lambda < 2.0$ Å^{-1}, all ions were fitted. In the ranges 2.0–4.0 and 4.0–6.0 Å^{-1}, the parameterization was necessary only for M^+, M^{2+} and X^- of the second period, M^{3+} and M^{4+} of the third and fourth periods, M^{5+} and M^{6+} of the fourth and fifth periods. In fact, the remaining ions have high-order scattering factors not significantly different from those of the corresponding neutral configurations (Su & Coppens, 1997).

The parameters of the six Gaussian expansion are reported in Table 1, while maximum and mean deviations for each fit have been deposited as supporting material.[2] In Figs. 1–6, scattering factors computed with the six Gaussian expansion coefficients are labeled 'fitted *f*'.

3. Discussion

As is well known, relativistic effects are particularly significant as the atomic number increases.

For each atom or ion, taking as reference the scattering factor *f* obtained from (4), the function

$$\Delta f\% = [(f - f^\dagger)/f] \times 100 \quad (6)$$

[2] See deposition footnote

was evaluated with $f^\dagger$ computed from a non-relativistic wave function, from the wave function fitted with (2) and from the six Gaussian function expansion (5).

Fig. 1 shows the Δf values for Li, Si and Xe. It is clear that the atomic scattering factor of ground-state Li from a non-relativistic wave function (Clementi & Roetti, 1974) does not contain substantial errors [$\Delta f\% < 0.2$ within the range $0.0 < \sin(\theta)/\lambda < 2.0$ Å^{-1}]. The two analytical expressions of the relativistic *f* ('fitted *f*' and 'fitted WF') produce minor improvements. The effects are more significant for a third-row atom such as Si, and they eventually become very important for subsequent periods (see Xe, which is the heaviest atom considered in this work). As illustrated in Fig. 2, the scattering factors of fifth-row neutral atoms, as calculated from non-relativistic wave functions, have within the range $0.0 < \sin(\theta)/\lambda < 2.0$ Å^{-1} average errors larger than 1.0% and maximum errors up to 3.0%. The analytical expressions for the relativistic *f* differ from the numerical solution by less than 0.2%.

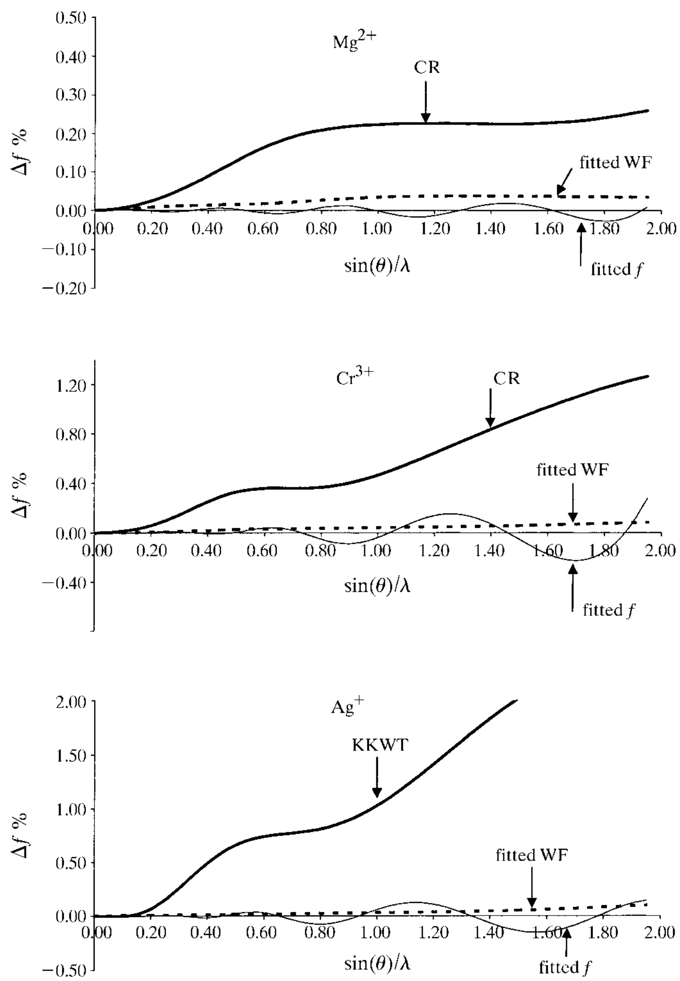

Figure 3
$\Delta f\%$ for Mg^{2+}, Cr^{3+} and Ag^+ as a function of $\sin(\theta)/\lambda$ (Å^{-1}). 'CR', 'fitted WF' and 'fitted *f*' have the same meaning as in Fig. 1; for Ag^+, the non-relativistic wave function was taken from Koga *et al.* (1999) and labelled 'KKWT'. Both analytical expressions of relativistic *f* come from this work.

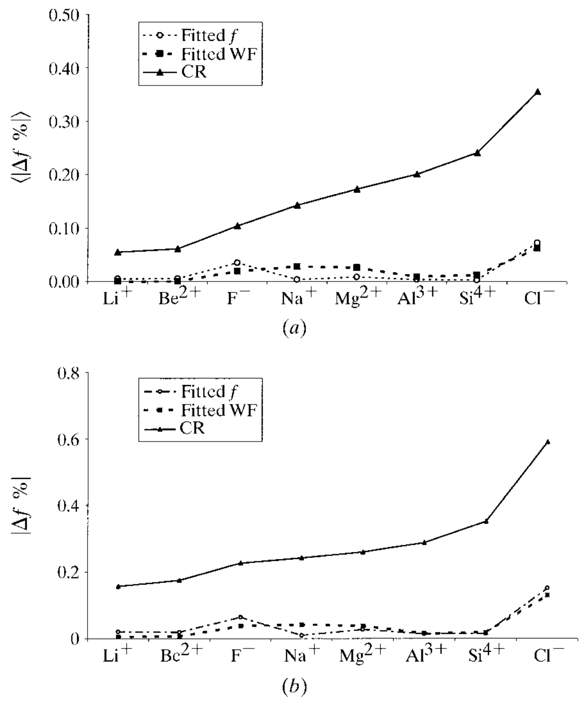

Figure 4
Average (*a*) and largest (*b*) absolute percentile differences of scattering factors for ions of the second and third rows. 'CR', 'fitted WF' and 'fitted *f*' have the same meaning as in previous figures. Both 'fitted WF' and 'fitted *f*' results come from this work.

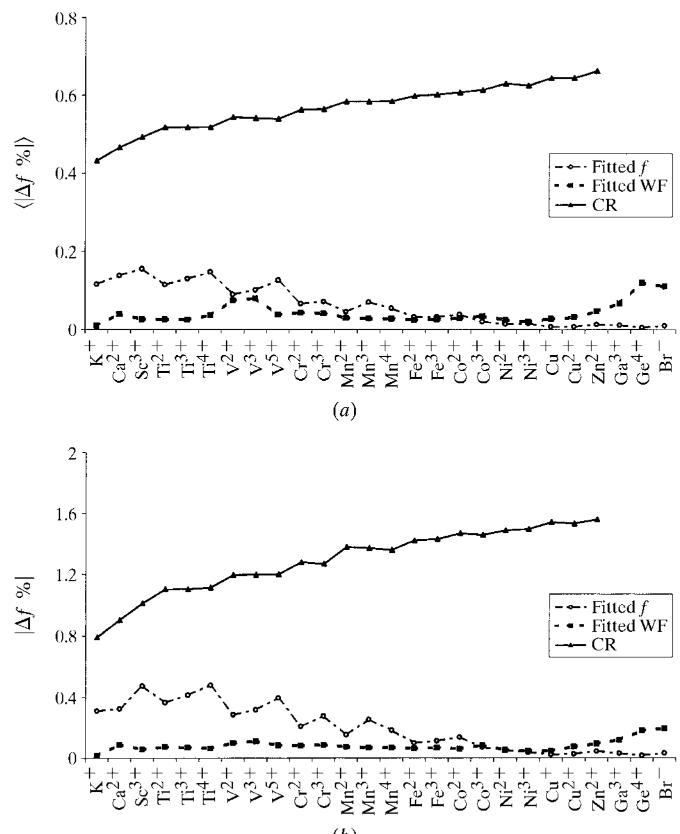

Figure 5
Average (*a*) and largest (*b*) absolute percentile differences of scattering factors for chemically relevant ions of the fourth row. Labels as in Fig. 4. (CR wave functions for Ga^{3+} and Ge^{4+} were not available in electronic format.)

Core-electron distributions are of course the most affected by relativistic effects, thus $\Delta f\%$ increases with $\sin(\theta)/\lambda$, as valence electrons contribute little to the high-order data. In the determination of an accurate electron-density distribution from X-ray intensities, the main error produced by the use of a non-relativistic wave function is therefore expected to occur in the thermal parameters. However, this in turn will affect the static density produced by the deconvolution of thermal motion from the experimental results.

Cations and anions up to $Z = 54$ show trends similar to those of neutral atoms (see Fig. 3 for plots of Mg^{2+}, Cr^{3+} and Ag^{+}). For second- and third-row ions, the largest error of the non-relativistic approach is 0.6% for Cl^{-} (Fig. 4). For fourth-row ions, the difference is quite significant (on average $|\Delta f\%| > 0.5$; largest $|\Delta f\%| > 1.2$). On the other hand, non-relativistic wave functions are not available for most of the fifth-row ions, thus a full comparison is not possible. For mono-cations, scattering factors based on the functions published by Koga *et al.* (1999) show a large difference compared with results from the relativistic approach (see Ag^{+} in Fig. 3). A test calculation for neutral Xe showed the scattering-factor curve based on the Koga wave function to be within 0.1% of the results from the Bunge wave function.

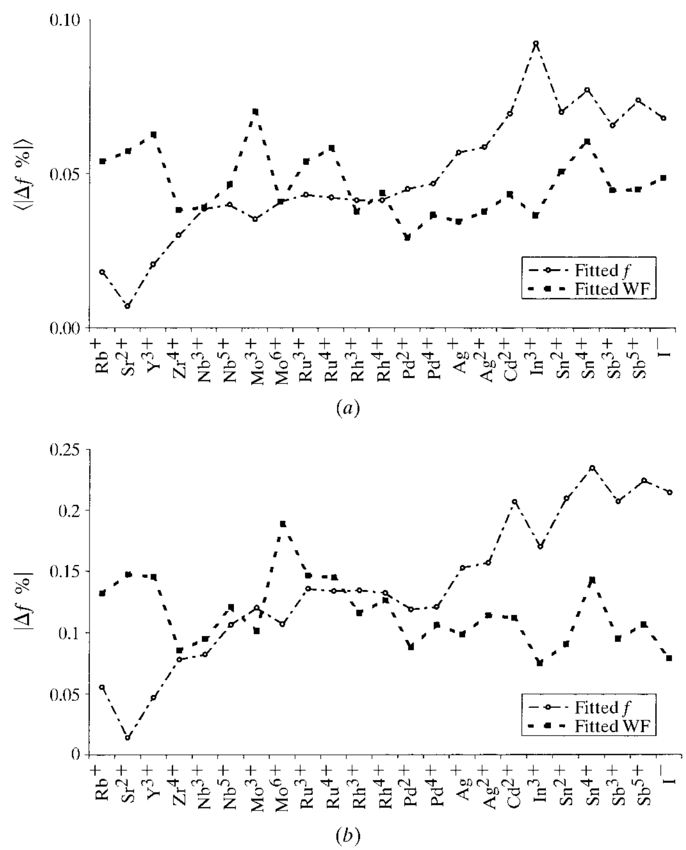

Figure 6
Average (*a*) and largest (*b*) absolute $\Delta f\%$ for chemically relevant ions of the fifth row. Only the relativistic analytical expressions are plotted as non-relativistic wave functions are not available for most of these ions. 'Fitted WF' and 'fitted *f*' have the same meaning as in the previous plots. Note that the scale here is much expanded with respect to the previous figures.

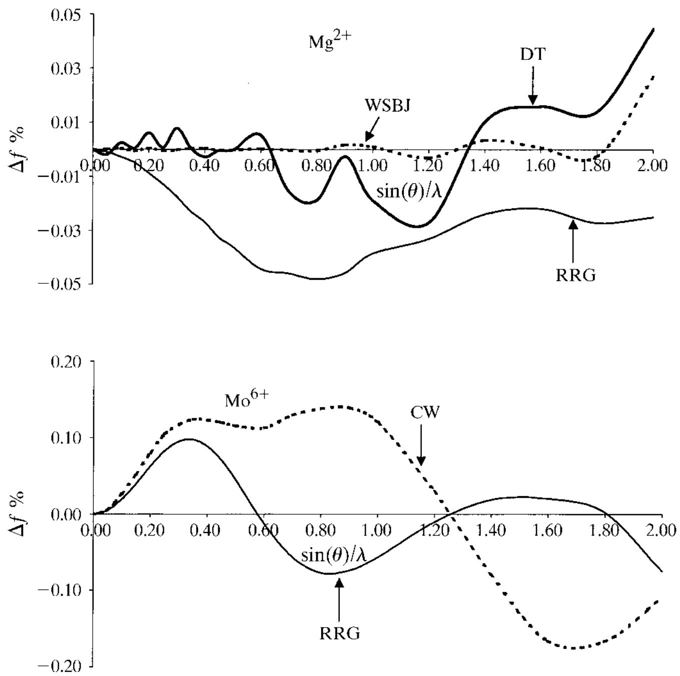

Figure 7
$\Delta f(= f^\dagger - f)$ % for Mg^{2+} and Mo^{6+} as a function of $\sin(\theta)/\lambda$ (Å^{-1}); the reference f is the relativistic scattering factor from the numerical solution evaluated in this work, $f^\dagger$ is the relativistic scattering factor tabulated in Rez *et al.* (1994), RRG, in Wang *et al.* (1996), WSBJ, in Doyle & Turner (1968), DT, and in Cromer & Waber (1968), CW.

It is of interest to compare the performances of the two kinds of analytically calculated relativistic scattering factors. The six-term Gaussian expansions ('fitted f') are usable only in spherical atom refinements. These expansions typically have somewhat larger errors, which reflects the oscillating behavior produced by the fitting (Figs. 1 and 3). They do not seem to be affected by any systematic effect along the $\sin\theta/\lambda$ axis. As judged from the percent errors, the worst agreement is found for Sc^{3+} and Ti^{4+}.

The starting point of the analytical wave-function fittings ('fitted WF') of the ions were the optimized wave functions for neutral atoms. The scattering factors calculated are very satisfactory, indicating that the fitting procedure has been quite successful (see Figs. 4–6). The error functions along $\sin(\theta)/\lambda$ show a systematic behavior, though it is quite negligible. The worst agreement is found for Mo^{6+}.

A comparison between the relativistic scattering factors reported in the literature is of interest for estimating the accuracy of these calculations. As discussed above, differences for anions are affected by the application of the method suggested by Watson (1958). For cations, the agreement between the different methods is within 0.05% for light atoms and within 0.2% for heavy atoms (see Fig. 7). It should be noticed, however, that the accuracy of calculations by Doyle & Turner (1968) and by Cromer & Waber (1968) was less than those reported here. Accordingly, our results are much closer to those of Wang *et al.* (1996) (which are however limited to atoms up to Ar) and those of Rez *et al.* (1994), which are extended to atoms beyond Xe, but do not contain all the cations.

Taking into account the average errors of the wave function fitting procedure based on (2), it is notable that the analytical expressions derived in this work reproduce the relativistic scattering factors within the range of 'uncertainty'. The use of these wave functions in electron-density analysis from experimental X-ray models will give more accurate results, especially when dealing with heavy atoms for which differences with non-relativistic treatments become more substantial.

The results of this work have been deposited as supporting material and are available at http://harker.chem.buffalo.edu.

Support of this work by the National Science Foundation (CHE9981864) is gratefully acknowledged.

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