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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 Slatertype 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].

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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 Slatertype 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 = 54and 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 higherorder 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



Figure 1

 $\Delta f \%$ 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).

400). The radial density of a given shell A can be easily computed as

$$R_A(r) = [P_A^2(r) + Q_A^2(r)].$$
 (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 nonrelativistic 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 nonrelativistic 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:

$$\chi^{2} = \sum_{i=1}^{npts} w(r_{i}) \left(R(r_{i}) - r_{i}^{2} \left\{ \sum_{j=1}^{m} [(2n_{j})!]^{-1/2} (2\zeta_{j})^{n_{j}+1/2} c_{j} r_{i}^{n_{j}-1} \right. \\ \left. \times \exp(-\zeta_{j} r_{i}) \right\} \right)^{2}.$$
(2)



Figure 2

Average (a) and largest (b) absolute $\Delta f \%$ 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 \AA^{-1} range).

$\begin{array}{c c c c c c c c c c c c c c c c c c c $	Atom	$egin{array}{c} a_1 \ b_1 \end{array}$	$egin{array}{c} a_2 \ b_2 \end{array}$	a_3 b_3	$egin{array}{c} a_4 \ b_4 \end{array}$	a_5 b_5	a_6 b_6
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	т.:+	0 70375	0.54736	0.46161	0 13018	0.05800	0.00010
$\begin{split} Ba^{1} & 0.22377 & 0.7397 & 0.22857 & 0.20135 & 0.00084 & 0.0007 \\ & 2.04212 & 0.86257 & 0.02186 & 0.66084 & 0.0018 \\ & 2.04302 & 1.64286 & 0.66080 & 0.67022 & 0.51650 & 0.54850 \\ & 0.53818 & 2.14850 & 0.1597 & 0.21862 & 0.1015 & 573087 \\ & 0.53987 & 1.17889 & 0.15013 & 0.97886 & 0.10015 & 573087 \\ & 0.23284 & 2.4411 & 0.5979 & 0.28490 & 0.11335 & 0.0008 \\ & 0.23284 & 2.4411 & 0.5979 & 0.28490 & 0.11335 & 0.0008 \\ & 0.23284 & 2.4411 & 0.5979 & 0.28490 & 0.11335 & 0.0008 \\ & 0.23284 & 0.44133 & 0.07267 & 0.12393 & 0.04149 & 0.65431 & 0.9008 \\ & 0.24418 & 0.24819 & 0.12797 & 1.53548 & 0.00470 & 0.0000 \\ & 0.24418 & 0.28192 & 0.12797 & 1.53548 & 0.00470 & 0.0000 \\ & 0.411 & 0.3377 & 0.12279 & 0.54334 & 0.14648 & 3.52838 \\ & 0.40187 & 0.10183 & 0.8699 & 0.35456 & 0.119770 \\ & 0.24818 & 0.3890 & 0.31640 & 0.52437 & 0.2000 \\ & 0.24818 & 0.3890 & 0.31640 & 0.52437 & 0.2000 \\ & 0.24818 & 0.3890 & 0.31640 & 0.32456 & 0.119770 \\ & 0.24818 & 0.3890 & 0.31640 & 0.32476 & 0.0000 \\ & 0.24818 & 0.3890 & 0.31640 & 0.32476 & 0.00758 \\ & 0.24818 & 0.3890 & 0.31640 & 0.32476 & 0.0000 \\ & 0.77 & 0.1993 & 0.5137 & 0.2537 & 0.52356 \\ & 0.24818 & 0.3890 & 0.31640 & 0.32476 & 0.0000 \\ & 0.0000 & 0.309476 & 0.00000 & 0.224420 & 0.909000 & 0.20000 \\ & 0.0000 & 0.309476 & 0.90000 & 0.00000 \\ & 0.0000 & 0.309476 & 0.90000 & 0.20000 \\ & 0.0000 & 0.309476 & 0.90000 & 0.20000 \\ & 0.0000 & 0.00000 & 0.309476 & 0.90000 & 0.00000 \\ & 0.0000 & 0.00000 & 0.309476 & 0.90000 & 0.00000 \\ & 0.0000 & 0.00000 & 0.309476 & 0.90000 & 0.00000 \\ & 0.0000 & 0.00000 & 0.309476 & 0.90000 & 0.20000 \\ & 0.0000 & 0.309476 & 0.90000 & 0.20000 \\ & 0.0000 & 0.309476 & 0.90000 & 0.20000 \\ & 0.0000 & 0.00000 & 0.309476 & 0.90000 & 0.20000 \\ & 0.0000 & 0.00000 & 0.309476 & 0.90000 & 0.00000 \\ & 0.0000 & 0.00000 & 0.309476 & 0.90000 & 0.00000 \\ & 0.0000 & 0.00000 & 0.309476 & 0.90000 & 0.00000 \\ & 0.0000 & 0.00000 & 0.309476 & 0.90000 & 0.00000 \\ & 0.0000 & 0.00000 & 0.204429 & 0.00000 & 0.20498 & 0.00000 \\ & 0.0000 & 0.00000 & 0.204429 & 0.00000 & 0.20498 & 0.0000$	LI	0.79575	1 16905	6 18250	0.13918	12 60983	28 15027
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	Be^{2+}	0.82577	0.73691	0.23557	0.20135	0.00034	0.00010
Cau 2.0902 1.04289 0.08000 0.07022 0.1509 0.45489 O" 3.65678 2.10950 1.52760 1.07980 0.01096 0.0000 F 3.20971 2.11192 1.02787 1.08853 0.01096 0.09868 F 3.20971 2.01192 1.02787 1.08853 0.02313 0.00978 Ma" 3.0483 7.0779 0.12279 15.35341 1.48641 35.2685 Ma" 4.0045 1.85304 0.10093 8.78523 35.8712 12.5005 At 1.93498 3.33770 2.28765 1.08840 0.0013 0.00013 St ₄ 3.49889 3.33770 2.28765 1.08944 1.01197 0.00013	Бе	2.04212	0.80252	4.60157	0.21162	43 68258	103 45510
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	Cural	2.03492	1.64286	0.68060	0.67022	0.51650	0.45488
O ⁻ 3.5578 2.14950 1.2790 1.2790 0.0000 H 10561 5.6491 0.23201 4.68862 0.00980 10.9888 F ⁻ 3.2064 2.47111 1.5959 1.28400 11.1135 0.9018 Na* 3.64293 3.94459 1.6333 0.04194 0.62131 0.0008 Mg ² 4.20945 1.85304 0.10693 8.78523 558712 0.25000 A ¹ 4.10967 3.00032 1.71590 1.08884 0.00171 0.0000 3.7734 1.5867 0.00158 0.99679 45.26456 1.137270 Sta 2.64002 7.46289 1.09847 0.04491 80.52377 50.2705 Sta 2.39802 3.54575 1.27888 0.99679 42.15456 0.19979 CT 7.13932 0.54113 2.23901 61.04550 0.06010 0.00010 0.00010 CT 7.13932 0.54113 2.23901 61.04550 0.00010 0.00010	Cval	25.99675	11.77809	0.51013	0.97866	0.16915	57.91874
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	0-	3.56378	2.14950	1.52760	1.47980	0.27065	0.00010
F ⁻ 3.2264i 2.47111 1.98939 1.23490 1.1353 0.03082 Na" 3.0352 3.24483 70177 0.12272 1.54534 1.44604 52.6833 Ma" 4.03053 2.24835 70177 0.12270 1.54534 1.44604 52.6833 Ma" 4.03055 2.53390 1.71397 1.29284 0.00167 0.00101 3.37314 1.58647 0.09188 6.99679 45.54546 0.19970 3.64012 3.74628 1.10647 0.06419 80.25375 55.2756 Stat 2.266612 3.734628 1.106471 0.13897 2.18252 0.0979 C1 2.36663 7.37473 0.00010 5.01644 5.21875 7.7583 C1 2.70467 0.77473 0.00010 3.03484 0.00010 0.00017 C2 ⁷⁴ 8.66633 7.39747 1.322160 0.35476 1.9999980 2.58524 C2 ⁷⁴ 8.66633 7.39747 1.322160 0.00010 <td></td> <td>14.10561</td> <td>5.60491</td> <td>0.32801</td> <td>46.88862</td> <td>0.00980</td> <td>10.98084</td>		14.10561	5.60491	0.32801	46.88862	0.00980	10.98084
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	F^{-}	3.22684	2.47111	1.59839	1.28490	1.11335	0.30182
Na* 3.06/32 3.04/93 1.06/33 0.06/149 0.02/151 0.02/151 Mg* 3.24/183 7.07/79 0.12279 1.53/534 1.46/64 5.52/683 Al* 4.00/045 8.53/530 0.17/1377 1.39/386 0.00/07 0.00/07 Al* 4.19/367 3.00/02 1.71/577 1.08/840 6.59/979 4.52/456 1.13/727 Stat 2.37/143 1.55/57 1.27/867 0.06/39 0.00/31 0.00/01 St* 3.93/32 5.5/57 1.27/868 0.07/910 0.00/33 0.00/01 Cl 7.13/92 6.5/2/37 7.40/75 0.22/84 0.00/00 0.00/01 Cl 7.13/92 6.5/2/37 0.00/01 0.00/01 0.00/01 0.00/01 0.00/01 Cl 7.13/92 7.4/2/3 0.00/01 0.00/01 0.00/01 0.00/01 Cl 2.2/7/6 6.66/83 0.3/77 0.10/83 0.3/82 0.00/83 0.00/93 Cl 2.0/777 <td></td> <td>4.95997</td> <td>14.45952</td> <td>0.17267</td> <td>11.39653</td> <td>43.30817</td> <td>0.96703</td>		4.95997	14.45952	0.17267	11.39653	43.30817	0.96703
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	Na ⁺	3.69529	3.30459	1.68333	0.69149	0.62431	0.00088
Mg ¹ 4.30385 2.58300 1.71397 1.9368 0.00470 0.00010 Al ¹⁺ 4.102457 3.30032 1.71590 1.08840 0.00167 0.000167 Stagi 3.57134 1.556577 0.09158 6.599677 4.52445 1.13370 Stagi 3.649488 3.33770 2.28755 1.59964 9.17386 0.00011 Staft 2.06468 3.34770 2.28755 1.59964 9.03373 S52705 Cl ² 2.06468 1.59488 0.05869 591644 60.23176 77.7529 Cl ² 8.03777 1.33825 0.05864 0.06867 2.03284 0.00010 Cl ² 1.60355 0.6336 0.03010 3.03877 0.332825 0.03010 0.00010 Cl ² 0.65687 7.7737 0.030179 0.00010 0.030179 Cl ² 0.65687 0.03886 2.388714 0.00010 0.231825 0.03018 Cl ² 0.65677 0.73554 1.66777 <		3.24183	7.07179	0.12279	15.45334	1.43664	35.26383
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Mg ²⁺	4.30385	2.58390	1.71397	1.39368	0.00470	0.00010
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	-	4.02045	1.85304	0.10693	8.78523	58.58712	125.50050
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Al ³⁺	4.19367	3.00032	1.71590	1.08840	0.00167	0.00010
S_{iat} 5.4986 5.3376 2.38765 1.59864 1.17866 0.00011 Si ¹⁺ 3.08392 3.33675 1.72848 0.07103 0.00013 0.00013 Cl ⁻ 7.13932 6.34213 2.29891 1.97826 0.22854 0.09875 Cl ⁻ 7.13932 6.34213 2.29891 0.197826 0.22854 0.09975 K ⁺ 8.09376 7.39747 1.42210 1.18991 0.00010 0.00010 C ² 8.69683 7.39747 1.32825 0.00010 0.00010 0.00010 0.00010 S ¹ 9.03957 7.36477 1.32160 0.00010 0.00010 0.00010 S ¹ 9.04664 0.55771 0.00010 2.998133 137.40030 5.36981 T ¹ 9.67667 7.53520 1.26997 0.81466 0.00010 0.00010 T ¹ 9.5676 7.35320 1.26997 0.81465 0.00010 0.00010 T ¹ 9.459747 0.35386 0.00		3.37134	1.58637	0.09158	6.99679	45.26456	113.97270
$\begin{array}{cccccc} 2 & 20902 & 37.46289 & 1.09647 & 0.06439 & 80.2237 & 56.27056 \\ & 2.94048 & 1.39488 & 0.08089 & 5.91604 & 56.23176 & 77.7658 \\ & 1.18073 & 1.922901 & 61.04859 & 0.00857 & 2.318225 & 0.00759 \\ & 1.270476 & 0.77473 & 0.0010 & 32.44270 & 19.99900 & 82.9829 \\ & 2.274 & 8.6683 & 7.97477 & 0.02010 & 32.44270 & 19.99900 & 82.9829 \\ & 2.62^{2*} & 8.6683 & 7.97477 & 0.02176 & 2.03182 & 0.00010 & 0.00011 \\ & 24^{2*} & 8.6683 & 7.97477 & 0.02176 & 2.03183 & 17.00010 & 0.00011 \\ & 24^{2*} & 9.67697 & 7.35574 & 1.66775 & 1.29843 & 0.00010 & 0.00011 \\ & 54^{3*} & 9.67697 & 7.35574 & 1.66775 & 1.29843 & 0.00010 & 0.00011 \\ & 7.9285 & 0.51988 & 0.38977 & 0.02176 & 0.02179 & 0.00010 & 0.00010 \\ & 7.9285 & 0.51988 & 2.38821 & 0.00010 & 0.20199 \\ & 7.42634 & 0.48955 & 0.05010 & 2.38931 & 0.20010 & 0.00010 \\ & 7^{4*} & 9.56376 & 7.3512 & 2.3561 & 1.23867 & 0.00010 & 0.00010 \\ & 7^{4*} & 9.22395 & 7.35117 & 1.23367 & 0.13935 & 0.00010 & 0.00010 \\ & 7^{4*} & 0.00572 & 7.3517 & 2.23561 & 1.23887 & 0.01533 & 0.00010 \\ & 7^{4*} & 0.00572 & 7.34875 & 0.00010 & 2.21700 & 0.50091 \\ & 7^{4*} & 0.0573 & 7.34875 & 0.00010 & 2.21700 & 0.50091 \\ & 7^{4*} & 0.0573 & 7.34875 & 0.00010 & 2.23881 & 0.00010 & 0.00010 \\ & 7^{4*} & 0.05723 & 7.34875 & 1.38759 & 1.20752 & 0.00010 & 0.00010 \\ & 7^{4*} & 0.05723 & 7.34875 & 1.38759 & 1.20752 & 0.00010 & 0.00010 \\ & 7^{4*} & 0.05723 & 7.34875 & 1.38759 & 1.20752 & 0.00010 & 0.00010 \\ & 7^{4*} & 0.3480 & 0.39867 & 0.33866 & 16.91988 & 0.00010 & 0.59840 \\ & 7^{4*} & 0.3459 & 7.36389 & 1.11621 & 0.14450 & 0.00010 & 0.59840 \\ & 7^{4*} & 0.3459 & 7.3587 & 1.38759 & 1.20752 & 0.00010 & 0.00010 \\ & 7^{4*} & 0.3480 & 0.3587 & 1.34875 & 2.87024 & 1.17229 & 0.06733 \\ & 7^{4*} & 0.34597 & 7.35874 & 1.45178 & 0.00010 & 0.00010 \\ & 7^{4*} & 1.04597 & 7.35874 & 1.45178 & 0.00010 & 0.59880 \\ & 0.13997 & 7.3789 & 1.34688 & 0.00010 & 0.00059 & 0.00359 \\ & 7^{5*} & 1.2031 & 0.33181 & 12.46389 & 0.00010 & 0.520860 & 3.939933 \\ & 7.5204 & 0.37840 & 0.35891 & 1.39285 & 0.00010 & 3.52086 & 3.000010 \\ & 7^{4*} & 1.$	Si _{val}	5.49488	3.33770	2.38765	1.59864	1.17986	0.00010
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		2.60802	37.46289	1.09647	0.06439	80.52337	56.27056
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	Si ⁴⁺	3.98392	3.53675	1.72808	0.75103	0.00013	0.00010
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		2.94648	1.39488	0.08069	5.91604	56.23176	79.76580
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Cl ⁻	7.13932	6.34213	2.29801	1.97826	0.22854	0.00983
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		1.18073	19.52901	61.04850	0.08057	23.18225	0.09759
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	K^+	8.00372	7.44077	1.42217	1.13491	0.00010	0.00010
$\begin{array}{c} Ca^2 & 8.6603 & 7.39747 & 1.38325 & 0.55348 & 0.00010 & 0.0001 \\ & 10.62955 & 0.66306 & 0.00010 & 30.98476 & 199.99808 & 8.237898 \\ Sc^4 & 9.01395 & 7.36477 & 1.32160 & 0.30179 & 0.00010 & 0.0001 \\ & 7.02258 & 0.50388 & 23.88214 & 0.00010 & 0.210388 & 14.558810 \\ & 7.2258 & 0.50388 & 23.88214 & 0.00010 & 0.210388 & 14.558810 \\ & 7.7272 & 0.40604 & 0.00010 & 22.37931 & 02.10560 & 14.558920 \\ & 7.74454 & 0.48595 & 0.00010 & 22.37931 & 02.10560 & 14.559920 \\ & 7.4454 & 0.48595 & 0.00010 & 28.20512 & 02.10930 & 14.559910 \\ & 7.4454 & 0.48595 & 0.00010 & 28.20512 & 0.00010 & 0.00010 \\ & 0.00010 & 7.35015 & 2.25541 & 1.23887 & 0.01533 & 0.00010 \\ & 6.00615 & 0.44224 & 2.014575 & 0.00010 & 120.21700 & 55.09812 \\ & 6.55290 & 0.43599 & 18.25122 & 0.00010 & 120.2159 & 55.11062 \\ & 6.55290 & 0.43599 & 18.25122 & 0.00010 & 120.2159 & 55.11062 \\ & 6.55290 & 0.43599 & 1.1621 & 0.14450 & 0.00010 & 0.00010 \\ & 6.0515 & 0.41588 & 0.00010 & 25.36044 & 199.99870 & 8.297847 \\ & 6.16125 & 0.41568 & 0.00010 & 25.36044 & 19.999870 & 8.297847 \\ & Cr^2 & 10.54130 & 4.41457 & 2.93456 & 2.87024 & 1.17229 & 0.06743 \\ & 6.64000 & 0.38967 & 0.38966 & 16.94938 & 0.00010 & 5.998400 \\ & Cr^4 & 10.45597 & 4.43683 & 2.29205 & 2.06149 & 1.11981 & 0.00120 \\ & 5.90641 & 0.38967 & 3.29866 & 16.94938 & 0.00010 & 5.968271 \\ & Ma^2 & 1.036580 & 7.35401 & 3.49267 & 1.09987 & 0.18537 & 0.00248 \\ & Ma^4 & 1.04597 & 4.3683 & 0.37041 & 15.34221 & 0.00010 & 5.968271 \\ & Ma^4 & 1.04597 & 7.37819 & 1.80548 & 1.00048 & 0.00010 & 0.90010 \\ & 5.9064 & 0.33896 & 0.31818 & 0.018560 & 0.00039 \\ & 6^2^4 & 1.13254 & 7.37819 & 1.80548 & 1.000418 & 0.00010 & 0.00010 \\ & 5.52604 & 9.37318 & 10.34578 & 0.00010 & 10.014660 & 3.86078 \\ & Fe^5 & 11.32594 & 7.3761 & 4.5131 & 0.95818 & 0.31843 & 0.00010 \\ & 6.7599 & 9.332058 & 0.94641 & 0.04263 & 0.00010 \\ & 6.7599 & 9.34593 & 0.31784 & 4.32027 & 2.5552 & 1.47560 & 0.03560 \\ & 7.37486 & 0.24588 & 9.52524 & 0.00100 & 3.53698 & 0.00140 & 0.00032 \\ & 7.5329 & 01619 & 9.25530 & 0.03019 & 0.05592 & 0.57552 & 0.4719 & 0.003$		12.70476	0.77473	0.00010	32.44270	199.99900	82.98298
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Ca ²⁺	8.66803	7.39747	1.38325	0.55348	0.00010	0.00010
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		10.62955	0.66306	0.00010	30.98476	199.99880	82.97898
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	Sc^{3+}	9.01395	7.36477	1.32160	0.30179	0.00010	0.00010
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		8.86658	0.56771	0.00010	29.98133	137.40030	53.69811
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Ti ²⁺	9.67607	7.35874	1.66775	1.29681	0.00010	0.00010
$\begin{array}{rrrr} \begin{tabular}{l l l l l l l l l l l l l l l l l l l $		7.92858	0.50388	23.88214	0.00010	92.10388	145.58810
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Ti ³⁺	9.56376	7.35320	1.26997	0.81496	0.00010	0.00010
$\begin{array}{cccccccccccccccccccccccccccccccccccc$.4.	7.72729	0.49604	0.00010	22.37931	92.10560	145.58920
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Ti ⁴⁺	9.22395	7.35117	1.23367	0.19305	0.00010	0.00010
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	2 -	7.44634	0.48595	0.00010	28.20512	92.10930	145.59010
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	V^{2+}	10.14209	7.35015	2.25361	1.23887	0.01533	0.00010
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	2 -	6.90615	0.44224	20.14575	0.00010	120.21700	55.09812
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	V^{3+}	10.05723	7.34875	1.38759	1.20752	0.00010	0.00010
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	* *5+	6.75290	0.43509	18.25122	0.00010	120.22150	55.11062
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	V^{3+}	9.37695	7.36389	1.11621	0.14450	0.00010	0.00010
$\begin{array}{c} {\rm Cr}^{-} & 10.54130 & 4.41457 & 2.93436 & 2.87024 & 1.17229 & 0.00743 \\ & 6.04009 & 0.38967 & 0.38966 & 16.94938 & 0.00010 & 59.98400 \\ {\rm Cr}^3 + & 10.45597 & 4.33683 & 2.92505 & 2.06149 & 1.11981 & 0.0120 \\ & 5.90641 & 0.38863 & 0.37041 & 15.34221 & 0.00010 & 59.68201 \\ {\rm Mn}^{3^2} & 10.86580 & 7.35401 & 3.49267 & 1.09987 & 0.18537 & 0.00249 \\ & 5.30450 & 0.34487 & 14.15718 & 0.00010 & 38.60730 & 100.13560 \\ {\rm Mn}^{3^4} & 11.04414 & 4.43611 & 4.06737 & 2.44502 & 0.00559 & 0.00189 \\ & 5.32462 & 0.15971 & 0.47488 & 13.90108 & 100.14020 & 38.59723 \\ {\rm Mr}^{4^4} & 10.80739 & 7.37819 & 1.80548 & 1.00948 & 0.00010 & 0.00010 \\ & 5.12031 & 0.33181 & 12.46589 & 0.00010 & 100.14660 & 38.60128 \\ {\rm 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 \\ {\rm 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 \\ {\rm Co}^{2^+} & 11.8338 & 5.16446 & 4.59215 & 3.72826 & 0.67719 & 0.00010 \\ & 4.13155 & 0.27012 & 10.32693 & 0.00010 & 35.20369 & 93.95908 \\ {\rm Ni}^{2^+} & 11.83838 & 5.16446 & 4.59215 & 3.72826 & 0.67719 & 0.00010 \\ & 3.7640 & 9.57707 & 0.31557 & 0.11646 & 25.17286 & 96.77010 \\ {\rm Ni}^{3^+} & 12.08932 & 7.37051 & 4.53328 & 0.89389 & 0.11440 & 0.00010 \\ & 3.7640 & 9.57707 & 0.31557 & 0.11646 & 25.17286 & 96.77103 \\ {\rm Ni}^{3^+} & 12.08932 & 7.37051 & 4.53328 & 0.89389 & 0.11440 & 0.00010 \\ {\rm Cu}^{*} & 11.74994 & 6.77249 & 6.21229 & 1.75552 & 1.47560 & 0.03461 \\ {\rm Cu}^{*} & 11.74994 & 6.77249 & 6.21229 & 1.75552 & 1.47560 & 0.03461 \\ {\rm Cu}^{*} & 11.42499 & 7.88148 & 4.9190 & 2.05602 & 0.05750 & 0.000010 \\ {\rm A}52509 & 0.16619 & 9.20541 & 1.71372 & 24.20427 & 82.21923 \\ {\rm Ga}^{3^+} & 12.08093 & 7.89470 & 5.30620 & 3.91156 & 0.06803 & 0.00010 \\ {\rm A}548 & 0.0515 & 9.934955 & 0.00010 \\ {\rm A}548 & 0.0515 & 9.31568 & 34.76155 & 9.93495 \\ {\rm A}67800 & 0.15468 & 2.08510 & 9.11568 & 34.76155 & 9.934957 \\ {\rm A}1849 & 0.05161 & 9.11568 & 34.76155$	G ²⁺	6.31625	0.41568	0.00010	25.36044	199.99870	82.97847
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Cr	10.54130	4.41457	2.93436	2.8/024	1.17229	0.06/43
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C 3+	6.04009	0.38967	0.38966	16.94938	0.00010	59.98400
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	Cr ³⁺	10.45597	4.43085	2.92505	2.06149	1.11981	0.00120
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	N 4 - 2+	5.90641	0.38803	0.37041	15.34221	0.00010	59.082/1
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	MIN	5 30450	0.34487	3.49207	0.00010	28 60720	100 12560
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	Mn ³⁺	11 04414	4 43611	4.06737	2 44502	0.00559	0.00180
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		5 32462	0.15071	4.00737	13 00108	100 14020	38 50723
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	Mn ⁴⁺	10 80730	7 37810	1 80548	1 00048	0.00010	0.00010
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	14111	5 12031	0.33181	12 46589	0.00010	100 14660	38 60185
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Fe ²⁺	11 32394	7 35828	4 08542	1 03934	0 19438	0.00103
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	1.6	4 71611	0.30793	12 87900	0.00024	43 73118	103 91920
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Fe ³⁺	11 27641	7 37595	3 32058	0.98461	0.04263	0.00010
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		4 63894	0.30169	11 63908	0.00010	44 10289	103 92070
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Co^{2+}	11 59539	7 37601	4 75131	0.95818	0 31843	0.00010
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0	4 18474	0.27510	11 19206	0.00010	36 27509	93 95933
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Co^{3+}	11.58135	7.38964	4.01201	0.91419	0.10353	0.00010
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	00	4.13155	0.27012	10.32693	0.00010	35.20369	93.95908
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Ni ²⁺	11.83838	5.16446	4.59215	3.72826	0.67719	0.00010
$\begin{array}{c c c c c c c c c c c c c c c c c c c $. 11	3,76040	9.57707	0.31557	0.11646	25.17286	96.76703
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Ni ³⁺	12.08932	7.37051	4.53328	0.89389	0.11440	0.00010
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		3.73486	0.24588	9.52524	0.00100	36.54998	96.77110
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	Cu^+	11.74994	6.77249	6,21229	1,75552	1.47560	0.03461
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$		3.34714	0.23831	8.32820	23.58346	0.04331	98.01738
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	Cu ²⁺ Zn ²⁺	11.83187	5.78192	5.77531	2.46041	1.14698	0.00353
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$		3.33965	0.25530	8.03031	0.08201	19.99327	98.02090
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$		12.49609	7.88148	4.99190	2.05602	0.57505	0.00010
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$		3.52509	0.16619	9.20541	1.71372	24.20427	82.21923
3.67800 0.15468 2.08510 9.11568 34.76155 99.34953	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

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Table 1 (continued)

	a_1	a_2	<i>a</i> ₃	a_4	<i>a</i> ₅	a_6
Atom	b_1	b_2	b_3	b_4	b_5	b_6
Ge ⁴⁺	8 64238	8 44015	7 88210	2 00085	0.03500	0.00010
Ge	3 75852	2 14505	0.14366	2.55505	30.03576	72 31440
Br ⁻	14 72800	7 73340	4.08153	3 80020	2 84005	2.31449
DI	1 97791	0.11285	4.08155	3.65207	21.50646	2.70412
Dh+	1.07/01	0.11265	23.43030	4.22220	0 10456	06.30430
KU	1/./2/30	7.70840	0.22707	4.25520	0.10430	0.00010
c2+	1.08258	0.09962	13.34/13	25.64859	1.47524	199.99860
Sr ⁻	13.56253	9.15282	7.57461	4.23621	1.4/524	0.00010
x z ³⁺	1.52639	13.37893	0.09009	1.50827	28.97999	162.86130
Y	17.83594	10.00061	7.34299	0.76995	0.05161	0.00010
- 4+	1.37290	11.94201	0.07979	27.59179	0.08311	137.72530
Zr	17.88797	10.57832	7.18/25	0.34750	0.00010	0.00010
. 2.	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
14	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
i u	0.69220	7 50980	0.00010	10 35021	0.62452	60.83056
Λa^+	10 20333	16 76786	5 18410	4 60146	0.05135	0.00010
Ag	0.64534	7 54710	0.00010	23 16034	100 32570	2 35114
Λa^{2+}	10 26038	16 76118	5 17728	3 80102	0.00010	0.00010
Ag	0.64383	7 44215	0.00010	21 24567	100 31/30	2 43002
$C d^{2+}$	0.04365	17.91622	5.07556	21.24307	0.00010	2.43992
Ca	19.24328	7.02822	0.00010	2.80228	0.00010	21.99594
T., 3+	0.39348	10.03622	5.11556	20.12258	87.00355	51.00304
In	19.15099	19.02664	5.11556	1./2840	1.00259	0.00010
- 21	0.55860	6.79490	0.00370	25.60539	8.23095	93.69624
Sn	19.14517	19.11002	4.80/20	4.48861	0.25075	0.20103
4.	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
5	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 1*s* 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 2*p* 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, 1*s*, 2*s 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), 1*s*, 2*s 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) Co²⁺ and Co³⁺: 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

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

$$f(\sin\theta/\lambda) = \int_{i=1}^{6} a_i \exp[-b_i(\sin\theta/\lambda)^2].$$
 (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 $0.0 < \sin(\theta)/\lambda < 2.0 \text{ Å}^{-1}$, 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 highorder 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

$$\Delta f\% = [(f - f^{\dagger})/f] \times 100$$
 (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 nonrelativistic wave function (Clementi & Roetti, 1974) does not contain substantial errors [$\Delta f \% < 0.2$ within the range $0.0 < \sin(\theta)/\lambda < 2.0 \text{ Å}^{-1}$]. 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 $0.0 < \sin(\theta)/\lambda < 2.0 \text{ Å}^{-1}$ 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%.





 $\Delta f\%$ for Mg²⁺, Cr³⁺ 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.



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 Mg²⁺, Cr³⁺ and Ag⁺). For second- and third-row ions, the largest error of the non-relativistic approach is 0.6% for Cl⁻ (Fig. 4). For fourthrow ions, the difference is quite significant (on average $|\Delta f \%| > 0.5$; largest $|\Delta f \%| > 1.2$). On the other hand, nonrelativistic 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 Mg²⁺ and Mo⁶⁺ as a function of sin(θ)/ λ (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 θ/λ axis. As judged from the percent errors, the worst agreement is found for Sc³⁺ and Ti⁴⁺.

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.

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