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Nonlinear Least-Squares Fitting of Numerical Relativistic Atomic Wave Functions by a Linear Combination of Slater-Type Functions for Atoms with $Z = 1$–36

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Abstract

New relativistic atomic ground-state wave functions calculated by using the Dirac–Fock program package *GRASP*92 [Parpia *et al.* (1996). *Comput. Phys. Commun*. **94**, 249–271; Su & Coppens (1997). *Acta Cryst.* A**53**, 749–762, (1998). *Acta Cryst.* A**54**, 357] for atoms H through Kr ($Z = 1$–36) have been fitted by a linear combination of Slater-type functions using a nonlinear least-squares procedure. These analytical expressions allow derivation of closed-form expressions for the X-ray scattering factors of the core and valence electrons and for the atomic densities and electrostatic properties of the pseudoatoms, the latter being required for the evaluation of physical properties from accurate X-ray diffraction data. All results are accessible *via* http://wings.buffalo.edu/~chem9982.

1. Introduction

We have recently calculated numerical relativistic atomic wave functions for the ground-state neutral atoms with $Z = 1$–54 (H through Xe) using the Dirac–Fock program *GRASP*92 (Parpia *et al.*, 1996; Su & Coppens, 1997). For X-ray charge-density refinements and the evaluation of the electrostatic and topological properties of the charge density, it is more convenient to parametrize the atomic radial wave functions so that the X-ray scattering factors and the expectation values of the atomic inner and outer moments as well as the total charge densities can be expressed analytically. Analytical expressions for atomic wave functions by Clementi & Roetti (1974) have been used extensively in theoretical calculations and charge-density analysis. More recent values are due to Bunge *et al.* (1993).

In this paper, we use the *L-BFGS-B* procedure (Zhu *et al.*, 1994) to fit the relativistic numerical radial wave functions to Slater-type functions. The algorithm is specifically designed for solving large nonlinear optimization problems and has limited memory requirements. The orbital expansions are tabulated for atoms H through Kr.

2. The computational method

The radial density $R(r)$ of a relativistic orbital A is defined by

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

where the radial functions P_A and Q_A are, respectively, the major and minor components of the relativistic wave function. $R(r)$ is normalized such that

$$\int_0^\infty R(r)\,\mathrm{d}r = 1. \tag{2}$$

The program *GRASP*92 solves the Dirac–Fock equations numerically and outputs P_A and Q_A for all orbitals A at selected exponential grid points, the number of which is typically less than 400.

We minimize

$$\chi^2 = \sum_{i=1}^{npts} w(r_i)\left(R(r_i) - r_i^2\left\{\sum_{j=1}^{m}[(2n_j)!]^{-1/2}(2\zeta_j)^{n_j+1/2} \times c_j r_j^{n_j-1}\exp(-\zeta_j r_j)\right\}\right)^2, \tag{3}$$

where $w(r)$ is a weighting function, n_j the principal quantum number of the basis function j and c_j and z_j are adjustable parameters. The weighting function $w(r)$ is taken as unity for all orbitals of the atoms except for the 1*s* orbitals of the atoms of the third and fourth periods (K through Kr).

For the 1*s* orbitals of these atoms, we have found it necessary to use the following weighting functions in order to get satisfactory convergence:

$$w(r) = \begin{cases} 0.001 & r \le 0.5\ \text{a.u.} \\ 1 & r > 0.5\ \text{a.u.} \end{cases} \tag{4a}$$

for third-period atoms, and

$$w(r) = \begin{cases} 0.00001 & r \le 0.5\ \text{a.u.} \\ 1 & r > 0.5\ \text{a.u.} \end{cases} \tag{4b}$$

for fourth-period atoms. The values of m, which define the size of the basis sets, are the same as in the non-relativistic Roothaan–Hartree–Fock atomic wave functions of Bunge *et al.* (1993).

It should be pointed out that in relativistic atomic structure theory the subshells nl with $l \neq 0$ are split, thus

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Table 1. *Slater-type expansions for a number of relativistic neutral atoms and χ^2 values from the fitting procedure for C, P and Fe*

(*a*) Slater-type expansions

6 C

	1*s*		2*s*	
n	*c*	ζ	*c*	ζ
1	0.363110	8.567411	−0.066035	8.493580
1	0.437999	4.888048	0.441836	4.879055
2	0.234039	6.992217	−0.087353	7.049887
2	0.005501	2.263845	−0.393509	2.263881
2	0.015065	1.475269	−0.578609	1.475239
2	−0.005056	1.164113	−0.125934	1.163509
3	−0.000015	15.468297	−0.000496	15.466018

	2*p*	
n	*c*	ζ
2	0.007068	7.047132
2	0.071982	3.224676
2	0.231920	2.182796
2	0.410597	1.439708
2	0.349870	1.023369

15 P

	1*s*		2*s*		3*s*	
n	*c*	ζ	*c*	ζ	*c*	ζ
1	0.397031	20.842263	0.049123	20.825855	0.023562	20.826392
1	0.425658	12.638955	−0.459439	12.639224	−0.149158	12.633020
2	0.209835	18.164218	0.041090	18.176774	0.019848	18.176785
2	0.007226	6.986503	0.173786	6.987225	0.068192	6.986357
2	0.004270	5.134081	0.827618	5.134590	0.122791	5.134227
2	0.001311	3.731156	0.110068	3.731743	0.271193	3.732359
3	−0.004278	39.546319	0.001415	39.540521	0.000133	39.539704
3	0.001839	2.955950	−0.006902	2.955877	−0.324658	2.957576
3	−0.005481	1.940809	0.006505	1.940738	−0.582309	1.941678
3	0.002028	1.361791	0.003038	1.361650	−0.291556	1.363710

	2*p*		3*p*	
n	*c*	ζ	*c*	ζ
2	0.001376	20.297579	0.000720	20.297400
2	0.164067	9.316383	−0.049247	9.316112
2	0.493203	5.517056	−0.087540	5.519837
2	0.393685	3.950373	−0.135964	3.951853
3	−0.006241	15.563888	0.004519	15.563314
3	−0.000611	2.282602	0.326209	2.284386
3	0.002051	1.496800	0.521881	1.495643
3	0.003802	1.052695	0.255577	1.053024

26 Fe

	1*s*		2*s*		3*s*		4*s*	
n	*c*	ζ	*c*	ζ	*c*	ζ	*c*	ζ
1	0.979867	26.733521	−0.304003	26.690155	0.117289	26.710497	0.025695	26.710310
2	−0.101240	22.735649	−0.148443	22.766754	0.070408	22.739063	0.015270	22.739408
2	0.077520	11.157480	0.998634	11.175217	−0.461960	11.158093	−0.101936	11.157920
3	0.096690	32.869671	−0.013148	32.869949	0.005098	32.859406	0.001471	32.859200
3	0.034980	8.227090	0.090178	8.226641	−0.077110	8.226805	−0.028579	8.226529
3	−0.019800	5.701970	−0.011523	5.701175	0.636882	5.706118	0.180214	5.699980
3	0.009940	3.840580	0.021227	3.839126	0.565836	3.846828	0.119361	3.843176
4	−0.062420	13.206350	0.084607	13.195103	−0.107495	13.207508	−0.022991	13.203642
4	−0.004740	2.268600	0.000314	2.267621	−0.000343	2.267640	−0.285227	2.275507
4	0.004360	1.438630	−0.002177	1.437800	0.002728	1.437820	−0.536533	1.443056
4	−0.001990	0.947530	−0.001122	0.946200	0.003742	0.946201	−0.306484	0.951968

Table 1 (*cont.*)

	2*p*		3*p*	
n	*c*	ζ	*c*	ζ
2	0.003817	42.328979	0.001274	42.292492
2	0.322259	16.140730	0.076649	16.333742
2	0.494804	8.719466	0.507928	8.722346
2	−0.020901	4.098303	−0.824261	4.096264
3	0.234972	13.386844	0.026310	13.252109
3	0.036566	3.369292	−0.401458	3.376440
3	−0.013667	2.192874	−0.041994	2.190422

	3*d*	
n	*c*	ζ
3	0.018030	12.746986
3	0.214103	6.625397
3	0.412689	4.019248
3	0.384281	2.405056
3	0.134867	1.474486

(*b*) χ^2 values

	1*s*	2*s*	3*s*	4*s*	2*p*	3*p*	3*d*
C	2.34E−07	6.74E−08	1.48E−08				
P	9.18E−10	3.65E−05	2.56E−07	1.97E−06	1.75E−08		
Fe	4.95E−12	1.67E−03	4.40E−05	1.57E−07	7.66E−05	3.12E−06	1.95E−07

Table 2. *Expectation values of* $\langle r^k \rangle$ *(k = −2, −1, 1, 2) for the orbitals of the atoms C, P and Fe*

a: values calculated from the numerical wave functions. *b*: values calculated from the converged fitting functions. *c*: values calculated from the non-relativistic wave functions of Bunge *et al.* (1993).

k		1*s*	2*s*	3*s*	4*s*	2*p*	3*p*	3*d*
Carbon								
−2	*a*	65.08845	3.59252			0.89295		
	b	65.06459	3.58926			0.89260		
	c	65.23416	3.25530			0.89207		
−1	*a*	5.64980	0.91726			0.78367		
	b	5.64959	0.91721			0.78364		
	c	5.66444	0.89680			0.78350		
1	*a*	0.27031	1.58649			1.71439		
	b	0.27031	1.58651			1.71446		
	c	0.26844	1.58934			1.71450		
2	*a*	0.09948	3.04668			3.74661		
	b	0.09946	3.04675			3.74707		
	c	0.09720	3.05206			3.74680		
Phosphorus								
−2	*a*	434.41106	35.32679	2.97370		10.35170	0.71905	
	b	432.37733	35.51897	2.95914		10.33619	0.71820	
	c	428.60626	33.05670	2.71283		10.28401	0.71576	
−1	*a*	14.61627	2.88656	0.70354		2.71160	0.57040	
	b	14.61005	2.88515	0.70342		2.71142	0.57040	
	c	14.57355	2.83171	0.69473		2.70627	0.57015	
1	*a*	0.10401	0.51385	1.92648		0.48284	2.32279	
	b	0.10400	0.51404	1.92657		0.48278	2.32274	
	c	0.10381	0.51566	1.93269		0.48340	2.32271	
2	*a*	0.01465	0.31463	4.32218		0.29124	6.39106	
	b	0.01464	0.31507	4.32261		0.29109	6.39050	
	c	0.01449	0.31592	4.34709		0.29180	6.38963	

Table 2 (*cont.*)

k		1s	2s	3s	4s	2p	3p	3d
Iron								
−2	a	1379.51881	135.47490	20.86895	1.101280	41.05179	5.80980	2.07240
	b	1364.79789	133.50997	20.56323	1.086771	40.84652	5.78087	2.07179
	c	1310.42041	123.69853	17.69893	0.914094	40.27350	5.43366	2.08596
−1	a	25.93213	5.62479	1.77547	0.39866	5.44571	1.60624	1.23172
	b	25.92596	5.61679	1.77378	0.39857	5.44332	1.60586	1.23169
	c	25.52120	5.49855	1.70991	0.39140	5.42209	1.57655	1.23692
1	a	0.058634	0.26712	0.80827	3.22238	0.23633	0.86091	1.07912
	b	0.058509	0.26731	0.80855	3.22248	0.23647	0.86091	1.07902
	c	0.059112	0.26846	0.81924	3.25849	0.23613	0.86586	1.07273
2	a	0.00464	0.08490	0.75494	12.11409	0.06889	0.87500	1.51031
	b	0.00463	0.08499	0.75598	12.11433	0.06911	0.87496	1.50974
	c	0.00469	0.08498	0.77333	12.38116	0.06838	0.88286	1.48997

Table 3. *Total scattering factors* $\langle j_0 \rangle$ *for free atoms C, P and Fe*

a, b and c are as given in Table 2.

$\sin\theta/\lambda$ (Å^{-1})	$\langle j_0 \rangle$		
	a	b	c
Carbon			
0.0000	6.0000	6.0000	6.0000
0.0500	5.7559	5.7559	5.7558
0.1000	5.1269	5.1268	5.1265
0.1500	4.3373	4.3372	4.3366
0.2000	3.5833	3.5832	3.5824
0.2500	2.9653	2.9653	2.9643
0.3000	2.5034	2.5033	2.5024
0.3500	2.1763	2.1763	2.1755
0.4000	1.9507	1.9507	1.9500
0.4500	1.7952	1.7951	1.7945
0.5000	1.6850	1.6849	1.6844
0.6000	1.5363	1.5363	1.5358
0.7000	1.4253	1.4252	1.4247
0.8000	1.3218	1.3218	1.3213
0.9000	1.2180	1.2180	1.2174
1.0000	1.1138	1.1138	1.1132
1.2000	0.9134	0.9134	0.9126
1.4000	0.7361	0.7360	0.7352
1.6000	0.5879	0.5879	0.5871
1.8000	0.4682	0.4682	0.4674
2.0000	0.3732	0.3732	0.3725
2.5000	0.2157	0.2157	0.2151
3.0000	0.1294	0.1294	0.1290
3.5000	0.0809	0.0809	0.0806
4.0000	0.0525	0.0525	0.0523
5.0000	0.0245	0.0245	0.0244
6.0000	0.0127	0.0127	0.0127
Phosphorus			
0.0000	15.0000	15.0000	15.0000
0.0500	14.4713	14.4713	14.4704
0.1000	13.1699	13.1697	13.1668
0.1500	11.6598	11.6594	11.6544
0.2000	10.3421	10.3417	10.3353
0.2500	9.3366	9.3361	9.3293
0.3000	8.5952	8.5946	8.5879
0.3500	8.0250	8.0235	8.0168
0.4000	7.5434	7.5429	7.5361
0.4500	7.1024	7.1019	7.0946
0.5000	6.6747	6.6743	6.6663
0.6000	5.8311	5.8308	5.8212

Table 3 (*cont.*)

$\sin\theta/\lambda$ (Å^{-1})	$\langle j_0 \rangle$		
	a	b	c
0.7000	5.0210	5.0207	5.0097
0.8000	4.2846	4.2843	4.2726
0.9000	3.6491	3.6488	3.6370
1.0000	3.1222	3.1219	3.1106
1.2000	2.3639	2.3637	2.3540
1.4000	1.9027	1.9025	1.8947
1.6000	1.6260	1.6258	1.6195
1.8000	1.4528	1.4526	1.4473
2.0000	1.3336	1.3335	1.3286
2.5000	1.1221	1.1220	1.1172
3.0000	0.9423	0.9422	0.9370
3.5000	0.7771	0.7770	0.7716
4.0000	0.6321	0.6320	0.6265
5.0000	0.4108	0.4107	0.4058
Iron			
0.0000	26.0000	26.0000	26.0000
0.0500	25.3037	25.3037	25.2965
0.1000	23.6826	23.6825	23.6675
0.1500	21.8428	21.8427	21.8299
0.2000	20.0668	20.0664	20.0585
0.2500	18.3764	18.3759	18.3686
0.3000	16.7652	16.7645	16.7531
0.3500	15.2497	15.2488	15.2309
0.4000	13.8559	13.8549	13.8302
0.4500	12.6045	12.6034	12.5729
0.5000	11.5052	11.5040	11.4694
0.6000	9.7522	9.7509	9.7129
0.7000	8.5099	8.5087	8.4713
0.8000	7.6431	7.6420	7.6067
0.9000	7.0217	7.0208	6.9869
1.0000	6.5444	6.5436	6.5099
1.2000	5.7746	5.7739	5.7370
1.4000	5.0699	5.0694	5.0274
1.6000	4.3869	4.3866	4.3406
1.8000	3.7519	3.7517	3.7042
2.0000	3.1942	3.1943	3.1477
2.5000	2.1963	2.1968	2.1588
3.0000	1.6575	1.6582	1.6300
3.5000	1.3768	1.3776	1.3559
4.0000	1.2133	1.2142	1.1956
5.0000	0.9955	0.9965	0.9788
6.0000	0.8125	0.8133	0.7950

the pairs $np_{3/2}$ and $np_{1/2}$ have slightly different radial densities, as have, for example, $nd_{5/2}$ and $nd_{3/2}$. We use a weighted average of $R(r)$ in (3), the weights being the generalized occupation numbers of the orbitals in the ground-state atom. This way the analytical Slater-type expansions are equivalent to their nonrelativistic counterparts.

The Fortran subroutine *L-BFGS-B* (Zhu *et al.*, 1994) has been used for the minimization of (3). The initial values of c_j and ζ_j are those from Bunge *et al.* (1993) and the n_j are kept at the nonrelativistic values.

The converged wave functions that give the minimum χ^2 are generally slightly unnormalized, although

$$N = \int_0^\infty r^2 \left\{ \sum_{j=1}^{m} [(2n_j)!]^{-1/2} (2\zeta_j)^{n_j+1/2}\, c_j r^{n_j-1} \exp(-\zeta_j r) \right\}^2 \mathrm{d}r \tag{5}$$

deviates from 1 by less than 0.05%. We use $N^{-1/2}$ to scale the c_i's so that the final expansion is perfectly normalized.

The final Slater-type expansion coefficients and the orbital exponents for C, P and Fe are listed in Table 1, together with the n_j's used. Note that the orbitals with the same l value are expanded using the same basis-function set. Therefore, only one set of n_j's is given for one l. But unlike the tabulation of Bunge *et al.* (1993), the present tabulation uses different ζ_j's for different orbitals with the same l, *i.e.* ζ_j's are optimized for each orbital separately. The χ^2 values for the fit, listed in Table 1(*b*), are evidence for the quality of the fit obtained.

Expectation values $\langle r^k \rangle$ for $k = -2$, -1, 1 and 2 are listed in Table 2. Three sets of values are given: those calculated directly from the numerical wave functions, from the converged fitting functions, and from the nonrelativistic wave functions. The expectation values of $\langle r^{-3} \rangle$ for the d orbitals of Fe, which are of importance for comparison of Mössbauer results with values calculated from the charge density (Coppens, 1997), are 4.949 65, 4.940 56 and 4.978 80 for the numerical relativistic wave functions, the relativistic fitting functions and the nonrelativistic wave functions, respectively.

In Table 3, we list the total scattering factors for C, P and Fe, while Table 4 contains the scattering factors $\langle j_k \rangle$, $k = 0$, 2 and 4, for orbitals of Fe. The scattering factor is defined as

$$\langle j_k(S) \rangle = \int_0^\infty R(r)\, j_k(2\pi S r)\, \mathrm{d}r,$$

where $S = 2 \sin \theta/\lambda$, with θ the Bragg angle of scattering and $j_k(x)$ the spherical Bessel function of the first kind (Arfken, 1970). Closed-form expressions for $\langle j_k \rangle$ given in Su & Coppens (1990) were used for the calculations. As in Table 2, values calculated with the converged fitting functions are compared with those obtained directly

Table 4. *Core and valence scattering factors $\langle j_k \rangle$ for Fe*

The core scattering factors are the sum of the contributions due to all the subshells that define the core. The valence orbital scattering factors are normalized to one electron. a, b and c are as given in Table 2.

$\sin\theta/\lambda$ (Å^{-1})	a	b	c
	$\langle j_0 \rangle$ [Ar] core of Fe		
0.0000	18.0000	18.0000	18.0000
0.0500	17.8655	17.8655	17.8641
0.1000	17.4741	17.4739	17.4684
0.1500	16.8592	16.8589	16.8473
0.2000	16.0702	16.0698	16.0508
0.2500	15.1646	15.1641	15.1376
0.3000	14.2001	14.1994	14.1662
0.3500	13.2283	13.2275	13.1887
0.4000	12.2906	12.2896	12.2470
0.4500	11.4167	11.4156	11.3708
0.5000	10.6247	10.6235	10.5781
0.6000	9.3103	9.3090	9.2657
0.7000	8.3304	8.3292	8.2900
0.8000	7.6095	7.6085	7.5732
0.9000	7.0617	7.0608	7.0279
1.0000	6.6154	6.6147	6.5823
1.2000	5.8486	5.8479	5.8124
1.4000	5.1232	5.1227	5.0819
1.6000	4.4203	4.4200	4.3749
1.8000	3.7714	3.7713	3.7244
2.0000	3.2052	3.2053	3.1592
2.5000	2.1989	2.1995	2.1617
3.0000	1.6583	1.6590	1.6308
3.5000	1.3770	1.3779	1.3561
4.0000	1.2133	1.2142	1.1955
5.0000	0.9951	0.9961	0.9785
6.0000	0.8120	0.8128	0.7946
	$\langle j_0 \rangle$ 4s(Fe), normalized to 1 electron		
0.0000	1.0000	1.0000	1.0000
0.0500	0.8008	0.8008	0.7969
0.1000	0.4119	0.4119	0.4035
0.1500	0.1219	0.1219	0.1148
0.2000	0.0071	0.0071	0.0103
0.2500	0.0369	0.0369	0.0370
0.3000	0.0278	0.0278	0.0265
0.3500	0.0108	0.0108	0.0094
0.4000	0.0028	0.0028	0.0039
0.4500	0.0107	0.0107	0.0112
0.5000	0.0138	0.0138	0.0139
0.6000	0.0119	0.0119	0.0114
0.7000	0.0067	0.0067	0.0061
0.8000	0.0025	0.0025	0.0019
0.9000	0.0000	0.0000	0.0005
1.0000	0.0009	0.0009	0.0013
1.2000	0.0004	0.0004	0.0006
1.4000	0.0008	0.0008	0.0006
1.6000	0.0015	0.0015	0.0014
1.8000	0.0016	0.0016	0.0015
2.0000	0.0014	0.0014	0.0013
2.5000	0.0005	0.0005	0.0004
3.0000	0.0000	0.0000	0.0000
3.5000	0.0001	0.0001	0.0001
4.0000	0.0000	0.0000	0.0000
5.0000	0.0002	0.0002	0.0001
6.0000	0.0002	0.0002	0.0002
	$\langle j_0 \rangle$ 3d(Fe), normalized to 1 electron		
0.0000	1.0000	1.0000	1.0000
0.0500	0.9728	0.9728	0.9731

Table 4 (*cont.*)

$\sin\theta/\lambda$ (Å^{-1})	a	b	c
0.1000	0.8974	0.8975	0.8987
0.1500	0.7900	0.7900	0.7922
0.2000	0.6684	0.6685	0.6714
0.2500	0.5476	0.5476	0.5508
0.3000	0.4368	0.4368	0.4400
0.3500	0.3405	0.3405	0.3435
0.4000	0.2599	0.2599	0.2626
0.4500	0.1944	0.1944	0.1966
0.5000	0.1422	0.1422	0.1439
0.6000	0.0697	0.0697	0.0707
0.7000	0.0277	0.0277	0.0282
0.8000	0.0048	0.0048	0.0050
0.9000	0.0067	0.0067	−0.0067
1.0000	0.0115	0.0115	−0.0116
1.2000	0.0122	0.0122	−0.0124
1.4000	0.0092	0.0092	−0.0093
1.6000	0.0061	0.0061	−0.0062
1.8000	0.0038	0.0038	−0.0039
2.0000	0.0023	0.0023	−0.0023
2.5000	0.0006	0.0006	−0.0006
3.0000	0.0001	0.0001	−0.0001
3.5000	0.0000	0.0000	0.0000
4.0000	0.0000	0.0000	0.0000
5.0000	0.0000	0.0000	0.0000
6.0000	0.0000	0.0000	0.0000
	$\langle j_2\rangle$ for $3d$(Fe) normalized to 1 electron		
0.0000	0.0000	0.0000	0.0000
0.0500	0.0108	0.0108	0.0107
0.1000	0.0396	0.0396	0.0391
0.1500	0.0777	0.0777	0.0770
0.2000	0.1161	0.1161	0.1154
0.2500	0.1484	0.1484	0.1478
0.3000	0.1715	0.1715	0.1711
0.3500	0.1850	0.1851	0.1850
0.4000	0.1902	0.1902	0.1905
0.4500	0.1886	0.1886	0.1892
0.5000	0.1821	0.1821	0.1829
0.6000	0.1604	0.1604	0.1614
0.7000	0.1341	0.1341	0.1352
0.8000	0.1084	0.1084	0.1094
0.9000	0.0856	0.0856	0.0864
1.0000	0.0664	0.0665	0.0672
1.2000	0.0387	0.0387	0.0392
1.4000	0.0219	0.0219	0.0222
1.6000	0.0121	0.0121	0.0123
1.8000	0.0066	0.0066	0.0067
2.0000	0.0036	0.0036	0.0036
2.5000	0.0007	0.0007	0.0006
3.0000	0.0000	0.0000	0.0000
3.5000	−0.0001	0.0001	0.0001
4.0000	−0.0001	0.0001	0.0001
5.0000	0.0000	0.0000	0.0000
6.0000	0.0000	0.0000	0.0000
	$\langle j_4\rangle$ for $3d$(Fe), normalized to 1 electron		
0.0000	0.0000	0.0000	0.0000
0.0500	0.0001	0.0001	0.0001
0.1000	0.0010	0.0010	0.0010
0.1500	0.0044	0.0044	0.0043
0.2000	0.0110	0.0110	0.0107
0.2500	0.0206	0.0206	0.0202
0.3000	0.0322	0.0322	0.0317
0.3500	0.0444	0.0444	0.0439

Table 4 (*cont.*)

$\sin\theta/\lambda$ (Å^{-1})	a	b	c
0.4000	0.0560	0.0560	0.0556
0.4500	0.0663	0.0663	0.0659
0.5000	0.0747	0.0747	0.0745
0.6000	0.0857	0.0857	0.0857
0.7000	0.0896	0.0896	0.0898
0.8000	0.0881	0.0881	0.0885
0.9000	0.0832	0.0832	0.0836
1.0000	0.0762	0.0762	0.0767
1.2000	0.0604	0.0604	0.0609
1.4000	0.0456	0.0456	0.0460
1.6000	0.0335	0.0335	0.0338
1.8000	0.0242	0.0242	0.0245
2.0000	0.0174	0.0174	0.0176
2.5000	0.0077	0.0077	0.0078
3.0000	0.0035	0.0035	0.0035
3.5000	0.0017	0.0017	0.0017
4.0000	0.0008	0.0008	0.0008
5.0000	0.0002	0.0002	0.0002
6.0000	0.0001	0.0001	0.0001

from the numerical wave functions and with values from nonrelativistic wave functions.

3. Concluding remarks

The results in Tables 2, 3 and 4 show that the wave functions listed in Table 1 give rise to accurate $\langle r^k\rangle$ for $k = -2, -1, 1$ and 2 and $\langle j_k\rangle$ for $k = 0, 2$ and 4. They are significantly more accurate than the values calculated directly from the nonrelativistic wave functions. The availability of the analytical wave functions allows the generalized X-ray scattering factors and the total charge density from pseudoatoms to be expressed in closed form. As a result, the topological properties of the electron density can be analyzed more accurately, especially for crystals containing heavier atoms such as the transition metals.

Analogous results for atoms 37–42 (Rb–Mo) have also been obtained. Complete results of this work are accessible at http://wings.buffalo.edu/~chem9982.

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