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Accurate Elastic Scattering Factors for Lithium to Argon Based on Correlated Wavefunctions

BY HERMANN MEYER, THOMAS MÜLLER AND ARMIN SCHWEIG*

Fachbereich Physikalische Chemie und Zentrum für Materialwissenschaften, Universität Marburg, Postfach, D-35032 Marburg, Germany

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Abstract

Elastic scattering factors (or atomic form factors) $f(s)$ for Li to Ar have been derived in the first Born approximation from *ab initio* MR-SDCI (multireference singly and doubly excited configuration interaction) calculations which recover between 90 and 99% of the estimated total correlation energy. The correlation effects on $f(s)$ are contrasted with the relativistic effects known from the literature. Atomic form factors are presented that take into account correlation and relativistic contributions in an additive manner.

Introduction

Elastic scattering factors (or atomic form factors) $f(s)$ listed in *International Tables for Crystallography* (Maslen, Fox & O'Keefe, 1992) are widely used in crystallographic structure calculations. Except for hydrogen, they were computed from relativistic Dirac–Fock wavefunctions which completely neglect electron correlation. However, at least for light atoms, correlation effects are expected to be more significant than relativistic corrections. For two-electron systems and, restricted to rather few s values, for Li and Be, accurate atomic form factors are available that account for more than 99% of the estimated total correlation energy (Thakkar & Smith, 1992; Schmider, Esquivel, Sagar & Smith, 1993; Esquivel & Bunge, 1987). For B to Ne, atomic form factors including correlation contributions were published but they either do not account for a sufficient amount of electron correlation (Tanaka & Sasaki, 1971; Peixoto, Bunge & Bonham, 1969) or they rely on non-variational configuration interaction schemes (Naon & Cornille, 1973). For Na to Ar, no correlation calculations of form factors have been published to date. In the present work, atomic form factors are derived based on *ab initio* MR-SDCI (multireference singly and doubly excited configuration interaction) calculations which recover between 90 and 99% of the estimated total correlation energy. The resulting correlation contributions to $f(s)$ are compared with corresponding relativistic contributions known from the literature.

Computational details

The atomic form factor in the framework of the first Born approximation (Waller & Hartree, 1929) is given by

$$f(\mathbf{s}) = \int \rho(\mathbf{r}) \exp(i\mathbf{s}\mathbf{r})\mathrm{d}\mathbf{r}, \qquad (1)$$

where $\mathbf{r}$ denotes the position vector of an electron, $\rho(\mathbf{r})$ the one-electron density and $\mathbf{s}$ the scattering vector. The magnitude of $\mathbf{s}$ is the scattering variable s which depends on the wavelength λ of the radiation and the scattering angle 2θ according to $s = (4\pi/\lambda)\sin\theta$. If the one-electron density is expanded in terms of GTOs (Gaussian-type orbitals), χ_μ, the spherically averaged form factor is obtained as

$$\begin{aligned} f(s) &= (1/4\pi)\int f(\mathbf{s})\mathrm{d}\Omega \\ &= (1/4\pi)\sum_{\mu\nu} P_{\mu\nu} \int\int \chi_\mu(\mathbf{r})\chi_\nu(\mathbf{r}) \exp(i\mathbf{s}\mathbf{r})\mathrm{d}\mathbf{r}\mathrm{d}\Omega, \end{aligned} \qquad (2)$$

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* To whom correspondence should be addressed.

Table 1. *Energetic results (in* hartrees) *for the atoms* Li *to* Ar *in the ground state*

Atom	GTO basis	RHF	SDCI			MR-SDCI^b			$E_{corr}(est.)^c$
		total energy	total energy	$E_{corr}{}^a$	virial ratio	total energy	$E_{corr}{}^a$	virial ratio	
Li	[14s10p7d6f]	-7.43273	-7.47729	98.3%	2.00022	7.47734	98.4%	2.00013	-0.04533
Be	[14s10p7d6f]	-14.57302	-14.66220	94.5%	2.00023	-14.66629	98.9%	2.00003	-0.09434
B	[15s10p7d6f4g]	-24.52903	-24.64656	94.1%	2.00013	-24.65181	98.3%	2.00007	-0.12485
C	[15s10p7d6f4g]	-37.68857	-37.83614	94.3%	2.00012	-37.84157	97.8%	2.00005	-0.15640
N	[15s10p7d6f4g]	-54.40086	-54.57935	94.8%	2.00017	-54.58243	96.4%	2.00004	-0.18831
O	[15s10p7d6f4g]	-74.80929	-75.05054	93.5%	2.00011	-75.05699	96.0%	2.00008	-0.25794
F	[15s10p7d6f4g]	-99.40921	-99.71109	93.0%	2.00010	-99.71933	95.5%	2.00001	-0.32453
Ne	[15s10p7d6f4g]	-128.54687	-128.90925	92.8%	2.00009	-128.92055	95.7%	2.00007	-0.39047
Na	[17s13p10d9f5g]	-161.85869	-162.22830	93.4%	2.00017	-162.23399	94.8%	2.00014	-0.39564
Mg	[17s13p10d9f5g]	-199.61440	-200.01484	91.3%	2.00022	-200.02520	93.7%	2.00015	-0.43828
Al	[18s13p10d9f5g]	-241.87643	-242.30250	90.7%	2.00021	-242.31673	93.7%	2.00014	-0.46960
Si	[18s13p10d9f5g]	-288.85406	-289.31031	90.3%	2.00018	-289.31971	92.1%	2.00013	-0.50503
P	[18s13p10d9f5g]	-340.71846	-341.20666	90.3%	2.00016	-341.21198	91.3%	2.00009	-0.54026
S	[18s13p10d9f5g]	-397.50454	-398.04634	89.5%	2.00014	-398.05254	90.6%	2.00008	-0.60476
Cl	[18s13p10d9f5g]	-459.48167	-460.07651	89.3%	2.00012	-460.08043	89.8%	2.00007	-0.66598
Ar	[18s13p10d9f5g]	-526.81706	-527.46256	89.3%	2.00010	-527.47738	91.4%	2.00005	-0.72216

[a] Recovered percentage of the estimated total correlation energy $E_{\mathrm{corr}}(\mathrm{est})$
[b] For the calculations concerning second-row atoms, see text.
[c] Chakravorty, Gwaltney, Davidson, Parpia & Froese-Fischer (1993).

where $P_{\mu\nu}$ and Ω denote one-electron density matrix elements and the solid angle, respectively.

Uncontracted basis sets were used throughout including spherical GTOs up to *g* functions. SDCI wavefunctions were calculated in a basis of RHF (Roothaan open-shell Hartree–Fock)-AOs (atomic orbitals); MR-SDCI calculations were performed in a basis of NOs (natural orbitals) obtained by diagonalization of the first-order density matrix of the corresponding SDCI wavefunction. The most important configurations were selected as reference configurations (for details about these computations, see Meyer, Müller & Schweig, 1995).

For most atoms, about ten reference configurations were included implying the generation of up to about 1.5 million TQ (triply and quadruply excited) configurations. TQ contributions to $f(s)$ and to all other quantities considered in this work are defined as differences between the corresponding MR-SDCI and SDCI results. For the second-row atoms, the TQ contributions were calculated in a reduced basis excluding all f and g GTOs (because of limited computer capacities). The final MR-SDCI results were then obtained by adding these TQ contributions to the corresponding SDCI results from the large basis-set calculations. All electrons (valence and core electrons) were included in the correlation treatment. The MR-SDCI calculations were carried out using the *COLUMBUS* program (Shepard *et al.*, 1988). The one-electron density matrix elements were computed by means of the MR-SDCI gradient program (Shepard, Lischka, Szalay, Kovar & Ernzerhof, 1992). The program for the calculation of the form factors originated from our group.

Results and discussion

All quantities representing electron correlation effects are taken as differences between results obtained on the MR-SDCI level (if not stated otherwise) and on the RHF level of approximation (throughout these differences are marked by the index corr).

Table 1 shows the energetic results obtained for Li to Ar in the ground state. The RHF energies differ less than 0.5×10^{-3} hartrees from the RHF limit (Froese-Fischer, 1977) yielding a virial ratio correct to at least six digits. Total SDCI and MR-SDCI energies for the elements Li to Ne deviate less than 1×10^{-3} hartrees from the best hitherto published CI results (Sasaki & Yoshimine, 1974; Feller & Davidson, 1988, 1989; Bunge, 1976). For the elements Na to Ar, no correlation calculations of comparable high quality have been published.

With regard to the reliability of the atomic form factors presented in this work, a partitioning of E_{corr} into the contributions due to the kinetic energy, the electron–nucleus attraction energy ($\Delta V^{\mathrm{ne}}_{\mathrm{corr}}$) and the electron–electron repulsion energy ($\Delta V^{\mathrm{ee}}_{\mathrm{corr}}$) is instructive. Contrary to E_{corr} itself, this partitioning is rather sensitive to the wavefunctions used. $\Delta V^{\mathrm{ne}}_{\mathrm{coor}}$ is closely related to the correlation contribution to the atomic form factor,

$\Delta f_{\mathrm{corr}}(s)$ (Tavard, 1965):

$$\Delta V^{\mathrm{ne}}_{\mathrm{corr}} = -(2Z/\pi)\int \Delta f_{\mathrm{corr}}(s)\mathrm{d}s, \qquad (3)$$

where Z refers to the nuclear charge.

Fig. 1 displays, for all atoms considered, the estimated total correlation energy $E_{\mathrm{corr}}(\mathrm{est.})$ as well as E_{corr}, $\Delta V^{\mathrm{ne}}_{\mathrm{corr}}$ and $\Delta V^{\mathrm{ee}}_{\mathrm{corr}}$ calculated from the MR-SDCI wavefunctions [which, for $\Delta V^{\mathrm{ne}}_{\mathrm{corr}}$, coincide with the values obtained through (3)]. For the first-row atoms, $\Delta V^{\mathrm{ne}}_{\mathrm{corr}}$ and $\Delta V^{\mathrm{ee}}_{\mathrm{corr}}$ values derived by means of the Z-expansion technique from experimental total energies (Bonham & Goruganthu, 1982) are available. Except for F, where somewhat larger deviations are found (-44×10^{-3} hartrees for $\Delta V^{\mathrm{ne}}_{\mathrm{corr}}$ and 64×10^{-3} hartrees for $\Delta V^{\mathrm{ee}}_{\mathrm{corr}}$), our results agree well with the Z-expansion data. For Ne, where results of other correlation calculations are available to us (Breitenstein, Meyer & Schweig, 1985), the deviations from these data amount to *ca* 200×10^{-3} hartrees although *ca* 80 to 100% of $E_{\mathrm{corr}}(\mathrm{est.})$ are recovered.

Unlike the correlation energy itself, which displays the expected dependence upon the number of electron pairs and doubly occupied SCF orbitals of the considered atoms, the corresponding data of $\Delta V^{\mathrm{ne}}_{\mathrm{corr}}$ and $\Delta V^{\mathrm{ee}}_{\mathrm{corr}}$ may be surprising. For Be to Ne, $\Delta V^{\mathrm{ne}}_{\mathrm{corr}}$ increases followed by a strong decrease which continues up to Cl. For Li to Ne, $\Delta V^{\mathrm{ee}}_{\mathrm{corr}}$, on the other hand, decreases rapidly followed by a small increase to Mg, subsequently decreasing again and finally reaching its lowest value for Ar. Thus, $\Delta V^{\mathrm{ne}}_{\mathrm{corr}}$ and $\Delta V^{\mathrm{ee}}_{\mathrm{corr}}$ exhibit markedly different behaviour for first-row and second-row atoms.

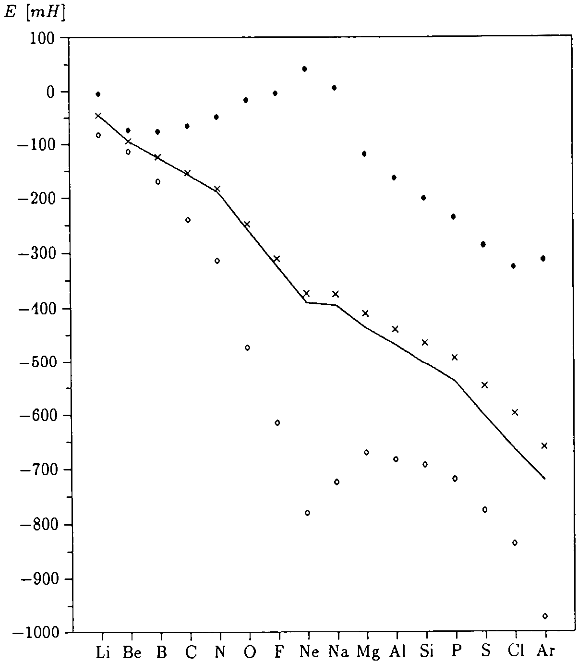

Fig. 1. Calculated values of E_{corr} (×), $\Delta V^{\mathrm{ne}}_{\mathrm{corr}}$ (●) and $\Delta V^{\mathrm{ee}}_{\mathrm{corr}}$ (○) for the atoms Li to Ar. The full line represents the values of $E_{\mathrm{corr}}(\mathrm{est.})$

Another quantity closely related to $f(s)$ is the radial electron density $D(r)$ (Bartell & Gavin, 1964):

$$D(r) = r^2 \int \rho(\mathbf{r})\mathrm{d}\Omega = (2r/\pi)\int f(s)s\sin(sr)\mathrm{d}s. \qquad (4)$$

With $f(s)$ substituted by $\Delta f_{\mathrm{corr}}(s)$ in (4), the correlation contribution $\Delta D_{\mathrm{corr}}(r)$ is obtained, Thus, the features of $\Delta f_{\mathrm{corr}}(s)$ in the region of high s values are predominantly affected by features of $\Delta D_{\mathrm{corr}}(r)$ in the region of low r values and *vice versa*.

$D(r)$ curves, with their characteristic maxima corresponding to the K, L and M shells [for a recent justification of such a correspondence, see Simas, Sagar, Ku & Smith (1988)] are shown in Fig. 2 for Ne and Ar (the MR-SDCI and RHF curves are indistinguishable for the chosen scales). The investigation of $\Delta D_{\mathrm{corr}}(r)$ for all atoms considered reveals that most of these functions are negative at large r values implying a contraction of the atomic electron density as a consequence of electron correlation. For N, O, F and Ne, however, an expansion of the electron density results (*cf.* the examples Ne and Ar in Fig. 2).

Fig. 3 shows, for all atoms considered, the correlation contributions $\Delta f_{\mathrm{corr}}(s)$ to the atomic form factors $f(s)$ which, on the RHF level of approximation, are in

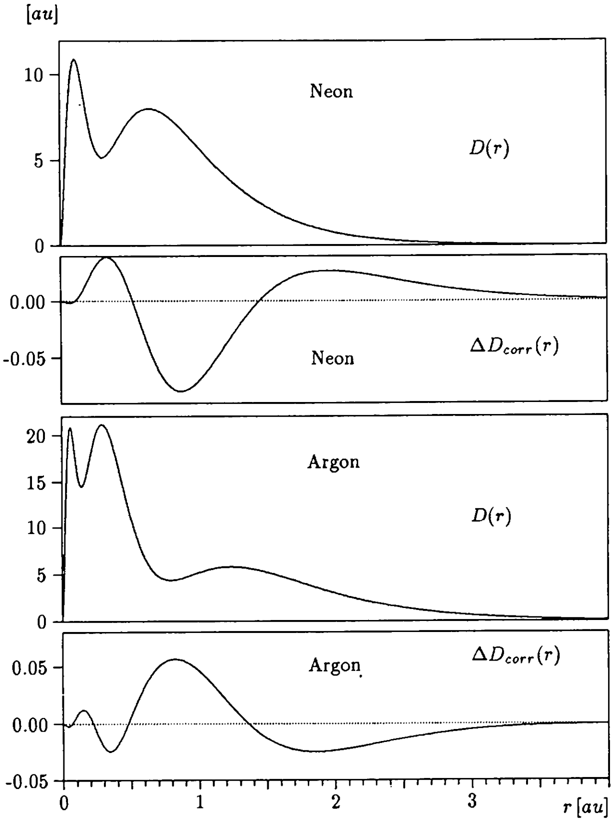

Fig. 2. Radial electron density $D(r)$ and the corresponding correlation contribution $\Delta D_{\mathrm{corr}}(r)$ for Ne and Ar.

excellent agreement with reported values (Wang, Sagar, Schmider & Smith, 1993; Tavard, Nicolas & Rouault, 1967). The $\Delta f_{\rm corr}(s)$ curves are most pronounced in the region of low s values (between 0 and *ca* 5 to 15 Å^{-1}) corresponding essentially to the valence-shell electrons. The maximum amount of $\Delta f_{\rm corr}(s)$ for the various atoms ranges from 0.005 to 0.039. The number of extrema increases from two to four when going from Li to Ar. The positions of the extrema continuously shift towards larger s values as the atomic number increases. This trend parallels the shrinking of the electron-density regions corresponding to the various shells with increasing

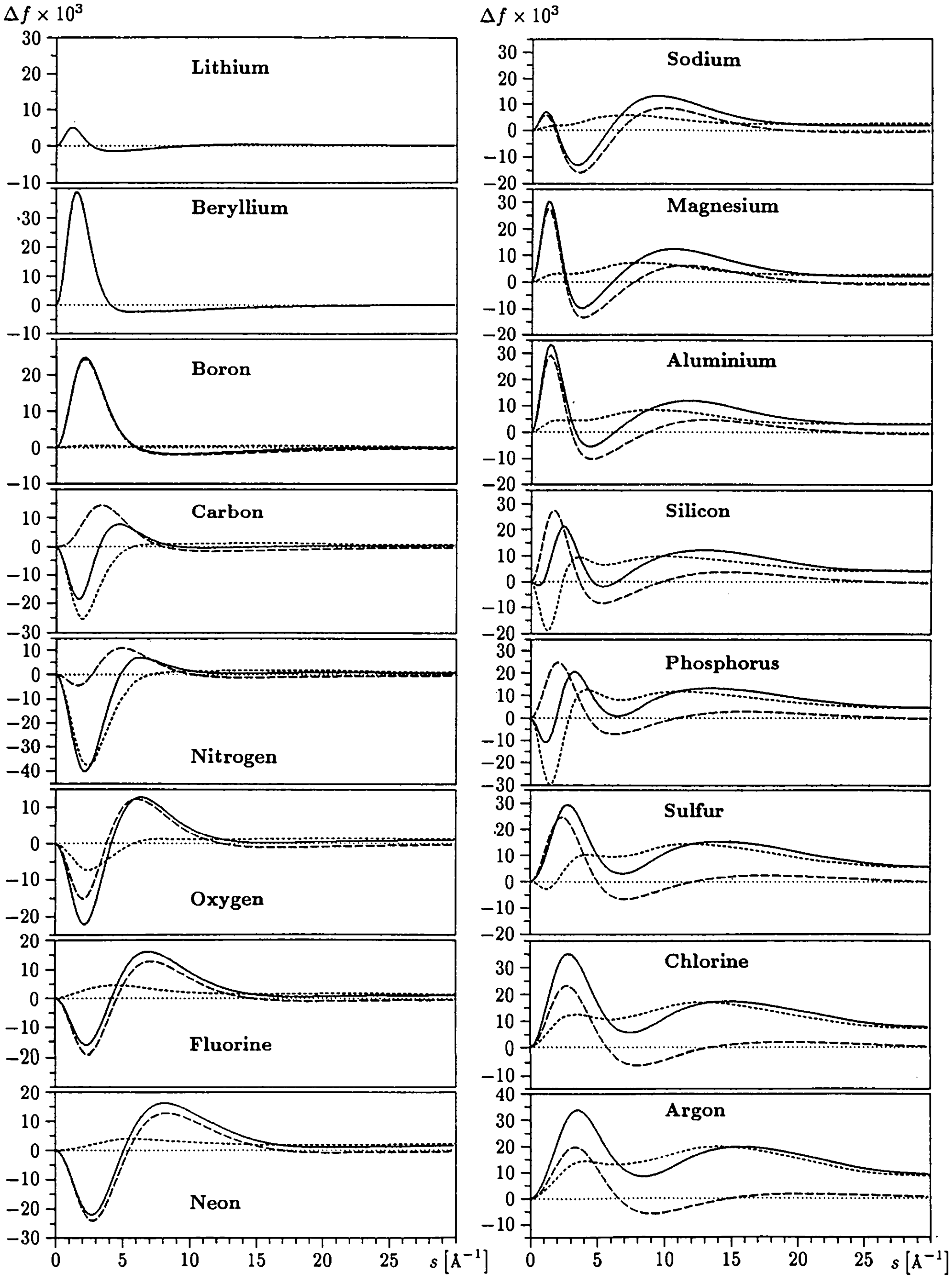

Fig. 3. Contributions to $f(s)$ due to electron correlation, $\Delta f_{\rm corr}(s)$ (– – –), and relativistic effects, $\Delta f_{\rm rel}(s)$ (- - -), as well as the sum of both contributions (——) for the atoms Li to Ar.

Table 2. *Atomic form factors $f(s)$ for* Li *to* Ar *including correlation and relativistic contributions*

$\sin\theta/\lambda$ [Å^{-1}]	Li	Be	B	C	N	O	F	Ne	Na	Mg	Al	Si	P	S	Cl	Ar
0.00	3.000	4.000	5.000	6.000	7.000	8.000	9.000	10.000	11.000	12.000	13.000	14.000	15.000	16.000	17.000	18.000
0.01	2.986	3.988	4.988	5.990	6.991	7.992	8.993	9.993	10.980	11.979	12.977	13.976	14.977	15.979	16.980	17.981
0.02	2.947	3.953	4.955	5.958	6.963	7.966	8.969	9.972	10.923	11.917	12.906	13.906	14.910	15.916	16.920	17.924
0.03	2.885	3.895	4.899	5.907	6.917	7.925	8.932	9.937	10.832	11.817	12.792	13.791	14.800	15.811	16.821	17.831
0.04	2.804	3.817	4.824	5.837	6.854	7.867	8.879	9.889	10.712	11.684	12.638	13.634	14.650	15.668	16.685	17.701
0.05	2.710	3.723	4.730	5.750	6.775	7.794	8.812	9.827	10.572	11.522	12.452	13.443	14.464	15.488	16.514	17.538
0.06	2.609	3.613	4.621	5.646	6.680	7.707	8.731	9.752	10.417	11.338	12.240	13.221	14.245	15.277	16.311	17.343
0.07	2.506	3.493	4.498	5.527	6.571	7.606	8.639	9.666	10.255	11.139	12.009	12.977	14.001	15.038	16.079	17.119
0.08	2.405	3.366	4.364	5.398	6.450	7.493	8.533	9.568	10.090	10.929	11.764	12.714	13.734	14.774	15.822	16.869
0.09	2.308	3.234	4.224	5.257	6.317	7.369	8.418	9.460	9.926	10.714	11.512	12.439	13.450	14.490	15.542	16.596
0.10	2.220	3.102	4.077	5.110	6.176	7.234	8.291	9.340	9.765	10.500	11.259	12.158	13.156	14.191	15.245	16.304
0.11	2.140	2.971	3.927	4.956	6.026	7.091	8.156	9.212	9.609	10.289	11.007	11.875	12.854	13.881	14.934	15.996
0.12	2.069	2.843	3.777	4.799	5.871	6.941	8.012	9.076	9.457	10.084	10.762	11.594	12.548	13.564	14.611	15.674
0.13	2.007	2.721	3.628	4.639	5.710	6.784	7.861	8.932	9.310	9.887	10.526	11.319	12.246	13.244	14.282	15.341
0.14	1.953	2.605	3.482	4.479	5.547	6.622	7.705	8.781	9.165	9.698	10.299	11.052	11.946	12.923	13.949	15.002
0.15	1.906	2.498	3.340	4.319	5.381	6.457	7.543	8.624	9.024	9.518	10.083	10.796	11.653	12.606	13.616	14.659
0.16	1.865	2.398	3.203	4.162	5.214	6.289	7.377	8.463	8.883	9.347	9.878	10.551	11.370	12.294	13.283	14.314
0.17	1.829	2.307	3.072	4.008	5.048	6.119	7.207	8.297	8.744	9.184	9.685	10.317	11.097	11.988	12.955	13.972
0.18	1.797	2.223	2.948	3.857	4.884	5.949	7.036	8.128	8.605	9.028	9.502	10.097	10.835	11.693	12.633	13.631
0.19	1.768	2.148	2.832	3.712	4.721	5.779	6.864	7.955	8.465	8.878	9.330	9.889	10.586	11.407	12.319	13.295
0.20	1.742	2.081	2.722	3.572	4.562	5.610	6.690	7.781	8.324	8.734	9.167	9.691	10.349	11.134	12.014	12.966
0.22	1.693	1.966	2.524	3.310	4.255	5.278	6.344	7.430	8.039	8.459	8.866	9.333	9.914	10.621	11.436	12.334
0.24	1.647	1.875	2.355	3.072	3.966	4.956	6.003	7.078	7.749	8.195	8.591	9.013	9.527	10.160	10.904	11.741
0.25	1.625	1.836	2.281	2.963	3.829	4.800	5.835	6.905	7.603	8.067	8.462	8.866	9.350	9.947	10.655	11.461
0.26	1.603	1.801	2.212	2.861	3.698	4.649	5.670	6.732	7.455	7.939	8.337	8.727	9.183	9.746	10.420	11.192
0.28	1.557	1.742	2.091	2.672	3.452	4.360	5.351	6.391	7.160	7.685	8.096	8.468	8.879	9.379	9.984	10.691
0.30	1.511	1.694	1.990	2.508	3.227	4.089	5.045	6.060	6.865	7.433	7.865	8.229	8.606	9.052	9.594	10.235
0.32	1.464	1.652	1.906	2.364	3.023	3.837	4.755	5.742	6.573	7.181	7.639	8.007	8.360	8.762	9.247	9.825
0.34	1.416	1.615	1.836	2.239	2.841	3.604	4.481	5.438	6.284	6.930	7.416	7.794	8.135	8.501	8.936	9.458
0.35	1.392	1.598	1.805	2.183	2.757	3.495	4.351	5.290	6.143	6.805	7.306	7.692	8.029	8.382	8.794	9.288
0.36	1.367	1.581	1.776	2.131	2.678	3.390	4.224	5.148	6.002	6.679	7.195	7.590	7.926	8.267	8.660	9.128
0.38	1.318	1.549	1.727	2.038	2.533	3.195	3.985	4.873	5.728	6.431	6.975	7.390	7.730	8.053	8.411	8.833
0.40	1.269	1.518	1.684	1.957	2.404	3.016	3.763	4.613	5.461	6.184	6.756	7.194	7.542	7.856	8.187	8.569
0.42	1.220	1.487	1.646	1.888	2.289	2.855	3.557	4.368	5.206	5.942	6.539	7.000	7.361	7.671	7.983	8.331
0.44	1.172	1.456	1.612	1.828	2.188	2.709	3.368	4.140	4.961	5.704	6.322	6.807	7.183	7.498	7.796	8.117
0.45	1.148	1.440	1.597	1.800	2.142	2.641	3.279	4.031	4.842	5.587	6.214	6.711	7.096	7.413	7.707	8.017
0.46	1.124	1.424	1.581	1.775	2.099	2.576	3.193	3.926	4.726	5.473	6.107	6.614	7.010	7.331	7.621	7.922
0.48	1.077	1.392	1.553	1.730	2.020	2.457	3.033	3.727	4.503	5.247	5.895	6.423	6.838	7.169	7.457	7.742
0.50	1.031	1.360	1.525	1.689	1.950	2.350	2.886	3.542	4.291	5.029	5.686	6.233	6.667	7.011	7.302	7.577
0.55	0.923	1.277	1.462	1.605	1.808	2.126	2.572	3.136	3.813	4.517	5.181	5.763	6.243	6.626	6.936	7.205
0.60	0.822	1.193	1.400	1.538	1.702	1.955	2.321	2.802	3.403	4.059	4.710	5.307	5.823	6.248	6.589	6.871
0.65	0.732	1.109	1.337	1.479	1.619	1.824	2.123	2.530	3.054	3.654	4.276	4.875	5.413	5.871	6.248	6.555
0.70	0.650	1.028	1.274	1.425	1.553	1.720	1.966	2.309	2.762	3.300	3.883	4.468	5.016	5.500	5.909	6.246
0.80	0.512	0.874	1.145	1.321	1.445	1.571	1.742	1.982	2.313	2.734	3.224	3.750	4.283	4.787	5.241	5.634
0.90	0.404	0.738	1.018	1.217	1.352	1.464	1.592	1.765	2.004	2.323	2.716	3.166	3.649	4.137	4.605	5.032
1.00	0.320	0.621	0.898	1.112	1.264	1.377	1.484	1.614	1.790	2.028	2.335	2.705	3.124	3.570	4.022	4.458
1.10	0.255	0.521	0.789	1.011	1.176	1.297	1.399	1.505	1.638	1.817	2.054	2.350	2.700	3.093	3.509	3.930
1.20	0.205	0.437	0.689	0.913	1.089	1.220	1.324	1.419	1.527	1.664	1.845	2.080	2.367	2.701	3.071	3.462
1.30	0.165	0.368	0.601	0.821	1.003	1.144	1.253	1.346	1.440	1.549	1.690	1.875	2.107	2.386	2.706	3.057
1.40	0.135	0.310	0.523	0.735	0.920	1.069	1.185	1.280	1.368	1.461	1.574	1.720	1.906	2.135	2.407	2.714
1.50	0.110	0.262	0.456	0.658	0.842	0.996	1.119	1.217	1.304	1.388	1.483	1.600	1.749	1.937	2.164	2.429
1.60	0.091	0.223	0.397	0.587	0.768	0.925	1.054	1.157	1.247	1.327	1.409	1.507	1.628	1.781	1.969	2.194
1.70	0.075	0.190	0.346	0.524	0.699	0.856	0.989	1.098	1.191	1.270	1.347	1.431	1.532	1.657	1.813	2.002
1.80	0.063	0.162	0.304	0.467	0.635	0.791	0.927	1.040	1.136	1.219	1.292	1.368	1.454	1.559	1.688	1.846
1.90	0.053	0.139	0.266	0.417	0.577	0.730	0.867	0.983	1.083	1.169	1.243	1.314	1.390	1.478	1.586	1.718
2.00	0.045	0.120	0.233	0.373	0.525	0.673	0.809	0.928	1.031	1.120	1.195	1.264	1.334	1.412	1.503	1.615
2.50	0.021	0.060	0.126	0.216	0.324	0.443	0.564	0.679	0.791	0.891	0.978	1.056	1.122	1.182	1.240	1.301
3.00	0.011	0.033	0.072	0.130	0.204	0.292	0.389	0.489	0.591	0.691	0.783	0.867	0.942	1.009	1.069	1.123
3.50	0.006	0.019	0.043	0.081	0.132	0.196	0.270	0.331	0.438	0.527	0.615	0.699	0.777	0.849	0.915	0.974
4.00	0.004	0.012	0.027	0.053	0.088	0.134	0.190	0.254	0.325	0.401	0.478	0.566	0.632	0.705	0.773	0.836
5.00	0.002	0.005	0.012	0.025	0.043	0.067	0.099	0.137	0.183	0.234	0.290	0.349	0.411	0.474	0.536	0.597
6.00	0.001	0.003	0.006	0.013	0.023	0.037	0.055	0.079	0.107	0.141	0.179	0.222	0.268	0.316	0.367	0.419

nuclear charge. The first extremum of $\Delta f_{\text{corr}}(s)$ is a maximum in cases where electron correlation causes contraction of the valence-shell electron density (Li to C and Na to Ar). For N to Ne, the opposite effects are observed (see above). Drastic changes in the $\Delta f_{\text{corr}}(s)$ curves occur at the transition from the first to the second row of the Periodic Table of elements (*cf.* the curves for Ne and Na or Mg, Fig. 3). This is in accord with corresponding strong changes in $\Delta D_{\mathrm{corr}}(r)$ (not shown) and in $\Delta V^{\mathrm{ne}}_{\mathrm{corr}}$ (and consequently in $\Delta V^{\mathrm{ee}}_{\mathrm{corr}}$, too, *cf.* Fig. 1).

Our $\Delta f_{\mathrm{corr}}(s)$ results agree qualitatively with the results of Tanaka & Sasaki (1971) for B to Ne based on *L*-shell CI calculations employing a rather small number of *s, p* and *d* functions and the results of Peixoto, Bunge & Bonham (1969) for Ne derived from a 65-term CI wavefunction. We obtained, however, much more pronounced correlation effects and observed a significant dependence of $\Delta f_{\mathrm{corr}}(s)$ on freezing the *K* electrons, even in the region of low *s* values. This indicates that rather small basis sets or restriction to *L*-shell correlation do not suffice to describe $\Delta f_{\mathrm{corr}}(s)$ adequately. The agreement with $\Delta f_{\mathrm{corr}}(s)$ results based on the independent electron-pair approximation (Naon & Cornille, 1973) is poor. The $\Delta f_{\mathrm{corr}}(s)$ results for Li and Be presented in this paper are in excellent agreement with those previously reported (Schmider, Esquivel, Sagar & Smith, 1993; Esquivel & Bunge, 1987); small deviations are observed in comparison with the data obtained from a slightly less accurate 55-term CI wavefunction (Benesch & Smith, 1970) for Be.

In addition to $\Delta f_{\mathrm{corr}}(s)$, Fig. 3 displays relativistic contributions $\Delta f_{\mathrm{rel}}(s)$ to the atomic form factors. These contributions were obtained from published $f(s)$ values which are based on relativistic Dirac–Fock calculations by subtracting the RHF results for $f(s)$. The relativistic data were taken from Doyle & Turner (1968). The significance of the relativistic effects is rather different for the various atoms considered. For Li, Be and B, practically no relativistic effects occur. Small effects are observed in the cases of F and Ne. The same is valid for the remaining first-row atoms in the region of higher *s* values. At low *s* values, however, significant minima in $\Delta f_{\mathrm{rel}}(s)$ occur for O and especially for C and N (*i.e.* for atoms in ^3P and ^4S states). Such minima are also characteristic of the corresponding second-row atoms (S, Si and P). For second-row atoms, in contrast to the first-row atoms, relativistic contributions are significant also at large *s* values. This obviously corresponds to the well known contraction of core-electron density by relativistic effects which increase with nuclear charge (the aforementioned minima in the $\Delta f_{\mathrm{rel}}(s)$ curves of C, N, O, Si, P and S imply a substantial valence-electron-density expansion).

For more accurate atomic form factors than those currently available, $\Delta f_{\mathrm{rel}}(s)$ and $\Delta f_{\mathrm{corr}}(s)$ are added to $f(s)$ calculated on the RHF level of approximation. From Fig. 3 where $\Delta f_{\mathrm{corr}}(s)$ and $\Delta f_{\mathrm{rel}}(s)$ and the sum of both contributions is displayed, we conclude that correlation effects are more important than the relativistic effects for all first-row atoms except for C and N. This, correspondingly, holds for the second-row atoms (*i.e.* with the exception of Si and P) as long as small *s* values are considered; at large *s* values, of course, relativistic effects dominate.

Table 2 presents the atomic form factors obtained in this work in a similar format to that in *International Tables for Crystallography* (Maslen, Fox & O'Keefe, 1992).

Some remarks are to be added concerning the reliability of our correlation calculations. The non-recovered correlation is due to the limited size of the basis set and the truncation of the CI expansion to all SD (singly and doubly excited) and a limited number of TQ configurations. The basis-set error with repect to $\Delta f_{\mathrm{corr}}(s)$ is negligible as systematic basis-set variations suggest. The limited number of higher excited configurations, however, implies larger uncertainties. In our calculations, $\Delta f_{\mathrm{corr}}(s)$ is always clearly dominated by the SD contributions (which generally correspond to more than 89% of the estimated total correlation energy, see Table 1). The TQ contributions, which essentially affect $\Delta f_{\mathrm{corr}}(s)$ only in the range of small *s* values (up to 5 Å^{-1}), are significant only in the case of Mg, Al and Si. The procedure of calculating the TQ contributions in the reduced bases (applied to the second-row atoms) seems to work rather reliably as investigations on first-row atoms as well as on Mg (where calculations in the large basis set were possible) suggest.

Concluding remarks

Atomic form factors $f(s)$ for Li to Ar were derived from *ab initio* MR-SDCI calculations which recover between 90 and 99% of the estimated total correlation energy. The correlation contributions $\Delta f_{\mathrm{corr}}(s)$ obtained are expected to be remarkably more precise than those hitherto known. For second-row atoms, correlation contributions of $f(s)$ have been calculated for the first time.

For all atoms considered, the correlation effects manifest themselves in the regions of low *s* values (between 0 and *ca* 5 to 15 Å^{-1}). In these regions, the correlation contributions $\Delta f_{\mathrm{corr}}(s)$ to $f(s)$ are generally more important than the relativistic contributions $\Delta f_{\mathrm{rel}}(s)$ known from the literature. The only exceptions are C, N, Si and P. At large *s* values, relativistic effects are generally more significant than the correlation effects, especially for second-row atoms.

The final atomic form factors presented in this work take into account correlation and relativistic contributions in an additive manner. The results are expected to be the most accurate ones available to date for first- and second-row atoms.

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The *Ab Initio* Crystal Structure Solution of Proteins by Direct Methods. III. The Phase Extension Process

By Carmelo Giacovazzo and Dritan Siliqi*

Dipartimento Geomineralogico, Università di Bari, Campus Universitario, Via Orabona 4, 70125 *Bari, Italy*

and Giuseppe Zanotti

Dipartimento di Chimica Organica, Università di Padova, Via Marzolo 1, *Padova, Italy*

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Abstract

In two preceding papers [Giacovazzo, Siliqi & Ralph (1994). *Acta Cryst.* A**50**, 503–510; Giacovazzo, Siliqi & Spagna (1994). *Acta Cryst.* A**50**, 609–621], a direct-phasing process was described which proved to be potentially able to solve *ab initio* crystal structures of proteins. The method uses the diffraction data of the native and of one isomorphous derivative. The main limitation of the approach was the small number of phased reflections rather than the quality of the assigned phases. In this paper, it is shown that the phasing process can be extended to about 40% of the measured reflections (up to the derivative resolution) without reducing significantly the quality of the new phases. Of the four test proteins examined, in one case it was possible to obtain fully interpretable electron-density maps.

Symbols and abbreviations

Symbols and notation are basically the same as in papers I and II (Giacovazzo, Siliqi & Ralph, 1994; Giacovazzo, Siliqi & Spagna, 1994). Since new symbols are necessary here and for the reader's convenience, we give a combined list below.

$F_p = \|F_p\| \exp(i\varphi)$	Structure factor of the protein
$F_d = \|F_d\| \exp(i\psi)$	Structure factor of the isomorphous derivative
$F_H = F_d - F_p$	Structure factor of the heavy-atom structure (*i.e.* the atoms added to the native protein)

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* Permanent address: Laboratory of X-ray Diffraction, Department of Inorganic Chemistry, Faculty of Natural Sciences, Tirana University, Tirana, Albania.