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Relativistic Hartree-Fock X-ray and Electron Scattering Factors

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Kinematic X-ray and electron scattering factors, found with the use of relativistic Hartree-Fock atomic fields, are tabulated for 76 atoms and ions. Parametric fits to these are given in the range of $\sin \theta/\lambda$ from 0.0 to 2.0 \AA^{-1} . A method is developed to obtain the electron structure factor for forward scattering for a crystal containing ionized atoms.

Introduction

A relativistic Hartree-Fock (R-HF) atomic wave function calculation has been programmed by Coulthard (1967). Results have been obtained by him and by the present authors for 76 atoms and ions. The calculation yields, among other data, the total charge densities $\rho(r)$ and atomic potentials $\varphi(r)$. From these, kinematic scattering factors for X-rays and electrons, $f_X(s)$ and $f_{el}(s)$, have been found by using the equations

$$f_X(s) = 4\pi \int_0^\infty r^2 \rho(r) \frac{\sin(4\pi sr)}{(4\pi sr)} dr \quad (1)$$

and

$$f_{el}(s) = \frac{8\pi^2 m_0 e}{h^2} \int_0^\infty r^2 \varphi(r) \frac{\sin(4\pi sr)}{(4\pi sr)} dr, \quad (2)$$

where $s = \sin \theta/\lambda \text{ \AA}^{-1}$.

Equation (2) was used only for neutral atoms. The case of ions will be dealt with separately. For asymmetric atoms, Harada & Kashiwase (1962) found $\lim_{s \rightarrow 0} f_{el}(s)$ depends on the direction in which the limit is taken. A single value is obtained in the present case, since the atom is considered as being spherically symmetrical.

A brief comparison, for mercury, between the R-HF scattering curves and those found from some other atomic models has been given previously (Doyle & Turner, 1967). Work by several authors (see Byron &

Joachim, 1967*a, b*) has taken some account of correlations between electrons in the atom. However, since this deals only with a few light atoms, the present tabulation may prove useful. The inclusion of correlations might be expected to decrease $f_X(s)$ for medium s , and to increase $f_{el}(s)$ for small and medium s . Except for the lightest atoms, the most sophisticated tables previously available were those based on the non-relativistic Hartree-Fock model by Freeman (1959) for lighter atoms, and on the Dirac-Slater model (relativ-

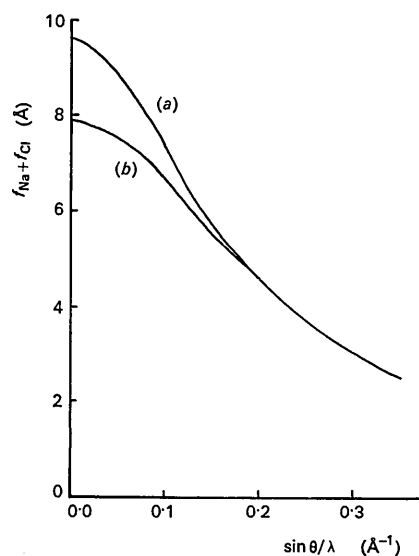


Fig. 1. $f_{Na}(s) + f_{Cu}(s)$ for (a) neutral and (b) ionized atoms.

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istic Hartree with a Slater statistical approximation to exchange) for all atoms (Cromer & Waber, 1965).

The atoms chosen in the accompanying tables represent a compromise between the desire to complete the periodic table, and the computing time available. Some light atoms such as helium for which better approximations have been calculated (see *International Tables for X-ray Crystallography*, Vol.III) were included, for completeness, and because they take little time. Coulthard's R-HF program is probably capable

of treating most atoms, though F- failed to converge, and difficulty may be met in dealing with some transition metals and rare earths.

Kinematic scattering from ionized atoms

$f_{el}(s)$ has generally been obtained from the Mott formula for $s \neq 0$. For $s=0$, the values $\pm \infty$ are found for an ion. It is desirable to find finite values at $s=0$ that can be used in a neutral unit cell containing ions.

Table 3. Parameters for the fit of $f_X(s)$

Table with 11 columns: Z, a1, b1, a2, b2, a3, b3, a4, b4, c, E. Rows list elements from He (Z=2) to U (Z=92) with corresponding numerical parameters.

Defining

$$\varphi^1(r) = \varphi(r) - \frac{e\Delta Z}{4\pi\epsilon_0 r}$$

where ΔZ is the ionic charge, (2) can be written as

$$f_{el}(s) = \frac{8\pi^2 m_0 e}{h^2} \int_0^\infty r^2 \varphi^1(r) \frac{\sin(4\pi sr)}{(4\pi sr)} dr + \frac{m_0 e^2 \Delta Z}{8\pi h^2 \epsilon_0 s^2} \quad (3)$$

This simply separates the coulomb field due to the excess or deficiency of charge on the nucleus from the remaining atomic field. The Fourier transform of a coulomb field, used to find the second term of (3), was evaluated originally by Bethe (1930). Values of $f_{el}(s)$ for $s \neq 0$ listed in Table 2 for ions were found by the use of (3), which is equivalent to using the Mott formula.

For $s=0$, the amplitude scattered from a crystal depends on the zero-order Fourier coefficient of potential

$$V_0 = \frac{1}{\Omega} \int V(\mathbf{r}) d\mathbf{r}$$

where Ω is the unit cell volume, and $V(\mathbf{r})$ the crystal field potential. V_0 is independent of ion positions in the unit cell. If all coulomb fields due to the excess and deficiency of charge on the nuclei in the unit cell are superimposed with their centres coincident, then they give a net contribution of zero to $V(\mathbf{r})$. Thus for any ion positions in a neutral unit cell, the structure factor depends only on the first term in (3), and it is these values which are given in Table 2 for $s=0$.

The (200), (400), ... structure factors for the fundamental cell of NaCl depend on $f_{Na}(s) + f_{Cl}(s)$. Fig. 1 shows this sum for neutral atoms and for singly ionized atoms. The value at $s=0$ is lower for the ionic case, showing the more effective screening of the nuclear fields by the ionized atoms.

Calculations

Values of $q(r)$ and $\varphi(r)$ are computed by Coulthard's program at up to 180 points, exponentially weighted towards the nucleus. Repeated use of an equal-interval formula based on 7 points (the 'six-strip rule') was employed for the numerical integration of (1) and (2) (see, for example, Abramowitz & Stegun (1965), p. 886). Although the third (and probably also the second)

Table 4(a). Parameters for the fit of $f_{el}(s)$. Neutral atoms

Z		a ₁	b ₁	a ₂	b ₂	a ₃	b ₃	a ₄	b ₄	E
2	HE	0.0906	18.1834	0.1814	6.2109	0.1095	1.8026	0.0362	0.2844	0.0220
3	LI	1.6108	107.6394	1.2460	30.4795	0.3257	4.5331	0.0946	0.4951	0.0849
4	BE	1.2498	60.8042	1.3335	18.5914	0.3603	3.6534	0.1055	0.4157	0.0629
5	P	0.9446	46.4438	1.3120	14.1778	0.4188	3.2228	0.1159	0.3767	0.0569
6	C	0.7307	36.9951	1.1951	11.2966	0.4563	2.8139	0.1247	0.3456	0.0500
7	N	0.5717	28.8465	1.0425	9.0542	0.4647	2.4213	0.1311	0.3167	0.0398
8	O	0.4548	23.7803	0.9173	7.6220	0.4719	2.1440	0.1384	0.2959	0.0326
9	F	0.3686	20.2390	0.8109	6.6093	0.4751	1.9310	0.1459	0.2793	0.0265
10	NE	0.3025	17.6396	0.7202	5.8604	0.4751	1.7623	0.1534	0.2656	0.0215
11	NA	2.2406	108.0039	1.3326	24.5047	0.9070	3.3914	0.2863	0.4346	0.1208
12	MG	2.2682	73.6704	1.8025	20.1749	0.8394	3.0191	0.2892	0.4046	0.0883
13	AL	2.2756	72.3220	2.4280	19.7729	0.8578	3.0799	0.3166	0.4076	0.0896
14	SI	2.1293	57.7748	2.5333	16.4756	0.8349	2.8796	0.3216	0.3860	0.0757
15	P	1.8882	44.8756	2.4605	13.5283	0.8046	2.6424	0.3204	0.3608	0.0617
16	S	1.6591	36.6500	2.3863	11.4881	0.7899	2.4686	0.3208	0.3403	0.0515
17	CL	1.4524	30.9352	2.2976	9.9798	0.7874	2.3336	0.3217	0.3228	0.0437
18	AR	1.2736	26.6823	2.1894	8.8130	0.7927	2.2186	0.3225	0.3071	0.0370
19	K	3.9507	137.0748	2.5452	22.4017	1.9795	4.5319	0.4617	0.4340	0.1379
20	CA	4.4696	99.5228	2.9708	22.6958	1.9696	4.1954	0.4818	0.4165	0.1094
21	SC	3.9659	98.9597	2.9169	20.6061	1.9254	3.8557	0.4802	0.3988	0.1043
22	TI	3.5653	81.9821	2.8181	19.0486	1.8930	3.5904	0.4825	0.3855	0.1019
23	V	3.2449	76.3789	2.6978	17.7262	1.8597	3.3632	0.4864	0.3743	0.0998
24	CR	2.3066	78.4051	2.3339	15.7851	1.8226	3.1566	0.4901	0.3636	0.1102
25	MN	2.7467	67.7862	2.4556	15.6743	1.7923	2.9998	0.4984	0.3569	0.0958
26	FE	2.5440	64.4244	2.3434	14.6806	1.7588	2.8539	0.5062	0.3502	0.0943
27	CC	2.3668	61.4306	2.2361	14.1798	1.7242	2.7247	0.5148	0.3442	0.0926
28	NI	2.2104	58.7267	2.1342	13.5530	1.6891	2.6094	0.5238	0.3388	0.0906
29	CU	1.5792	62.9403	1.8197	12.4527	1.6576	2.5042	0.5323	0.3331	0.1004
30	ZN	1.9418	54.1621	1.9501	12.5177	1.6192	2.4164	0.5434	0.3295	0.0869
31	GA	2.3205	65.6019	2.4855	15.4577	1.6879	2.5806	0.5992	0.3510	0.1035
32	GE	2.4467	55.8930	2.7015	14.3930	1.6157	2.4461	0.6009	0.3415	0.0870
33	AS	2.3989	45.7179	2.7898	12.8166	1.5288	2.2799	0.5936	0.3277	0.0712
34	SE	2.2980	38.8296	2.8541	11.5359	1.4555	2.1463	0.5895	0.3163	0.0597
35	BR	2.1659	33.8987	2.9037	10.4996	1.3951	2.0413	0.5886	0.3070	0.0519
36	KR	2.0338	29.9992	2.9271	9.5977	1.3425	1.9520	0.5888	0.2986	0.0452
37	RB	4.7760	140.7821	3.8588	18.9910	2.2339	3.7010	0.8683	0.4194	0.1558
38	SR	5.8478	104.9721	4.0026	19.3666	2.3420	3.7368	0.8795	0.4142	0.1313
42	MG	3.1199	72.4642	3.9061	14.6424	2.3615	3.2370	0.8504	0.3662	0.1089
47	AC	2.0355	61.4970	3.2716	11.8237	2.5105	2.8456	0.8372	0.3271	0.0948
48	CC	2.5737	55.6752	3.2586	11.8376	2.5468	2.7842	0.8379	0.3217	0.0856
49	IN	3.1528	66.6492	3.5565	14.4494	2.8180	2.9758	0.8842	0.3345	0.1025
50	SN	3.4495	59.1042	3.7349	14.1787	2.7779	2.8548	0.8786	0.3270	0.0900
51	SB	3.5644	50.4869	3.8437	13.3156	2.6866	2.6909	0.8638	0.3161	0.0764
53	I	3.4728	39.4411	4.0602	11.8161	2.5215	2.4148	0.8398	0.2976	0.0581
54	XE	3.3656	35.5094	4.1468	11.1170	2.4430	2.2940	0.8293	0.2892	0.0513
55	CS	6.0620	155.8336	5.9861	19.6951	3.3033	3.3354	1.0958	0.3793	0.1567
56	BA	7.8212	117.6575	6.0040	18.7782	3.2803	3.2634	1.1030	0.3760	0.1375
63	EU	6.2667	100.2983	4.8440	16.0662	3.2022	2.9803	1.2009	0.3674	0.1375
79	AG	2.3880	42.8656	4.2259	9.7430	2.6886	2.2641	1.2551	0.3067	0.0774
80	FG	2.6817	42.8217	4.2414	9.8557	2.7549	2.2951	1.2708	0.3067	0.0754
82	PB	3.5099	52.9141	4.5523	11.8840	3.1539	2.5713	1.3591	0.3205	0.0907
83	BI	3.8412	50.2608	4.6794	11.9988	3.1924	2.5598	1.3625	0.3177	0.0849
86	RN	4.0779	38.4058	4.9776	11.0204	3.0955	2.3549	1.3259	0.2991	0.0617
92	L	6.7668	85.9510	6.7287	15.6415	4.0135	2.9364	1.5607	0.3346	0.1187

Table 4(b). Parameters for the fit of $f_{el}(s)$. Ionized atoms

Z	ΔZ	a_1	b_1	a_2	b_2	a_3	b_3	a_4	b_4	E	
3	Li+	1	0.0538	1.0860	0.0206	7.6853	0.0587	3.1378	0.0237	0.1923	0.0082
4	Be2+	2	-0.0002	0.2171	0.0169	3.3691	0.0407	1.1282	0.0243	0.2008	0.0194
11	Na+	1	0.1677	11.2946	0.4740	4.2735	0.3590	1.4135	0.1289	0.2262	0.0092
12	Mg2+	2	0.0989	8.1847	0.3315	3.3711	0.2886	1.1900	0.1118	0.1984	0.0045
17	Cl-	-1	1.9290	50.1174	3.2667	13.4759	1.1666	3.0567	0.3972	0.3713	0.0729
19	K+	1	0.8880	18.3273	1.6382	6.7637	0.6271	1.8497	0.2816	0.2713	0.0220
20	Ca2+	2	0.6443	13.8112	1.2902	5.5116	0.5242	1.6178	0.2523	0.2453	0.0135
23	V2+	2	0.4754	19.2254	1.3279	5.9361	0.7998	1.8605	0.2496	0.2538	0.0241
25	Mn2+	2	0.4523	17.3232	1.2228	5.4583	0.8599	1.7444	0.3102	0.2422	0.0203
26	Fe2+	2	0.4328	16.4991	1.1715	5.2529	0.8819	1.6870	0.3157	0.2373	0.0187
26	Fe3+	3	0.3133	12.3214	0.9929	4.3988	0.7149	1.5040	0.2771	0.2174	0.0106
27	Co2+	2	0.4149	15.6581	1.1218	5.0435	0.8959	1.6265	0.3208	0.2323	0.0169
28	Ni2+	2	0.3932	14.9689	1.0741	4.8695	0.9086	1.5730	0.3266	0.2283	0.0156
29	Cu+	1	0.5401	20.5410	1.2368	5.9307	1.1176	1.7355	0.3843	0.2501	0.0276
30	Zn2+	2	0.3509	13.7756	0.9852	4.5632	0.9235	1.4749	0.3387	0.2212	0.0135
35	Br-	-1	2.8044	52.9153	4.1294	13.8053	1.7053	2.5144	0.7016	0.3511	0.0846
37	Rb+	1	1.5652	21.4061	2.3080	7.6576	1.1424	1.6782	0.5270	0.2693	0.0285
38	Sr2+	2	1.2452	16.6652	1.9124	6.4532	1.0007	1.4964	0.4833	0.2483	0.0190
50	Sn2+	2	1.4363	25.5762	2.2527	6.9676	1.7685	2.0370	0.6836	0.2641	0.0363
50	Sn4+	4	0.6327	10.3654	1.8013	4.0965	1.0063	1.3935	0.5307	0.2129	0.0078
53	I-	-1	4.2495	59.6448	5.6512	15.5905	2.9603	2.7837	0.9489	0.3300	0.0873
55	Cs+	1	2.7761	26.0552	3.3558	9.0139	2.1398	2.0273	0.7588	0.2654	0.0352

decimal places have no physical significance, the $f(s)$ values are tabulated to three places as an aid to interpolation. Tables 1 and 2 list $f_X(s)$ and $f_{el}(s)$ respectively, for values of s up to 6.0 \AA^{-1} . Values of $f_{el}(0)$ for ions are as described in the previous section.

Analytical approximations to $f(s)$, of the form

$$f(s) = \sum_{i=1}^n a_i \exp(-b_i s^2) + c \quad (4)$$

where the a_i , b_i and c are parameters determined by curve fitting procedures, were introduced by Vand, Eiland & Pepinsky (1957) for X-ray scattering factors. Tables of $f_X(s)$ parameters for $n=2$ were published by Forsyth & Wells (1959), while Cromer & Waber (1965) fitted the Dirac-Slater $f_X(s)$ curves with the use of 9 parameters ($n=4$). Smith & Burge (1962) used six parameters ($n=3$, $c=0$) in fitting electron scattering factors.

A non-linear least-squares curve fitting computer program due to Marquardt* (1963) has been used to determine 9-parameter approximations to $f_X(s)$ and 8-parameter approximations ($c=0$) to $f_{el}(s)$. These are listed in Table 3 and Table 4(a) respectively. 201 values of the functions, evaluated in the range $s=0.00$ to 2.00 were used. For $f_{el}(s)$, for ions, an additional term $0.023934\Delta Z/s^2$ was added to (4) for non-zero values of s . This is the contribution to $f_{el}(s)$ from the excess nuclear charge. The remaining eight parameters fit the Fourier transform of the non-coulombic atomic field, including $s=0$. Table 4(b) lists the eight parameters and the ionic charge for ionized electron scattering factors.

Since $f_{el}(s)$ asymptotes to a Lorentzian, a parametric fit using four Lorentzians was attempted. However, for s from 0.00 to 2.00 , the fit was significantly inferior,

so that the Gaussian parameters of (4) were retained.

For each atom, the root mean square value E of the deviation δ_i between theoretical and fitted f -values is expressed as a percentage of $f(0)$, i.e.

$$E = \frac{100}{f(0)} \left[\frac{\sum_{i=1}^{201} \delta_i^2}{201} \right]^{1/2}$$

These are listed in the last columns of Tables 3 and 4. The difference between actual and predicted values is rarely greater than 0.02, and is usually about 0.005.

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* This program is available through SHARE [number 3094(PA)].