Acta Cryst. (1999). A**55**, 648–651

Modified form factors from multiconfiguration Dirac–Fock wave functions for neutral atoms with Z = 70–100

Sylvian Kahane

Physics Department, Nuclear Research Center – Negev, PO Box 9001, Beer-Sheva 84190, Israel.
E-mail: skahane@bgumail.bgu.ac.il

(*Received 16 July 1998; accepted 7 December 1998*)

Abstract

Tables of modified X-ray scattering factors for neutral elements with Z = 70–100 have been calculated using multiconfiguration Dirac–Fock wave functions. The physical approximation is a next step beyond the usual form-factor approximation in calculating elastic scattering photon intensities. Differences as large as 3–6% compared to previous calculations of the same kind are obtained; differences from the usual form factors are much larger.

1. Introduction

The major form of interaction between photons and atoms, at the X-ray energies of interest in crystallography, is the elastic Rayleigh scattering. For these nonrelativistic energies, the Rayleigh scattering amplitude is approximated by the form factor of the charge distribution (Franz, 1935, 1936; Levinger, 1952; Florescu & Gavrila, 1976). These form factors are the most important components of the structure factors $F(hkl)$ used to analyse and interpret the crystallographic data.

A great deal of effort and ingenuity has been invested in obtaining accurate predictions of the atomic form factors. Earlier calculations were produced by Freeman (1959), based on nonrelativistic Hartree–Fock–Slater wave functions (Herman & Skillman, 1963), by Cromer & Waber (1965), using the Dirac–Slater model (Liberman, Cromer & Waber, 1971), and by Doyle & Turner (1968), using the relativistic Hatrtree–Fock wave functions of Coulthard (1967). More recent theoretical studies were performed by Thakkar & Smith (1992), including electron correlations by Wang *et al.* (1993), starting from nonrelativistic Hartree–Fock wave functions by Rez *et al.* (1994), using relativistic wave functions and interactions by Wang *et al.* (1995), including electron correlations by Meyer *et al.* (1995), including electron correlations, and by Wang *et al.* (1996), using multiconfiguration Dirac–Hartree–Fock (DHF). Comprehensive tabulations have been published by Hubbell *et al.* (1975) (non-relativistic) and Hubbell & Øverbø (1979) (relativistic), and the standard of crystallographic usage by Cromer & Waber (1974).

All of the above effort was concentrated on using improved wave functions in the calculation of the form factors. Comparatively much less attention has been paid to obtaining Rayleigh scattering amplitudes in formalisms going beyond the form-factor approximation. The most complete calculations of the Rayleigh scattering amplitudes are the S-matrix calculations. They were pioneered by Brown and co-workers (Brown *et al.*, 1955; Brenner *et al.*, 1955; Brown & Mayers, 1956, 1957) for pure Coulomb potential fields, improved by Johnson and co-workers (Johnson & Feiock, 1968; Lin *et al.*, 1975; Johnson & Cheng, 1976) for self-consistent potential fields, and continued in a systematic investigation by Kissel and co-workers (Kissel *et al.*, 1980, 1995; Kissel & Pratt, 1985; Kane *et al.*, 1986; Roy *et al.*, 1983; Zhou *et al.*, 1990). These kinds of calculations are extremely difficult to perform and as such are restricted to particular electronic shells (K, L, M) and to a restricted number of elements.

An approximation of considerably less complexity than the S matrix but representing an improvement over the form factor (FF) is the modified form-factor (MFF) approximation (Franz, 1936; Brown & Mayers, 1957), which takes into account corrections due to the electron binding and reproduces the zero-angle infinite energy amplitude calculated by Levinger & Rustgi (1956). Moreover, expanding MFF in powers of $Z\alpha$, the first two terms in the Born-approximation calculation of Brown & Woodward (1952) are also reproduced. A tabulation of MFFs, based on the wave functions of Liberman, Cromer & Waber (1971) has been presented by Schaupp *et al.* (1983) [a similar tabulation can be found at the Livermore Laboratory World-Wide Web (WWW) site http://www.phys.llnl.gov/pub/rayleigh/mftab].

The aim of the present work is to present new calculations of MFFs based on improved and more modern wave functions. We used the multiconfiguration Dirac–Fock package of Grant *et al.* (1980), which calculates the exchange terms correctly, giving a considerable improvement over the local Slater approximation of Liberman, Cromer & Waber (1971). Moreover, we used true multiconfigurations, as opposed to the single configuration used by Schaupp *et al.* (1983), and maintained the correct nonrelativistic limit.

2. Form-factor and modified form-factor approximations

The scattering of a photon by a bound electron is described by the two Feynman diagrams of Fig. 1. The corresponding second-order *S*-matrix scattering amplitude is given by (Akhiezer & Berestetskii, 1965)

$$A_{i\to f} = \frac{2\pi\alpha}{\omega}\sum_n\left[\frac{\langle i|O_f^*|n\rangle\langle n|O_i|i\rangle}{E_n-E_i-\omega} + \frac{\langle i|O_i|n\rangle\langle n|O_f^*|i\rangle}{E_n-E_i+\omega}\right], \tag{1}$$

where ω is the photon energy, $O_i = \varepsilon_i\exp(-i\mathbf{k}_i\cdot\mathbf{r})$ is the initial electromagnetic field, and $|i\rangle$ is the initial and final electron state.

In the limit of high energy and small momentum transfer $\mathbf{q} = \mathbf{k}_f - \mathbf{k}_i$, this expression can be simplified to (Goldberger & Low, 1968)

$$A^R = -r_0(\varepsilon_i\varepsilon_f^*)\left\langle i\left|\exp(-i\mathbf{q}\cdot\mathbf{r})\frac{mc^2}{E_i-V-c(\mathbf{q}\cdot\mathbf{p})}\right|i\right\rangle, \tag{2}$$

where $\mathbf{p}$ is the electron momentum and V the potential seen by the electron. Under the assumption that the binding energy $B_i = |E_i - mc^2|$, the potential V and the electron momentum $\mathbf{p}$ are all much smaller than mc^2, the denominator reduces to mc^2 and one obtains the form-factor (FF) approximation

$$A^{\mathrm{FF}} = -r_0(\varepsilon_i\varepsilon_f^*)f(q) \tag{3}$$

with

$$f(q) = 4\pi\sum_i\int\rho_i(r)\frac{\sin qr}{qr}r^2\,\mathrm{d}r. \tag{4}$$

The summation is over all the electronic shells.

In the modified form-factor (MFF) approximation, the $E_i - V$ term is kept and only the $c(\mathbf{q}\cdot\mathbf{p})$ term is dropped:

$$A^{\mathrm{MFF}} = -r_0(\varepsilon_i\varepsilon_f^*)g(q) \tag{5}$$

with

$$g(q) = 4\pi\sum_i\int\rho_i(r)\frac{\sin qr}{qr}\left[\frac{mc^2}{E_i-V(r)}\right]r^2\,\mathrm{d}r. \tag{6}$$

In terms of linear polarization, the amplitudes are $A_\parallel = r_0h(q)\cos\theta$ and $A_\perp = r_0h(q)$, with θ the scattering angle. $h(q)$ stands for $f(q)$ or $g(q)$ depending on the approximation employed. The differential cross section will be:

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} = \tfrac{1}{2}(A_\parallel^2 + A_\perp^2). \tag{7}$$

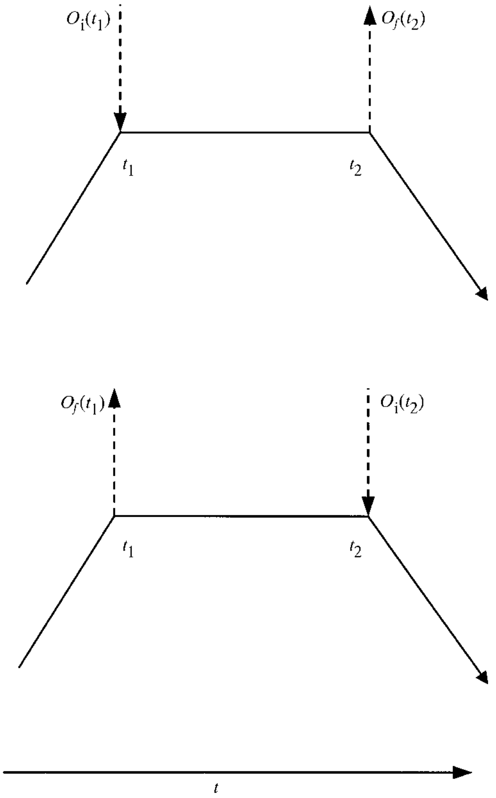

Fig. 1. Feynman diagrams describing the elastic scattering process. Each diagram corresponds to one of the terms appearing in equation (1).

3. MFF calculations

As stated before, the wave functions were calculated with the multiconfiguration Dirac–Fock package of Grant *et al.* (1980). In a recent calculation of form factors by Wang *et al.* (1996), a point was made that it is necessary for the wave functions employed to approach the correct nonrelativistic limit when $c \to \infty$. This is so for closed shells, when only a single configuration is present. For open shells, when more than one relativistic configuration corresponds to the nonrelativistic term,

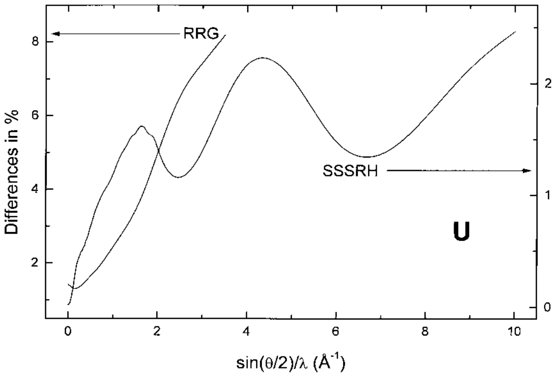

Fig. 2. Differences, in percent, compared with the FF calculations of Rez *et al.* (1994) (RRG) and the MFF calculations of Schaupp *et al.* (1983) (SSSRH).

one has to consider all the relativistic configurations in order to obtain the desired nonrelativistic limit. The wave functions were calculated in the OL mode when only one configuration was present (*i.e.* optimizing the single atomic level energy), and in the EOL mode when more than one relativistic configuration was considered (*i.e.* the optimization was performed on a number of atomic levels, but no more than ten at once). The nonrelativistic ground-state terms, used to decide which relativistic configurations to employ, were taken from the WWW site of Sheffield University (http://www.shef.co.uk/chem/web-elements). They are mentioned in the tables together with the number of relativistic configurations generated.

A consequence of using the Dirac–Fock program is that the potential appearing in equation (6) is different for each shell. This is distinct from the case of Slater-type exchange, where the potential is universal for all the electrons.

The present work may be compared with the work of Rez *et al.* (1994) (RRG), who used the same type of wave functions but calculated the FFs, and with that of Schaupp *et al.* (1983) (SSSRH), who calculated MFFs but used single-configuration Slater-type exchange. In Fig. 2, we present a comparison of the present calculations for uranium with those of RRG and SSSRH. As expected, the differences, in percent, with respect to RRG are quite large, climbing rapidly to 8% at 4 Å^{-1}. This is to be expected because of the different physics involved in the two types of calculations. Even compared to SSSRH, we observe a 1.5% average difference over most of the interval. According to equation (7), a 1.5% difference in the scattering amplitude corresponds to 3–6% differences in the scattering cross sections (*i.e.* in the expected X-ray scattering intensities). The smallest difference is at $\theta = 90^\circ$ scattering where $\cos\theta = 0$ and only the $A_\perp$ amplitude contributes. The maximum difference is at $\theta = 0^\circ$ scattering, where both $A_\parallel$ and $A_\perp$ contribute fully.

In Table 1, we present a small sample of the calculations. The full calculations, for all the elements in the Z = 70–100 interval and for an extended range of $\sin(\theta/2)/\lambda$, have been deposited.†

4. Conclusions

We have presented a tabulation of the modified X-ray sattering factor for all the neutral elements with Z = 70–100. This approximation is believed to be a better one than the usual form-factor approximation in describing the elastic scattering of X-rays from bounded electrons. We have also improved on a previous tabulation of the same quantities by employing better wave functions in the relativistic multiconfiguration mode with a proper nonrelativistic limit.

Table 1. *Modified form factors*

Elemental notation, atomic number Z, ground-state term and the number of relativistic configurations (rel. config.) used in the calculations are specified.

$\sin(\theta/2)/\lambda$ (Å^{-1})	Pa ($^4K_{11/2}$) 13 rel. config. $Z = 91$	U ($^5L_6$) 44 rel. config. $Z = 92$	Np ($^5L_{11/2}$) 126 rel. config. $Z = 93$
0.00	89.6769	90.7123	91.6773
0.01	89.5975	90.6339	91.6007
0.02	89.3630	90.4020	91.3746
0.03	88.9843	90.0270	91.0083
0.04	88.4774	89.5246	90.5166
0.05	87.8621	88.9138	89.9175
0.06	87.1597	88.2153	89.2302
0.07	86.3905	87.4489	88.4739
0.08	85.5730	86.6328	87.6658
0.09	84.7225	85.7822	86.8206
0.10	83.8511	84.9091	85.9503
0.11	82.9677	84.0226	85.0639
0.12	82.0786	83.1290	84.1677
0.13	81.1876	82.2325	83.2663
0.14	80.2973	81.3357	82.3624
0.15	79.4092	80.4402	81.4580
0.16	78.5241	79.5467	80.5543
0.17	77.6425	78.6561	79.6521
0.18	76.7650	77.7688	78.7521
0.19	75.8922	76.8852	77.8551
0.20	75.0245	76.0061	76.9617
0.22	73.3080	74.2642	75.1896
0.24	71.6221	72.5500	73.4435
0.26	69.9738	70.8709	71.7314
0.28	68.3694	69.2338	70.0607
0.30	66.8135	67.6443	68.4376
0.32	65.3089	66.1062	66.8664
0.34	63.8569	64.6214	65.3495
0.36	62.4570	63.1904	63.8880
0.38	61.1077	61.8121	62.4811
0.40	59.8065	60.4847	61.1272
0.42	58.5505	59.2054	59.8240
0.44	57.3367	57.9714	58.5686
0.46	56.1620	56.7796	57.3580
0.48	55.0237	55.6269	56.1892
0.50	53.9190	54.5106	55.0591
0.55	51.2908	51.8630	52.3865
0.60	48.8340	49.3967	49.9056
0.65	46.5332	47.0914	47.5923
0.70	44.3792	44.9345	45.4309

References

Akhiezer, A. I. & Berestetskii, V. B. (1965). *Quantum Electrodynamics*. New York/London/Sydney: Interscience.

Brenner, S., Brown, G. E. & Woodward, J. B. (1955). *Proc. R. Soc. London Ser. A*, **227**, 59–72.

---

† Supplementary data for this paper are available from the IUCr electronic archives (Reference: HR0040). Services for accessing these data are described at the back of the journal.

Brown, G. E. & Mayers, D. F. (1956). *Proc. R. Soc. London Ser. A*, **234**, 387–390.

Brown, G. E. & Mayers, D. F. (1957). *Proc. R. Soc. London Ser. A*, **242**, 89–95.

Brown, G. E., Peierls, R. E. & Woodward, J. B. (1955). *Proc. R. Soc. London Ser. A*, **227**, 51–58.

Brown, G. E. & Woodward, J. B. (1952). *Proc. Phys. Soc. London Ser. A*, **65**, 977–983.

Coulthard, M. A. (1967). *Proc. Phys. Soc.* **91**, 44–49.

Cromer, D. T. & Waber, J. T. (1965). *Acta Cryst.* **18**, 104–109.

Cromer, D. T. & Waber, J. T. (1974). *International Tables for X-ray Crystalliography*, Vol. IV, pp. 71–74. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

Doyle, P. A. & Turner, P. S. (1968). *Acta Cryst.* A**24**, 390–397.

Florescu, V. & Gavrila, M. (1976). *Phys. Rev. A*, **14**, 211–235.

Franz, W. (1935). *Z. Phys.* **95**, 652–668.

Franz, W. (1936). *Z. Phys.* **98**, 314–320.

Freeman, A. J. (1959). *Acta Cryst.* **12**, 261–271.

Goldberger, M. L. & Low, F. E. (1968). *Phys. Rev.* **176**, 1778–1781.

Grant, I. P., McKenzie, B. J., Norrington, P. H., Mayers, D. F. & Pyper, N. C. (1980). *Comput. Phys. Commun.* **21**, 207–231.

Herman, F. & Skillman, S. (1963). *Atomic Structure Calculations.* Englewood Cliffs, NJ: Prentice Hall.

Hubbell, J. H. & Øverbø, I. (1979). *J. Phys. Chem. Ref. Data*, **8**, 69–109.

Hubbell, J. H., Veigele, W. J., Briggs, E. A., Brown, R. T., Cromer, D. T. & Howerton, R. J. (1975). *J. Phys. Chem. Ref. Data*, **4**, 471–538; erratum (1977), **6**, 615–616.

Johnson, W. R. & Cheng, K. T. (1976). *Phys. Rev. A*, **13**, 692–698.

Johnson, W. R. & Feiock, F. D. (1968). *Phys. Rev.* **168**, 22–31.

Kane, P. P., Kissel, L., Pratt, R. H. & Roy, S. C. (1986). *Phys. Rep.* **140**, 75–159.

Kissel, L. & Pratt, R. H. (1985). *Atomic Inner-Shell Physics*, edited by B. Crasemann, pp. 465–532. New York: Plenum Press.

Kissel, L., Pratt, R. H. & Roy, S. C. (1980). *Phys. Rev. A*, **22**, 1970–2004.

Kissel, L., Zhou, B., Roy, S. C., Sen Gupta, S. K. & Pratt, R. H. (1995). *Acta Cryst.* A**51**, 271–288.

Levinger, J. S. (1952). *Phys. Rev.* **87**, 656–662.

Levinger, J. S. & Rustgi, M. L. (1956). *Phys. Rev.* **103**, 439–442.

Liberman, D. A., Cromer, D. T. & Waber, J. T. (1971). *Comput. Phys. Commun.* **2**, 107–113.

Lin, C. P., Cheng, K. T. & Johnson, W. R. (1975). *Phys. Rev. A*, **11**, 1946–1956.

Meyer, H., Müller, T. & Schweig, A. (1995). *Acta Cryst.* A**51**, 171–177.

Rez, D., Rez, P. & Grant, I. (1994). *Acta Cryst.*, A**50**, 481–497.

Roy, S. C., Kissel, L. & Pratt, R. H. (1983). *Phys. Rev. A*, **27**, 285–290.

Schaupp, D., Schumacher, M., Smend, F., Rullhusen, P. & Hubbell, J. H. (1983). *J. Phys. Chem. Ref. Data*, **12**, 467–512.

Thakkar, A. J. & Smith, V. H. Jr (1992). *Acta Cryst.* A**48**, 70–71.

Wang, J., Esquivel, R. O., Smith, V. H. Jr & Bunge, C. F. (1995). *Phys. Rev. A*, **51**, 3812–3818.

Wang, J., Sagar, R. P., Schmider, H. & Smith, V. H. Jr (1993). *At. Data Nucl. Data Tables*, **53**, 233–269.

Wang, J., Smith, V. H. Jr, Bunge, C. F. & Jáuregui, R. (1996). *Acta Cryst.* A**52**, 649–658.

Zhou, B., Pratt, R. H., Roy, S. C. & Kissel, L. (1990). *Phys. Scr.* **41**, 495–498.