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Investigation of the Angle Dependence of the Photon–Atom Anomalous Scattering Factors

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Abstract

The angle dependence of the elastic photon–atom scattering amplitude is investigated using full relativistic S-matrix calculations for guidance. A simple quantitative approach is developed based on the full nonrelativistic amplitude for Rayleigh scattering from the ground state of a hydrogenic ion and it is successfully applied to neutral atoms of low and intermediate nuclear charge. This framework is useful for scattering of X-rays with energies above the K-shell ionization threshold but below energies where major relativistic corrections are necessary. The generalized anomalous scattering factors presented here go beyond the usual angle-independent anomalous-scattering-factor approximation, permitting a discussion of the full angular dependence of the anomalous scattering factors. Simple formulas, expressed in terms of elementary functions and a lookup table, are presented for these generalized anomalous scattering factors. Numerical examples illustrate that the angle dependence can be substantial. A fairly good representation of full numerical results is achieved.

1. Introduction

Elastically scattered photons are used extensively as a tool for determining the composition and structure of materials. These procedures utilize relatively simple approximations to the Rayleigh scattering amplitude for elastic photon scattering from bound atomic electrons. Perhaps the most commonly used approximation to the cross section (where the incident beam of photons is unpolarized and where the polarization of the scattered photons is not observed), described as form-factor approximation with angle-independent anomalous scattering factors (FF + ASF), may be written

$$d\sigma/d\Omega = (r_0^2/2)(1+\cos^2\theta)\Big|\sum_j M_j(\mathbf{k}_1\cdot\mathbf{k}_2)\Big|^2, \quad (1)$$

where the sum is over all electrons in the target, r_0 is the classical electron radius, $\theta = 2\Theta$ (θ is the photon scattering angle and Θ is the Bragg angle) and

$$M_j(\mathbf{k}_1\cdot\mathbf{k}_2) = -[f_j(q) + f_j'(q) + if_j''(\omega)]. \quad (2)$$

Equations (1) and (2) are exact for forward scattering and, as will be seen subsequently, approximate for finite angles. In (2), we may make the nonrelativistic approximation

$$f_j(q) = \textstyle\int d\mathbf{r}\rho_j(\mathbf{r})\exp(i\mathbf{q}\cdot\mathbf{r}), \quad (3)$$

where f_j is the form factor (a function of photon momentum transfer $\mathbf{q}$), obtained by evaluating the 'A^2' term of the nonrelativistic photon–electron interaction in lowest nonvanishing order. Equation (1) gives most of the total cross section for elastic scattering, particularly at high energy. Because the scattering is elastic, occurring coherently from all of the electrons of the target, and owing to its particularly simple form, the form factor has been used extensively in determining the structure of macromolecular systems, sometimes simply taken as $M_j \simeq -f_j$.

The other quantities in (2), f' and f'', are called the anomalous scattering factors. They are real and are given, nonrelativistically, by

$$f_j'(\omega) = (2/\pi)\textstyle\int[\omega' f_j''(\omega')/(\omega'^2-\omega^2)]\,d\omega' \quad (4)$$

and

$$f_j''(\omega) = -(\omega/4\pi c)\sigma_j(\hbar\omega), \quad (5)$$

where σ_j is the total cross section for a photon interacting with an electron bound in the jth subshell. Equation (4) is a dispersion relation connecting the real and imaginary parts of the forward-scattering amplitude. Equation (5) may be obtained from the optical theorem, which related the imaginary part of the forward-scattering amplitude to the total photon–atom cross section, σ. The choice of sign in (5) has recently been discussed by Kissel, Zhou, Roy, Sen Gupta & Pratt (1995). These anomalous scattering factors con-

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tain information about the edge structure of atoms, where f'' includes a Rydberg series of resonances, and are useful in identifying the composition of scattering systems (Materlik, Sparks & Fischer, 1994).

Within a nonrelativistic description, the FF + ASF scheme gives the exact forward elastic scattering amplitude. However, at finite angles, this method approximates the second-order evaluation of the $\mathbf{p} \cdot \mathbf{A}$ terms of the elastic scattering amplitude with the forward-angle values. A full nonrelativistic treatment of elastic photon scattering (in lowest order) is obtained by evaluating these $\mathbf{p} \cdot \mathbf{A}$ terms exactly together with the form factor. Such nonrelativistic calculations have been done, without further approximation, only for photons scattering from the K shell of hydrogenic ions by Gavrila & Costescu (1970) (as discussed below there have been numerical, not analytic, relativistic calculations). In addition to neglecting the angle dependence of the $\mathbf{p} \cdot \mathbf{A}$ terms of the transition amplitude, the FF + ASF approximation also omits relativistic effects in the amplitude.

Full independent-particle-approximation (IPA) S-matrix (SM) calculations, performed within the framework of relativistic quantum electrodynamics, have been available for some time (Brown, Peierls & Woodward, 1955; Brenner, Brown & Woodward, 1955; Brown & Mayers, 1956, 1957; Johnson & Feiock, 1968; Kissel, Pratt & Roy, 1980; Kane, Kissel, Pratt & Roy, 1986; Kissel *et al.*, 1995). Agreement between this approach and experiment is rather good over most regimes of X-ray and γ-ray energy – not too close to edges – and all scattering angles, for all elements that have been tested (Kane *et al.*, 1986; Basavaraju, Kane, Kissel & Pratt, 1994; Basavaraju, Kane, Lad, Kissel & Pratt, 1995). Although these calculations require considerable computing resources, a substantial body of S-matrix data has been accumulated (see for example the description of Kissel *et al.*, 1995) and continuing improvements to the code and method have made evaluation much less costly.

The FF + ASF scheme has been used extensively but its region of validity has only recently been examined relative to the accumulating body of S-matrix data (Kissel *et al.*, 1995). The data indicates that, although the FF + ASF approach is useful, the region of its validity is smaller than was previously assumed. For example, Kissel & Pratt (1990) pointed out that a Z-dependent energy-independent correction is necessary to bring agreement with the S-matrix calculations. This correction is needed for all elements but is particularly significant at high Z. A version of the FF + ASF approach that more accurately represents the S-matrix data makes use of the modified form factor (Franz, 1936) and corresponding modified anomalous scattering factors (MF + ASF). The modified form factor accounts for additional electron binding effects beyond the form factor. It includes the correction of Kissel & Pratt (1990). Even this MF + ASF scheme breaks down for γ-rays scattered into back angles from heavy elements; the assumption of angle-independent anomalous scattering factors is not quantitatively correct at higher energies. Data for the form factor, the modified form factor and the corresponding anomalous scattering factors are accessible electronically at http://www-phys.llnl.gov/V_Div/scattering/elastic.html.

Recently, Costescu, Bergstrom, Dinu & Pratt (1994) have greatly simplified the full nonrelativistic hydrogenic ground-state amplitude, obtaining results in a series expansion in terms of elementary functions and the dipole nonrelativistic hydrogenic ground-state amplitude that had first been obtained by Gavrila (1967). The nonrelativistic dipole approximation suffices to predict the dominant s-state photoionization across sections (Oh, McEnnan & Pratt, 1976; Ron, Goldberg, Stein, Manson, Pratt & Yin, 1994) and consequently, from (4) and (5), forward anomalous scattering amplitudes, to quite high energies. However, the results of Costescu *et al.* (1994) made clear the importance of retardation and multipole corrections in determining the angular distribution of the scattered photons. (At the same time, it may still be supposed that, well above the K edge, K-shell contributions still dominate the full anomalous amplitudes.) The nonrelativistic framework used was expected to be valid in regimes where retardation corrections are larger than relativistic corrections, *i.e.* for scattering of photons with energies up to several times the K-shell photoionization threshold from elements of low to moderate nuclear charge. Costescu *et al.* (1994) demonstrated this explicitly by comparisons with S-matrix data.

In the next section, we used the results of Costescu *et al.* (1994) to explicitly obtain the angle dependence of the K-shell anomalous scattering factors. At energies above the K-shell ionization threshold, the total photon–atom cross section and, as a consequence of (4) and (5), the anomalous scattering factors are dominated by the ionization of the K-shell electrons. Hence, the K-shell results of Costescu *et al.* should also provide neutral-atom anomalous scattering factors and their angle dependence that is needed to correct the FF + ASF scheme. In the last section, we present numerical examples illustrating the nature of these corrections. We also give conclusions regarding our results, including when angle-dependent corrections to the FF + ASF scheme are necessary and when one needs to go beyond the formulas given here.

2. Formalism

The full angle-dependent matrix element – relativistic or nonrelativistic – for elastic photon scattering from bound electrons in a closed-shell atom is

$$A_{\varepsilon 1 \varepsilon 2} = (\varepsilon_1 \cdot \varepsilon_2^*) M(\mathbf{k}_1 \cdot \mathbf{k}_2) + (\varepsilon_1 \cdot \mathbf{k}_2)(\varepsilon_2^* \cdot \mathbf{k}_1) N(\mathbf{k}_1 \cdot \mathbf{k}_2), \quad (6)$$

where ε_1 and ε_2 are the directions of the initial and final photon polarizations and where $\mathbf{k}_1$ and $\mathbf{k}_2$ are the directions of the incident and scattered photon momenta.

Comparing this equation to (1)–(5), one sees that the FF + ASF scheme is an exact evaluation of the nonrelativistic amplitude for forward scattering only. The only dynamical contribution to the angle dependence in this approximation comes from the form factor. The remaining real and imaginary parts of M are approximated by their value at $\theta = 0$. N does not contribute to the full scattering amplitude at forward angle and, since it is not determined from the photoeffect cross section, is normally neglected in FF + ASF at all angles. (It is true as we will see later that N is smaller in magnitude than M.) In order to obtain the angle dependence of the anomalous scattering factors, the full angle dependence of the amplitude M needs to be retained as does the contribution of N.

Costescu *et al.* (1994) have derived the following approximate expressions for the non-relativistic Coulomb K-shell amplitudes, using the first three terms in an expansion of the exact nonrelativistic amplitude in the parameter $(k\alpha Z \sin\theta/2)^2$:

$$\begin{aligned} M(k, \alpha Z, \theta) &= -f(q, \alpha Z) + [1 - (\alpha Z)^2 \\ &\quad + (\tfrac{5}{8}k^2 + 1)(\alpha Z)^4][Q(k) + R(k)] \\ &\quad + k(\alpha Z)^2[1 - \tfrac{7}{4}(\alpha Z)^2][Q(k) - R(k)] + (\alpha Z)^2 \\ &\quad - (\alpha Z)^4 - \{\tfrac{6}{5}(\alpha Z)^2[1 - 2(k^2 + 1) + (\alpha Z)^2] \\ &\quad \times [1 - Q(k) - R(k)] + (k/5)(\alpha Z)^2 \\ &\quad \times [8 - 25(\alpha Z)^2][Q(k) - R(k)] \\ &\quad + (23/10)k^2(\alpha Z)^4\} \sin^2(\theta/2) \\ &\quad + [2(\alpha Z)^4/35]\{12(3k^2 + 2)[Q(k) + R(k)] \\ &\quad - 59k[Q(k) - R(k)] - 4(k^2 + 6)\} \sin^4(\theta/2) \quad (7) \end{aligned}$$

and

$$\begin{aligned} N(k, \alpha Z, \theta) &= \{\tfrac{6}{10}(\alpha Z)^2[1 - 2(k^2 + 1)(\alpha Z)^2][1 - Q(k) - R(k)] \\ &\quad + (k/10)(\alpha Z)^2[8 - 25(\alpha Z)^2][Q(k) - R(k)] \\ &\quad + (23/20)k^2(\alpha Z)^4\} \\ &\quad - [2(\alpha Z)^4/35]\{12(3k^2 + 2)[Q(k) + R(k)] \\ &\quad - 59k[Q(k) - R(k)] - 4(k^2 + 6)\} \sin^2(\theta/2), \quad (8) \end{aligned}$$

where

$$k = 2\hbar\omega/[(\alpha Z)^2 mc^2]. \quad (9)$$

Table 1. *Values of R and of the real and imaginary parts of the functions Q for scaled photon energies* $1.05 \le k \le 274$

k	Re Q	Im Q	R
1.05	−0.370	1.131	0.254
1.10	−0.395	1.046	0.248
1.20	−0.425	0.902	0.238
1.30	−0.439	0.785	0.229
1.40	−0.442	0.690	0.220
1.50	−0.438	0.611	0.212
1.75	−0.415	0.463	0.194
2.00	−0.386	0.363	0.180
2.50	−0.328	0.239	0.156
3.00	−0.280	0.168	0.138
4.50	−0.189	7.572E−02	1.036E−01
6.00	−0.140	4.218E−02	8.305E−02
12.00	−6.596E−02	9.774E−03	4.672E−02
24.00	−3.102E−02	2.126E−03	2.513E−02
48.00	−1.482E−02	4.394E−04	1.313E−02
96.00	−7.198E−03	8.725E−05	6.733E−03
274.00	−2.467E−03	7.145E−06	2.404E−03

The functions Q and R are universal functions of the photon energy, $\hbar\omega$, and the nuclear charge, Z, through the variable k, restricted by the condition $k \ll 2/\alpha Z$ if the results are to be used for all angles. Detailed expressions for these functions may be found in the work of Costescu *et al.* (1994). We give values of these functions in Table 1 for $k > 1$. This table was compiled to give values of Q and R accurate to at least 1% using linear interpolation on the logarithms of the energies and values. Note that the amplitude N is essentially contained in the calculation of M. The isotropic part of N is given by the negative of half the coefficient of the $\sin^2(\theta/2)$ term of M and the negative of the coefficient of the $\sin^2(\theta/2)$ term of N is precisely the coefficient of the $\sin^4(\theta/2)$ in M.

The term anomalous scattering refers to that part of the scattering that goes beyond the form-factor (or modified-form-factor) approximation. The expressions usually used to describe the anomalous part of the scattering give the exact nonrelativistic result at forward angle. As can be seen from (6), the amplitude N does not contribute to the overall scattering amplitude at $\theta = 0°$ even though N may not be zero there. In extending the notion of anomalous scattering factors to finite angles, where M and N both contribute to the overall scattering amplitude, the anomalous scattering factors include contributions both from M and N. However, the relative mix of M and N in the overall scattering amplitude depends in detail on the scattering geometry (*i.e.* on the polarization of the incident beam and on the polarization of the observed scattered photons). In what follows, we shall use the symbols $f'(\omega, \theta)$ and $f''(\omega, \theta)$ to denote the real (excluding the form factor) and the imaginary parts of M, so

$$M_j(\mathbf{k}_1 \cdot \mathbf{k}_2) = -[f_j(q) + f_j'(\omega, \theta) + i f_j''(\omega, \theta)]. \quad (10)$$

Similarly, we shall use the symbols $f'''(\omega, \theta)$ and $f''''(\omega, \theta)$ to denote the real and the imaginary parts of N, so

$$N_j(\mathbf{k}_1 \cdot \mathbf{k}_2) = -[f_j'''(\omega, \theta) + i f_j''''(\omega, \theta)]. \qquad (11)$$

All of these quantities contribute to anomalous scattering and should be considered 'generalized anomalous scattering factors' for scattering at arbitrary angles.

3. Numerical results

In order to illustrate the angle dependence of the non-form-factor or anomalous terms in elastic scattering, we calculate the angle-dependent anomalous scattering factors given by the real and imaginary parts of (7) and (8) for scattering from calcium over a wide range of photon energies (from the nonrelativistic hydrogenic K-shell binding energy $k = 1$ to 10 times this threshold).

In Figs. 1 and 2, the angle-dependent corrections to f' and to f'' are shown. The angle dependence that is displayed here is normalized to the forward values. These forward values are just the quantities that have usually been called the anomalous scattering factors. Hence, these figures give an idea of the magnitude of some of the needed corrections (those arising from f' and f'' alone) to the assumption of angle-independent anomalous scattering factors for calcium. For lighter elements, the corrections are smaller and for heavier elements they are larger, scaling approximately as $(\alpha Z)^2$. As expected, angle-independent predictions are valid to within a few percent for low energies or for small departures from forward scattering, although this region decreases with increasing photon energy. For energies several times threshold and for finite angles, the departures from the forward result are large, reaching more than 40% for f' and more the 25% for f''. There are 3% corrections in the threshold region to the usual real anomalous scattering factor at back angles, whereas there are no corresponding corrections to the imaginary anomalous scattering factor. The lack of retardation corrections to the imaginary anomalous scattering factor is an artifact of the hydrogenic formalism used here. It has been shown that such corrections do exist in neutral atoms (Bechler & Pratt, 1989). Figs. 3 and 4 present similar data for the amplitudes $f'''(\omega, \theta)$ and $f''''(\omega, \theta)$. Note that these amplitudes are completely neglected in the schemes that utilize angle-independent anomalous scattering factors. The angle dependence of these quantities is larger than for f' and f''. An equivalent way of writing the Rayleigh amplitudes is

$$A_\perp = M \qquad (12)$$

and

$$A_\parallel = M \cos\theta - N \sin^2\theta, \qquad (13)$$

where $A_{\perp(\parallel)}$ is the amplitude for scattering when the polarization vectors are perpendicular (parallel) to the scattering plane. Clearly, the relative mixture of M and N is highly dependent on the scattering geometry and only N will contribute whenever $\varepsilon_1 \cdot \varepsilon_2^* = 0$. From (12) and (13), it may be seen that one geometry where N will dominate is the case for scattering of photons that are linearly polarized in the scattering plane into angle near 90°. The unpolarized differential cross section may be expressed in terms of these amplitudes as

$$\mathrm{d}\sigma/\mathrm{d}\Omega = (r_0^2/2)(|A_\perp|^2 + |A_\parallel|^2). \qquad (14)$$

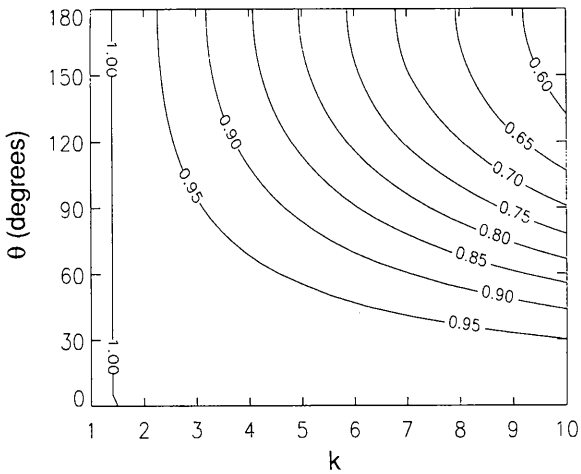

Fig. 1. The angular dependence $f'(\omega, \theta)/f'(\omega, 0)$ is shown for scattering of photons with energies from near the nonrelativistic K-shell hydrogenic threshold to ten times this threshold from calcium.

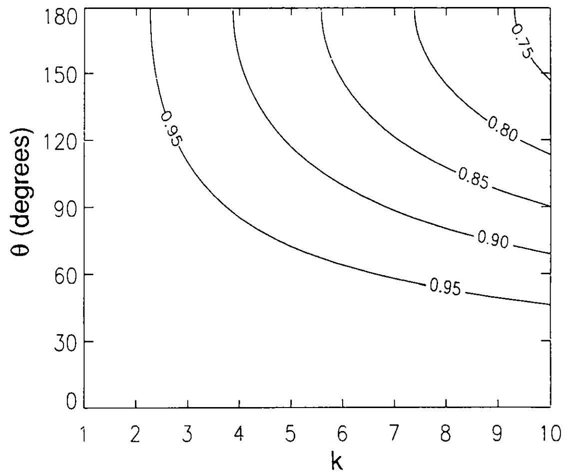

Fig. 2. The angular dependence $f''(\omega, \theta)/f''(\omega, 0)$ is shown for scattering of photons with energies from near the nonrelativistic K-shell hydrogenic threshold to ten times this threshold from calcium.

The utility of the present approach depends on the dominance of K-shell anomalous amplitudes and the accuracy of their representation by hydrogenic amplitudes in describing photon scattering from neutral atoms. As stated above, this follows from the dominance of the K-shell photoeffect cross section above the K-shell threshold, from the fact that the anomalous scattering factors at forward angle are largely determined by the photoeffect cross section [see (4) and (5)] and because, qualitatively, anomalous scattering factors are largely angle independent. As an example of the application of this assumption, we discuss the scattering of Mo $K\alpha$ radiation ($\hbar\omega = 17.48$ keV) from neutral calcium ($Z = 20$). The scaled photon energy,

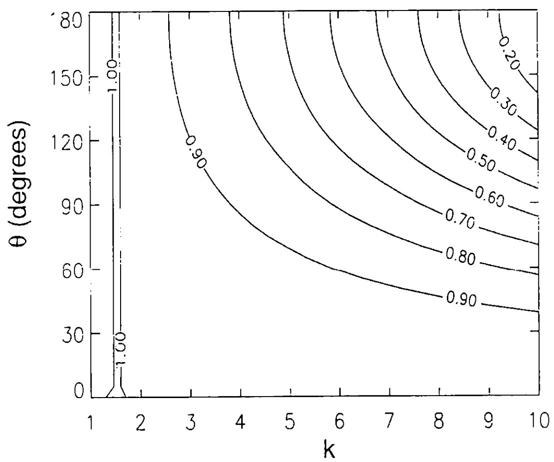

Fig. 3. The angular dependence $f'''(\omega, \theta)/f'''(\omega, 0)$ is shown for scattering of photons with energies from near the nonrelativistic K-shell hydrogenic threshold to ten times this threshold from calcium.

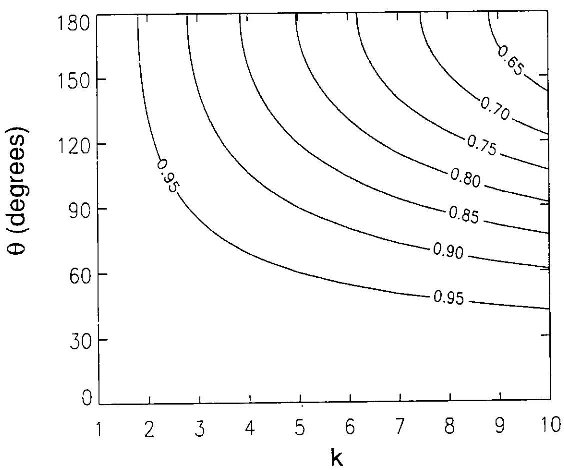

Fig. 4. The angular dependence $f''''(\omega, \theta)/f''''(\omega, 0)$ is shown for scattering of photons with energies from near the nonrelativistic K-shell hydrogenic threshold to ten times this threshold from calcium.

Table 2. *Calculated anomalous scattering factors times r_0 for the scattering for Mo $K\alpha$ photons from a K-shell electron of calcium*

θ	f'	f''	f'''	f''''
0	0.133	−1.154	0.007	−0.007
10	0.133	−0.154	0.007	−0.007
20	0.133	−0.154	0.007	−0.007
30	0.132	−0.153	0.007	−0.006
40	0.132	−0.152	0.007	−0.006
50	0.131	−0.152	0.007	−0.006
60	0.130	−0.151	0.007	−0.006
70	0.129	−0.150	0.007	−0.006
80	0.128	−0.149	0.007	−0.006
90	0.126	−0.148	0.007	−0.006
100	0.125	−0.147	0.007	−0.006
110	0.124	−0.146	0.007	−0.006
120	0.123	−0.145	0 006	−0.006
130	0.122	−0.144	0.006	−0.006
140	0.121	−0.143	0.006	−0.006
150	0.121	−0.142	0.006	−0.006
160	0.120	−0.142	0.006	−0.006
170	0.120	−0.142	0.006	−0.006
180	0.120	−0.142	0.006	−0.006

$k = 3.212$, is determined using (9). Interpolating in Table 1, we obtain $Q = -0.262 + i0.147$ and $R = 0.131$. Use of these values in (7) and (8) yields the full angle-dependent amplitudes given in Table 2. We see that f' and f'' are dominant and fairly angle independent. However, the angle-dependent corrections of these factors reach nearly 10% of the forward values. Contributions from f''' and f'''' enter at the same level in situations where the interference between N and M matters. We may find such cases by examining (12) and (13). Clearly, the interference between M and N only matters for those cases where the polarization vector is in the scattering plane and in a limited range of angles.

The amplitudes of Table 2, multiplied by 2 to account for the filled K shell in neutral calcium, are compared with the predictions of the (angle-independent) FF + ASF and SM schemes for the scattering of 17.48 keV photons from neutral calcium in Fig. 5. In the first panel, f' is displayed for all angles. While the FF + ASF scheme agrees with the current predictions and those of the SM approach – where the modified form factor (Schaupp, Schumacher, Smend, Rullhusen & Hubbell, 1983) has been subtracted – at forward angles, there is a reasonably strong angular dependence that goes beyond the FF + ASF scheme. The small differences between the neutral-atom results derived from the S-matrix calculations and the present results are mainly due to higher-shell contributions. The lower (dotted) curves give the SM results when the form factor (Hubbell, Veigele, Briggs, Brown, Cromer & Howerton, 1975) has been subtracted. Subtracting the form factor rather than the modified form factor does not change the shape of f' much. However, the magnitude does change. This change in magnitude results from the difference between the

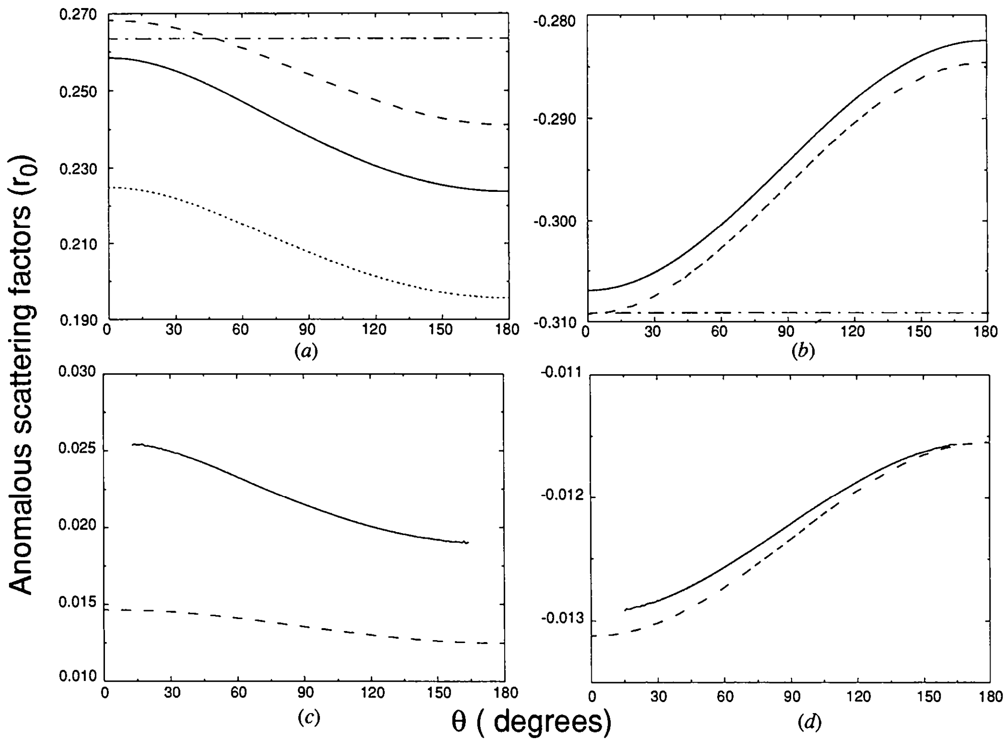

Fig. 5. (a) f', (b) f'', (c) f''' and (d) f'''' are shown for the scattering of Mo $K\alpha_1$ radiation (17.48 keV) by calcium. The solid (dotted) curve refers to the SM predictions where the modified form factor (form factor) has been subtracted. The dashed curve represents the present results. The dot-dashed curve gives the results of the (angle-independent) FF + ASF scheme.

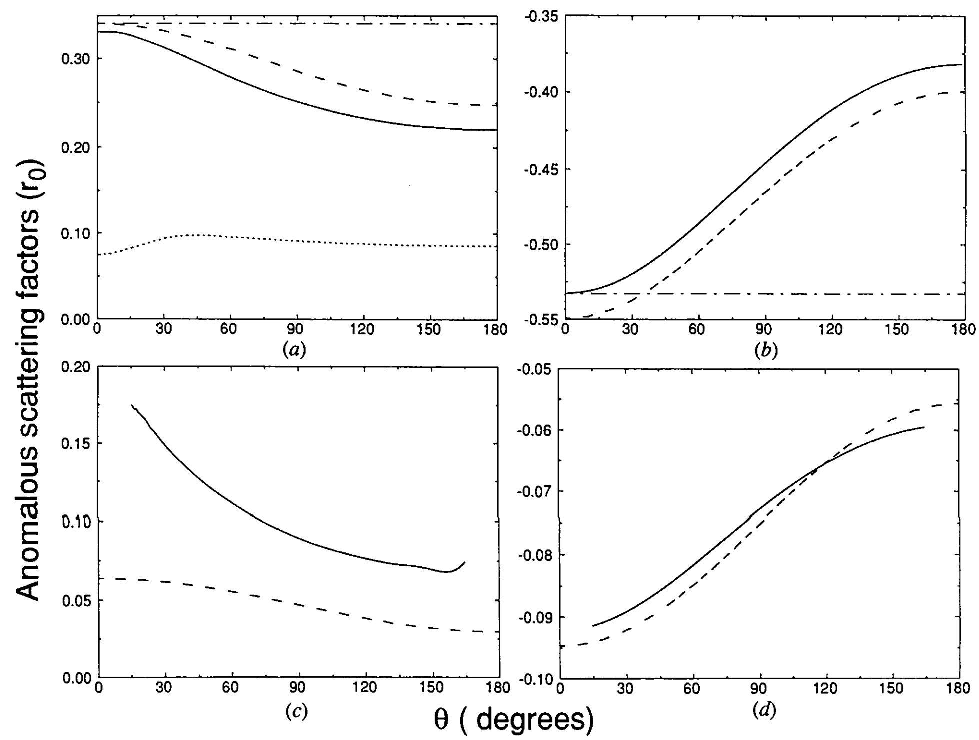

Fig. 6. (a) f', (b) f'', (c) f''' and (d) f'''' are shown for the scattering of 76.47 keV photons by silver. The solid (dotted) curve refers to the SM predictions where the modified form factor (form factor) has been subtracted. The dashed curve represents the present results. The dot-dashed curve gives the results of the (angle-independent) FF + ASF scheme.

form factor and the modified form factor at zero momentum transfer. As discussed by Kissel & Pratt (1990), the former suffers from an improper high-energy limit. Measurements of f' for forward scattering exist for this case (Creagh, 1984). The method used in this experiment actually measures the real forward amplitude. When the form factor is subtracted from the experimental data, the results agree with the dotted curve. If the modified form factor is subtracted, the other curves would agree with the observed value within the experimental uncertainty at forward angle.

As in the case of the real anomalous scattering factor, f'' has a substantial angle dependence that is well reproduced by the present theory. The angular dependence of the S-matrix result is nicely reproduced by the imaginary part of (7). The final two panels show the small f''' and f'''' factors. The error in the real part, f''', is significant and is mostly due to L-shell contributions, particularly to $2p$ (which becomes unimportant for low Z). It is important to note that (7), based on the work of Gavrila & Costescu (1970), gives the only available simple prediction of this quantity. The imaginary part of the amplitude is reasonably well reproduced by the K-shell result.

In Fig. 6, we present data for these amplitudes for 76.47 keV photons scattering from silver (three times the K-shell binding energy). The angular dependence of f' predicted here is again quite similar to that obtained from the SM results (after the modified form factor has been subtracted). If the form factor is subtracted from the SM results, however, the resulting angular dependence is quite different. This reinforces the argument that, in determining f' from the real scattering amplitude, as is done in interferometric measurements of this quantity, the modified form factor rather than the form factor should be subtracted. It is especially important to do this away from forward angles where corrections such as those given by Kissel & Pratt (1990) are not available. As before, higher-shell contributions slightly affect the agreement between the present results and the neutral-atom S-matrix results.

The range of validity of the scheme presented in this work is restricted by the condition $k < 2/\alpha Z$ and by the onset of relativistic effects. These criteria have been discussed by Costescu *et al.* (1994). In that work, good agreement between these amplitudes and S-matrix calculations was observed over a wide range of k for aluminium and silver.

As discussed above, the agreement of the Coulombic K-shell approach presented here with the results obtained for a neutral atom is not surprising and may be understood using the optical theorem and knowledge of the photoeffect. The optical theorem relates the subshell amplitudes for forward elastic photon–atom scattering to the total subshell photon–atom cross sections, here mostly photoionization. Above the K-shell photoionization threshold, the K-shell contribution is by far the largest part of the total photoionization cross section. This means that the K-shell should dominate the corresponding anomalous scattering factors. The qualitative angle independence of these factors means that K-shell dominance persists at all angles. This justifies our quantitative calculation of the angle-dependent part.

In summary, we have given simple formulas for the angle dependence of the anomalous scattering factors in the elastic photon–atom scattering amplitude at arbitrary angle. Numerical examples have illustrated the need for these angle-dependent corrections to the FF + ASF scheme and the simplicity with which they may be determined. In the real amplitudes, outer shells (mostly L) affect the agreement in both magnitude and shape between the K-shell Coulombic results derived here and those obtained from relativistic S-matrix calculations. More precise agreement requires treatment of at least the L-shell (particularly $2p$) contributions. However, for most purposes, reasonable agreement is obtained using only the present K-shell amplitudes. Extension of this formalism to include relativistic effects, necessary for calculations at higher energies or nuclear charge is in progress.

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References

Basavaraju, G., Kane, P. P., Kissel, L. & Pratt, R. H. (1994). *Phys. Rev. A*, **49**, 3664–3672.

Basavaraju, G., Kane, P. P., Lad, S. M., Kissel, L. & Pratt, R. H. (1995). *Phys. Rev. A*, **51**, 2608–2610.

Bechler, A. & Pratt, R. H. (1989). *Phys. Rev. A*, **39**, 1774–1779.

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

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*, **234**, 51–58.

Costescu, A., Bergstrom, P. M. Jr, Dinu, C. & Pratt, R. H. (1994). *Phys. Rev. A*, **50**, 1390–1398.

Creagh, D. (1984). *Phys. Lett.* **103**A, 52–56.

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

Gavrila, M. (1967). *Phys. Rev.* **163**, 147–155.

Gavrila, M. & Costescu, A. (1970). *Phys. Rev. A*, **2**, 1752–1758; erratum (1971), **4**, 1688.

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. & 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. (1990). *Acta Cryst.* A**46**, 170–175.

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.

Materlik, G., Sparks, C. J. & Fischer, K. (1994). *Resonant Anomalous X-ray Scattering: Theory and Applications*. Amsterdam: Elsevier.

Oh, S. D., McEnnan, J. & Pratt, R. H. (1976). *Phys. Rev. A*, **14**, 1428–1436.

Ron, A., Goldberg, I. B., Stein, J., Manson, S. T., Pratt, R. H. & Yin, R. Y. (1994). *Phys. Rev. A*, **50**, 1312–1320.

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