

## Recent Advances in the Calculation and Measurement of the X-ray Dispersion Corrections\*

D. C. Creagh

Department of Physics, University College,  
University of New South Wales, Australian Defence Force Academy,  
Campbell, A.C.T. 2600, Australia.

### Abstract

This paper discusses some modern techniques for the calculation of the X-ray dispersion corrections and compares the calculated data with experimental data taken near to, and remote from, the absorption edges of atoms.

### 1. Introduction

Twenty-five years ago the principal theory describing the scattering of X-ray photons by atoms was the nonrelativistic theory developed by Hönl (1933*a*, 1933*b*) and extended by Eisenlohr and Muller (1954) and Wagenfeld (1966, 1975). At that time few experimental measurements had been made, and the extent of the agreement between theory and experiment was poor, as can be seen by reference to James (1955). Because of the suggestion by Bijvoet *et al.* (1953) that anomalous dispersion could be used by crystallographers for the solution of crystal structures, there was strong interest in the production of a better theory of X-ray scattering and in the development of better techniques for the measurement of the dispersion corrections.

The advent of the X-ray interferometer (Bonse and Hart 1965, 1966) and its use for the measurement of the X-ray refractive index (and hence the real part of the dispersion correction) by a number of authors (Bonse and Hellkötter 1969; Creagh 1970; Creagh and Hart 1970) gave a real impetus to the understanding of photon scattering.

With the development of a relativistic dipole theory of X-ray scattering (RDP) by Cromer and Liberman (1970) crystallographers had access, for the first time, to a self-consistent modern theory of photon scattering. Their tabulations of both the real part  $f'$  and the imaginary part  $f''$  of the dispersion corrections have been actively used (with revisions by Cromer and Liberman in 1981 and 1983) for the last 17 years, and are still used as benchmark data by theoreticians and experimentalists alike. Their results for  $f''$  were in accord with the relativistic Hartree-Fock-Dirac-Slater calculations of Storm and Israel (1970) and the relativistic Hartree-Fock calculations of Scofield (1973).

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The development of both theoretical and experimental techniques for the determination of the dispersion corrections has been outlined by Gavrilu (1981) and Creagh (1986). The use of the dispersion corrections to enhance the measurement of a wide range of physical systems has been described recently by Creagh (1987*b*).

Rather than re-iterate the information given in those review articles, I want to discuss developments in both theory and experiment which have occurred in the past decade comparing the predictions of two theories [the *S*-matrix approach of Kissel *et al.* (1980) and the relativistic multipole with retardation approach (RMP) suggested by Creagh (1984) and Smith (1987)] with the RDP theory of Cromer and Liberman (1970, 1981, 1983). I shall then compare these theoretical predictions with the results of recent experiment.

## 2. Theory

The scattering power  $f(\omega, \Delta)$  of an isolated atom relative to that of a free electron is

$$f(\omega, \Delta) = f_0(\Delta) + f'(\omega, \Delta) + i f''(\omega, \Delta). \quad (1)$$

Here  $f_0(\Delta)$  is the atomic form factor (or atomic scattering factor) for a change in photon momentum  $\hbar\Delta = \hbar k_0 - \hbar k_i$ ,  $k_0$  being the wave vector of the scattered photon and  $k_i$  the wave vector of the incident wave. The other two terms are the (anomalous) dispersion corrections which become significant when the photon energy  $\hbar\omega$  becomes significant compared with the electron energy levels of the atom.

In the classical and the nonrelativistic quantum mechanical theories the atomic form factor is given, for a spherically symmetrical atom containing one electron, by

$$f_0(\Delta) = 4\pi \int_0^\infty \rho(r) (\sin \Delta r / \Delta r) r^2 dr,$$

where  $\rho(r)$  is the electron density at a distance  $r$  from the centre of the atom. For an atom containing  $Z$  electrons the atomic form factor becomes

$$f_0(\Delta) = 4\pi \sum_{n=1}^Z \int_0^\infty \rho_n(r) (\sin \Delta r / \Delta r) r^2 dr. \quad (2)$$

The real part of the dispersion correction  $f'(\omega, \Delta)$  is given by

$$f'(\omega, \Delta) = (2/\pi) \sum_n P \int_{\omega_n}^\infty \{ \omega f''(\omega, \Delta) / (\omega^2 - \omega_n^2) \} d\omega. \quad (3)$$

Equation (3) implies that the principal value of the integral is taken and the integral is made over a range of photon angular frequencies from the angular frequency  $\omega_n$  of the  $n$ th energy level of the atom to infinity. The angular frequency of the incident photon is  $\omega_i$  and

$$f''(\omega, \Delta) = (\omega/4\pi r_e c) \sigma(\omega, \Delta), \quad (4)$$

where  $\sigma(\omega, \Delta)$  is the atomic photoelectric scattering cross section and  $r_e$  is the classical radius of the electron.

In the relativistic theories the atomic form factor needs to be modified to take account of electron binding effects, as suggested by Franz (1935, 1936). In this representation, the modified relativistic form factor (MRFF) for each subshell,  $g(q, Z)$ , is given by

$$g(q, Z) = 4\pi \int \rho(r)(\sin qr/qr)[1/\{1-\epsilon-V(r)\}]r^2 dr, \quad (5)$$

where  $q = \Delta$ . Recent tabulations by Schaupp *et al.* (1983) and Hubbell and Øverbø (1979) have been calculated using a screened Dirac–Hartree–Fock–Slater (DHFS) potential. In all the form factor theories a term  $\frac{1}{2}(1+\cos^2\theta)$  occurs because they do not consider the change in polarisation which occurs during the photon scattering process.

The reduced scattering cross section for a photon of angular frequency  $\omega$  and wave vector  $q = \Delta$  is, in the form factor approximation,

$$\sigma(\omega, \Delta) = |f(\omega, \Delta)|^2. \quad (6)$$

The derivation of the dispersion corrections  $f'(\omega, \Delta)$  and  $f''(\omega, \Delta)$  is discussed in the following Sections for two different relativistic approximations.

### 3. Relativistic Dipole Theory

The relativistic approach developed by Cromer and Liberman (1970) is based on the scattering formula for the scattering of photons by bound electrons given by Akhiezer and Berestetsky (1959):

$$S_{i \rightarrow f} = -2\pi i \delta(\epsilon_1 + \hbar\omega_1 - \epsilon_2 - \hbar\omega_2) \{4\pi(e\hbar c)^2/2mc^2\hbar(\omega_1\omega_2)^{\frac{1}{2}}\} f. \quad (7)$$

Here the angular frequencies of the incident and scattered photons are  $\omega_1$  and  $\omega_2$  respectively, and the initial and final energy states are  $\epsilon_1$  and  $\epsilon_2$ .

The scattering factor  $f'$  is a complicated expression which includes the initial and final polarisation states  $e_1$  and  $e_2$ , the Dirac velocity operator  $c^\alpha$ , and the phase factors  $\exp(i k_1 \cdot r)$  and  $\exp(i k_2 \cdot r)$ . Summation is over all positive and negative intermediate states except those energy states occupied by other atomic electrons. The expression is not easily related to the form factor formalism and Cromer and Liberman manipulated it to relate more directly to the form used by crystallographers:

$$f = mc^2 \sum_+ \left( \frac{\langle 2 | e_2 \cdot \alpha \exp(-i k_2 \cdot r) | n^+ \rangle}{\epsilon_1 - \epsilon_n^+ + \hbar\omega_1} + \frac{\langle n^+ | e_1 \cdot \alpha \exp(i k_1 \cdot r) | 1 \rangle}{\epsilon_1 - \epsilon_n^+ - \hbar\omega_2} \right) \\ + mc^2 \sum_- \left( \frac{\langle 2 | e_2 \cdot \alpha \exp(-i k_2 \cdot r) | n^- \rangle}{\epsilon_1 - \epsilon_n^- + \hbar\omega_1} + \frac{\langle n^- | e_1 \cdot \alpha \exp(i k_1 \cdot r) | 1 \rangle}{\epsilon_1 - \epsilon_n^- - \hbar\omega_2} \right). \quad (8)$$

Cromer and Liberman limited their discussion to coherent ( $|k_1| = |k_2|$ ) forward scattering ( $\Delta = 0$ ), and the electric dipole approximation  $\exp(i k \cdot r) = 1$ . Using these assumptions they showed that

$$f(\omega, 0) = f_0(0) - f^+(\omega, 0) + \frac{5}{3} E_{\text{tot}}/mc^2 + i f''(\omega, 0). \quad (9)$$

Here  $f_0(0)$  is the atomic form factor for forward scattering and the term  $\frac{5}{3}E_{\text{tot}}/mc^2$  arises from the application of the relativistic dipole approximation. The term  $f''(\omega, 0)$  is related to the photoelectric scattering cross section  $\sigma(\hbar\omega)$  by

$$f''(\omega, 0) = (mc/4\pi\hbar e^2)\hbar\omega \sigma(\hbar\omega), \quad (10)$$

and

$$f^+(\omega, 0) = \frac{1}{2}\pi^2\hbar r_e c P \int_{mc^2}^{\infty} (\epsilon^+ - \epsilon_1)\sigma(\epsilon^+ - \epsilon_1)/\{(\hbar\omega)^2 - (\epsilon^+ - \epsilon_1)^2\} d\epsilon^+. \quad (11)$$

Equations (11) and (10) are in the mathematical form referred to as the Kramers-Kronig transform.

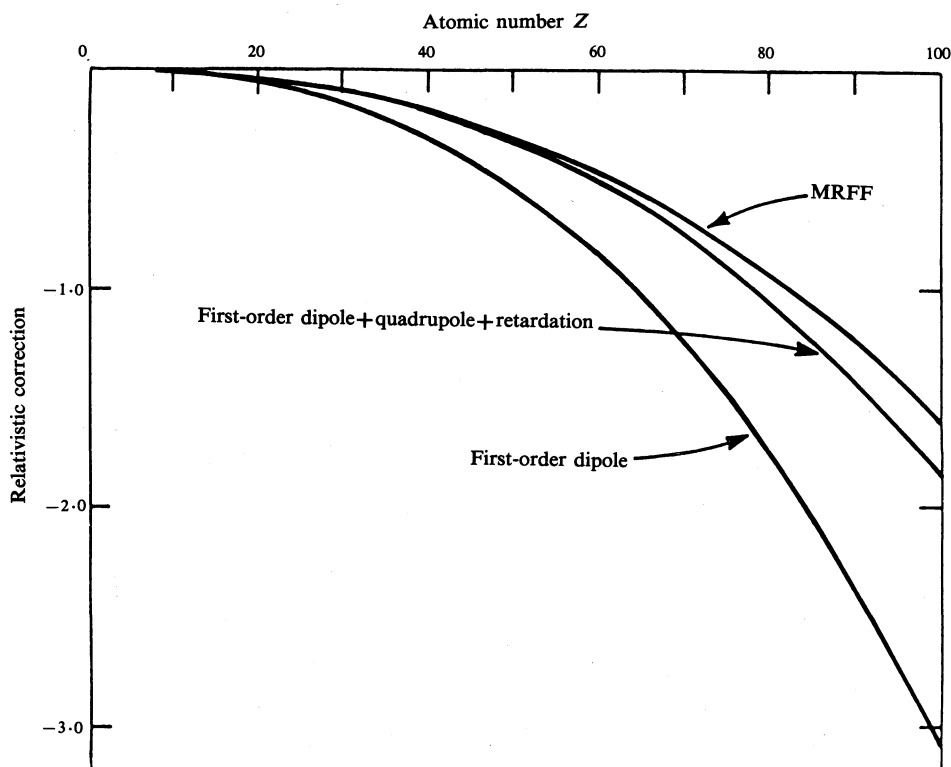


Fig. 1. Relativistic correction  $f'(\infty, 0)$  in electrons per atom for the modified form factor approach, the relativistic multipole approach, and the relativistic dipole approach.

Relating (10) and (11) to equation (1) we see that

$$f'(\omega, 0) = f^+(\omega, 0) + \frac{5}{3}E_{\text{tot}}/mc^2. \quad (12)$$

The magnitude of the relativistic correction in the dipole approximation is plotted in Fig. 1 as a function of atomic number.

In developing their tables Cromer and Liberman (1970) used the Brysk and Zerby (1968) computer code for the calculation of photoelectric cross sections. This was based on Dirac-Slater relativistic wavefunctions developed by Liberman *et al.* (1965) in which an exchange potential of  $0.667\rho^{1/3}(r)$  was used. However, instead of using the computed energy eigenvalues in their calculations they used the experimentally determined values. Their values for the photoelectric scattering cross section are almost identical to those found by Storm and Israel (1970) using similar DHFS techniques and the Hartree-Fock calculations of Scofield (1973). Both of these use the computed energy eigenvalues.

Stibius-Jensen (1979) drew attention to the fact that the dipole approximation was used at an unnecessarily early stage and that an error of  $-\frac{1}{2}Z(\hbar\omega/mc^2)$  existed in the tabulated values. A more recent paper by Cromer and Liberman (1981) includes the Stibius-Jensen correction term. Computer programs based on the Cromer and Liberman (1983) program are used throughout the world.

#### 4. Scattering Matrix Formalism

In an attempt to provide an accurate technique for predicting total-atom Rayleigh scattering amplitudes, Kissel *et al.* (1980) have developed a computer program based on the second order *S*-matrix formalism suggested by Brown *et al.* (1955). Their model treated Rayleigh scattering by considering second order single transitions by electrons bound in a relativistic self-consistent central potential of the DHFS type with the inclusion of the Kohn-Sham (1965) exchange model. Radiative corrections were omitted in their formalism.

In the photon scattering process both momentum and polarisation changes can occur. The complex polarisation vectors *e* satisfy the conditions

$$e^* \cdot e = 1; \quad e \cdot k = 0. \quad (13)$$

Scattering is described in terms of the differential scattering amplitude

$$M = M_1(e_1 \cdot e_2^*) + M_2(e_1 \cdot k_2)(e_2 \cdot k_1), \quad (14)$$

where the subscripts 1 and 2 refer to the initial and final states of the photon. If polarisation is not an observable then the expression for the differential scattering cross section takes the form

$$d\phi/d\Omega = \frac{1}{2}r_e^2(|M_1|^2 + |M_2|^2). \quad (15)$$

All tabulations have, to date, assumed that polarisation is not an observable. However, recent experiments using synchrotron radiation sources show that, particularly in the neighbourhood of an absorption edge, the full equation (14) should be used in the calculation of the dispersion corrections.

The principle of causality implies that the forward scattering amplitude  $M(\omega, 0)$  should be analytical in the upper half of the  $\omega$ -plane and that

$$\operatorname{Re} M(\omega, 0) = (2\omega^2/\pi) \int_0^\infty \{\operatorname{Im} M(\omega', 0)/\omega'(\omega'^2 - \omega^2)\} d\omega', \quad (16)$$

with the consequence that

$$\operatorname{Re} M(\infty, 0) = -(2/\pi) \int_0^\infty \{\operatorname{Im} M(\omega', 0)/\omega'\} d\omega'. \quad (17)$$

This may be rewritten as

$$M(\omega, 0) - M(\infty, 0) = f'(\omega, 0) + i f''(\omega, 0), \quad (18)$$

with the value of  $f'(\omega, 0)$  defined by equation (1). Using the conservation of probability we have

$$\operatorname{Im} M(\omega, 0) = (\omega/4\pi c r_e) \sigma,$$

which is to be compared with equation (10).

If one starts with Furry's extension of the Feynman and Dyson formalism for the total Rayleigh scattering amplitude, the value of the scattering amplitude of the  $n$ th level is

$$M_n = \sum_p \left( \frac{\langle n | T_1^* | p \rangle \langle p | T_1 | n \rangle}{E_n - E_p + \hbar\omega} + \frac{\langle n | T_2 | p \rangle \langle n | T_2^* | p \rangle}{E_n - E_p + \hbar\omega} \right), \quad (19)$$

where

$$T_1 = \alpha \cdot e_1 \exp(i k_1 \cdot r), \quad T_2 = \alpha \cdot e_2^* \exp(i k_2 \cdot r).$$

The  $|p\rangle$  are the complete set of bound and continuum states in the external field of the atomic potential. Singularities occur at all photon energies which correspond to transitions between bound  $|n\rangle$  and bound state  $|p\rangle$ . These singularities are removed if the finite widths of these states are considered and the energies  $E$  are replaced by  $i E \Gamma/2$ , where  $\Gamma$  is the total radiative plus nonradiative width of the state.

Using the approach suggested by Brown *et al.* (1955), Kissel *et al.* (1980) were able to reduce the numerical problems to the solution of one-dimensional radial integrals and differential equations. The required multipole expansions of  $T_1$  and the specification of the radial perturbed orbitals has been discussed by Kissel (1977). Finally, all the angular dependence on the photon scattering angle is written in terms of the associated Legendre functions and all the energy dependence is written in terms of multiple amplitudes.

Solutions to the inhomogeneous radial wave equations were not, however, found. Rather, Kissel (1977) expressed the solution as the linear sum of two solutions of the inhomogeneous equation, one regular at the origin and the other regular at infinity.

Although the  $S$ -matrix approach is by far the most sophisticated of all the techniques for computing Rayleigh scattering amplitudes, it is also by far the most demanding in terms of computer time. To reduce the computer time Kissel and Pratt (1985) used the  $S$ -matrix formalism for the inner subshells and estimates for the outer shell contributions based on the modified form factor approach. A recent tabulation of modified relativistic form factors has been presented by Schaupp *et al.* (1983).

## 5. Relativistic Multipole Approach

It has been pointed out earlier that the relativistic dipole approach has some limitations to its accuracy. The error in estimating the scattering amplitude at infinite frequency made by using the dipole approximation was thought to have been taken into account by use of the Stibius-Jensen correction. This, however, is not the case, and many authors (Kissel and Pratt 1985; Omote and Kato 1987; Creagh 1980, 1984, 1986) have shown that a major source of the discrepancies between the modern theories lies in the inaccuracy in determining the scattering amplitude at infinite frequency  $f'(\infty, \Delta)$ .

**Table 1.** Comparison of the imaginary part of the forward scattering amplitude  $f''(\omega, 0)$  computed using different theoretical approaches

Atom	Radiation	RDP <sup>A</sup>	Storm & Israel (1970)	$f''(\omega, 0)$ Scofield (1973)	S-matrix formalism <sup>B</sup>	RMP <sup>C</sup>
C	Cr $K\alpha_1$					
	Cu $K\alpha_1$	0.0091	0.0091	0.0093		0.0091
	Ag $K\alpha_1$	0.0009	0.0009	0.0009		0.0009
Al	Cr $K\alpha_1$	0.522		0.513	0.514	0.512
	Cu $K\alpha_1$	0.246		0.244	0.243	0.246
	Ag $K\alpha_1$	0.031		0.030	0.031	0.031
Si	Cr $K\alpha_1$	0.694		0.694		0.692
	Cu $K\alpha_1$	0.330	0.331	0.332		0.330
	Ag $K\alpha_1$	0.043	0.043	0.043		0.043
Cu	Cr $K\alpha_1$	1.194		1.189		1.193
	Cu $K\alpha_1$	0.589		0.586		0.588
	Ag $K\alpha_1$	0.826		0.826		0.826
Zn	Cr $K\alpha_1$	1.373		1.371	1.370	1.371
	Cu $K\alpha_1$	0.678		0.678	0.678	0.678
	Ag $K\alpha_1$	0.938		0.938	0.932	0.938

<sup>A</sup> Cromer and Liberman (1981).

<sup>B</sup> Kissel *et al.* (1980).

<sup>C</sup> Relativistic multipole approach.

There are not any significant systematic discrepancies between the several different methods for computing the photoelectric scattering cross section (see e.g. Table 1). The computation of  $f'(\omega, \Delta)$  follows from the use of the causality relation (15) using the values  $f''(\omega, \Delta)$  derived from the photoelectric cross-section data. The chief difference between the relativistic dipole and the relativistic multipole approach lies in the evaluation of the scattering amplitude at infinite frequency. The most detailed formal exposition of the multipole approach results from the series expansion for a single Dirac electron in a Coulomb field. Florescu and Gavrila (1976) derived a corrected version of the Goldberger and Low (1968) expression for  $f'(\infty, \Delta)$  of an electron bound in the ground state to a nucleus having atomic number  $Z$ :

$$f'(\infty, \Delta) = 1 - \frac{1}{2}a^2 + \frac{13}{24}a^4 + O(a^5), \quad (20)$$

where  $a = Ze^2/\hbar c$ . The second term evidently corresponds to the Stibius-Jensen correction.

When the multipole expansion is performed the magnitude of  $f'(\infty, 0)$  is  $E_{\text{tot}}/mc^2$  to the fifth order multipole expansion. This is three-fifths of the magnitude of that calculated using the relativistic dipole approach. [The relativistic multipole results reported here are due to Creagh and McAuley and are to be published in 'International Tables for Crystallography' (Volume C).]

## 6. Comparison of Theories

In comparisons between the theories it is possibly best to commence with the imaginary part of the dispersion correction  $f''(\omega, 0)$ , which is directly proportional to the photoelectric scattering cross section. Table 1 compares the values of  $f''(\omega, 0)$  for the relativistic dipole, the  $S$ -matrix, and the relativistic multipole cases for the elements carbon, aluminium, silicon, copper and zinc at the wavelengths of Ag  $K\alpha_1$ , Cu  $K\alpha_1$  and Cr  $K\alpha_1$ . Also shown are relativistic calculations from Storm and Israel (1970) and Scofield (1973). Despite the great differences which exist in making the various calculations there is, overall, close agreement between the results. No significant systematic differences appear to exist.

The real part of the dispersion correction  $f'(\omega, 0)$  is related to  $f''(\omega, 0)$  through the causality relation (15) and its limiting condition (17). Given that there are no significant differences between the  $f''(\omega, 0)$  values predicted by the three models, the value of the integral would be expected to be the same in each case. Differences do exist in the value of the limiting condition. That these are significant can be seen in Fig. 1 which shows the variation of the relativistic correction  $f'(\omega, 0)$  as a function of atomic number for the relativistic dipole, relativistic multipole, and modified form factor models.

**Table 2.** Comparison between the  $S$ -matrix calculations and the form factor calculations for the noble gases and several common metals  
 $f'(\omega, 0)$  values are given for two frequently used photon energies

Energy (keV)	Element	RDP <sup>A</sup>	$S$ -matrix <sup>B</sup>	RMP <sup>C</sup>
17.479 (Mo $K\alpha_1$ )	Ne	0.021	0.024	0.026
	Ar	0.155	0.170	0.174
	Kr	-0.652	-0.478	-0.557
	Xe	-0.684	-0.416	-0.428
22.613 (Ag $K\alpha_1$ )	Al	0.032	0.039	0.041
	Zn	0.260	0.323	0.324
	Ta	-0.937	-0.375	-0.383
	Pb	-1.910	-1.034	-1.162

<sup>A</sup> Cromer and Liberman (1970, 1981, 1983).

<sup>B</sup> Kissel (1987).

<sup>C</sup> Creagh and McAuley (unpublished).

Table 2 compares the predictions of the three models for the rare gases and some common metals. For the rare gases the RMP and  $S$ -matrix models are in good agreement with one another for neon, argon and xenon. There is no agreement between the models for krypton. For the common metals aluminium, zinc, tantalum and lead, the RMP theory is in better accord with the  $S$ -matrix theory than the RDP theory.



Considering the very significant differences in the techniques used for computing the RMP and  $S$ -matrix values, the agreement between the theories is surprisingly good. Because the  $S$ -matrix approach is the more complete of the three, it seems logical to use it as the bench-mark against which comparisons are made. Large amounts of time are required to compute  $S$ -matrix values with the result that relatively few results have been reported (see e.g. Creagh 1987*b*). In contrast the code for the RMP calculations has been compressed to enable it to run on a (large) personal computer. It would be therefore a more useful data set for experimentalists, if substantial agreement can be shown to exist between theory and experiment. In the following section comparisons will be made between the predictions of the RMP theory and experimental data.

## 7. Experimental Results

Most modern techniques for the measurement of  $f'(\omega, 0)$  make use of devices for determining the X-ray refractive index  $n$ , which is related to the dielectric susceptibility  $\chi$  by

$$n = (1 + \chi)^{\frac{1}{2}}, \quad (21)$$

where

$$\chi = -(r_e^2 \lambda^2 / \pi) \sum_j N_j f_j(\omega, \Delta). \quad (22)$$

It is not my intention here to describe these techniques since I have reviewed the subject recently (Creagh 1986). Suffice to say that direct measurements of  $f'(\omega, 0)$  using X-ray interferometers have been made by, *inter alia*, Cusatis and Hart (1975), Siddons and Hart (1983), Begum *et al.* (1986), Bonse and Materlik (1975), Bonse and Hartmann-Lotsch (1984), Bonse and Henning (1985) and Creagh (1984).

An alternative approach is the measurement of refractive index by the deviation of the prism method and recent measurements have been made by Deutsch and Hart (1985) and Katoh *et al.* (1985*a*, 1985*b*). Another technique uses measurements of  $f''(\omega, 0)$ . The deficiencies of this approach have been discussed by Creagh (1980, 1984, 1986). However, serious attempts to determine  $f'(\omega, 0)$  through measurements of  $f''(\omega, 0)$  have been made by Gerward *et al.* (1979), Dreier *et al.* (1984), Creagh (1980), Bonse and Henning (1985), Bonse and Hartmann-Lotsch (1984), Kawamure and Fukamachi (1978) and Fukamachi *et al.* (1978).

One other approach uses refinement of the diffraction pattern of crystal structures, for which the structure is known, to determine  $f'(\omega, \Delta)$  and  $f''(\omega, \Delta)$ . This technique has been used by, *inter alia*, Engel and Sturm (1975), Templeton and Templeton (1978), Phillips *et al.* (1978), Phillips and Hodgson (1985) and Chapuis *et al.* (1985). Inherent in this approach is the assumption that  $f'(\omega, \Delta)$  is not a function of the scattering vector  $\Delta$ . Fortunately, it has been demonstrated theoretically by Kissel *et al.* (1980) using the  $S$ -matrix theory, and experimentally by Suortti *et al.* (1985) and Omote and Kato (1987), that  $f'(\omega, \Delta)$  is not a function of  $\Delta$ .

The experiment by Omote and Kato (1987) used X-ray pendellösung techniques to determine the atomic form factor for silicon. They showed that, not only is there no dependence of  $f'(\omega, \Delta)$  on  $\Delta$ , but that the Stibius-Jensen correction is not appropriate.

8. Comparison of Experimental Results with Theoretical Predictions

In this section discussion focusses on:

- (i) the scattering of photons having energies considerably greater than that of the K-absorption edge of the atom from which they are scattered; and
- (ii) scattering of photons having energies in the neighbourhood of an absorption edge of the scattering atom.

Table 3. Comparison of measurements of  $f''(\omega, 0)$  for C, Si and Cu with theoretical predictions  
The measurements are from the IUCr X-ray Attenuation Project Report (Creagh and Hubbell 1987) corrected for the effects of Compton, Laue-Bragg and small angle scattering.

Sample	Reference	$f''(\omega, 0)$		
		Cu $K\alpha_1$	Mo $K\alpha_1$	Ag $K\alpha_1$
$^{6}\text{C}$	<i>Theory</i>			
	RMP	0.0091	0.0016	0.0009
	RDP	0.0091	0.0016	0.0009
	<i>Experiment</i>			
	IUCr Project	0.0093	0.0016	0.0009
$^{14}\text{Si}$	<i>Theory</i>			
	RMP	0.330	0.070	0.043
	RDP	0.330	0.0704	0.0431
	<i>Experiment</i>			
	IUCr Project	0.332	0.0696	0.0429
$^{29}\text{Cu}$	<i>Theory</i>			
	RMP	0.588	1.265	0.826
	RDP	0.589	1.265	0.826
	<i>Experiment</i>			
	IUCr Project	0.588	1.267	0.826

The imaginary part of the dispersion correction  $f''(\omega, 0)$  is proportional to the photoelectric scattering cross section. In Table 1 a comparison was made between the predictions of the various theories of scattering, and it was shown that the theories yielded results in substantial agreement. In Table 3 the predictions of the relativistic dipole (RDP) and the relativistic multipole (RDM) approaches are compared with measurements made by laboratories participating in the IUCr X-ray Attenuation Project (Creagh and Hubbell 1987). The results have been corrected for the effects of Compton, Laue-Bragg thermal diffuse, and small angle X-ray scattering. Experiment and theory are in excellent agreement.

Let us consider first the real part of the dispersion correction  $f'(\omega, 0)$  for the case where  $\omega/\omega_K \rightarrow 0$ , i.e. the high energy limit. In Table 4 measurements of  $f'(\omega, 0)$  for lithium fluoride, silicon, aluminium and germanium are presented for the characteristic  $K\alpha_1$  wavelengths of copper, molybdenum and silver. Summarised are measurements using a variety of X-ray interferometer, deviation by a prism, pendellösung and Kramers-Kronig experiments. The theoretical predictions of the relativistic multipole and relativistic dipole theories are shown.

In general the agreement between theory and experiment is good, but the predictions of the RMP theory are in better accord with experiment than the RDP theory. Exceptions occur for Si and Al for the wavelength of  $\text{Cu } K\alpha_1$ . The discrepancy

**Table 4.** Comparison of measurements of the real part of the dispersion correction for LiF, Si, Al and Ge with theoretical predictions

The experimental accuracy (in per cent) claimed for the experiments is given in parentheses

Sample	Reference	$f'(\omega, 0)$		
		Cu $K\alpha_1$	Mo $K\alpha_1$	Ag $K\alpha_1$
LiF	<i>Theory</i>			
	This work	0.075	0.017	0.010
	Cromer & Liberman (1981)	0.068	0.014	0.006
	<i>Experiment</i>			
	Creagh (1984)	0.085(5)	0.020(10)	0.014(10)
Si	Deutsch & Hart (1985)	—	0.0217(1)	0.0133(1)
	<i>Theory</i>			
	This work	0.254	0.0817	0.052
	Cromer & Liberman (1981)	0.242	0.071	0.042
	<i>Experiment</i>			
	Cusatis & Hart (1975)	—	0.0863(2)	0.0568(2)
	Price <i>et al.</i> (1978)	—	0.085(7)	0.047(7)
	Gerward <i>et al.</i> (1979)	0.244(7)	0.099(7)	0.070(7)
	Creagh (1984)	0.236(5)	0.091(5)	0.060(5)
Al	Deutsch & Hart (1985)	—	0.0847(1)	0.0537(1)
	<i>Theory</i>			
	This work	0.213	0.0645	0.041
	Cromer & Liberman (1981)	0.203	0.0486	0.020
	<i>Experiment</i>			
	Creagh (1984)	—	0.065(20)	0.044(20)
Ge	Takama <i>et al.</i> (1982)	0.20(5)	0.07(5)	0.035(10)
	<i>Theory</i>			
	This work	-1.089	0.155	0.302
	Cromer & Liberman (1981)	-1.167	0.062	0.197
	<i>Experiment</i>			
	Gerward <i>et al.</i> (1979)	-1.04	0.30	0.43

between the theories is about 5%. Neither theory appears in reasonable agreement with experiment for Ge, although the RMP theory is in better accord than the RDP theory.

Remote from the edge the RMP theory successfully predicts the experimental values of  $f'(\omega, 0)$  to within 5% for all the elements of the periodic table. Close to the absorption edge of an atom, processes other than photoelectric scattering occur and extended X-ray absorption fine structure (EXAFS) and X-ray near-edge structure (XANES) are observed in  $f''(\omega, 0)$  and (consequently) in  $f'(\omega, 0)$ . Although the origins of these processes are well known, there are still some problems in making quantitative predictions (Creagh 1980). It is a tribute to the techniques of experimentalists that measurements can be made in the neighbourhood of the edges where the scattering powers of the atoms vary quite considerably from the classically expected values.

In Table 5 data from many different experiments are collated. Measurements for Cu, Ni and Nb made at, or near, an absorption edge, are compared with the predictions of both the RDP and RDM theories. For Cu a considerable range of experimental values (-7.84 to -10.0) exists although -8.3 appears to be a

Table 5. Comparison of  $f'(\omega_K, 0)$  for copper, nickel and niobium for theoretical and experimental datasets

Reference	Method <sup>A</sup>	Cu	$f'(\omega, 0)$ Ni	Nb <sup>B</sup>
<i>Experiment</i>				
Freund (1975)	BR	-8.2		
Begum <i>et al.</i> (1986)	IN	-7.84	-7.66	
Bonse & Materlik (1975)	IN		-8.1	
Bonse <i>et al.</i> (1983)	IN	-8.3		
Siddons & Hart (1983)	IN	-9.3	-9.2	-4.396†
Kawamura & Fukamachi (1978)	KK		-7.9	
Dreier <i>et al.</i> (1984)	KK	-8.2	-7.8	
Bonse & Hartmann (1984)	{ IN	-8.3	-8.1	
	{ KK	-8.3	-7.7	
Fukamachi <i>et al.</i> (1978)	{ KK	-8.8		
	{ CA	-10.0		
Bonse & Henning (1985)	{ IN			-7.37;* -7.73*
	{ KK			-7.21;* -7.62*
<i>Theory</i>				
Linewidth calculation <sup>C</sup>		-13.50	-9.45	-4.20;† -7.39*
This work		-13.45	-9.40	-4.04;† -7.23*

<sup>A</sup> Here BR is the Bragg reflection, IN the interferometer, KK the Kramers-Kronig, and CA the critical angle. Measurements have been made for the K-absorption edges of copper and nickel and near the K-absorption edge of niobium. Claimed experimental errors are not worse than 5%.

<sup>B</sup> Here † and \* are used to indicate values which are to be compared, the former were taken near the absorption edge of niobium, the latter at the absorption edge of niobium.

<sup>C</sup> Calculation made in conjunction with the Cromer-Liberman (1981) program by replacing the energies in equation (11) by  $iE\Gamma/2$ , where  $\Gamma$  is the total radiative plus nonradiative linewidth.

commonly found value. These are not in accord with theory, even when account is taken of the radiative linewidth. A recent measurement by K. Ishida (1987, personal communication) gives a value of -10.5. A similar situation occurs for Ni, although the range in the measurements is not so great (-7.66 to -9.2) and the disagreement between theory and experiment not so pronounced.

A variety of explanations have been given for the discrepancies between theoretical and experimental values for  $f'(\omega, 0)$ . They range from theories concerning the band pass of the measuring equipment (Creagh 1986) to theories based on the fact that the XANES structure overlaps the edge. No completely satisfactory explanation exists at present.

Slightly away from the edge in Nb agreement between theory and experiment is better than 10%, and at the edge somewhat better (about 5%) agreement is found. Four values are given for the measurement at the edge. One set is for the interferometer measurement of  $f'(\omega, 0)$  and the other for the Kramers-Kronig transform of  $f''(\omega, 0)$ . The two values for each set correspond to two different polarisation states of the incident and scattered photon. The *S*-matrix theory takes account of polarisation changes in scattering. Both the RDP and RMP theory, however, are derived only for the case of averaged polarisation. Polarisation effects can apparently be quite significant, a fact pointed out by Chapuis *et al.* (1985) and Templeton and Templeton (1986). Note that when the Kramers-Kronig integral was performed the relativistic correction term was not incorporated into the final

expression for  $f'(\omega, 0)$ . The difference between the two could be construed to be an estimate of  $f'(\infty, 0)$  which is related to  $E_{\text{tot}}/mc^2$ , which is 0.20 in this case. This brings the two sets of measurements into close agreement.

## 9. Conclusions

In this paper I have described briefly three modern techniques for calculating the dispersion corrections for photon scattering from isolated, spherical atoms, for averaged polarisation states. It has been demonstrated that, for the imaginary part of the dispersion corrections,  $f''(\omega, 0)$ , there is little to choose between the theories, and in particular agreement between theory and experiment is excellent.

Remote from an absorption edge the results of the relativistic multipole theory are in slightly better agreement with experiment than the relativistic dipole theory. At the absorption edge the choice of theory does not appear to be so clear. One must point out, however, that in most cases the RMP theory gives better agreement with experiment away from the edge.

The difference between the RDP and the RMP theory lies chiefly in the evaluation of  $f'(\infty, 0)$ , the matrix element for the scattering at infinite energy. The inclusion of the higher order multipoles reduced this from  $\frac{5}{3}E_{\text{tot}}/mc^2$  to  $E_{\text{tot}}/mc^2$ . The effect of the inclusion of still higher order multipoles may alter this value somewhat, and it is estimated that there is an inaccuracy of  $0.25E_{\text{tot}}/mc^2$  in the RMP calculations. Errors in calculating  $f'(\infty, 0)$  shift the  $f'(\omega, 0)$  versus  $\omega$  graph up or down the *vertical axis*.

It should be appreciated by users of tables of dispersion corrections that the absorption edge energy of an atom varies with its oxidation state. This shifts the graph along the  $\omega$ -axis. This can have a significant effect on the value of  $f'(\omega, 0)$  particularly in the neighbourhood of the edge where  $f'(\omega, 0)$  is varying rapidly with  $\omega$ . Attention is also drawn to the fact that it has been demonstrated that  $f'(\omega, \Delta)$  is *not* a function of  $\Delta$ .

The excellent agreement which exists between the RMP and *S*-matrix theories indicates that RMP is more reliable than the RDP theory. When this was considered in conjunction with the good agreement it has with experimental results for a wide range of atoms and photon energies, it was decided to use the RMP formalism to produce the tables of the dispersion corrections in the forthcoming 'International Tables for Crystallography' (Volume C). It is hoped that programs for computing the dispersion corrections, capable of running in a (large) personal computer, will be available in the near future.

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