

4.2. X-RAYS

terms in the analytical expression for the photoelectric scattering cross section.

The values of the cross section so obtained were used to calculate the values of $f'(\omega, \Delta)$ using the Kramers–Kronig transform [equation (4.2.6.22)] and $f''(\omega, \Delta)$ using equation (4.2.6.23). The work of Wagenfeld (1975) predicts that the values of $f'(\omega, \Delta)$ and $f''(\omega, \Delta)$ are functions of Δ . Whether or not this is a correct prediction will be discussed in Subsection 4.2.6.3.

Wang & Pratt (1983) have drawn attention to the importance of bound–bound transitions in the dispersion relation for the calculation of forward-scattering amplitudes. Their inclusion is especially important for elements with small atomic numbers. In a later paper, Wang (1986) has shown that, for silicon at the wavelengths of Mo $K\alpha$ and Ag $K\alpha_1$, values for $f'(\omega, 0)$ of 0.084 and 0.055, respectively, are obtained. These values should be compared with those listed in Table 4.2.6.4.

4.2.6.2.3. Relativistic theories

4.2.6.2.3.1. Cromer and Liberman: relativistic dipole approach

It is necessary to consider relativistic effects for atoms having all but the smallest atomic numbers. Cromer & Liberman (1970) produced a set of tables based on a relativistic approach to the scattering of photons by isolated atoms that was later reproduced in *IT IV* (1974). Subsequent experimental determinations drew attention to inaccuracies in these tables in the neighbourhood of absorption edges owing to the poor convergence of the Gaussian integration technique, which was used to evaluate the real part of the dispersion correction. In a later paper, Cromer & Liberman (1981) recalculated 34 instances for which the incident radiation lay close to the absorption edges of atoms using a modified integration procedure. Care should be exercised when using the Cromer & Liberman computer program, especially for calculations of $f'(\omega, 0)$ for high atomic weight elements at low photon energies. As Creagh (1990) and Chantler (1994) have shown, incorrect values of $f'(\omega, 0)$ can be calculated because an insufficient number of values of $f''(\omega, 0)$ are calculated prior to performing the Kramers–Kronig transform. In a new tabulation, Chantler (1995) presents the Cromer & Liberman data using a finer integrating grid. It should be noted that the relativistic correction is the same as that used in this tabulation.

These relativistic calculations are based on the scattering formula developed by Akhiezer & Berestetsky (1957) for the scattering amplitude for photons by a bound electron, viz:

$$S_{i \rightarrow f} = -2\pi i \delta(\varepsilon_1 + \hbar\omega_1 - \varepsilon_2 - \hbar\omega_2) \frac{4\pi(e\hbar c)^2}{2mc^2\hbar(\omega_1\omega_2)^{1/2}} f. \quad (4.2.6.24)$$

Here the angular frequencies of the incident and scattered photons are ω_1 and ω_2 , respectively, and the initial and final energy states of the atom are ε_1 and ε_2 , respectively. The scattering factor f is a complicated expression that includes the initial and final polarization states of the photon, the Dirac velocity operator, and the phase factors $\exp(i\mathbf{k}_1 \cdot \mathbf{r})$ and $\exp(i\mathbf{k}_2 \cdot \mathbf{r})$ for the incident and scattered waves, respectively. Summation is over all positive and negative intermediate states except those positive energy states occupied by other atomic electrons. The form of this expression is not easily related to the form-factor formalism that is most widely used by crystallographers, and a number of manipulations of the formula for the scattering factor are necessary to relate it more directly to the crystallographic formalism. In doing so, a number of assump-

tions and simplifications were made. Cromer & Liberman restricted their study to coherent, forward scatter in which changes in photon polarization did not occur. With these approximations, and using the electrical dipole approximation [$\exp(i\mathbf{k} \cdot \mathbf{r}) = 1$], they were able to show that

$$f(\omega, 0) = f(0) + f^+(\omega, 0) + \frac{5}{3} \frac{E_{\text{tot}}}{mc^2} + if''(\omega, 0). \quad (4.2.6.25)$$

In equation (4.2.6.25), $f(0)$ is the atomic form factor for the case of forward scatter ($\Delta = 0$), and the term $[+\frac{5}{3}(E_{\text{tot}}/mc^2)]$ arises from the application of the dipole approximation to determine the contribution of bound electrons to the scattering process. The term $f''(\omega, 0)$ is related to the photoelectric scattering cross section expressed as a function of photon energy $\sigma(\hbar\omega)$ by

$$f''(\omega, 0) = \frac{mc}{4\pi\hbar e^2} \hbar\omega \sigma(\hbar\omega) \quad (4.2.6.26)$$

and

$$f^+(\omega, 0) = \left(\frac{1}{2\pi^2\hbar r_e c} \right) P \int_{mc^2}^{\infty} \frac{(\varepsilon^+ - \varepsilon_1)\sigma(\varepsilon + -\varepsilon_1)}{(\hbar\omega)^2 - (\varepsilon^+ - \varepsilon_1)^2} d\varepsilon^+. \quad (4.2.6.27)$$

These equations may be compared with equations (4.2.6.23) and (4.2.6.22), respectively. But equation (4.2.6.25) differs from equation (4.2.6.21) by the term $\frac{5}{3}(E_{\text{tot}}/mc^2)$, which is constant for each atomic species, and is related to the total Coulomb energy of the atom. Evidently, to keep the formalism the same, one must write

$$f'(\omega, 0) = f^+(\omega, 0) + \frac{5}{3} \frac{E_{\text{tot}}}{mc^2}. \quad (4.2.6.28)$$

In Table 4.2.6.1, values of E_{tot}/mc^2 are set out as a function of atomic number for elements ranging in atomic number from 3 to 98.

To develop their tables, Cromer & Liberman (1970) used the Brysk & Zerby (1968) computer code for the calculation of photoelectric cross sections, which was based on Dirac–Slater relativistic wavefunctions (Liberman, Waber & Cromer, 1965). They employed a value for the exchange potential of $0.667\rho(\mathbf{r})^{1/3}$ and experimental rather than computed values of the energy eigenvalues for the atoms.

The wide use of their tables by crystallographers inevitably meant that criticism of the accuracy of the tables was forthcoming on both theoretical and experimental grounds. Stibius-Jensen (1979) drew attention to the fact that the use of the dipole approximation too early in the argument caused an error of $-\frac{1}{2}Z(\hbar\omega/mc^2)^2$ in the tabulated values. More recently, Cromer & Liberman (1981) include this term in their calculations. Some experimental deficiencies of the tabulated values of $f'(\omega, 0)$ have been discussed by Cusatis & Hart (1977), Hart & Siddons (1981), Creagh (1980, 1984, 1985, 1986), Deutsch & Hart (1982), Dreier, Rabe, Malzfeldt & Niemann (1984), Bonse & Hartman-Lotsch (1984), and Bonse & Henning (1986).

In the latter two cases, the Kramers–Kronig transformation of photoelectric scattering results has been performed without taking into account the term that arises in the relativistic case for the total Coulomb energy of the atom. Although good agreement with the Cromer & Liberman tables is claimed, their failure to include this term is an implied criticism of the Cromer & Liberman tables. That this is unjustified can be seen by references to Fig. 4.2.6.2 taken from Bonse & Henning (1986), which shows that their interferometer results [which measure $f'(\omega, 0)$ directly] and the Kramers–Kronig results differ

4. PRODUCTION AND PROPERTIES OF RADIATIONS

from one another by $\sim E_{\text{tot}}/mc^2$ in the neighbourhood of the K -absorption edge of niobium in the compound lithium niobate.

Further theoretical objections have been made by Creagh (1984) and Smith (1987), who has shown that the Stibius-Jensen correction is not valid, and that, when higher-order multipolar expansions and retardation are considered, the total self-energy correction becomes E_{tot}/mc^2 rather than $\frac{5}{3}E_{\text{tot}}/mc^2$. Fig. 4.2.6.1 shows the variation of the self-energy correction with atomic number for the modified form factor (Creagh, 1984; Smith, 1987; Cromer & Liberman, 1970).

For the imaginary part of the dispersion correction $f''(\omega, 0)$, which depends on the calculation of the photoelectric scattering cross section, better agreement is found between theoretical results and experimental data. Details of this comparison have been given elsewhere (Section 4.2.4). Suffice it to say that Creagh & Hubbell (1990), in reporting the results of the IUCr X-ray Attenuation Project, could find no rational basis for preferring the Scofield (1973) Hartree-Fock calculations to the Cromer & Liberman (1970, 1981) and Storm & Israel (1970) Dirac-Hartree-Fock-Slater calculations.

Computer programs based on the Cromer & Liberman program (Cromer & Liberman, 1983) are in use at all the major synchrotron-radiation laboratories. Many other laboratories have also acquired copies of their program. This program must be modified to remove the incorrect Stibius-Jensen correction term, and, as will be seen later, the energy term should be modified to be E_{tot}/mc^2 .

4.2.6.2.3.2. The scattering matrix formalism

Kissel, Pratt & Roy (1980) have developed a computer program based on the second-order S -matrix formalism suggested by Brown, Peierls & Woodward (1955). Their aim was to provide a prescription for the accurate ($\sim 1\%$) prediction of the total-atom Rayleigh scattering amplitudes.

Their model treats the elastic scattering as the sum of bound electron, nuclear, and Delbrück scattering cross sections, and treats the Rayleigh scattering by considering second-order, single-electron transitions from electrons bound in a relativistic, self-consistent, central potential. This potential was a Dirac-Hartree-Fock-Slater potential, and exchange was included by use of the Kohn & Sham (1965) exchange model. They omitted radiative corrections.

In principle, the observables in an elastic scattering process are momentum ($\hbar\mathbf{k}$) and polarization $\boldsymbol{\varepsilon}$. The complex polarization vectors $\boldsymbol{\varepsilon}$ satisfy the conditions

$$\boldsymbol{\varepsilon}^* \cdot \boldsymbol{\varepsilon} = 1'; \quad \boldsymbol{\varepsilon} \cdot \mathbf{k} = 0. \quad (4.2.6.29)$$

In quantum mechanics, elastic scattering is described in terms of a differential scattering amplitude, M , which is related to the elastic cross section by equation (4.2.6.16).

If polarization is not an observable, then the expression for the differential scattering cross section takes the form of equation (4.2.6.17). If polarization is taken into account, as may be the case when a polarizer is used on a beam scattered from a sample irradiated by the linearly polarized beam from a synchrotron-radiation source, the full equation, and not equation (4.2.6.17), must be used to compute the differential scattering cross section.

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

$$\text{Re } M(\omega, 0) = \frac{2\omega^2}{\pi} \int_0^\infty \frac{\text{Im } M(\omega', 0)}{\omega'(\omega'^2 - \omega^2)} d\omega' \quad (4.2.6.30)$$

Table 4.2.6.1. Values of E_{tot}/mc^2 listed as a function of atomic number Z

Z	Symbol	E_{tot}/mc^2	Z	Symbol	E_{tot}/mc^2
3	Li	-0.0004	49	In	-0.318
4	Be	-0.0006	50	Sn	-0.330
5	B	-0.0012	51	Sb	-0.348
6	C	-0.0018	52	Te	-0.363
7	N	-0.0030	53	I	-0.384
8	O	-0.0042	54	Xe	-0.396
9	F	-0.0054			
10	Ne	-0.0066	55	Cs	-0.414
			56	Ba	-0.438
11	Na	-0.0084			
12	Mg	-0.0110	57	La	-0.456
13	Al	-0.0125	58	Ce	-0.474
14	Si	-0.0158	59	Pr	-0.492
15	P	-0.0180	60	Nd	-0.516
16	S	-0.0210	61	Pm	-0.534
17	Cl	-0.0250	62	Sm	-0.558
18	Ar	-0.0285	63	Eu	-0.582
			64	Gd	-0.610
19	K	-0.0320	65	Tb	-0.624
20	Ca	-0.0362	66	Dy	-0.648
			67	Ho	-0.672
21	Sc	-0.0410	68	Er	-0.696
22	Ti	-0.0460	69	Tm	-0.723
23	V	-0.0510	70	Yb	-0.750
24	Cr	-0.0560	71	Lu	-0.780
25	Mn	-0.0616			
26	Fe	-0.0680	72	Hf	-0.804
27	Co	-0.0740	73	Ta	-0.834
28	Ni	-0.0815	74	W	-0.864
29	Cu	-0.0878	75	Re	-0.900
30	Zn	-0.0960	76	Os	-0.919
			77	Ir	-0.948
31	Ga	-0.104	78	Pt	-0.984
32	Ge	-0.114	79	Au	-1.014
33	As	-0.120	80	Hg	-1.046
34	Se	-0.132			
35	Br	-0.141	81	Tl	-1.080
36	Kr	-0.150	82	Pb	-1.116
			83	Bi	-1.149
37	Rb	-0.159	84	Po	-1.189
38	Sr	-0.171	85	At	-1.224
			86	Rn	-1.260
39	Y	-0.180			
40	Zr	-0.192	87	Fr	-1.296
41	Nb	-0.204	88	Ra	-1.332
42	Mo	-0.216			
43	Tc	-0.228	89	Ac	-1.374
44	Ru	-0.246	90	Th	-1.416
45	Rh	-0.258	91	Pa	-1.458
46	Pd	-0.270	92	U	-1.470
47	Ag	-0.285	93	Np	-1.536
48	Cd	-0.300	94	Pu	-1.584
			95	Am	-1.626
			96	Cm	-1.669
			97	Bk	-1.716
			98	Cf	-1.764

should hold, with the consequence that

$$\text{Re } M(\infty, 0) = -\frac{2}{\pi} \int_0^\infty \frac{\text{Im } M(\omega', 0)}{\omega'} d\omega'. \quad (4.2.6.31)$$

4.2. X-RAYS

This may be rewritten as

$$M(\omega, 0) - M(\infty, 0) = f'(\omega, 0) + if''(\omega, 0), \quad (4.2.6.32)$$

with the value of $f'(\omega, 0)$ defined by equation (4.2.6.15). Using the conservation of probability,

$$\text{Im } M(\omega, 0) = \frac{\omega}{4\pi r_e c} \sigma_{\text{tot}}, \quad (4.2.6.33)$$

which is to be compared with equation (4.2.6.23).

Starting with Furry's extension of the formalism of quantum mechanics proposed by Feynman and Dyson, the total Rayleigh amplitude may be written as

$$M_n = \sum_p \left[\frac{\langle n|T_1^*|p\rangle \langle p|T_1|n\rangle}{E_n - E_p + \hbar\omega} + \frac{\langle n|T_2|p\rangle \langle n|T_2^*|p\rangle}{E_n - E_p + \hbar\omega} \right], \quad (4.2.6.34)$$

where

$$T_1 = \mathbf{a} \cdot \boldsymbol{\varepsilon}_i \cdot \exp(i\mathbf{k}_i \cdot \mathbf{r})$$

and

$$T_2 = \mathbf{a} \cdot \boldsymbol{\varepsilon}_f^* \cdot \exp(-i\mathbf{k}_f \cdot \mathbf{r}).$$

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 that 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 $iE\Gamma/2$, where Γ is the total (radiative plus non-radiative) width of the state (Gavrila, 1981). By use of the formalism suggested by Brown *et al.* (1955), it is possible to reduce the numerical problems to one-dimensional radial integrals and differential equations. The required multipole expansions of T_1 and the specification of the radial perturbed orbitals that are characterized by angular-momentum quantum numbers have been discussed by Kissel (1977). Ultimately, all the angular dependence on the photon scattering angle is written in terms of the associated Legendre functions, and all the energy dependence is in terms of multipole amplitudes.

Solutions are not found for the inhomogeneous radial wave equations, and Kissel (1977) expressed the solution as the linear sum of two solutions of the homogeneous equation, one of which was regular at the origin and the other regular at infinity.

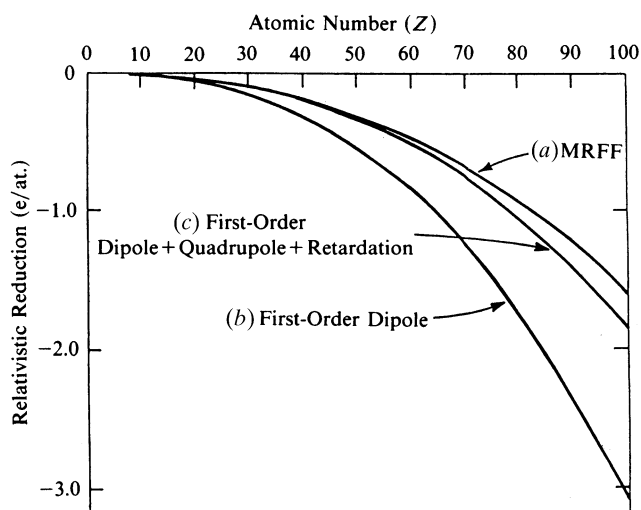


Fig. 4.2.6.1. The relativistic correction in electrons per atom for: (a) the modified form-factor approach; (b) the relativistic multipole approach; (c) the relativistic dipole approach.

Because excessive amounts of computer time are required to use these direct techniques for calculating the amplitudes from all the subshells, simpler methods are usually used for calculating outer-shell amplitudes. Kissel & Pratt (1985) used estimates for outer-shell amplitudes based on the predictions of the modified form-factor approach. A tabulation of the modified relativistic form factors has been given by Schaupp, Schumacher, Smend, Rullhusen & Hubbell (1983).

Because of the generality of their approach, the computer time required for the calculation of the scattering amplitudes for a particular energy is quite long, so that relatively few calculations have been made. Their approach, however, does not confine itself solely to the problem of forward scattering of photons as does the Cromer & Liberman (1970) approach. Using their model, Kissel *et al.* (1980) have been able to show that it is incorrect to assign a dependence of the dispersion corrections on the scattering vector Δ . This is at variance with some established crystallographic practices, in which the dispersion corrections are accorded the same dependence on Δ as $f_0(\Delta)$, and also at

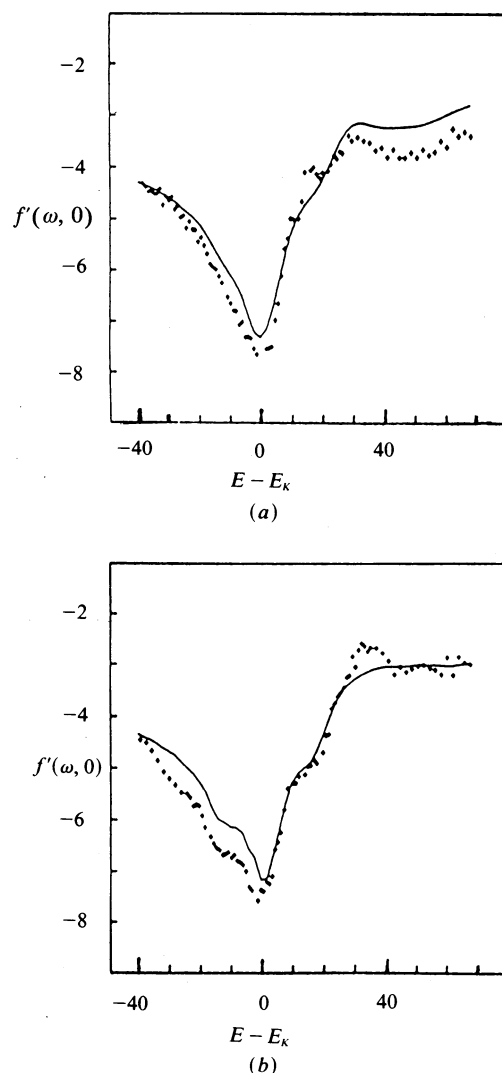


Fig. 4.2.6.2. Measured values of $f'(\omega, 0)$ at the K -edge of Nb in LiNbO_3 and the Kramers-Kronig transformation of $f''(\omega, 0)$. The curve is obtained by transformation and the points are measured by interferometry. For (a), the polarization of the incident radiation is parallel to the hexagonal c axis, and for (b) it is at right angles to the hexagonal c axis. After Bonse & Henning (1986). Note that the distortion of the dispersion curve is due to X-ray absorption near-edge structure (XANES) effects (Section 4.2.4).

4. PRODUCTION AND PROPERTIES OF RADIATIONS

variance with the predictions of Wagenfeld's (1975) non-relativistic model.

4.2.6.2.4. *Intercomparison of theories*

A discussion of the validity of the non-relativistic dipole approximation for the calculation of forward Rayleigh scattering amplitudes has been given by Roy & Pratt (1982). They compared their relativistic multipole calculations with the relativistic dipole approximation and with the non-relativistic dipole approximation for two elements, silver and lead. They concluded that a relativistic correction to the form factor of order $(Z\alpha)^2$ persists in the high-energy limit, and that this constant correction accounts for much of the deviation from the non-relativistic dipole approximation at all energies above threshold. In addition, their results illustrate that cancelling occurs amongst the relativistic, retardation, and higher multipole contributions to the scattering amplitude. This implies that care must be taken in assessing where to terminate the series that describes the multipolarity of the scattering process.

In a later paper, Roy, Kissel & Pratt (1983) discussed the elastic photon scattering for small momentum transfers and the validity of the form-factor theories. In this paper, which compares the relativistic modified form factor with experimental results for lead and a relativistic form factor and the tabulation by Hubbell, Veigele, Briggs, Brown, Cromer & Howerton (1975), it is shown that the modified relativistic form-factor approach gives better agreement with experiment for high momentum transfers ($< 104 \text{ \AA}^{-1}$) than the non-relativistic, form-factor theories.

Kissel *et al.* (1980) used the S -matrix technique to calculate the real part of the forward-scattering amplitude $f'(\omega, 0)$ for the inert gases at the wavelength of Mo $K\alpha_1$. These values are compared with the predictions of the relativistic dipole theory (RDP) and the relativistic multipole theory (RMP) in Table 4.2.6.2(a). In most cases, the agreement between the S matrix and the RMP theory is excellent, considering the differences in the methodology of the two sets of calculations. Table 4.2.6.2(b) shows comparisons of the real part of the forward-scattering amplitude $f'(\omega, 0)$ calculated for the atoms aluminium, silicon, zinc, germanium, silver, samarium, tantalum and lead using the approach of Kissel *et al.* (1980) with that of Cromer & Liberman (1970, 1981), with tabulations by Wagenfeld (1975), and with values taken from the tables in this section. Although reasonably satisfactory agreement exists between the relativistic values, large differences exist between the non-relativistic value (Wagenfeld, 1975) and the relativistic values. The major difference between the relativistic values occurs because of differences in estimation of the self-consistent-field term, which is proportional to E_{tot}/mc^2 . The Cromer & Liberman (1970) relativistic dipole value is $+\frac{2}{3}(E_{\text{tot}}/mc^2)$, whereas the tabulation in this section uses the relativistic multipole value of $(+E_{\text{tot}}/mc^2)$. This causes a vertical shift of the curve, but does not alter its shape. Should better estimates of the self-energy term be found, the correction is simply that of adding a constant to each value of $f'(\omega, 0)$ for each atomic species. There is a significant discrepancy between the Kissel *et al.* (1980) result for ^{62}Sm and the other theoretical values. This is the only major point of difference, however, and the results are better in accord with the relativistic multipole approach than with the relativistic dipole approach. Note that the relativistic multipole approach does not include the Stibius-Jensen correction, which alters the shape of the curve.

In §4.2.6.3.3, some examples are given to illustrate the extent to which predictions of these theories agree with experimental data for $f''(\omega, 0)$.

That there is little to choose between the different theoretical approaches where the calculation of $f''(\omega, 0)$ is concerned is illustrated in Table 4.2.6.3. In most cases, the agreement between the scattering matrix, relativistic dipole, and relativistic multipole values is within 1%. In contrast, there are some significant differences between the relativistic and the non-relativistic values of $f''(\omega, 0)$. The extent of the discrepancies is greater the higher the atomic number, as one might expect from the assumptions made in the formulation of the non-relativistic model. Some detailed comparisons of theoretical and experimental data for linear attenuation coefficients [proportional to $f''(\omega, 0)$] have been given by Creagh & Hubbell (1987) for silicon, and for copper and carbon by Gerward (1982, 1983). These tend to confirm the assertion that, at the 1% level of accuracy, there is little to choose between the various relativistic models for computing scattering cross sections.

Further discussion of this is given in §4.2.6.3.3.

4.2.6.3. *Modern experimental techniques*

The atomic scattering factor enters directly into expressions for such macroscopic material properties as the *refractive index*, n , and the *linear attenuation coefficient*, μ_1 . The refractive index depends on the dielectric susceptibility χ through

$$n = (1 + \chi)^{1/2}, \quad (4.2.6.35)$$

where

$$\chi = -\frac{r_e \lambda^2}{\pi} \sum_j N_j f_j(\omega, \Delta) \quad (4.2.6.36)$$

and N_j is the number density of atoms of type j .

The imaginary part of the dispersion correction $f''(\omega, \Delta)$ for the case where $\Delta = 0$ is related to the atomic scattering cross section through equation (4.2.6.23).

Experimental techniques that measure refractive indices or X-ray attenuation coefficients to determine the dispersion corrections involve measurements for which the scattering vector, Δ , is zero or close to it. Data from these experiments may be compared *directly* with data sets such as Cromer & Liberman (1970, 1981).

Other techniques measure the intensities of Bragg reflections from crystalline materials or the variation of intensities within one particular Laue reflection (*Pendellösung*). For these cases, $\Delta = g_{hkl}$, the reciprocal-lattice vector for the reflection or reflections measured. These techniques can be compared only indirectly with existing relativistic tabulations, since these have been developed for the $\Delta = 0$ case. Data are available for elements having atomic numbers less than 20 in the non-relativistic case (Wagenfeld, 1975).

The following sections will discuss some modern techniques for the measurement of dispersion corrections, and an inter-comparison will be made between experimental data and theoretical calculations for a representative selection of atoms and at two extremes of photon energies: near to and remote from an absorption edge of those atoms.

4.2.6.3.1. *Determination of the real part of the dispersion correction: $f'(\omega, 0)$*

X-ray interferometer techniques are now used extensively for the measurement of the refractive index of materials and hence