

4. PRODUCTION AND PROPERTIES OF RADIATIONS

if the atom is assumed to have an infinite number of energy states. For an atom containing κ electrons, it is assumed that the overall value of f' is the coherent sum of the contribution of each individual electron, whence

$$f' = \sum_{\kappa} \int_{\omega_{\kappa}}^{\infty} \frac{\omega'^2 (dg_{\kappa}/d\omega')}{\omega^2 - \omega'^2} d\omega' \quad (4.2.6.12)$$

and the oscillator strength of the κ th electron

$$g_{\kappa} = \int_{\omega_{\kappa}}^{\infty} \left[\frac{dg}{d\omega} \right]_{\kappa} d\omega$$

is not unity, but the total oscillator strength for the atom must be equal to the total number of electrons in the atom.

The imaginary part of the dispersion correction f'' is associated with the damping of the incident wave by the bound electrons. It is therefore functionally related to the linear absorption coefficient, μ_l , which can be determined from experimental measurement of the decrease in intensity of the photon beam as it passes through a medium containing the atoms under investigation. It can be shown that the attenuation coefficient per atom μ_a is related to the density of the oscillator states by

$$\mu_a = \frac{2\pi^2 e^2}{\epsilon_0 mc} \left[\frac{dg}{d\omega} \right], \quad (4.2.6.13)$$

whence

$$f'' = \frac{\pi}{2} \omega \left[\frac{dg_{\kappa}}{d\omega} \right]. \quad (4.2.6.14)$$

An expression linking the real and imaginary parts of the dispersion corrections can now be written:

$$f' = \frac{2}{\pi} \sum_{\kappa} P \int_{\omega_{\kappa}}^{\infty} \frac{\omega' f''(\omega', 0)}{\omega^2 - \omega'^2} d\omega'. \quad (4.2.6.15)$$

This is referred to as the Kramers–Kronig transform. Note that the term involving the restoring force has been omitted from this equation.

Equations (4.2.6.12), (4.2.6.14), and (4.2.6.15) are the fundamental equations of the classical theory of photon scattering, and it is to these equations that the predictions of other theories are compared.

4.2.6.2.2. Non-relativistic theories

The matrix element for Rayleigh scattering from an atom having a radially symmetric charge distribution may be written as

$$M = M_1(\boldsymbol{\epsilon}_i \cdot \boldsymbol{\epsilon}_f^*) + M_2(\boldsymbol{\epsilon}_i \cdot \boldsymbol{\kappa}_f)(\boldsymbol{\epsilon}_f^* \cdot \boldsymbol{\kappa}_i), \quad (4.2.6.16)$$

where $\boldsymbol{\epsilon}_i$ and $\boldsymbol{\epsilon}_f$ represent the initial and final states of the photon. The matrix element M_1 represents scattering for polarizations $\boldsymbol{\epsilon}_i$ and $\boldsymbol{\epsilon}_f$ perpendicular to the plane of scattering and M_2 represents scattering for polarization states lying in the plane of scattering.

Averaged over polarization states, the differential scattering cross section takes the form

$$\frac{d\sigma}{d\Omega} = \frac{r_e^2}{2} (|M_1|^2 + |M_2|^2). \quad (4.2.6.17)$$

Here σ is the photoelectric scattering cross section, which is related to the mass attenuation coefficient μ_m by

$$\sigma = (M/N_A)\mu_m \times 10^{-24}, \quad (4.2.6.18)$$

where M is the molecular weight and N_A is Avogadro's number.

Using the vector potential of the wavefield \mathbf{A} , an expression for the perturbed Hamiltonian of a hydrogen-like atom coupled to the radiation field may be written as

$$\hat{\mathcal{H}} = \hat{\mathcal{H}}_0 - r_e c \mathbf{A} \cdot \mathbf{P} + \frac{r_e^2}{2} \mathbf{A}^2, \quad (4.2.6.19)$$

where $\hat{\mathcal{H}}_0$ is the Hamiltonian for the unperturbed atom and $\mathbf{P} = i\hbar \nabla$.

After application of the second-order perturbation theory, the matrix element may be deduced to be

$$M = (\boldsymbol{\epsilon}_i \cdot \boldsymbol{\epsilon}_f^*) f_0(\Delta) + \frac{1}{m} \langle 1|T_1|1 \rangle + \frac{1}{m} \langle 1|T_2|1 \rangle. \quad (4.2.6.20)$$

In this equation, the initial and final wavefunctions are designated as $\langle 1|$ and $|1 \rangle$, respectively, and the terms T_1 and T_2 are given by

$$T_1 = \boldsymbol{\epsilon}_f \cdot \mathbf{P} \exp(-i\mathbf{k}_f \cdot \mathbf{r}) \frac{1}{E_1 - \mathcal{H}_0 + \hbar\omega + i\xi} \boldsymbol{\epsilon}_i \cdot \mathbf{P} \exp(-i\mathbf{k}_i \cdot \mathbf{r})$$

and

$$T_2 = \boldsymbol{\epsilon}_i \cdot \mathbf{P} \exp(-i\mathbf{k}_i \cdot \mathbf{r}) \frac{1}{E_1 - \mathcal{H}_0 + \hbar\omega + i\xi} \boldsymbol{\epsilon}_f \cdot \mathbf{P} \exp(-i\mathbf{k}_f \cdot \mathbf{r})$$

where ξ is an infinitesimal positive quantity.

The first term of equation (4.2.6.20) corresponds to the atomic scattering factor and is identical to the value given by classical theory. The terms involving T_1 and T_2 correspond to the dispersion corrections. Equation (4.2.6.20) contains no terms to account for radiation damping. More complete theories take the effect of the finite width of the radiating level into account.

It is necessary to realize that the atomic scattering factor depends on both the photon's frequency ω and the momentum vector Δ . To emphasize this dependence, equation (4.2.6.7) is rewritten as

$$f(\omega, \Delta) = f_0(\Delta) + f'(\omega, \Delta) + if''(\omega, \Delta). \quad (4.2.6.21)$$

In the dipole approximation, it can be shown that

$$f'(\omega, 0) = \frac{2}{\pi} P \int_0^{\infty} \frac{\omega' f''(\omega', 0)}{\omega^2 - \omega'^2} d\omega', \quad (4.2.6.22)$$

which may be compared with equation (4.2.6.15) and

$$f''(\omega, 0) = \frac{\omega}{4\pi r_e c} \sigma(\omega), \quad (4.2.6.23)$$

which may be compared with equation (4.2.6.14).

There is a direct correspondence between the predictions of the classical theory and the theory using second-order perturbation theory and non-relativistic quantum mechanics.

The extension of Hönl's (1933a,b) study of the scattering of X-rays by the K shell of atoms to other electron shells has been presented by Wagenfeld (1975).

In these calculations, the energy of the photon was assumed to be such that relativistic effects do not occur, nor do transitions within the discrete states of the atom occur. Transitions to continuum states do occur, and, using the analytical expressions for the wavefunctions of the hydrogen-like atom, analytical expressions may be developed for the photoelectric scattering cross sections. By expansion of the retardation factor $\exp(-i\mathbf{k} \cdot \mathbf{r})$ as the power series $1 - i\mathbf{k} \cdot \mathbf{r} - \frac{1}{2}(\mathbf{k} \cdot \mathbf{r})^2 + \dots$, it is possible to determine dipolar, quadrupolar, and higher-order

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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