7.4. CORRECTION OF SYSTEMATIC ERRORS

$$H = \frac{e}{me}\mathbf{p}\cdot\mathbf{A} + \frac{e^2}{2me^2}\mathbf{A}\cdot\mathbf{A}. \qquad (7.4.3.3)$$

It produces photoelectric absorption through the $\mathbf{p}\cdot\mathbf{A}$ term taken in first order, Compton and Raman scattering through the $\mathbf{A}\cdot\mathbf{A}$ term and resonant Raman scattering through the $\mathbf{p}\cdot\mathbf{A}$ terms in second order.

If resonant scattering is neglected for the moment, the expression for the incoherent scattering cross section becomes

$$S = \sum_f (E_2/E_1)^2 \left| \langle\psi_f| \sum_j \exp(i\mathbf{K}\cdot\mathbf{r}_j)|\psi_i\rangle \right|^2 \delta(E_f - E_i - \Delta E),$$

$$(7.4.3.4)$$

where the Born operator is summed over the j target electrons and the matrix element is summed over all final states accessible through energy conservation. In the high-energy limit of $\Delta E \gg E_B$, $S(E_1, E_2, \mathbf{K}, Z) \to Z$ but as Table 7.4.3.1 shows this condition does not hold in the X-ray regime.

The evaluation of the matrix elements in equation (7.4.3.4) was simplified by Waller & Hartree (1929) who (i) set $E_2 = E_1$ and (ii) summed over all final states irrespective of energy conservation. Closure relationships were then invoked to reduce the incoherent scattering factor to an expression in terms of form factors f_{jk}:

$$S = \sum_j [1 - |f_j(\mathbf{K})|^2] - \sum_j \sum_k^{j \neq k} |f_{jk}(\mathbf{K})|^2, \qquad (7.4.3.5)$$

where

$$f_j(\mathbf{K}) = \langle\psi_j|\exp(i\mathbf{K}\cdot\mathbf{r}_j)|\psi_j\rangle$$

and

$$f_{jk} = \langle\psi_k|\exp[i\mathbf{K}\cdot(\mathbf{r}_k - \mathbf{r}_j)]|\psi_j\rangle,$$

the latter term arising from exchange in the many-electron atom.

According to Currat, DeCicco & Weiss (1971), equation (7.4.3.5) can be improved by inserting the prefactor $(E_2/E_1)^2$, where E_2 is calculated from equation (7.4.3.1); the factor is an average for the factors inside the summation sign of equation (7.4.3.4) that were neglected by Waller & Hartree. This term has been included in a few calculations of incoherent intensities [see, for example, Bloch & Mendelsohn (1979)]. The Waller–Hartree method remains the chosen basis for the most extensive compilations of incoherent scattering factors, including those tabulated here, which were calculated by Cromer & Mann (1967) and Cromer (1969) from non-relativistic Hartree–Fock self-consistent-field wavefunctions. Table 7.4.3.2 is taken from the compilation by Hubbell, Veigele, Briggs, Brown, Cromer & Howerton (1975).

7.4.3.2.2. *Thomas–Fermi model*

This statistical model of the atomic charge density (Thomas, 1927; Fermi, 1928) considerably simplifies the calculation of coherent and incoherent scattering factors since both can be written as universal functions of $\mathbf{K}$ and Z. Numerical values were first calculated by Bewilogua (1931); more recent calculations have been made by Brown (1966) and Veigele (1967). The method is less accurate than Waller–Hartree theory, but it is a much simpler computation.

7.4.3.2.3. *Exact calculations*

The matrix elements of (7.4.3.4) can be evaluated exactly for the hydrogen atom. If one-electron wavefunctions in many-electron atoms are modelled by hydrogenic orbitals [with a

Table 7.4.3.3. *Compton scattering of Mo Kα X-radiation through 170° from 2s electrons*

Element	S_{exact}	S_{imp}	S_{W-H}
Li	0.879	0.878	0.877
B	0.879	0.878	0.877
O	0.878	0.877	0.876
Ne	0.875	0.875	0.875
Mg	0.863	0.863	0.872
Si	0.851	0.850	0.868
Ar	0.843	0.826	0.877
V	0.663	0.716	0.875
Cr	0.568	0.636	0.875

S_{exact} is the incoherent scattering factor calculated analytically from a hydrogenic atomic model. S_{imp} is the incoherent scattering factor calculated by taking the Compton profile derived in the impulse approximation and truncating it for $\Delta E < E_B$. S_{W-H} is the Waller–Hartree incoherent scattering factor. Data taken from Bloch & Mendelsohn (1974).

suitable choice of the orbital exponent; see, for example, Slater (1937)], an analytical approach can be used, as was originally proposed by Bloch (1934).

Hydrogenic calculations have been shown to predict accurate K- and L-shell photoelectric cross sections (Pratt & Tseng, 1972). The method has been applied in a limited number of cases to K-shell (Eisenberger & Platzman, 1970) and L-shell (Bloch & Mendelsohn, 1974) incoherent scattering factors, where it has served to highlight the deficiencies of the Waller–Hartree approach. In chromium, for example, at an incident energy of $\sim 17\,\text{keV}$ and a Bragg angle of 85°, the L-shell Waller–Hartree cross section is higher than the 'exact' calculation by $\sim 50\%$. A comparison of Waller–Hartree and exact results for $2s$ electrons, taken from Bloch & Mendelsohn (1974), is given in Table 7.4.3.3 for illustration. The discrepancy is much reduced when all electrons are considered.

In those instances where the exact method has been used as a yardstick, the comparison favours the 'relativistic integrated impulse approximation' outlined below, rather than the Waller–Hartree method.

7.4.3.3. *Relativistic treatment of incoherent scattering*

The Compton effect is a relativistic phenomenon and it is accordingly more satisfactory to start from this basis, *i.e.* the Klein & Nishina (1929) theory and the Dirac equation (see Jauch & Rohrlich, 1976). In second-order relativistic perturbation theory, there is no overt separation of $\mathbf{p}\cdot\mathbf{A}$ and $\mathbf{A}\cdot\mathbf{A}$ terms. The inclusion of electron spin produces additional terms in the Compton cross section that depend upon the polarization (Lipps & Tolhoek, 1954); they are generally small at X-ray energies. They are of increasing interest in synchrotron-based experiments where the brightness of the source and its polarization characteristics compensate for the small cross section (Blume & Gibbs, 1988).

Somewhat surprisingly, it is the spectral distribution, $\text{d}^2\sigma/\text{d}\Omega\,\text{d}E_2$, rather than the total intensity, $\text{d}\sigma/\text{d}\Omega$, which is the better understood. This is a consequence of the exploitation of the Compton scattering technique to determine electron momentum density distributions through the Doppler broadening of the scattered radiation [see Cooper (1985) and Williams (1977) for reviews of the technique]. Manninen, Paakkari & Kajantie (1976) and Ribberfors (1975) have shown that the

references