$$\sigma_{\rm inel}(s) = 4S(s)/a^2s^4.$$

Inelastic scattering factors for X-rays and electrons are given in Table 4.3.3.2 in the Morse (1932) approximation for elements $Z = 1$ to $Z = 92$ with HF wave functions (Bunge, Barrientos & Bunge, 1993; McLean & McLean, 1981).

There are two kinds of relativistic correction that can be made on inelastic scattering factors. The first is for relativistic effects on the atomic field and has been neglected. This should not be too serious since HF wavefunctions are used and the corrections are only large for the heavier atoms where the contribution to the total scattering for $s > 3 - 4\,\text{Å}^{-1}$ tends to be negligible. The other correction is for effects in the scattering process, which can be significant above 40 keV, but again these corrections tend to be localized to the small-angle region ($s < 3\,\text{Å}^{-1}$) (Yates, 1970). Hence the tables of inelastic scattering factors given here are based on HF atomic fields since these appear to be the most accurate results presently available.

The inelastic scattering equations must be modified in order to compare theory with experiment. First, the Morse theory is corrected to ensure that both energy and momentum are conserved in the scattering process. In the description of the elastic scattering process, no transformation is required from the centre-of-mass system (CMS), where the scattering factors are calculated, to the laboratory system (LS), where data are taken, since the nuclei are heavy compared with the incident electrons. In the inelastic channels, a similar argument holds for scattering involving the bound states. However, for ionizing processes, the interaction can be assumed to take place between the incident electron and the ejected electron, so that the CMS is entirely different from the LS. Considering the atomic electrons as free particles and considering only the ionization process, the transformation between the CMS and the LS is possible and leads to the Bethe modification (Tavard & Bonham, 1969) for inelastic scattering. The inelastic cross section can now be given by

$$\sigma_{\rm inel} = \frac{4\cos(2\theta)S(s\cos\theta)}{a^2s^4\cos^4\theta}$$

for $\theta < \pi/4$ and by $\sigma_{\rm inel} = 0$ for $\theta > \pi/4$.

Another modification is necessary because the average energy of inelastically scattered electrons varies with energy and is given from approximate conservation of energy and momentum for a fast incident particle by $k^2\cos^2(2\theta)$. This means that for $s > 30\text{Å}^{-1}$ at 40 keV the average energy of inelastically scattered electrons may be around 30 keV and the fact that the response of the detector may be different for the 40keV inelastically scattered electrons and the elastic ones may have to be considered (Fink, Bonham, Lee & Ng, 1969).

In addition to the values given in Table 4.3.3.2, a few calculations of $S(s)$ have been carried out with very exact wavefunctions that include more than 85% of the correlation energy (Kohl & Bonham, 1967; Bartell & Gavin, 1964; Peixoto, Bunge & Bonham, 1969; Thakkar & Smith, 1978; Wang, Esquivel, Smith & Bunge, 1995).

4.3.3.2.3. *Corrections for defects in the theory of atomic scattering*

Errors in the inelastic scattering factors from the three approximations made in the Morse theory have been investigated (Tavard & Bonham, 1969; Bonham, 1965*b*). The Morse theory breaks down at very large scattering angles ($\theta > 30^\circ$), and is incorrect at small angles. Investigations carried out so far indicate that the small-angle failure is not serious outside $s = 1\,\text{Å}^{-1}$. It must be stressed that these uncertainties do not introduce important errors into the analysis of molecular structure using theoretical atomic scattering amplitudes. This is mainly because such deviations are smooth compared with molecular features and thus do not interfere with the analysis of molecular structure.

4.3.3.3. *Molecular scattering factors for electrons*

The simplest theory of molecular scattering assumes that a molecule consists of spherical atoms and that each electron is scattered by only one atom in the molecule. If only single scattering is allowed within each atom, the molecular intensity can be written as

$$\begin{aligned} I(s) &= I_a(s) + I_m(s) \\ &= \left[\frac{4I_0}{a^2s^4R^2}\right]\left[\sum_{i=1}^{M}\{[Z_i - F_i(s)]^2 + S_i(s)\}\right. \\ &\quad + \sum_{i}^{M}\sum_{j\neq i}^{M}[Z_i - F_i(s)][Z_j - F_j(s)] \\ &\quad \left.\times \int_0^\infty {\rm d}r\, P_{ij}(r,T)(\sin sr)/sr\right], \end{aligned} \tag{4.3.3.1}$$

where M is the number of constituent atoms in the molecule, $F_i(s)$ and $S_i(s)$ are the coherent and incoherent X-ray scattering factors, and $P_{ij}(r,T)$ is the probability of finding atom i at a distance r from atom j at the temperature T (Bonham & Su, 1966; Kelley & Fink, 1982*b*; Mawhorter, Fink & Archer, 1983; Mawhorter & Fink, 1983; Miller & Fink, 1985; Hilderbrandt & Kohl, 1981; Kohl & Hilderbrandt, 1981). The constant I_0 is proportional to the product of the intensities of the electron and molecular beams and R is the distance from the point of scattering to the detector. The single sum is the atomic intensity $I_a(s)$ and the double sum is the molecular intensity $I_m(s)$. This expression, referred to here as the independent atom model (IAM), may be improved by replacing the atomic elastic electron scattering factors by their partial wave counterparts. This modification is necessary to explain the failure of the Born approximation observed in molecules containing light and heavy atoms in proximity (Schomaker & Glauber, 1952; Seip, 1965), and may be written as

$$\begin{aligned} I(s) &= I_a(s) + I_m(s) \\ &= \frac{I_0}{R^2}\left\{\sum_{i=1}^{M}[|f_i|^2 + 4S_i(s)/(a^2s^4)]\right. \\ &\quad + \sum_{i}^{M}\sum_{j\neq i}^{M}|f_i|\,|f_j|\cos(\eta_i - \eta_j) \\ &\quad \left.\times \int_0^\infty {\rm d}r\, P_{ij}(r,T)(\sin sr)/sr\right\}. \end{aligned} \tag{4.3.3.2}$$

This is the most commonly used expression for the interpretation of molecular gas electron-diffraction patterns in the keV energy range. If it is necessary to consider relativistic effects in the scattering intensity, equation (4.3.3.2) becomes (Yates & Bonham, 1969)

$$I(s) = I_a(s) + I_m(s)$$
$$= \frac{I_0}{R^2}\left\{\sum_{i=1}^{M}[|f_i|^2 + |g_i|^2 + 4S_i(s)/(a^2s^4)] + \sum_{i}^{M}\sum_{j\neq i}^{M}[|f_i|\,|f_j|\cos(\eta_i^f - \eta_j^f) + |g_i|\,|g_j|\cos(\eta_i^g - \eta_j^g)] \times \int_0^\infty \mathrm{d}r\, P_{ij}(r,T)(\sin sr)/sr\right\}, \quad (4.3.3.3)$$

where $|g_i|$ and η_i^g refer to the scattering-factor magnitude and phase for electrons that have changed their electron spin state during the scattering process and $|f_i|$ and η_i^f refer to retention of spin orientation. The incident electron beam is assumed to be unpolarized and no attempt has been made to consider relativistic effects on the inelastic scattering cross section, which is usually negligible in the structural s range.

If it is necessary to consider binding effects, the first Born approximation may usually be used in describing molecular scattering, since binding effects are largest for molecules containing small atoms where the Born approximation is most valid.

The exact expression for $I(s)$ in the first Born approximation can be written as (Bonham & Fink, 1974; Tavard & Roux, 1965; Tavard, Rouault & Roux, 1965; Iijima, Bonham & Ando, 1963; Bonham, 1967)

$$I(s) = \frac{4I_0}{a^2s^4R^2}\left\{\sum_{i=1}^{M}(Z_i^2 + Z_i) + \sum_{i}^{M}\sum_{j\neq i}^{M} Z_iZ_j\int_0^\infty \mathrm{d}r\, P_{ij}(r,T)(\sin sr)/sr - 2\sum_{i=1}^{M} Z_i\left\langle\int \mathrm{d}r\,\rho(r+r_i)(\sin sr)/sr\right\rangle_{\mathrm{vib}} + \left\langle\int \mathrm{d}r\,\rho_c(r)(\sin sr)/sr\right\rangle_{\mathrm{vib}}\right\},$$

where

$$\rho(r) = \sum_{i=1}^{N}\int \mathrm{d}r_1 \ldots \int \mathrm{d}r_N\,|\psi(r_1,\ldots,r_N)|^2\delta(r - r_i)$$

and

$$\rho_c(r) = \sum_{i}^{N}\sum_{j\neq i}^{N}\int \mathrm{d}r_1 \ldots \int \mathrm{d}r_N\,|\psi(r_1,\ldots,r_N)|^2\delta(r - r_i + r_j).$$

The brackets $\langle\,\rangle_{\mathrm{vib}}$ denote averaging over the vibrational motion, $\delta(r)$ is the Dirac delta function, and $\psi(r_i,\ldots,r_n)$ is the molecular wavefunction. Binding effects appear to be proportional to the ratio of the number of electrons involved in binding to the total number of electrons in the system (Kohl & Bonham, 1967; Bonham & Iijima, 1965) so that binding effects in molecules containing mainly heavy atoms should be quite small.

The intensities, $I(s)$, for many small molecules have been calculated based on molecular Hartree–Fock wavefunctions. In most cases, a distinctive minimum has been found at about $s = 3 - 4\,\text{Å}^{-1}$ and a much small maximum at $s = 8 - 10\,\text{Å}^{-1}$ in the cross-sectional difference curve between the IAM and the molecular HF results (Pulay, Mawhorter, Kohl & Fink, 1983; Kohl & Bartell, 1969; Liu & Smith, 1977; Epstein & Stewart, 1977; Sasaki, Konaka, Iijima & Kimura, 1982; Shibata, Hirota, Kakuta & Muramatsu, 1980; Horota, Kakuta & Shibata, 1981; Xie, Fink & Kohl, 1984). Further studies using correlated wavefunctions (accounting for up to 60% of the correlation energy) showed that in the elastic channel the binding effects are only weakly modified; only the maximum at $s = 8 - 10\,\text{Å}^{-1}$ is further reduced. However, strong effects are seen in the inelastic channel, deepening the minimum at $s = 3 - 4\,\text{Å}^{-1}$ significantly (Breitenstein, Endesfelder, Meyer, Schweig & Zittlau, 1983; Breitenstein, Endesfelder, Meyer & Schweig, 1984; Breitenstein, Mawhorter, Meyer & Schweig, 1984; Wang, Tripathi & Smith, 1994). Detailed calculations on CO_2 and H_2O averaging over many internuclear distances and applying the pair distribution functions $P_{ij}(r)$ showed that vibrational effects do not alter the binding effects (Breitenstein, Mawhorter, Meyer & Schweig, 1986). For CO_2, the calculations have been confirmed in essence by an experimental set of data (McClelland & Fink, 1985). However, more molecules and more detailed analysis will be available in the future. The binding effects make it desirable to avoid the small-angle-scattering range when structural information is the main goal of a diffraction analysis.

The problem of intramolecular multiple scattering may necessitate corrections to the molecular intensity when three or more closely spaced heavy atoms are present. This correction (Karle & Karle, 1950; Hoerni, 1956; Bunyan, 1963; Gjønnes, 1964; Bonham, 1965*a*, 1966) appears to be more serious for three atoms in a right triangular configuration than for a collinear arrangement of three atoms. A case study by Kohl & Arvedson (1980) on SF_6 showed the importance of multiple scattering. However, their approach is too cumbersome to be used in routine structure work. A very good approximate technique is available utilizing the Glauber approximation (Bartell & Miller, 1980; Bartell & Wong, 1972; Wong & Bartell, 1973; Bartell, 1975); Kohl's results are reproduced quite well using the atomic scattering factors only. Several applications of the multiple scattering routines showed that the internuclear distances are rather insensitive to this perturbation, but the mean amplitudes of vibration can easily change by 10% (Miller & Fink, 1981; Kelley & Fink, 1982*a*; Ketkar & Fink, 1985).

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4.3.4. Electron energy-loss spectroscopy on solids (By C. Colliex)

4.3.4.1. *Definitions*

4.3.4.1.1. *Use of electron beams*

Among the different spectroscopies available for investigating the electronic excitation spectrum of solids, inelastic electron scattering experiments are very useful because the range of accessible energy and momentum transfer is very large, as illustrated in Fig. 4.3.4.1 taken from Schnatterly (1979). Absorption measurements with photon beams follow the photon dispersion curve, because it is impossible to vary independently the energy and the momentum of a photon. In a scattering experiment, a quasi-parallel beam of monochromatic particles is incident on the specimen and one measures the changes in energy and momentum that can be attributed to the creation of a given excitation in the target. Inelastic neutron scattering is the most

references