

3.3. Atomic Scattering Factors

3.3.1. Atomic Scattering Factors for X-rays (corrected to November 1961)

The coherent scattering of X-rays from an atom may be described in terms of the atomic scattering factor f , which is the ratio of the amplitude of the radiation scattered by the atom to the amplitude of the radiation which an electron would scatter under the same conditions according to the classical theory. (See James [4] for a detailed discussion of such scattering and of the atomic scattering factor.) The atomic scattering factor is a function of the electron density of the atom. Since the density function is known exactly only for the hydrogen atom, scattering factors for all other atoms are approximate, and are reliable only in so far as the electron-density function employed in their calculation is a reliable representation of the true density function. The various methods of approximating the total wave function (and hence the electron density function) of an atom are discussed in the literature, and here we only mention those methods upon which the atomic factors in the following tables are based.

Improvements in wave functions are generally judged in accordance with the variation principle by minimization of total energy. It is by no means true that those wave functions which lead to the lowest energy, and hence are "best" in that sense, are necessarily the most reliable ones for the calculation of atomic scattering factors. Nevertheless, the energy criterion is a useful one, and there is no evidence at present to suggest that wave functions selected on such a criterion will lead to inferior atomic scattering factors. Accordingly, atomic scattering factors for Table 3.3.1A were generally selected according to the following order of preference of the wave functions: (1) Boys' analytic approach [1]; (2) improved (e.g. by considering correlation effects) Hartree-Fock self-consistent fields with exchange; (3) Hylleraas-Eckart type analytic wave functions; (4) Hartree-Fock self-consistent fields with exchange; (5) Hartree self-consistent fields; (6) Slater-type analytic wave functions with parameters determined from the variation principle. (See [3] [5] for a thorough discussion of many of these approaches to the calculation of atomic wave functions.) It should be noted that this order of pre-

ference is not always reflected in the selection of the data for Table 3.3.1A. Other factors, e.g. the availability and numerical accuracy of the scattering-factor data, were also considered. On the other hand, all the atomic scattering factors of Table 3.3.1A were based on those approaches to the calculation of atomic wave functions listed above. Atomic scattering factors obtained experimentally or by interpolation methods have not been included in the table. The reasons for this are twofold. First, it is generally quite difficult to assess the reliability of such atomic scattering factors; second, there is widespread interest in the calculation of atomic wave functions, and it is reasonable to suppose that many of the gaps to be found in Table 3.3.1A will be filled in the near future.

Another general approach to the calculation of atomic structures is the statistical one, either by the Thomas-Fermi or the Thomas-Fermi-Dirac methods. The latter method includes the effects of exchange and is generally believed to lead to better electron distributions. (Relevant discussions of the statistical approach are to be found in [2] [6] [8].) In Table 3.3.1B are presented atomic scattering factors based on the Thomas-Fermi-Dirac statistical model.

The atomic scattering factors of Tables 3.3.1A and B embody certain assumptions that are worth noting. First, the atoms are assumed to be at rest. Second, with only a few exceptions so noted in Table 3.3.1A, the atoms are assumed to be in their ground states. Third, it is assumed that the frequency of the scattered radiation is large in comparison with the transition frequencies within the atom. Fourth, the electron density of the atom is assumed to be spherically symmetric, and in the case of atoms known to be aspherical, the values of Tables 3.3.1A and B are mean atomic scattering factors.* In the case of aspherical atoms the atomic scattering factor is a function of the orientation of the atom, but such so-called orientation effects are important only in the later stages of refinement of a crystal structure [7]. Therefore, orientation effects are considered to be outside the immediate purpose of the present tables; however, in Table 3.3.1A there are indicated those aspherical atoms for which orientation effects have been considered in the literature.

* Averaged over orientation.