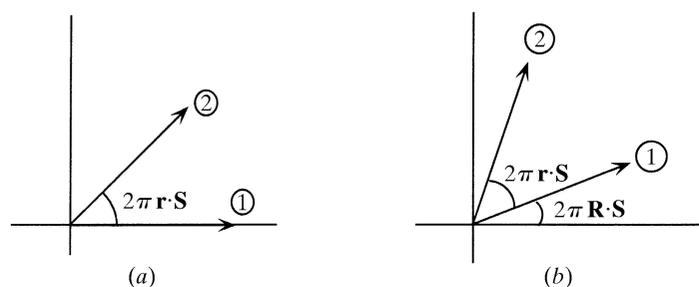


2. BASIC CRYSTALLOGRAPHY

**Figure 2.1.4.4**

An Argand diagram for the scattering by two electrons. In (a), the origin is at electron 1; electron 2 is at position \mathbf{r} with respect to electron 1. In (b), electron 1 is at position \mathbf{R} with respect to the new origin, and electron 2 is at position $\mathbf{R} + \mathbf{r}$.

The total scattering from the two-electron system is $1 + 1 \times \exp(2\pi i \mathbf{r} \cdot \mathbf{S})$ if the resultant amplitude of the waves from electrons 1 and 2 is set to 1. In an Argand diagram, the waves are represented by vectors in a two-dimensional plane, as in Fig. 2.1.4.4(a).¹ Thus far, the origin of the system was chosen at electron 1. Moving the origin to another position simply means an equal change of phase angle for all waves. Neither the amplitudes nor the intensities of the reflected beams change (Fig. 2.1.4.4b).

2.1.4.3. Scattering by atoms

2.1.4.3.1. Scattering by one atom

Electrons in an atom are bound by the nucleus and are – in principle – not free electrons.

However, to a good approximation, they can be regarded as such if the frequency of the incident radiation ν is greater than the natural absorption frequencies, ν_n , at the absorption edges of the scattering atom, or the wavelength of the incident radiation is shorter than the absorption-edge wavelength (Section 2.1.4.4). This is normally true for light atoms but not for heavy ones (Table 2.1.4.1).

If the electrons in an atom can be regarded as free electrons, the scattering amplitude of the atom is a real quantity, because the electron cloud has a centrosymmetric distribution, *i.e.* $\rho(\mathbf{r}) = \rho(-\mathbf{r})$.

A small volume, dv_r , at \mathbf{r} contains $\rho(\mathbf{r}) \times dv_r$ electrons, and at $-\mathbf{r}$ there are $\rho(-\mathbf{r}) \times dv_r$ electrons. The combined scattering of the two volume elements, in units of the scattering of a free electron, is

$$\rho(\mathbf{r})dv_r\{\exp(2\pi i \mathbf{r} \cdot \mathbf{S}) + \exp[2\pi i (-\mathbf{r}) \cdot \mathbf{S}]\} = 2\rho(\mathbf{r}) \cos(2\pi \mathbf{r} \cdot \mathbf{S})dv_r;$$

this is a real quantity.

The scattering amplitude of an atom is called the atomic scattering factor f . It expresses the scattering of an atom in terms of the scattering of a single electron. f values are calculated for spherically averaged electron-density distributions and, therefore, do not depend on the scattering direction. They are tabulated in *ITC* (2004) as a function of $\sin \theta/\lambda$. The f values decrease appreciably as a function of $\sin \theta/\lambda$ (Fig. 2.1.4.5). This is due to interference effects between the scattering from the electrons in the cloud. In the direction $\theta = 0$, all electrons scatter in phase and

¹ The plane is also called the ‘imaginary plane’. The real part of the vector in an Argand diagram is along the horizontal or real axis; the imaginary part is along the vertical or imaginary axis. Note also that $\exp(2\pi i \mathbf{r} \cdot \mathbf{S}) = \cos(2\pi \mathbf{r} \cdot \mathbf{S}) + i \sin(2\pi \mathbf{r} \cdot \mathbf{S})$. The cosine term is the real component and the sine term is the imaginary component.

Table 2.1.4.1

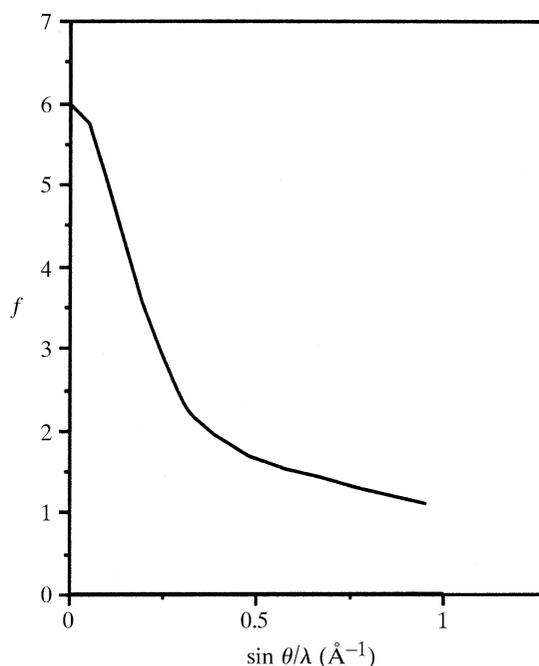
The position of the $K\alpha$ edge of different elements

Atomic number	Element	$K\alpha$ edge (\AA)
6	C	43.68
16	S	5.018
26	Fe	1.743
34	Se	0.980
78	Pt	0.158

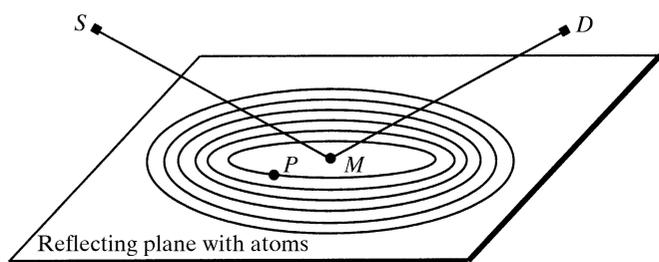
the atomic scattering factor is equal to the number of electrons in the atom.

2.1.4.3.2. Scattering by a plane of atoms

A plane of atoms reflects an X-ray beam with a phase retardation of $\pi/2$ with respect to the scattering by a single atom. The difference is caused by the difference in path length from source (S) to atom (M) to detector (D) for the different atoms in the plane (Fig. 2.1.4.6). Suppose the plane is infinitely large. The shortest connection between S and D *via* the plane is $S-M-D$. The plane containing S , M and D is perpendicular to the reflecting plane, and the lines SM and MD form equal angles with the reflecting plane. Moving outwards from atom M in the reflecting plane, to P for instance, the path length $S-P-D$ is longer. At the edge of the first Fresnel zone, the path is $\lambda/2$ longer (Fig. 2.1.4.6). This edge is an ellipse with its centre at M and its major axis on the line of intersection between the plane SMD and the reflecting plane. Continuing outwards, many more elliptic Fresnel zones are formed. Clearly, the beams radiated by the many atoms in the plane interfere with each other. The situation is represented in the Argand diagram in Fig. 2.1.4.7. Successive Fresnel zones can be subdivided into an equal number of subzones. If the distribution of electrons is sufficiently homogeneous, it can be assumed that the subzones in one Fresnel zone give the same amplitude at D . Their phases are spaced at regular intervals and their vectors in the Argand diagram lie in a half circle. In the lower part of Fig. 2.1.4.7, this is illustrated for the first Fresnel zone. For the second Fresnel zone (upper part),

**Figure 2.1.4.5**

The atomic scattering factor f for carbon as a function of $\sin \theta/\lambda$, expressed in units of the scattering by one electron. Reproduced with permission from Drenth (1999). Copyright (1999) Springer-Verlag.

**Figure 2.1.4.6**

S is the X-ray source and D is the detector. The scattering is by the atoms in a plane. The shortest distance between S and D via a point in the plane is through M . Path lengths via points in the plane further out from M are longer, and when these beams reach the detector they lag behind in phase with respect to the MD beam. The plane is divided into zones, such that from one zone to the next the path difference is $\lambda/2$.

the radius is slightly smaller, because the intensity radiated by more distant zones decreases (Kauzmann, 1957). Therefore, the sum of vectors pointing upwards is shorter than that of those pointing downwards, and the resulting scattered wave lags $\pi/2$ in phase behind the scattering by the atom at M .

2.1.4.4. Anomalous dispersion

In classical dispersion theory, the scattering power of an atom is derived by supposing that the atom contains dipole oscillators. In units of the scattering of a free electron, the scattering of an oscillator with eigen frequency ν_n and moderate damping factor κ_n was found to be a complex quantity:

$$f_n = \nu^2 / (\nu^2 - \nu_n^2 - i\kappa_n\nu), \quad (2.1.4.4)$$

where ν is the frequency of the incident radiation [James, 1965; see also *IT C* (2004), equation (4.2.6.8)]. When $\nu \gg \nu_n$ in equation (2.1.4.4), f_n approaches unity, as is the case for scattering by a free electron; when $\nu \ll \nu_n$, f_n approaches zero, demonstrating the lack of scattering from a fixed electron. Only for $\nu \cong \nu_n$ does the imaginary part have an appreciable value.

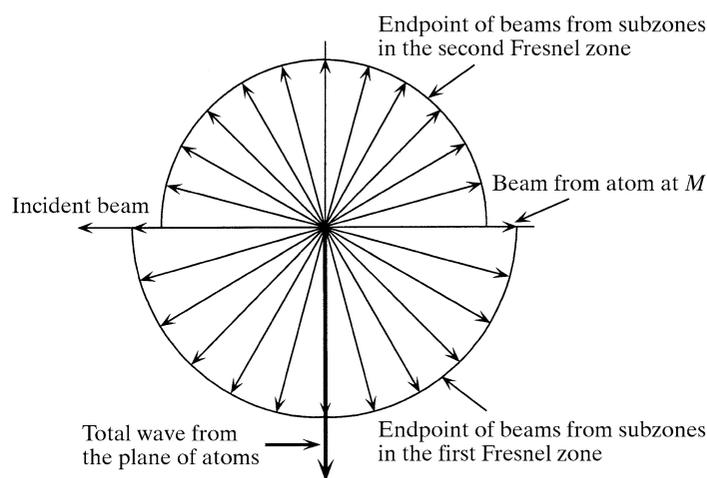
Fortunately, quantum mechanics arrives at the same result by adding a rational meaning to the damping factors and interpreting ν_n as absorption frequencies of the atom (Hönl, 1933). For heavy atoms, the most important transitions are to a continuum of energy states, with $\nu_n \geq \nu_K$ or $\nu_n \geq \nu_L$ etc., where ν_K and ν_L are the frequencies of the K and L absorption edges.

In practice, the complex atomic scattering factor, $f_{\text{anomalous}}$, is separated into three parts: $f_{\text{anomalous}} = f + f' + if''$. f is the contribution to the scattering if the electrons are free electrons and it is a real number (Section 2.1.4.3). f' is the real part of the correction to be applied and f'' is the imaginary correction; f'' is always $\pi/2$ in phase ahead of f (Fig. 2.1.4.8). $f + f'$ is the total real part of the atomic scattering factor.

The imaginary correction if'' is connected with absorption by oscillators having $\nu_n \cong \nu$. It can be calculated from the atomic absorption coefficient of the anomalously scattering element. For each of the K , L etc. absorption edges, f'' is virtually zero for frequencies below the edge, but it rises steeply at the edge and decreases gradually at higher frequencies.

The real correction f' can be derived from f'' by means of the Kramers–Kronig transform [*IT C* (2004), Section 4.2.6.2.2]. For frequencies close to an absorption edge, f' becomes strongly negative.

Values for f , f' and f'' are always given in units equal to the scattering by one free electron. f values are tabulated in *IT C* (2004) as a function of $\sin \theta/\lambda$, and the anomalous-scattering

**Figure 2.1.4.7**

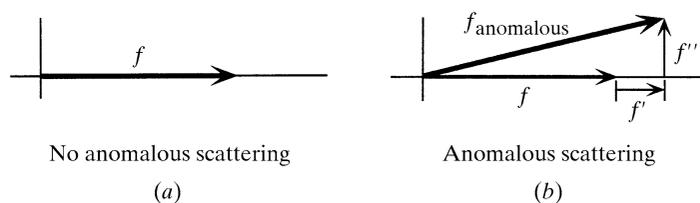
Schematic picture of the Argand diagram for the scattering by atoms in a plane. All electrons are considered free. The vector of the incident beam points to the left. The atom at M (see Fig. 2.1.4.6) has a phase difference of π with respect to the incident beam. Subzones in the first Fresnel zone have the endpoints of their vectors on the lower half circle. For the next Fresnel zone, they are on the upper half circle, which has a smaller radius because the amplitude decreases gradually for subsequent Fresnel zones (Kauzmann, 1957). The sum of all vectors points down, indicating a phase lag of $\pi/2$ with respect to the beam scattered by the atom at M .

corrections for forward scattering as a function of the wavelength. Because the anomalous contribution to the atomic scattering factor is mainly due to the electrons close to the nucleus, the value of the corrections diminishes much more slowly than f as a function of the scattering angle.

2.1.4.5. Scattering by a crystal

A unit cell contains a large number of electrons, especially in the case of biological macromolecules. The waves scattered by these electrons interfere with each other, thereby reducing the effective number of electrons in the scattered wave. The exception is scattering in the forward direction, where the beams from all electrons are in phase and add to each other. The effective number of scattering electrons is called the *structure factor* F because it depends on the structure, i.e. the distribution of the atoms in the unit cell. It also depends on the scattering direction. If small electron-density changes due to chemical bonding are neglected, the structure factor can be regarded as the sum of the scattering by the atoms in the unit cell, taking into consideration their positions and the corresponding phase differences between the scattered waves. For n atoms in the unit cell

$$F(\mathbf{S}) = \sum_{j=1}^n f_j \exp(2\pi i \mathbf{r}_j \cdot \mathbf{S}), \quad (2.1.4.5)$$

**Figure 2.1.4.8**

The atomic scattering factor as a vector in the Argand diagram. (a) When the electrons in the atom can be regarded as free. (b) When they are not completely free and the scattering becomes anomalous with a real anomalous contribution f' and an imaginary contribution if'' . Reproduced with permission from Drenth (1999). Copyright (1999) Springer-Verlag.