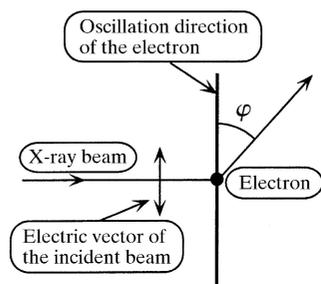## 2.1. INTRODUCTION TO BASIC CRYSTALLOGRAPHY

Figure 2.1.4.1
The electric vector of a monochromatic and polarized X-ray beam is in the plane. It hits an electron, which starts to oscillate in the same direction as the electric vector of the beam. The oscillating electron acts as a source of X-rays. The scattered intensity depends on the angle φ between the oscillation direction of the electron and the scattering direction [equation (2.1.4.1)]. Reproduced with permission from Drenth (1999). Copyright (1999) Springer-Verlag.
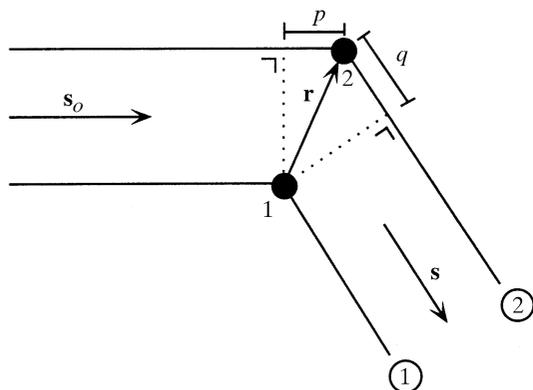
Figure 2.1.4.2
The black dots are electrons. The origin of the system is at electron 1; electron 2 is at position $\mathbf{r}$. The electrons are irradiated by an X-ray beam from the direction indicated by vector $\mathbf{s}_o$. The radiation scattered by the electrons is observed in the direction of vector $\mathbf{s}$. Because of the path difference $p + q$, scattered beam 2 will lag behind scattered beam 1 in phase. Reproduced with permission from Drenth (1999). Copyright (1999) Springer-Verlag.

radiation, and this is the radiation responsible for the interference effects in diffraction. It was shown by Thomson that if the electron is completely free the following hold:

(1) The phase difference between the incident and the scattered beam is π, because the scattered radiation is proportional to the displacement of the electron, which differs by π in phase with its acceleration imposed by the electric vector.
(2) The amplitude of the electric component of the scattered wave at a distance r which is large in comparison with the wavelength of the radiation is

$$E_{el} = E_o \frac{1}{r} \frac{e^2}{mc^2} \sin \varphi,$$

where E_o is the amplitude of the electric vector of the incident beam, e is the electron charge, m is its mass, c is the speed of light and φ is the angle between the oscillation direction of the electron and the scattering direction (Fig. 2.1.4.1). Note that $E_o \sin \varphi$ is the component of E_o perpendicular to the scattering direction.

In terms of energy,

$$I_{el} = I_o \frac{1}{r^2} \left(\frac{e^2}{mc^2} \right)^2 \sin^2 \varphi. \qquad (2.1.4.1a)$$

The scattered energy per unit solid angle is

$$I_{el}(\Omega = 1) = I_{el} r^2. \qquad (2.1.4.1b)$$

It was shown by Klein & Nishina (1929) [see also Heitler (1966)] that the scattering by an electron can be discussed in terms of the classical Thomson scattering if the quantum energy $h\nu \ll mc^2$. This is not true for very short X-ray wavelengths. For $\lambda = 0.0243$ Å, $h\nu$ and mc^2 are exactly equal, but for $\lambda = 1.0$ Å, $h\nu$ is 0.0243 times mc^2. Since wavelengths in macromolecular crystallography are usually in the range 0.8–2.5 Å, the classical approximation is allowed. It should be noted that:

(1) The intensity scattered by a free electron is independent of the wavelength.
(2) Thomson's equation can also be applied to other charged particles, *e.g.* a proton. Because the mass of a proton is 1800 times the electron mass, scattering by protons and by atomic nuclei can be neglected.
(3) Equation (2.1.4.1a) gives the scattering for a polarized beam. For an unpolarized beam, $\sin^2 \varphi$ is replaced by a suitable polarization factor.

2.1.4.2. Scattering by a system of two electrons

This can be derived along classical lines by calculating the phase difference between the X-ray beams scattered by each of the two electrons. A derivation based on quantum mechanics leads exactly to the same result by calculating the transition probability for the scattering of a primary quantum $(h\nu)_o$, given a secondary quantum $h\nu$ (Heitler, 1966, p. 193). For simplification we shall give only the classical derivation here. In Fig. 2.1.4.2, a system of two electrons is drawn with the origin at electron 1 and electron 2 at position $\mathbf{r}$. They scatter the incident beam in a direction given by the vector $\mathbf{s}$. The direction of the incident beam is along the vector $\mathbf{s}_o$. The length of the vectors can be chosen arbitrarily, but for convenience they are given a length $1/\lambda$. The two electrons scatter completely independently of each other.

Therefore, the amplitudes of the scattered beams 1 and 2 are equal, but they have a phase difference resulting from the path difference between the beam passing through electron 2 and the beam passing through electron 1. The path difference is $p + q = \lambda[\mathbf{r} \cdot (\mathbf{s}_o - \mathbf{s})]$. Beam 2 lags behind in phase compared with beam 1, and with respect to wave 1 its phase angle is

$$-2\pi\lambda[\mathbf{r} \cdot (\mathbf{s}_o - \mathbf{s})]/\lambda = 2\pi\mathbf{r} \cdot \mathbf{S}, \qquad (2.1.4.2)$$

where $\mathbf{S} = \mathbf{s} - \mathbf{s}_o$.

From Fig. 2.1.4.3, it is clear that the direction of $\mathbf{S}$ is perpendicular to an imaginary plane reflecting the incident beam at an angle θ and that the length of $\mathbf{S}$ is given by

$$|\mathbf{S}| = 2 \sin \theta / \lambda. \qquad (2.1.4.3)$$
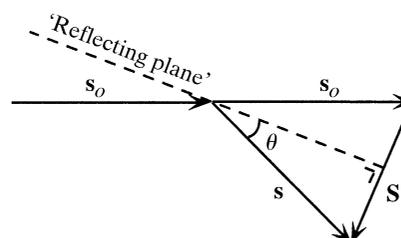
Figure 2.1.4.3
The direction of the incident wave is indicated by $\mathbf{s}_o$ and that of the scattered wave by $\mathbf{s}$. Both vectors are of length $1/\lambda$. A plane that makes equal angles with $\mathbf{s}$ and $\mathbf{s}_o$ can be regarded as a mirror reflecting the incident beam. Reproduced with permission from Drenth (1999). Copyright (1999) Springer-Verlag.
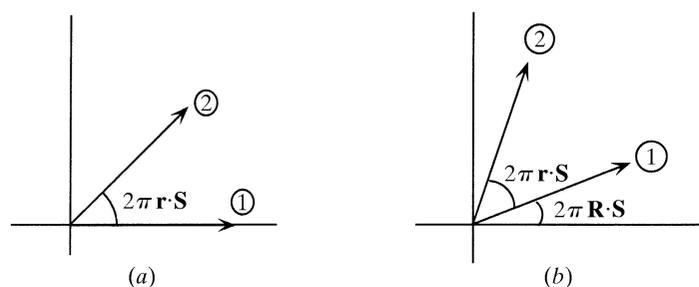
Figure 2.1.4.4
An Argand diagram for the scattering by two electrons. In (*a*), the origin is at electron 1; electron 2 is at position **r** with respect to electron 1. In (*b*), electron 1 is at position **R** with respect to the new origin, and electron 2 is at position **R** + **r**.

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. 2.1.4.4*b*).

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 **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 *IT* C (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

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[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 *Kα* edge of different elements

Atomic number	Element	*Kα* edge (Å)
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),
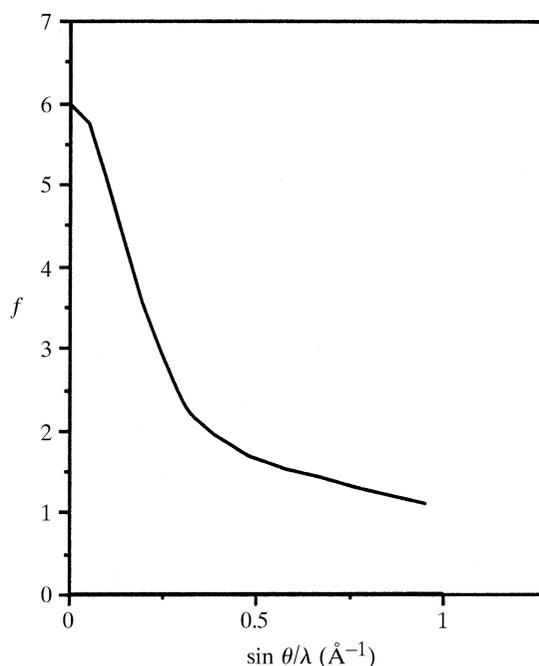

Figure 2.1.4.5
The atomic scattering factor *f* for carbon as a function of $\sin\theta/\lambda$, expressed in units of the scattering by one electron. Reproduced with permission from Drenth (1999). Copyright (1999) Springer-Verlag.