X-ray and Neutron Scattering
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Theoretical aspects of X-ray and neutron scattering are presented and discussed in this chapter. Theoretical concepts are linked to the most actual and critical aspects of materials science.

2.1 Unperturbed Beams

X-rays

X-rays or Röntgen rays are a form of electromagnetic radiation with a wavelength $\lambda$ in the range of 0.05 to 0.2 nm (corresponding to energies in the range 6 to 25 keV). X-rays with a wavelength longer than approximately 0.1 nm are called soft X-rays. At shorter wavelengths, they are called hard X-rays. Let us consider a monochromatic X-ray radiation propagating in vacuum. From a classical standpoint, the wave is constituted by oscillations of the electric field vector, $E$, and of the magnetic field vector, $B$, over perpendicular planes, which are mutually perpendicular to the direction of the wave propagation. Both $E$ and $B$ can be obtained by d’Alembert’s equation

$$\nabla^2 E = -\nabla \times \nabla \times E = \frac{1}{c^2} \frac{\partial E}{\partial t}, \quad (2.1)$$

where $\nabla$ is the gradient operator and $c$ is the speed of light in vacuum. The general solution of $E$ at the point $r$ and at the time $t$ is

$$E(r, t) = E_0 e^{i(k_0 \cdot r - \omega t)}, \quad (2.2)$$

where $k_0$ is the so-called wave vector, with modulus $k_0 = 2\pi/\lambda$ and collinear with the direction of the wave propagation, and $\omega$ is the angular frequency, $\omega = 2\pi \nu$, being $\nu$ the wave frequency (Fig. 2.1). Notice that the relation $c = \omega/k_0$ holds for any reference frame. It is also known that electromagnetic waves have a corpuscular nature: the transported energy is quantized in bundles (called photons) of energy $E = h\nu = \hbar \omega$, where $h$ is Planck’s constant and $\hbar = h/2\pi$. 

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Neutrons

Neutrons are elementary particles with mass $m_N = 1.67 \times 10^{-27}$ kg and spin $I_N = \frac{1}{2}$. Their properties are described in the framework of material wave mechanics. In particular, if their speed is much lower than $c$, the non-relativistic quantum mechanics theory can be adopted. The material wave function $\Psi(r, t)$ is solution of the time-dependent Schrödinger equation

$$\hat{H}\Psi = \frac{i\hbar}{\partial t},$$

(2.3)

where $\hat{H}$ is the Hamiltonian operator

$$\hat{H} = -\frac{\hbar^2}{2m_N} \nabla^2 + U,$$

(2.4)

$U$ being the potential energy. In particular, if $U$ does not depend on time $t$, the wave function can be factorised in a product between a space wavefunction $\psi(r)$ and a time wavefunction $\phi(t)$. The space wavefunction is the solution of the time-independent Schrödinger equation

$$\hat{H}\psi = E\psi,$$

(2.5)

where $E$ is the energy associated with the state $\psi(r)$. The time wavefunction is the straightforward solution of

$$i\hbar \frac{\partial \phi}{\partial t} = E\phi \Leftrightarrow \phi(t) = e^{-iEt/\hbar}.$$  

(2.6)

For a free neutron beam ($U = 0$), the easy solution of Eq. 2.5 is

$$\psi(r) = \frac{1}{L^{3/2}} e^{i\mathbf{k}_0 \cdot \mathbf{r}},$$

(2.7)

where the wave vector $\mathbf{k}_0$ represents the momentum of the neutron in $\hbar$ units, with modulus $k_0 = (2m_NE)^{1/2}/\hbar$. In Eq. 2.7 the constant $L$ represents the
side of the box that contains the portion of the sample that is irradiated by the neutron beam, as will soon be described. The whole wave function is then

\[ \Psi(r, t) = \frac{1}{L^{3/2}} e^{i(k_0 \cdot r - Et/h)}. \]  

(2.8)

It is important to note the resemblance of this equation with Eq. 2.2: both relations represent plane stationary waves. For neutrons, \( \Psi \) is a scalar field; for X-rays, \( E \) is a vectorial field. Moreover, for neutrons the energy and the wavelength are given by the classical kinetic energy and by de Broglie’s equation

\[ E = \frac{1}{2} m_N v^2 = \frac{\hbar^2 k_0^2}{2 m_N}, \]  

and

\[ \lambda = \frac{\hbar}{m_N v} = \frac{2\pi}{k_0}, \]  

(2.9)

(2.10)

\( v \) being the neutron velocity. Typical \( \lambda \) values for non-relativistic neutrons (also called cold or thermal neutrons) are between 0.1 and 1 nm.

2.2 Interactions

2.2.1 X-rays

Let us now consider the interaction between X-rays and matter. Due to their electromagnetic nature, X-rays will essentially interact with charged particles. Here we consider in detail the elastic interaction of X-rays with an electron, from a classical standpoint. This electron belongs to a material system and we suppose that, classically, it has its own (natural) angular frequency \( \omega_0 \equiv (\kappa/m)^{1/2} \), \( \kappa \) being the elastic force constant and \( m \) the electron mass. The average position of the electron is conveniently chosen as the origin of the reference frame (Fig. 2.2). For the sake of simplicity, we consider an X-ray beam that propagates along the \( z \) axis with a unique non-zero electric component \( E_x \) oscillating on the \( xz \) plane (polarized X-ray). From Eq. 2.2, we can write

\[ E_x = E_0 e^{i(k_0 z - \omega t)}. \]  

(2.11)

The electric field that acts on the electron at the origin \( (z = 0) \) is \( E_x = E_0 e^{-i\omega t} \), and the corresponding electric force will be \( F_x = -eE_x = -eE_0 e^{-i\omega t} \), where \(-e\) is the charge of the electron. Newton’s equation of motion will contain the electric force and the elastic (Hooke) force,

\[ m \frac{d^2x}{dt^2} = -eE_0 e^{-i\omega t} - m\omega_0^2 x. \]  

(2.12)

The general solution of the equation of motion is
Fig. 2.2 Thompson scattering. The scattering particle becomes a source of a spherical wave, according to Eq. 2.17

\[ x(t) = -E_0 e^{-i\omega t} \frac{e}{m} \frac{1}{\omega_0^2 - \omega^2}, \] (2.13)

and the corresponding acceleration is

\[ a_x(t) = \frac{d^2x}{dt^2} = E_0 e^{-i\omega t} \frac{e}{m} \frac{\omega^2}{\omega_0^2 - \omega^2}. \] (2.14)

According to the classical electromagnetic theory, an accelerated electron will irradiate its own electromagnetic wave. The electric component of this wave at the position \( \mathbf{r} \) (where we will place the detector, Fig. 2.2) and at the time \( t \) can be calculated from the general expression

\[ E(\mathbf{r}, t) = -\frac{e}{e^2 r^3} \mathbf{r} \times [\mathbf{r} \times \mathbf{a}(t - r/c)], \] (2.15)

which, for our particular system, leads to the following expression for the modulus of \( E(\mathbf{r}, t) \):

\[ E(\mathbf{r}, t) = E_0 e^{-i\omega t} \frac{e^2}{mc^2} \frac{\omega^2}{\omega_0^2 - \omega^2} \sin \alpha \frac{e^{ik_0 r}}{r}, \] (2.16)

\( \alpha \) being the angle between \( \mathbf{r} \) and the \( x \) axis. Equation 2.16 represents the classical expression of Rayleigh scattering. The first factor \( r_0 = \frac{e^2}{mc^2} \) is called classical radius of the electron, \( r_0 = 0.28 \times 10^{-12} \) cm. The second term \( \omega^2/(\omega_0^2 - \omega^2) \) is the frequency factor. Two cases can be distinguished. If the natural frequency \( \omega_0 \) of the electron is much higher than the electromagnetic field frequency \( \omega \), as occurs for visible light, the lower \( \omega_0 \) is, the higher the frequency factor. This is the blue-shift phenomenon, responsible, for example, for blue sky. On the other hand, when \( \omega_0 \ll \omega \) (as occurs essentially for X-rays) the frequency factor is -1. This is the case of Thompson scattering.
\[ E(\mathbf{r}, t) = -E_0 e^{-i\omega t} \frac{e^{i k_0 r}}{r} r_0 \sin \alpha. \] (2.17)

The angular factor \( \sin \alpha \) indicates that the maximum amplitude occurs for \( \alpha = \pi/2 \). Finally and very importantly, we have the factor \( \frac{e^{i k_0 r}}{r} \), which represents a spherical wave. Thus the electron becomes a source of a spherical wave, with the same frequency (and \( \lambda \)) of the impinging X-ray. The incident power per unit surface (i.e. the beam intensity) \( I_0 \) is represented by the time-average modulus of the Poynting vector \( \mathbf{S} \equiv \frac{c}{4\pi} \mathbf{E} \times \mathbf{B} \), which is 
\[
I_0 = \langle S \rangle = \langle (\text{Re} \, E_x)^2 \rangle_t / 4\pi = E_0^2 \langle \cos^2 \omega t \rangle_t / 4\pi = E_0^2 / 8\pi.
\]
Similarly, on the basis of Eq. (2.17), the scattered intensity will be
\[
I = \frac{1}{4\pi} \langle (\text{Re} \, E_x)^2 \rangle_t = \left( \frac{r_0}{r} \right)^2 \sin^2 \alpha \frac{E_0^2}{8\pi} = I_0 \left( \frac{r_0}{r} \right)^2 \sin^2 \alpha. \quad (2.18)
\]
The ratio between the power scattered by the electron on the surface element at distance \( r \), \( dS = r^2 d\Omega \) (\( \Omega \) is the solid angle) and the average incident power per unit surface is defined as a cross section (Fig. 2.3)

\[ d\sigma \equiv \frac{I r^2 d\Omega}{I_0}. \quad (2.19) \]

From a corpuscular point of view, because \( d\sigma \) is the energy transported by photons, it can be also viewed as the ratio between the number of photons per unit of time that fall in the surface \( dS \) and the so-called photon-flux \( \Phi_0 \), i.e. the number of incident photons per unit of time and per unit of area, with \( I_0 = \hbar \omega \Phi_0 \). Moreover, the frequency of the scattered beam being equal to that of the incident beam, we can say that the interaction between the photon and the electron has not changed the photon energy; we are dealing with an elastic collision. Combining it with Eq. 2.18, the differential cross section is also defined as
\[
\frac{d\sigma}{d\Omega} = r_0^2 \sin^2 \alpha. \quad (2.20)
\]

It is easy to show that in the case of unpolarized X-rays, the Thompson scattering of an electron reads
\[
\frac{d\sigma}{d\Omega} = r_0^2 \frac{1 + \cos^2(2\theta)}{2}, \quad (2.21)
\]
where \(2\theta\) is the scattering angle, i.e. the angle between the direction of the incident beam \(z\) and the vector \(\mathbf{r}\). The square root of \(\frac{d\sigma}{d\Omega}\) is called the scattering length of the electron
\[
b_X = r_0 \left[ \frac{1 + \cos^2(2\theta)}{2} \right]^{1/2} \approx r_0 \quad \text{for small } \theta. \quad (2.22)
\]

The total Thompson scattering cross section is the integral over \(d\Omega\), which reads
\[
\sigma = \int d\Omega \frac{d\sigma}{d\Omega} = r_0^2 \int_0^{2\pi} \int_0^\pi \sin(2\theta) \frac{1 + \cos^2(2\theta)}{2} d\theta = \frac{8\pi}{3} r_0^2. \quad (2.23)
\]

It can be observed from Eq. 2.16 that the scattered field \(E(\mathbf{r}, t)\) is inversely proportional to the electron mass \(m\). All other particles, starting from the proton, have a mass bigger than \(\approx 2000m\). Hence, their contribution to the elastic scattering of X-ray is negligible.

If the average position of the electron is now in the arbitrary position \(\mathbf{r}_n\), it is straightforward to show that the Thompson scattering Eq. 2.17 transforms to
\[
E_n(\mathbf{r}, t) = -E_0 e^{-i\omega t} \frac{e^{ik_0|\mathbf{r} - \mathbf{r}_n|}}{|\mathbf{r} - \mathbf{r}_n|} e^{i\mathbf{k}_0 \cdot \mathbf{r}_n} r_0 \sin \alpha, \quad (2.24)
\]
and, for unpolarized X-rays,
\[
E_n(\mathbf{r}, t) = -E_0 e^{-i\omega t} \frac{e^{ik_0|\mathbf{r} - \mathbf{r}_n|}}{|\mathbf{r} - \mathbf{r}_n|} e^{i\mathbf{k}_0 \cdot \mathbf{r}_n} b_X. \quad (2.25)
\]
Notice that in these equations \(\mathbf{r}\) still represents the position of, say, the detector with respect to the origin of the reference frame. Let us suppose now that the distance \(r_n\) is orders of magnitude lower than the distance \(r\). The first is in fact of the order of some tenths of nanometers, the latter of some meters. We can thus write \(|\mathbf{r} - \mathbf{r}_n| \approx r - \hat{\mathbf{r}} \cdot \mathbf{r}_n\), \(\hat{\mathbf{r}}\) being the unit vector of \(\mathbf{r}\). The spherical wave in Eq. 2.25 becomes
\[
\frac{e^{ik_0|\mathbf{r} - \mathbf{r}_n|}}{|\mathbf{r} - \mathbf{r}_n|} \approx \frac{e^{ik_0r}}{r} e^{-i\mathbf{k} \cdot \mathbf{r}_n}, \quad (2.26)
\]
where, as shown in Fig. 2.4, \(\mathbf{k} \equiv k_0\hat{\mathbf{r}}\). The amplitude of the electric field
where we have introduced the so-called scattering vector $Q \equiv k_0 - k$, with modulus $Q = 4\pi \sin \theta / \lambda$ (Fig. 2.4). The factor $e^{iQ \cdot r_n}$, called the structure factor of the electron in $r_n$, represents the ratio between the amplitudes of two electromagnetic fields, that generated by the electron in $r_n$ and that of the electron at the origin.

Instead of an electron, we now consider the interaction between X-rays and a “blob” of matter, which will be viewed by X-rays as a set of electrons. We suppose that the scattering originated by each electron is weak, and is only due to the interaction with the direct beam and not with the X-ray waves generated by the other electrons. This approximation is called single scattering approximation. In $r$ the amplitude of $E$ will be due to the sum between all the amplitudes of single electrons. The structure factor will be

$$F(Q) = \sum_{n=1}^{N} e^{iQ \cdot r_n}. \quad (2.28)$$

According to Eq. 2.22, the scattering length can be defined as

$$A(Q) = b_X F(Q) = b_X \sum_{n=1}^{N} e^{iQ \cdot r_n} \quad (2.29)$$

and, similarly to Eq. 2.21, the cross section is

$$\frac{d\sigma}{d\Omega}(Q) = |A(Q)|^2 \equiv b_X^2 \sum_{m,n=1}^{N} e^{iQ \cdot r_{mn}}, \quad (2.30)$$
where \( r_{mn} \equiv r_m - r_n \).

More properly, the position of electrons is not exactly known. Thus introducing the electron density function \( \rho_e(r) \), we can write

\[
F(Q) = \int d^3r \rho_e(r) e^{iQ \cdot r}.
\] (2.31)

Form a mathematical point of view, the latter integral is the so-called Fourier transform of \( \rho_e(r) \). Through the inverse Fourier transform, the electron density \( \rho_e(r) \) is determined by \( F(Q) \),

\[
\rho_e(r) = \frac{1}{(2\pi)^3} \int d^3Q F(Q) e^{-iQ \cdot r}.
\] (2.32)

We can also add an equation that gives the scattering length of a blob of matter in an integral form

\[
A(Q) = b_X \int d^3r \rho_e(r) e^{iQ \cdot r}.
\] (2.33)

Let us consider now that our blob of matter is an atom. If this atom is at the center of the reference frame, with good approximation, its electronic density will have a spherical symmetry, \( \rho_e(r) \equiv \rho_e(r) \), where the polar coordinates of \( r \) are \((r, \theta, \phi)\). The atomic structure factors (indicated as \( f(Q) \)) become real functions that only depend on the modulus \( Q \)

\[
f(Q) = \frac{4\pi}{Qr} \int_0^\infty r^2 dr \int_0^\pi \sin \theta d\theta \int_0^{2\pi} d\phi \rho_e(r) e^{iQ \cdot r} \\
= \int_0^\infty r^2 dr \rho_e(r) \frac{\sin(Qr)}{Qr} \equiv f(Q).
\] (2.34)

In Fig. 2.5 the elastic structure factors of some atoms are reported [140]. It can easily be shown that if the atom is translated in the position \( r_n \), its structure factor transforms to \( f(Q)e^{iQ \cdot r_n} \). Hence, if we now take as blob of matter a molecule and, as a first approximation, we suppose that the electronic clouds around the atoms do not change, the molecular form factor and the molecular scattering length (Eqs. 2.31 and 2.33) reduce to

\[
F(Q) = \sum_{n=1}^N f_n(Q) e^{iQ \cdot r_n},
\] (2.35)

and

\[
A(Q) = b_X \sum_{n=1}^N f_n(Q) e^{iQ \cdot r_n}.
\] (2.36)
2.2.2 Neutrons

We turn now to study the interaction between neutrons and matter. In particular, we only describe the elastic scattering of neutrons. The energy of incident and scattered neutrons remains unchanged and its value is expressed by Eq. 2.10. In this condition, neutrons can only transfer momentum to the material system. The *time-independent Schrödinger equation* 2.5 can be written as

\[(\nabla^2 + k_0^2)\psi(r) = \frac{2mN}{\hbar^2} U(r) \psi(r).\] (2.37)

The latter is a second-order non-homogeneous differential equation. It can be transformed in an integral equation with the method of *Green’s functions*,

\[\psi(r) = \psi^0(r) + \frac{2mN}{\hbar^2} \int dr' G(r, r') \psi(r') U(r'),\] (2.38)

where \(\psi^0(r)\) stands for the unperturbed state (Eq. 2.7) and \(G(r, r')\) represents a spherical wave with the same \(k_0\) originating from the position \(r'\),

\[G(r, r') = \frac{e^{ik_0|r-r'|}}{4\pi|r-r'|}.\] (2.39)

The sense of Eq. 2.38 is clear: after the elastic collision, the new state \(\psi(r)\) results from a superposition of the unperturbed wave \(\psi^0(r)\) and spherical waves that are generated in \(r'\) with an amplitude depending on the value of
ψ(r′) and the potential U(r′). Some approximations can be introduced. Firstly, the range of the distances where the potential U(r′) is different from zero will be of the typical order of atomic distances, say some tenths of nanometers. Hence, since we wish to calculate the unknown function ψ(r) at the typical sample-to-detector distance r, say some meters, the inequality r′ ≪ r will be true. On the basis of Eq. 2.26 we have

\[ G(r, r′) \approx \frac{e^{ik_0 r}}{4\pi r} e^{-ikr′}. \]  

Secondly, Eq. 2.38 is only a formal solution of the Schrödinger equation, ψ(r) being still unknown in both members. Nevertheless, an iterative procedure can be written,

\[ \psi = \psi^0 + \hat{G}U \psi \approx \psi^0 + \hat{G}U\psi^0 + \hat{G}U\hat{G}U\psi^0 + \ldots \]

where \( \hat{G} \), defined as Green’s operator, represents the integral in Eq. 2.38. Each step can be thought as an elastic scattering event. In the so-called Born approximation only the first term \( \psi^1 = \hat{G}U\psi^0 \) is considered. Similarly to the X-rays, this view is also called single scattering approximation and the smaller the thickness of the sample that neutrons cross, the more valid the Born approximation. Combining Eqs. 2.38, 2.40 and 2.7, the first-order approximation reads

\[ \psi^1(r) = \frac{1}{L^{3/2}} e^{ik_0 r} \frac{1}{r} \frac{2m_N}{\hbar^2} \int dr′ U(r′) e^{iQ·r′}, \]

where the scattering vector \( Q \equiv k_0 - k \) represents the momentum (in \( \hbar \) units) that the neutron has transferred to the sample (Fig. 2.4). For the sake of completeness, we also report the first-order approximation of the whole wave function,

\[ \Psi^1(r, t) = \frac{1}{L^{3/2}} e^{-iEt/\hbar} \frac{e^{ik_0 r}}{r} \frac{1}{4\pi} \frac{2m_N}{\hbar^2} \int dr′ U(r′) e^{iQ·r′}. \]

Neutrons mainly interact with nuclei. The interaction potential due to a nucleus at position \( r_n \) is described by the Fermi pseudo-potential

\[ U(r) = \frac{2\pi\hbar^2}{m_N} b_n \delta(r - r_n), \]

where \( b_n \) is the scattering length of the nth nucleus and \( \delta(r) \) is the well-known three-dimensional Dirac delta function. The Fourier transform in Eq. 2.43 is straightforward,

\[ \Psi^1_n(r, t) = \frac{1}{L^{3/2}} e^{-iEt/\hbar} \frac{e^{ik_0 r}}{r} b_n e^{iQ·r_n}. \]
The similarity with Eq. 2.27 is noticeable, which, for X-rays, gives the amplitude of the electric field scattered by the electron in \( r_n \). This analogy makes a unique mathematical treatment of the two types of radiations possible.

The incident neutron flux over a box of side \( L \) will be \( \Phi_0 = v/L^3 \). Considering the meaning in quantomechanics of \( \Psi \), the cross section due to the neutron nucleus elastic interaction is, similarly to Eq. 2.19,

\[
d\sigma \equiv \frac{v |\Psi_1^n(r, t)|^2 r^2 d\Omega}{\Phi_0} = b_n^2 d\Omega.
\]

Hence, the differential and the total scattering cross section are

\[
\frac{d\sigma}{d\Omega} = b_n^2,
\]

and

\[
\sigma = 4\pi b_n^2.
\]

Turning now to a blob of matter, say a molecule, its interaction with a nuclear beam will be described by a sum of all the Fermi potentials due to each \( n \)th atom. Hence, Eq. 2.45 becomes

\[
\Psi_1^n(r, t) = \frac{1}{L^{3/2}} e^{-iEt/\hbar} e^{i\mathbf{k}_0 \cdot \mathbf{r}} \sum_{n=1}^{N} b_n e^{i\mathbf{Q} \cdot \mathbf{r}_n},
\]

and the scattering length of the system will be

\[
A(Q) = \sum_{n=1}^{N} b_n e^{i\mathbf{Q} \cdot \mathbf{r}_n},
\]

or, turning to an integral form, we find a deep analogy with Eq. 2.33

\[
A(Q) = \int d^3 r \rho(r) e^{i\mathbf{Q} \cdot \mathbf{r}},
\]

where \( \rho(r) \) is defined as the scattering length density

\[
\rho(r) = \lim_{V \to \infty} \frac{1}{V} \sum_{n=\text{atoms in } V}^{N} b_n = \sum_{n=1}^{N} b_n \delta(\mathbf{r} - \mathbf{r}_n).
\]

### Coherent and Incoherent Neutron Scattering

The neutron nucleus interaction also depends on the total angular momentum operator \( \hat{J} = \hat{I} + \hat{I}_N \), where \( \hat{I} \) is the operator associated with the isotope spin \( I \neq 0 \) and \( \hat{I}_N \) the operator associated with the neutron spin \( I_N = \frac{1}{2} \). Hence, there are two different scattering lengths associated with two different values of \( J \).
The corresponding spin multiplicities are

\[ g^+ = 2J^+ + 1 = 2I + 2, \]
\[ g^- = 2J^- + 1 = 2I. \] (2.54)

The differential cross section depends on the average over the position \( r_n \) and the spin state \( J_n \) of all the nuclei. Assuming that no correlation exists between \( r_m \) and \( J_m \), or between \( J_m \) and \( J_n \), we have

\[
\frac{d\sigma}{d\Omega} (Q) = \langle |A(Q)|^2 \rangle = \sum_{m,n=1}^{N} \langle b_m b_n \rangle \langle e^{iQ \cdot (r_m - r_n)} \rangle \langle b_m b_n \rangle
\]
\[ = \langle b_m \rangle \delta_{m,n} \langle \langle b^2_m \rangle - \langle b_m \rangle^2 \rangle, \] (2.55)

where \( \delta_{m,n} \) is Kronecker’s delta function. In the absence of nuclear or neutron polarization, the spin states are weighted on their multiplicities,

\[ b^\text{coh}_m \equiv \langle b_m \rangle = \frac{g^+_m b^+_m + g^-_m b^-_m}{g^+_m + g^-_m} = \frac{1}{2I_m + 1} [(I_m + 1)b^+_m + I_m b^-_m], \]
\[ (b^\text{incoh}_m)^2 \equiv \langle b^2_m \rangle - \langle b_m \rangle^2 = \frac{g^+_m b^+_m + g^-_m b^-_m}{g^+_m + g^-_m} \]
\[ - \left( \frac{g^+_m b^+_m + g^-_m b^-_m}{g^+_m + g^-_m} \right)^2 = \frac{I_m (I_m + 1)}{2I_m + 1} (b^+_m - b^-_m)^2, \] (2.56)

where the two coherent and incoherent scattering lengths of the \( m \) nucleus have been introduced. The total scattering cross section is then constituted by a coherent component, which depends on \( Q \) and contains information on the structure \( \{r_m\} \), and a flat incoherent contribution, independent of \( Q \),

\[
\frac{d\sigma}{d\Omega} (Q) = \sum_{m,n} b^\text{coh}_m b^\text{coh}_n \langle e^{iQ \cdot (r_m - r_n)} \rangle + \sum_{i=1}^{N} (b^\text{incoh}_m)^2
\]
\[ = \left( \frac{d\sigma}{d\Omega} \right)^\text{coh} (Q) + \left( \frac{d\sigma}{d\Omega} \right)^\text{incoh}. \] (2.57)

The values of \( b^\text{coh} \) and \( b^\text{incoh} \) for some isotopes are reported in Table 2.1.

**Table 2.1** Neutron scattering lengths of selected isotopes (units of \( 10^{-12} \text{ cm} \)) [264]

<table>
<thead>
<tr>
<th>Isotope</th>
<th>( I )</th>
<th>( b^\text{coh} )</th>
<th>( b^\text{incoh} )</th>
<th>Isotope</th>
<th>( I )</th>
<th>( b^\text{coh} )</th>
<th>( b^\text{incoh} )</th>
</tr>
</thead>
<tbody>
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<td>(^1\text{H})</td>
<td>( \frac{1}{2} )</td>
<td>-0.37406</td>
<td>2.5274</td>
<td>(^{16}\text{O})</td>
<td>0</td>
<td>0.5803</td>
<td>0</td>
</tr>
<tr>
<td>(^2\text{H})</td>
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<td>0.6671</td>
<td>0.404</td>
<td>(^{31}\text{P})</td>
<td>( \frac{1}{2} )</td>
<td>0.513</td>
<td>0.2</td>
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<td>0</td>
<td>(^{32}\text{S})</td>
<td>0</td>
<td>0.2804</td>
<td>0</td>
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<tr>
<td>(^{14}\text{N})</td>
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<td>0.937</td>
<td>0.2</td>
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</tr>
</tbody>
</table>

The values of \( b^\pm \) associated with \( J^\pm = I \pm \frac{1}{2} \). (2.53)
2.3 Introduction to Crystallography

Examples of elastic scattering for some ordered systems are now described. In the following we will indicate by $a_n(Q)$ the scattering length of an atom: for X-rays $a_n(Q) \equiv b_X f_n(Q)$, for neutrons $a_n(Q) \equiv b_n^{\text{coh}}$.

2.3.1 Monodimensional Array of Atoms

![Monodimensional array of atoms](image)

Fig. 2.6 Monodimensional array of atoms

The first, simplest example of an ordered system is a monodimensional lattice of identical atoms. Let $\mathbf{u}$ be the translational vector that gives the position of the $n$th atom with respect to the $(n-1)$th one and $N$ the total number of atoms (Fig. 2.6). The scattering length of the system is

$$A(Q) = a(Q) \sum_{n=1}^{N} e^{i(n-1)Q \cdot \mathbf{u}} = a(Q) e^{i(N-1) Q \cdot \mathbf{u}} \sin \left( \frac{N Q \cdot \mathbf{u}}{2} \right),$$

(2.58)

and the corresponding differential cross section will be

$$\frac{d\sigma}{d\Omega}(Q) = A(Q) A^*(Q) = [a(Q)]^2 S(Q),$$

(2.59)

where

$$S(Q) = \left[ \frac{\sin \left( \frac{N Q \cdot \mathbf{u}}{2} \right)}{\sin \left( \frac{Q \cdot \mathbf{u}}{2} \right)} \right]^2,$$

(2.60)

where the so-called interference function $S(Q)$ has been introduced. In Fig. 2.7 the behaviour of this function for different values of $N$ is reported. It is clear that the higher $N$ is, the higher and narrower the peaks centered at integer values of $\frac{Q \cdot \mathbf{u}}{2\pi}$ are. In other words, for large $N$, the conditions of constructive interference take place only for particular orientations of the array, say $\mathbf{u}$, with respect to $Q$. Those conditions are referred to as von Laue conditions

$$\frac{Q \cdot \mathbf{u}}{2\pi} = h, \quad h = 0, \pm 1, \pm 2, \ldots$$

(2.61)
2.3.2 Three-Dimensional Array of Atoms

We will restrict ourselves to the case of the so-called Bravais lattice with one atom at the origin of the unit cell. The position of the atoms is given by \( \mathbf{R} = n_a \mathbf{a} + n_b \mathbf{b} + n_c \mathbf{c} \), where \( n_a, n_b \) and \( n_c \) are three integer numbers that label the atom. The three primitive vectors \( \mathbf{a}, \mathbf{b} \) and \( \mathbf{c} \) define the lattice. Considering the ratios between the primitive vectors’ lengths and the angles among them, in all, there are 14 Bravais lattices that fill three-dimensional space. According to Eq. 2.58, the scattering length of the crystal results

\[
A(Q) = a(Q) \sum_{n_a=1}^{N_a} \sum_{n_b=1}^{N_b} \sum_{n_c=1}^{N_c} e^{iQ \cdot (n_a \mathbf{a} + n_b \mathbf{b} + n_c \mathbf{c})}
\]

\[
= a(Q) e^{i[(N_a-1) \frac{Q \cdot \mathbf{a}}{2} + (N_b-1) \frac{Q \cdot \mathbf{b}}{2} + (N_c-1) \frac{Q \cdot \mathbf{c}}{2}]} \left( \frac{\sin(N_a \frac{Q \cdot \mathbf{a}}{2})}{\sin \frac{Q \cdot \mathbf{a}}{2}} \right) \left( \frac{\sin(N_b \frac{Q \cdot \mathbf{b}}{2})}{\sin \frac{Q \cdot \mathbf{b}}{2}} \right) \left( \frac{\sin(N_c \frac{Q \cdot \mathbf{c}}{2})}{\sin \frac{Q \cdot \mathbf{c}}{2}} \right),
\]

(2.62)

Fig. 2.7 Scattering of a monodimensional array of atoms. Dotted, dashed and solid lines refer to functions \( |a(Q)|^2, S(Q)/N^2 \) and \( S(Q)|a(Q)|^2/N^2 \), respectively.
where the three numbers $N_{a,b,c}$ define the size of the lattice. The differential cross section of a three-dimensional array of atoms will be

$$\frac{d\sigma}{d\Omega}(Q) = [a(Q)]^2 S_a(Q)S_b(Q)S_c(Q),$$  \hspace{1cm} (2.63)

where the three interference functions $S_{a,b,c}(Q)$ have the form of Eq. 2.60. For large values of $N_{a,b,c}$, the three-dimensional extension of the von Laue conditions indicates that $A(Q)$ is different from zero only when

$$\begin{align*}
Q \cdot a &= 2\pi h \quad h = 0, \pm 1, \pm 2, \ldots \\
Q \cdot b &= 2\pi k \quad k = 0, \pm 1, \pm 2, \ldots \\
Q \cdot c &= 2\pi l \quad l = 0, \pm 1, \pm 2, \ldots
\end{align*} \Rightarrow e^{iQ \cdot R} = 1.$$  \hspace{1cm} (2.64)

The three integer numbers $h, k,$ and $l$ are defined Miller indexes. When the von Laue conditions (Eq. 2.64) are respected one finds

$$A(Q_{h,k,l}) \equiv A_{h,k,l} = N a(Q_{h,k,l}),$$  \hspace{1cm} (2.65)

where $N = N_a N_b N_c$ is the total number of atoms in the lattice. In other words, the atomic scattering length $a(Q)$ is “sampled” only for $Q$ values that respect the von Laue conditions.

### 2.3.3 The Reciprocal Lattice

The scattering pattern appears constituted by a series of “spots” at regular positions. It can be demonstrated that in the reciprocal space (i.e. the space of the scattering vector $Q$), these regular positions will constitute a Bravais lattice, defined as a reciprocal lattice. The primitive vectors of this lattice are

$$\begin{align*}
a^\ast &= 2\pi \frac{b \times c}{V}, \\
b^\ast &= 2\pi \frac{c \times a}{V}, \\
c^\ast &= 2\pi \frac{a \times b}{V},
\end{align*}$$  \hspace{1cm} (2.66)

where $V = a \cdot (b \times c)$ is the unit cell volume. Values of $Q$ belonging to the reciprocal lattice and thus respecting the von Laue conditions can be calculated by

$$Q_{h,k,l} = h a^\ast + k b^\ast + l c^\ast.$$  \hspace{1cm} (2.67)

### 2.3.4 Crystals

A crystal is made up of one or more atoms (the “basis”, for example, one or a few molecules), which are repeated at each lattice point. It is straightforward to show that the scattering length of a crystal is

$$A(Q) = A_{h,k,l} = N A_m(Q_{h,k,l}),$$  \hspace{1cm} (2.68)

where $A_m(Q)$ is the scattering length of the unit cell.
\[ A_m(Q) = \sum_n a_n(Q) e^{iQ \cdot r_n}. \] (2.69)

\( r_n \) is now the vector of the \( n \)th atoms in the unit cell. This vector can be represented in terms of the primitive vectors \( r_n = x_n a + y_n b + z_n c, \) leading to

\[ A_m(Q) = \sum_n a_n(Q) e^{iQ \cdot (x_n a + y_n b + z_n c)}. \] (2.70)

Finally, by applying the von Laue condition, we have

\[ A_{h,k,l} = \sum_n a_n(Q) e^{2\pi i (hx_n + ky_n + lz_n)}, \] (2.71)

which represents the scattering length of the unit cell sampled at the lattice points \( h, k, \) and \( l. \)

**Determination of the Scattering Length Density**

The scattering length density within the unit cell is calculated through the inverse Fourier transform of the scattering length. The result reads

\[ \rho(r) = \frac{1}{NV} \sum_{h=-\infty}^{\infty} \sum_{k=-\infty}^{\infty} \sum_{l=-\infty}^{\infty} A_{h,k,l} e^{-2\pi i (hx + ky + lz)}. \] (2.72)

Nevertheless from scattering experiments only the cross section \( \frac{d\sigma}{d\Omega} \) can be calculated, so that only the modulus \( |A_{h,k,l}| \) is known but not its phase \( e^{i\phi}. \) The phase problem is one the biggest problems in crystallography.

**2.3.5 The Ideal Paracrystal**

The rigorous periodicity of a crystal lattice is altered by the presence of imperfections. Let us suppose that we have a perfect crystal and displace the atoms away from their theoretical positions, the displacements being small compared with the interatomic distance. This kind of disorder is generally referred to as *first-kind disorder*. An example is that of thermal agitation. In such crystals the average distance between, for example, the lattice point at the origin and the \( n_a \) neighbor along the \( a \) direction is simply \( n_a a, \) and the fluctuation of its position is independent of \( n_a. \) Hence, a long-range order is preserved.

On the contrary, in the second-kind imperfection, there is no long-range order; the fluctuation of the position depends on \( n_a. \) This is the case of many organic or biological materials composed of large molecules that dispose themselves in ordered structures because of weak van der Waals’ forces.

A theoretical model to describe the scattering pattern of a *second-kind disorder* is the so-called ideal *paracrystal* proposed by Hosemann [129]. In the
model it is assumed that the lattice fundamental vectors a, b and c fluctuate according to three independent three-dimensional Gaussian distributions. The general lattice vector \( \mathbf{R} = n_a \mathbf{a} + n_b \mathbf{b} + n_c \mathbf{c} \) is built up by adding \( n_a \) fluctuating vectors \( \mathbf{a} \), \( n_b \) fluctuating vectors \( \mathbf{b} \) and \( n_c \) fluctuating vectors \( \mathbf{c} \). Hence the higher \( n_{a,b,c} \) are, the higher will be the fluctuation of \( \mathbf{R} \) with respect to the origin (Fig. 2.8).

![Fig. 2.8 Schematic illustration of the distribution of lattice points in an ideal two-dimensional paracrystal](image)

The differential cross section is still expressed by Eq. 2.63, where the interference functions are replaced by quantities of the form [199]

\[
S_{a,\text{parac}}(\mathbf{Q}) = N_a \frac{1 - H_a^2(\mathbf{Q})}{1 - 2 \cos(\mathbf{Q} \cdot \mathbf{a}) H_a(\mathbf{Q}) + H_a^2(\mathbf{Q}) - 2 H_a(\mathbf{Q}) - H_a^{N_a}(\mathbf{Q}) \cos((N_a + 1) \mathbf{Q} \cdot \mathbf{a}) + 2 H_a^{N_a+1}(\mathbf{Q}) \cos((N_a + 1) \mathbf{Q} \cdot \mathbf{a}) - H_a^{N_a+2}(\mathbf{Q}) \cos((N_a - 1) \mathbf{Q} \cdot \mathbf{a})},
\]

(2.73)

and

\[
H_a(\mathbf{Q}) = e^{-\frac{1}{2} \mathbf{Q}^T \sigma_a^2 \mathbf{Q}},
\]

(2.74)

where \( H_a(\mathbf{Q}) \) is the Fourier transform of the three-dimensional Gaussian that gives the fluctuation around the vector \( \mathbf{a} \), \( \sigma_a^2 \) being the variance matrix (the elements of \( \sigma^2 \) transformed in a diagonal form are the squared semi-axes of the fluctuation ellipsoid around \( \mathbf{a} \)) and \( \mathbf{Q}^T \) the vector transpose of \( \mathbf{Q} \). A comparison of three \( S_{a,\text{parac}}(\mathbf{Q}) \) functions and the perfect crystal interference function is shown in Fig. 2.9.
2.4 Introduction to Powder Diffraction

In the powder diffraction technique X-ray or neutron scattering is performed on powders or polycrystalline samples. Ideally, the crystallites are randomly oriented, and it is thus not possible to see individual scattering spots as in single-crystal crystallography. Instead one observes rings of diffracted intensity as a function of momentum transfer $Q$, i.e. as a function of $2\theta$.

2.4.1 Bragg’s Law

*Bragg’s law* is a formulation equivalent to that of von Laue. It can be shown that for each vector $Q_{h,k,l}$ of the reciprocal lattice there is a corresponding family of planes in the direct lattice at regular distances

$$d_{h,k,l} = \frac{2\pi}{Q_{h,k,l}}. \quad (2.75)$$

Bragg’s law is a relation between the value of $d_{h,k,l}$, the scattering angle $2\theta$ and the wavelength

$$2d_{h,k,l} \sin \theta = n\lambda, \quad n = \pm 1, \pm 2, \ldots, \text{diffraction order}. \quad (2.76)$$

The recorded intensity as a function of the scattering angle $2\theta$ shows a series of diffraction peaks. By applying Bragg’s law it is possible to determine the distances $d_{h,k,l}$ and then to assign the correct crystal structure of the sample. The technique is very powerful for the identification of crystalline solids and can be used for many microcrystalline and amorphous solid state materials if adequate references have been characterized.
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