

Crystal Structure and Dynamics

Paolo G. Radaelli, Michaelmas Term 2015

Part 2: Scattering theory and experiments

Lectures 6-8

Web Site:

<http://www2.physics.ox.ac.uk/students/course-materials/c3-condensed-matter-major-option>

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1 Lecture 6 — Scattering from individual atoms and spins

In order to extract information about the *atomic* structure of a crystal, liquid or glass by diffraction, **the wavelength of the probe must be comparable or smaller than the interatomic distances**, which are typically a few Ångstroms (10^{-10} m, or 10^{-1} nm). Tab. 1 illustrates the typical wavelengths and energies employed for X-ray, neutron and electron diffraction.

Table 1: Typical wavelengths and energies employed for X-ray, neutron and electron diffraction. For electromagnetic radiation, $E = hc/\lambda$, with $hc = 12.4$ KeV · Å; for a non-relativistic particle beam, $E = \frac{2\pi^2\hbar^2}{m\lambda^2}$, where $\frac{2\pi^2\hbar^2}{m} = 82$ meV · Å² for neutrons and 150 eV · Å² for electrons. A typical Transmission Electron Microscope (TEM) can operate at 200 KV raising the electron velocity to 70 % of the speed of light, and some state-of-the-art microscopes can reach the MV range; therefore, relativistic effects need to be taken into account in converting between energy and wavelength.

	λ	E
X-rays	0.1–6 Å	2–150 KeV
neutrons	0.3–10 Å	1–1000 meV
electrons	0.02–3 Å	20 eV–200 KeV

Powerful X-ray, neutron and electron sources and diffraction instruments are available to the experimentalists.

1.1 Thomson scattering of X-rays from a single electron

- Bragg diffraction of X-rays is primarily due to the scattering from electrons bound to the atoms of the crystal structure. It is generally a very good approximation to employ the so-called Thomson formula (from J.J. Thomson, Nobel Prize 1906) to calculate the relevant scattering amplitudes and cross sections. This is a bit of a paradox, since the Thomson formula assumes *free* electrons¹, but the agreement with experiments is nonetheless very good. The Thomson formula is valid in the non-relativistic limit (velocity of the particle $\ll c$).
- By using classical electrodynamics, we can calculate the time-dependent amplitude of the electric field generated at a distance R from an electron that has been accelerated by an electromagnetic plane wave.
- If the time-dependent electric field at the position of the electron is

¹A description of the scattering process beyond the free electron approximation is contained in Appendix II.

$$\mathbf{E} = \epsilon E_0 e^{-i\omega t} \quad (1)$$

and the incident polarisation (see fig. 11) is

$$\epsilon = \cos \xi \epsilon_\sigma + \sin \xi \epsilon_\pi \quad (2)$$

then²

$$\mathbf{E}(\mathbf{R}, t) = -r_0 \mathbf{E}_0 \frac{e^{i(\mathbf{kR}-\omega t)}}{R} [\cos \xi \epsilon'_\sigma + \sin \xi \cos \gamma \epsilon'_\pi] \quad (3)$$

where

$$r_0 = \frac{e^2}{4\pi\epsilon_0 mc^2} = 2.82 \times 10^{-15} \text{ m} \quad (4)$$

is the *classical radius of the electron*.

- The *scattering angle* γ is the angle between the incident and scattered wavevector (this angle is also known, by longstanding diffraction convention, as 2θ). Based on eq. 55, we can make the following observations:

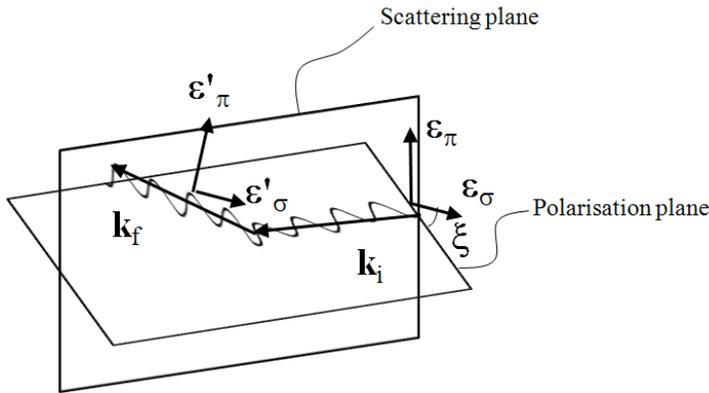


Figure 1: Diagram illustrating the conventional σ and π reference directions for the incident and scattered polarisation. Note that $\epsilon_\sigma \cdot \epsilon'_\sigma = 1$ *always*. Conversely, $\epsilon_\pi \cdot \epsilon'_\pi = \cos \gamma$ **depends on the scattering angle** γ , and **vanishes** for $\gamma = \pi/2$.

- A plane wave impinging on a quasi-free charge produces a scattered *spherical* wave $\frac{e^{i(kR-\omega t)}}{R}$, with an amplitude that in general depends on the scattering angle γ .

²See Appendix I for a complete derivation.

- If the incident wave is σ -polarised, the scattered wave is σ' -polarised, and has amplitude $\frac{r_0}{R} E_0$.
- If the incident wave is π -polarised, the scattered wave is π' -polarised, and has amplitude $\frac{r_0}{R} E_0 \cos \gamma$.
- The intensity of the scattered wave is zero for scattering of π polarisation at 90° .
- The scattered wave has a phase shift of π upon scattering (*minus* sign).
- For generic incident polarisation, the *scattering amplitude* (amplitude of the spherical wave) in each scattered polarisation can be written as:

$$A = r_0[\epsilon \cdot \epsilon'] \quad (5)$$

- The *cross section* is defined as the average power radiated per unit solid angle divided by the average incident power per unit area (power flux, Φ)
- For an *unpolarised* X-ray beam, all the angles ξ are equally represented (i.e., there will be photons with all polarisations). The cross section in this case is

$$\boxed{\frac{d\sigma}{d\Omega} = r_0^2 \left[\frac{1 + \cos^2 \gamma}{2} \right]} \quad (6)$$

1.2 Thomson scattering from many quasi-free electrons

- When many electrons are in close proximity to each other, the spherical waves emitted by them will interfere.
- The combined effect of these waves can be calculated in the following approximations:
 - ◊ The amplitude of the motion of the electrons is much smaller than the wavelength.
 - ◊ The distance at which the process is observed is also much larger than the distance between electrons (Fraunhofer diffraction or far-field limit).
 - ◊ The distribution of electrons can be considered continuous, with number density $\rho(\mathbf{x})$ [electrons/m³].

With these approximations, which are always obeyed for the electron cloud around an atom and reasonable values of the electric field)

$$\mathbf{E}(\mathbf{R}, t) = -r_0 \mathbf{E}_0 \frac{e^{i(\mathbf{kR} - \omega t)}}{R} [\cos \xi \epsilon'_\sigma + \sin \xi \cos \gamma \epsilon'_\pi] \int \rho(\mathbf{x}) e^{-i\mathbf{q} \cdot \mathbf{x}} d\mathbf{x} \quad (7)$$

- The vector $\mathbf{q} = \mathbf{k}_f - \mathbf{k}_i$ is the **scattering vector** and \mathbf{k}_i and \mathbf{k}_f are the incident and scattered wavevectors.
- Note the important formula, valid for elastic scattering (we recall that $\gamma = 2\theta$):

$$q = |\mathbf{q}| = \frac{4\pi \sin \theta}{\lambda} \quad (8)$$

Eq. 8 is illustrated graphically in fig. 2

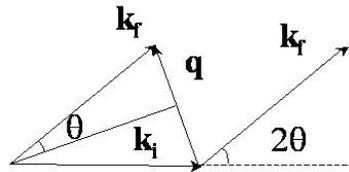


Figure 2: Scattering triangle for elastic scattering.

- The integral

$$f(\mathbf{q}) = \int \rho(\mathbf{x}) e^{-i\mathbf{q} \cdot \mathbf{x}} d\mathbf{x} \quad (9)$$

is known as the **atomic scattering factor or form factor**.

We have arrived here at an important result: **the scattering amplitude for many quasi-free electrons is proportional to the Fourier transform of the charge density**. Note that the integral for $\mathbf{q} = 0$ is the **total charge**, which for an atom is the atomic number Z (fig. 3).

A key fact to remember: the more spread out the charge is around the atom, the faster $f(\mathbf{q})$ will decay at high \mathbf{q} .

High $\mathbf{q} \equiv$ high scattering angles, short wavelengths.

- The cross sections are obtained in the same way as for a single charge — for instance, the unpolarised cross section for an atom is:

$$\left(\frac{d\sigma}{d\Omega}\right)_{atom} = r_0^2 |f(\mathbf{q})|^2 \left[\frac{1 + \cos^2 \gamma}{2}\right] \quad (10)$$

which, in forward scattering, becomes:

$$\left(\frac{d\sigma}{d\Omega}\right)_{atom} = r_0^2 Z^2 \quad (11)$$

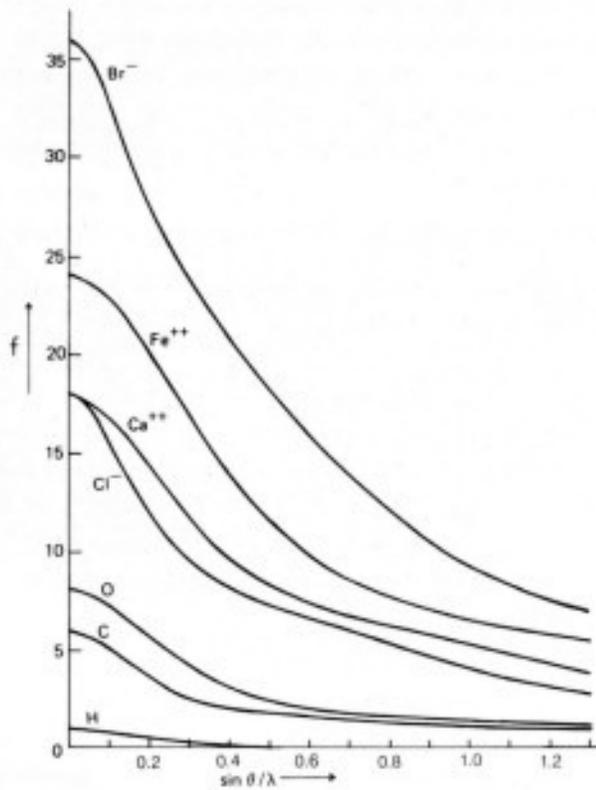


Figure 3: Atomic scattering factors (form factors) for selected neutral atoms and ions. Note that $\sin \theta/\lambda = q/4\pi$.

- One can find tabulated values of the form factors for neutral and ionised atoms in the International Tables for Crystallography, volume C, p 555 and p 566, respectively.

1.3 X-ray scattering from bound electrons — anomalous scattering

- Truly “free” electrons (e.g., conduction electrons in a metal) hardly contribute to the scattering of X-rays, because their probability distribution

extends a long way throughout the crystal, and, from eq. 9, the form factor decays very rapidly away from forward scattering (fig. 3).

- The largest contribution to X-ray scattering from atoms is given by “core” electrons, which are close to the nucleus and have slowly decaying form factors — but these electrons are certainly not free!
- There are large departures from the Thomson scattering formula near *atomic resonances*, where the energy of the photon is just sufficient to eject an electron from a core state into the continuum. Away from resonances, the Thomson formula can be corrected to a very good approximation by replacing the form factor by the *complex* quantity

$$f(\mathbf{q}) = f_{\text{Thom}}(\mathbf{q}) + f'(\hbar\omega) + i f''(\hbar\omega) \quad (12)$$

where the so-called *anomalous terms*, f' and f'' , away from atomic resonances do not depend on q and are weak functions of the photon energy³.

It can be shown, as a consequence of the so-called optical theorem, that the imaginary part of the scattering factor is proportional to the linear absorption coefficient due to the photoelectric effect.

$$f''(\hbar\omega) = \frac{\omega}{4\pi r_0 c N_a} \mu \quad (13)$$

where N_a is the number of atoms per unit volume, and the other symbols have the usual meaning. The quantity μ is the *linear absorption coefficient*, defined as:

$$I = I_0 e^{-\mu L} \quad (14)$$

1.4 Thermal neutron scattering from atoms and spins

- As in the case of X-rays, the neutron scattering process generates a *spherical wave*, the *squared* amplitude of which is proportional to the cross section.
- *Thermal neutrons*, with energies in the meV range, are commonly used to probe condensed matter. Their properties can be summarised as follows:
 - ◊ Free neutrons are unstable, with half-life $\tau = 10.6$ min. (β -decay)

³See Appendix II for more details about resonant X-ray scattering.

- ◇ Neutrons bound in nuclei are (generally) stable.
- ◇ Mass: $1.67492729(28) \times 10^{-27}$ kg
- ◇ Electric dipole moment $D < 10^{-25}$ (e cm)
- ◇ Spin: $s = \frac{1}{2}$ — neutrons are *fermions*.
- ◇ Magnetic dipole moment: $\mu = -1.9130418 \mu_N$, where $\mu_N = \frac{e\hbar}{2m_p} = 5.05078324(13) \times 10^{-27}$ JT⁻¹ is the **nuclear magneton**.

Table 2: Neutron wavelenghts and kinetic energies in different “slow” ranges. The thermal energy per particle at room temperature is 25 meV.

	λ (Å)	E (meV)
Cold	3–30	0.1–10
Thermal	1–3	10–100
Hot	0.4–1	100–500
Epithermal	< 0.4	> 500

- Neutrons are elastically or inelastically scattered by the condensed matter through two completely different mechanisms, but, as it turns out, yielding comparable scattering lengths.
 1. By **nuclear interaction with the atomic nuclei**.
 2. By **dipole interaction with the unpaired spin and orbital magnetic moments of the atoms**. This is only present if the atom or ion has a magnetic moment.
- A summary of the key results is provided here below⁴.

⁴See Appendix III for a complete derivation of the nuclear and magnetic neutron cross sections

Neutron-nuclear interaction

- The neutron-nuclear interaction is **isotope and elements specific**, and **depends on the mutual orientation of the neutron and the nuclear spin**.
- As far as neutron crystallography is concerned, **the key parameter is the scattering amplitude averaged over the nuclear spin states**, known as the **coherent scattering amplitude**.
- The neutron nuclear coherent scattering amplitude **is independent on q** — it carries **no form factor**, and is therefore expressed by a single number, known as the **Fermi length**.
- **Fermi lengths can be positive or negative, depending on whether the neutron-nuclear interaction is attractive or repulsive**. For typical nuclei, they are of the order of a few fm (10^{-15} m) (see fig 4), which means that they **are comparable to the classical electron radius**. However, atoms have a single nucleus and many electrons, so X-ray scattering cross sections in the *forward* direction are typically much larger than neutron cross sections (X-ray cross sections decay at high q due to the form factor).
- Fermi lengths do not vary in a systematic way across the periodic table (fig 4), which means that **with respect to X-rays, neutrons are uniquely sensitive to some light elements** — **notably oxygen**. The different scattering lengths of different isotopes is also widely exploited in the so-called **contrast variation techniques**.

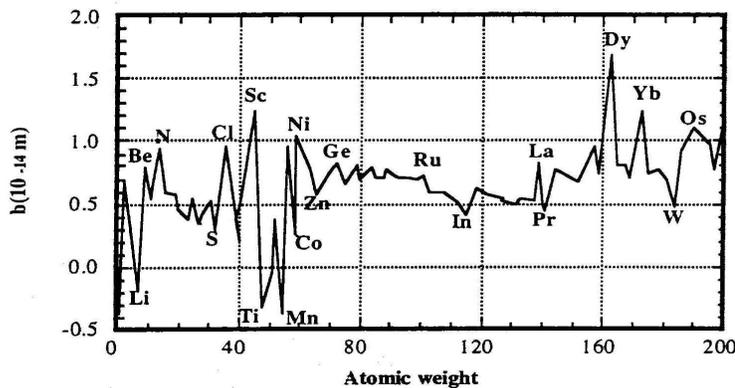


Figure 4: Variation of the Fermi length as a function of atomic weight.

Neutron-magnetic interaction

- When the scatterer carries a magnetic moment, in addition to the normal nuclear interaction, neutrons are also scattered by dipole-dipole interaction from the magnetic moment of the atom.
- Magnetic scattering of neutrons is governed by the following **vector** scattering amplitude.

$$\mathbf{A}_n = \gamma_N r_0 f_m(\mathbf{q}) \mathbf{M}_\perp \quad (15)$$

where γ_N is the neutron gyromagnetic ratio (-1.9130418), r_0 is the familiar **classical electron radius** and \mathbf{M}_\perp is the **projection of the atomic magnetic moment perpendicular to the wavevector transfer \mathbf{q}** , and is expressed in **Bohr magnetons**.

- The quantity $f_m(\mathbf{q})$ is known as the **neutron magnetic form factor**, and is normalised so that $f_m(0) = 1$. It is similar to the X-ray form factor, except for the fact that it only includes the more extended **density of unpaired electrons**. Therefore **magnetic neutron scattering decays very rapidly at high q** .
- From eq. 15 one can obtain a **number of cross sections**, accounting for the different orientations of the neutron spin with respect to the atomic magnetic moment (**neutron polarisation**). The most important cross section is the **unpolarised neutron cross section** (averaged over all the possible neutron polarisations), which, for a *single* atom, is:

$$\frac{d\sigma}{d\Omega} = \gamma_N^2 r_0^2 f_m^2(\mathbf{q}) |\mathbf{M}_\perp|^2 = \gamma_N^2 r_0^2 f_m^2(\mathbf{q}) M^2 \sin^2 \alpha \quad (16)$$

where α is the angle between \mathbf{M} and \mathbf{q} . Note that **the cross section is zero if \mathbf{q} is parallel to \mathbf{M}** .

- Typical magnetic moments for atoms and ions are **a few Bohr magnetons**. Therefore, from eq. 16, one finds that **neutron nuclear and magnetic scattering cross sections are typically comparable in magnitude for magnetic atoms**.

2 Lecture 7 - Scattering from crystals

2.1 Cross section for a “small” perfect single crystal

- We want to calculate the scattering cross section from a “small” single crystal. Here, “small” means that we can ignore multiple scattering events. We still consider the crystal as perfectly periodic.
- We will employ the same approximations that we have used for the scattering from many quasi-free electrons (the far-field approximation is not obeyed in some relevant cases, but we will not concern ourselves with them).
- We will consider the case of X-rays, but the calculation is analogous for neutrons. The scattering amplitude in each final polarisation direction is obtained by integrating over the whole crystal (instead that around an atom, as for eq. 7):

$$A(\mathbf{q}) = r_0 \int_{\text{Crystal}} d\mathbf{r} \rho(\mathbf{r}) e^{-i\mathbf{q} \cdot \mathbf{r}} [\boldsymbol{\epsilon} \cdot \boldsymbol{\epsilon}'] \quad (17)$$

- We can exploit the fact that the charge density is periodic, so that, if \mathbf{r}_i is a lattice translation and \mathbf{x} is restricted to the unit cell containing the origin:

$$\rho(\mathbf{r}) = \rho(\mathbf{r}_i + \mathbf{x}) = \rho(\mathbf{x}) \quad (18)$$

whence the scattering amplitude becomes

$$\begin{aligned} A(\mathbf{q}) &= r_0 \sum_i \int_{\text{Unit Cell}} d\mathbf{x} \rho(\mathbf{x}) e^{-i\mathbf{q} \cdot (\mathbf{r}_i + \mathbf{x})} [\boldsymbol{\epsilon} \cdot \boldsymbol{\epsilon}'] \\ &= r_0 \sum_i e^{-i\mathbf{q} \cdot \mathbf{r}_i} \int_{\text{Unit Cell}} d\mathbf{x} \rho(\mathbf{x}) e^{-i\mathbf{q} \cdot \mathbf{x}} [\boldsymbol{\epsilon} \cdot \boldsymbol{\epsilon}'] \end{aligned} \quad (19)$$

where the summation runs over all the unit cells in the crystal. The expression

$$F(\mathbf{q}) = r_0 \int_{\text{Unit Cell}} d\mathbf{x} \rho(\mathbf{x}) e^{-i\mathbf{q} \cdot \mathbf{x}} \quad (20)$$

is known as the **structure factor**. Note the close analogy with eq. 32, Part I.

The structure factor is proportional to the Fourier transform of the charge density (or, more in general, scattering density) integrated over the unit cell.

- If the electron density $\rho(\mathbf{r})$ is a superposition of atomic-like electron densities (i.e., a series of δ functions), $F(\mathbf{q})$ can be written as

$$F(\mathbf{q}) = r_0 \sum_n f_n(\mathbf{q}) e^{-i\mathbf{q} \cdot \mathbf{x}_n} \quad (21)$$

where the sum runs over all the atoms in the unit cell and $f_n(\mathbf{q})$ are the form factors of each species and \mathbf{x}_n are their positions within the unit cell.

- We can now calculate the **cross section**:

$$\frac{d\sigma}{d\Omega} = A(\mathbf{q}) \mathbf{A}^*(\mathbf{q}) = \left(\sum_j \sum_i e^{-i\mathbf{q} \cdot (\mathbf{r}_i - \mathbf{r}_j)} \right) |\mathbf{F}(\mathbf{q})|^2 [\boldsymbol{\epsilon} \cdot \boldsymbol{\epsilon}']^2 \quad (22)$$

- We now introduce the fact that the double summation in parentheses can be considered as running over an infinite lattice. Consequently, all the summations over i labelled by \mathbf{r}_j are the same (they only differ by a shift in origin), and the summation over j can be replaced by multiplication by N_c — the number of unit cells in the crystal ($\rightarrow \infty$).
- The remaining single summation is only non-zero when \mathbf{q} is a RL vector. If \mathbf{q} is restricted to the first Brillouin zone, we can write:

$$\delta(\mathbf{q}) = \frac{1}{(2\pi)^3} \int d\mathbf{x} e^{-i\mathbf{q} \cdot \mathbf{x}} \simeq \frac{v_0}{(2\pi)^3} \sum_i e^{-i\mathbf{q} \cdot \mathbf{r}_i} \quad (23)$$

where v_0 is the unit cell volume. For an unrestricted \mathbf{q} , the same expression holds with the left-hand member replaced by a sum of delta functions centred at all reciprocal lattice nodes, indicated with $\boldsymbol{\tau}$ in the remainder. With this, we can write the final expression for the cross section:

$$\frac{d\sigma}{d\Omega} = N_c \frac{(2\pi)^3}{v_0} \sum_{\boldsymbol{\tau}} \delta(\mathbf{q} - \boldsymbol{\tau}) |F(\boldsymbol{\tau})|^2 [\boldsymbol{\epsilon} \cdot \boldsymbol{\epsilon}']^2 \quad (24)$$

- The term $[\boldsymbol{\epsilon} \cdot \boldsymbol{\epsilon}']^2$ needs to be averaged over all this incident and scattered polarisations, yielding a **polarisation factor** $\mathcal{P}(\gamma)$, which depends on the experimental setting. For example, for an unpolarised incident beam and no polarisation analysis:

$$\mathcal{P}(\gamma) = \left[\frac{1 + \cos^2 \gamma}{2} \right] \text{ unpolarised beam} \quad (25)$$

- The final general expression for the average cross section is:

$$\frac{d\sigma}{d\Omega} = N_c \frac{(2\pi)^3}{v_0} \sum_{\tau} \delta(\mathbf{q} - \tau) |F(\tau)|^2 \mathcal{P}(\gamma) \quad (26)$$

Let's recap the key points to remember:

- ◇ **The cross section is proportional to the number of unit cells in the crystal. The bigger the crystal, the more photons or particles will be scattered. We can clearly see that this result *must* involve an approximation: the scattered intensity must reach a limit when all the particles in the beam are scattered.**
- ◇ **The cross section is proportional to the squared modulus of the structure factor (no surprises here — you should have learned this last year).**
- ◇ **Scattering only occurs at the nodes of the *RL*. For a perfect, infinite crystal, this is in the form of delta functions.**
- ◇ **The cross section contains the unit-cell volume in the denominator. This is necessary for dimensional reasons, but it could perhaps cause surprise. After all, we could arbitrarily decide to *double* the size of the unit cell by introducing a “basis”. The answer is, naturally, that the $|F(\tau)|^2$ term exactly compensates for this.**

- The limitations of the *small crystal approximation* can be overcome by complete description of the scattering process, including *multiple scattering*, in what is known as **dynamical theory of diffraction** (see extended version of the notes for a very short introduction).

2.2 Laue and Bragg equations

- The δ function in eq. 24 expresses the fact that the cross section is zero unless \mathbf{q} is equal to one of the *RLV*.
- This is more traditionally expressed by the *Laue equations*:

$$\mathbf{q} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^* \quad (27)$$

$$\begin{aligned} \mathbf{q} \cdot \mathbf{a}_1 &= (\mathbf{k}_f - \mathbf{k}_i) \cdot \mathbf{a}_1 = 2\pi h \\ \mathbf{q} \cdot \mathbf{a}_2 &= (\mathbf{k}_f - \mathbf{k}_i) \cdot \mathbf{a}_2 = 2\pi k \\ \mathbf{q} \cdot \mathbf{a}_3 &= (\mathbf{k}_f - \mathbf{k}_i) \cdot \mathbf{a}_3 = 2\pi l \end{aligned} \quad (28)$$

- h, k and l are the **Miller indices** that we have already encountered.
- The *modulus* of the scattering vector (fig. 2 and eq. 8) is:

$$q = |\mathbf{q}| = \frac{4\pi \sin \theta}{\lambda} \quad (29)$$

- Given a *RLV* \mathbf{q} with Miller indices hkl , it can be shown by simple geometry that there exist a family of *parallel real-lattice planes* perpendicular to it, and that the distance between two adjacent planes is $d = 2\pi n/q$, where n is the greatest common divisor of h, k and l .
- From this and eq. 29, one can deduce that the scattering process can be thought as a mirror reflection from this family of planes, with the addition of **Bragg law**:

$$2d \sin \theta = n\lambda \quad (30)$$

2.3 The effect of atomic vibrations — the Debye-Waller factor

- Atoms are always displaced away from their “ideal” positions, primarily due to thermal vibrations, but also due to crystal defects. This has an effect on the scattering cross section.
- We can re-write the expression of the scattering amplitude (eq. 19), taking into account the effect of these displacements (we omit the polarisation factor $[\boldsymbol{\epsilon} \cdot \boldsymbol{\epsilon}']$ for simplicity):

$$A(\mathbf{q}) = r_0 \sum_i e^{-i\mathbf{q} \cdot \mathbf{r}_i} \sum_n f_n(\mathbf{q}) e^{-i\mathbf{q} \cdot (\mathbf{x}_n + \mathbf{u}_{n,i})} \quad (31)$$

where $\mathbf{u}_{n,i}$ is the *displacement vector* characterising the position of the atom with label n in the i^{th} unit cell.

- Bragg scattering results from **time averaging of the scattering amplitude** (*not* the cross section). The effect of this is:

Atomic vibrations “smear out” the scattering density, acting, in a sense as an additional “form factor”.

- ◇ **The higher the temperature, the more the atoms will vibrate, the more the intensity will decay at high q . This is easily understood by analogy with the form factor $f(q)$: the more the atoms vibrate, the more “spread” out the scattering density will be, the faster the scattering will decay at high q .**
- ◇ **The *softer* the spring constants, the more the atoms will vibrate, the more the intensity will decay at high q .**
- ◇ **The *lighter* the atoms, the more the atoms will vibrate, the more the intensity will decay at high q .**

- The time averaging can be expressed as:

$$A(\mathbf{q}) = r_0 \sum_i e^{-i\mathbf{q}\cdot\mathbf{r}_i} \sum_n f_n(\mathbf{q}) e^{-i\mathbf{q}\cdot\mathbf{x}_n} \langle e^{-i\mathbf{q}\cdot\mathbf{u}_{n,i}} \rangle \quad (32)$$

- The term in $\langle \rangle$ represents the time averaging and does not depend on the specific atomic site i . One can show (see extended version of the notes on web site) that

$$\langle e^{-i\mathbf{q}\cdot\mathbf{u}_{n,i}} \rangle = e^{-W(\mathbf{q},n)}. \quad (33)$$

where, in the simple isotropic case

$$W(\mathbf{q}, n) = U_n q^2 \quad (34)$$

- With this, we obtain the **general expression for the X-ray structure factor in the isotropic case**

$$F(\mathbf{q}) = r_0 \sum_n f_n(q) e^{-i\mathbf{q}\cdot\mathbf{x}_n} e^{-U_n q^2} \quad (35)$$

- A very similar expression is found for the **coherent neutron structure factors for nuclear scattering**.

$$F(\mathbf{q}) = \sum_n b_n e^{-i\mathbf{q}\cdot\mathbf{x}_n} e^{-U_n q^2} \quad (36)$$

- The corresponding formula for **magnetic scattering of neutrons from a collinear ferromagnet or antiferromagnet** is

$$F(\mathbf{q}) = \gamma_N r_0 \sum_n f_n(\mathbf{q}) M_n \sin \alpha e^{-i\mathbf{q} \cdot \mathbf{x}_n} e^{-U_n q^2} \quad (37)$$

where M_n (expressed in Bohr magnetons) reflects both the magnitude and the sign of the magnetic moment of atom n , and $f_{m_n}(\mathbf{q})$ is the corresponding magnetic form factor and α is the angle between \mathbf{M} and \mathbf{q}

- Real crystals are not perfectly periodic, due to the presence of *defects*, *lattice vibrations* and, quite simply, the fact that they are of finite size.
- In scattering experiments, *deviation from perfect periodicity results in scattering outside the RL nodes*.
- *Static defects* produce elastic *elastic scattering*, known as *diffuse scattering* because of the fact that it not strongly peaked as Bragg scattering.
- *Dynamic effects* (such as lattice vibrations) produce *inelastic scattering*.
- In a diffraction experiment, one does not analyse the energy of the scattered particle, and both effects contribute to the diffuse scattering. Scattering from phonons is known as *thermal diffuse scattering*.
- *Extended defects* (involving planes or lines of defects) are described in the extended version of the notes.

2.4 Finite size effects

- In the case of an infinite perfect crystal, the cross section is a series of δ functions centred at the *RL nodes*, This is a result of the infinite summation over all the real lattice nodes.
- If we carry out a *finite* summation instead, for example over N_1, N_2 and N_3 unit cell in the $\mathbf{a}_1, \mathbf{a}_2$ and \mathbf{a}_3 directions, and remembering that

$$\sum_{n=-N}^N e^{-inx} = \frac{\sin\left(\left(2N+1\right)\frac{x}{2}\right)}{\sin\frac{x}{2}} \quad (38)$$

we obtain (in each direction, x in eq. 38 is $= \mathbf{q} \cdot \mathbf{a}_i$)

$$\frac{d\sigma}{d\Omega} = \left[\prod_i \frac{\sin^2\left(N_i \frac{1}{2} \mathbf{q} \cdot \mathbf{a}_i\right)}{\sin^2\left(\frac{1}{2} \mathbf{q} \cdot \mathbf{a}_i\right)} \right] |F(\mathbf{q})|^2 [\boldsymbol{\varepsilon} \cdot \boldsymbol{\varepsilon}']^2 \quad (39)$$

- This oscillatory function will be in general smeared out by coherence effects (see long versions of the notes), and can be approximated as

$$\frac{d\sigma}{d\Omega} = N_c^2 \left[\prod_i e^{-(N_i \frac{1}{2} \mathbf{q} \cdot \mathbf{a}_i)^2 / \pi} \right] |F(\mathbf{q})|^2 [\boldsymbol{\varepsilon} \cdot \boldsymbol{\varepsilon}']^2 \quad (40)$$

where the Gaussian functions have variance and FWHM

$$\begin{aligned} \sigma_i^2 &= \frac{2\pi}{N_i^2 a_i^2} \\ FWHM &= \frac{4\sqrt{\pi \ln 2}}{N_i a_i} \end{aligned} \quad (41)$$

- We can therefore conclude that:
 - ◊ The **cross section at a given \mathbf{q}** is proportional to N_c^2 .
 - ◊ The **width** in \mathbf{q} is *inversely proportional to the number of unit cells along that direction*.
 - ◊ The **integrated cross section** in three dimensions (remember the Gaussian integral $\sqrt{2\pi\sigma^2}$) is therefore proportional to N_c , which reproduces the result we obtained for the infinite crystal (eq. 8, lecture 6).

3 Lecture 8 - Diffraction experiments and data analysis

3.1 Geometries for diffraction experiments - single crystal diffraction

In general, the experimental apparatus to perform a diffraction experiment on a single crystal or a collection of small crystals (powder diffraction) will consist of (fig. 5):

- ◇ An **incident beam**, which can be **monochromatic** or **polychromatic**.
- ◇ A **sample stage**, which enables the sample to be oriented and also incorporates the **sample environment** to control a variety of physical (P , T , $H...$) and/or chemical parameters.
- ◇ A **detector**, which includes a detector of photons or particles. This is normally mounted on a separate arm, enabling the 2θ angular range to be varied.

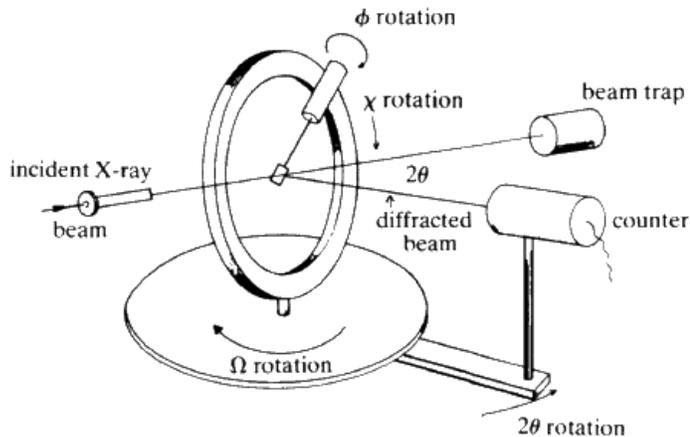


Figure 5: The geometry of a “four circle” single-crystal diffractometer. The “four circles” (actually four axes) are marked “ ϕ ”, “ χ ”, “ Ω ” and “ 2θ ”. The 2θ and Ω angles are also known as γ and η .

3.1.1 Scattering triangles for elastic scattering and the Ewald construction

- As we have seen, the scattering cross section for a single crystal is a series of delta functions in reciprocal space, centred at the nodes of the reciprocal lattice.

- When a single crystal is illuminated with monochromatic radiation, the scattering conditions are satisfied only for particular orientations of the crystal itself — in essence, the specular (mirror-like) reflection from a family of lattice planes must satisfy Bragg law at the given wavelength.

With monochromatic radiation, for a generic crystal orientation, no Bragg scattering will be observed at all.

- Fig. 6 show the geometrical construction used to establish when the scattering conditions are satisfied. Note that here we employ the **diffraction convention**: $\mathbf{q} = \mathbf{k}_f - \mathbf{k}_i$ (see below for the inelastic conventions).
- A typical problem will state the wavelength λ of the incident and scattered radiation (which are the same, since the scattering is elastic), the symmetry and the lattice parameters of the material and the Bragg reflection to be measured (given in terms of the Miller indices hkl). These data are sufficient to determine $k_i = k_f = 2\pi/\lambda$ and q (for a right-angle lattice $q = 2\pi\sqrt{h^2/a^2 + k^2/b^2 + l^2/c^2}$; see previous lectures for formulas to calculate q in the general case).
- Since all the sides of the scattering triangle are known, it is possible to determine all the angles — in particular the scattering angle $\gamma = 2\theta$ and the orientation of the incident beam with respect to the lattice required to be in scattering condition.
- The circle shown in fig. 6 is actually a sphere in 3D, and defines the *locus* of all the possible scattering vectors for a given \mathbf{k}_i . This is known as the **Ewald sphere**, from the German physicist Paul Peter Ewald (1888, 1985).
- The maximum value of q is achieved for $\gamma = 2\pi$ (*backscattering*), and is $\mathbf{q} = -2\mathbf{k}_i$
- The nodes "accessible" by scattering are contained within a sphere of radius $2k_i = 4\pi/\lambda$, centered on the origin of reciprocal space, so that

$$0 \leq q \leq 2k_i \quad (42)$$

3.2 Scattering triangles for inelastic scattering

- For inelastic scattering, the **inelastic convention**: $\mathbf{q} = \mathbf{k}_i - \mathbf{k}_f$ is generally employed, so that $\mathbf{q}_{\text{dif}} = -\mathbf{q}_{\text{ine}}$.

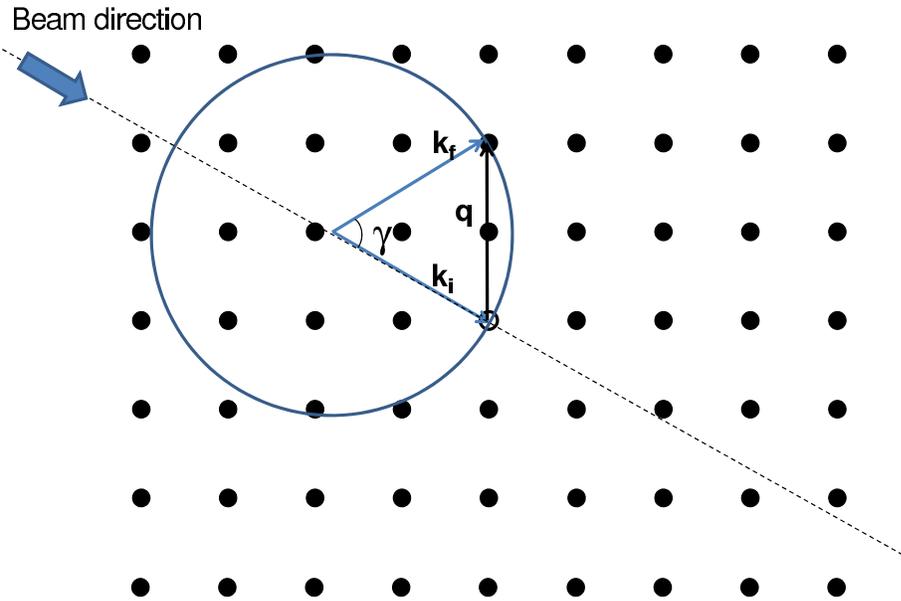


Figure 6: The procedure to construct the scattering triangle for elastic scattering.

- In an inelastic scattering experiment, the scattered particle loses (**energy loss scattering**) or gains (**energy gain scattering**) part of its energy, and a corresponding amount of energy is transferred to or from an excitation in the crystal such as a *phonon* or a *magnon*. In constructing the scattering triangle, we should therefore allow for the fact that k_f will be either larger or smaller than k_i .

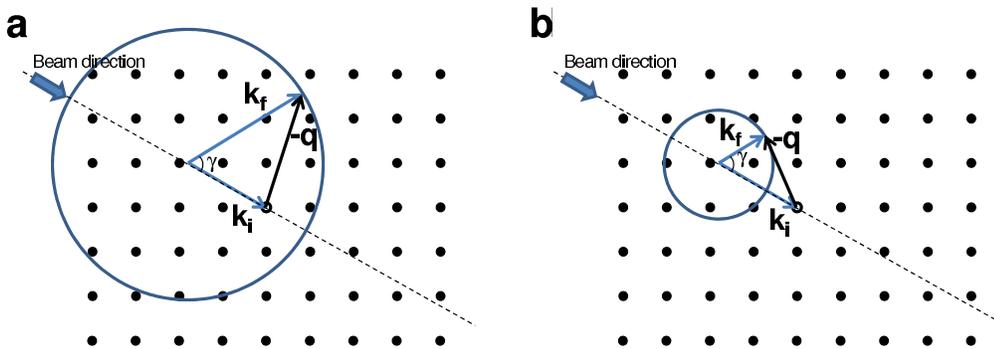


Figure 7: The procedure to construct the scattering triangle for inelastic scattering. (a) energy gain; (b) energy loss.

- The corresponding constructions are shown in 7. One can see that eq. 42 should be replaced by

$$|k_i - k_f| \leq q \leq k_i + k_f \quad (43)$$

- The region of reciprocal space "accessible" by scattering is bounded by

two spheres of radius $k_i + k_f$ and $|k_i - k_f|$, centered on the origin of reciprocal space.

- Maximum and minimum q are achieved in backscattering and forward scattering, respectively.

3.3 Powder diffraction and the Debye-Scherrer cones

- A “powder” sample is a more or less “random” collection of small single crystals, known as “crystallites”.
- The cross section for the whole powder sample depends on the *modulus* of the scattering vector q but not on its direction. Therefore, when a powder sample is illuminated, scattering is always observed (unlike the case of a single crystal).
- For a monochromatic incident beam, the 2θ angle *between* the incident and scattered beam is fixed for a given Bragg reflection, but the angle *around* the incident beam is arbitrary. The *locus* of all the possible scattered beams is a **cone** around the direction of the incident beam (fig. 8).
- All the symmetry-equivalent RL nodes, having the same q , *contribute to the same D-S cone* (fig. 9).
- *Accidentally degenerate* reflections, having the same q but unrelated hkl 's, also contribute to the same D-S cone. This is the case for example, for reflections $[333]$ and $[115]$ in the cubic system, since $3^2 + 3^2 + 3^2 = 1^2 + 1^2 + 5^2$.

Key points to retain about powder diffraction

- ◇ In powder diffraction methods, the intensity around the D-S cones is *always integrated*, yielding a 1-dimensional pattern.
- ◇ Powder diffraction peaks are usually well-separated at low q , but become increasingly crowded at high q often becoming completely overlapped. This substantially reduce the amount of information available to solve or refine the structure precisely (see below).

3.4 Integrated Intensities

- Exam problems will not be concerned with peak fitting, and you will be given integrated intensities of some form. These intensities will be usually

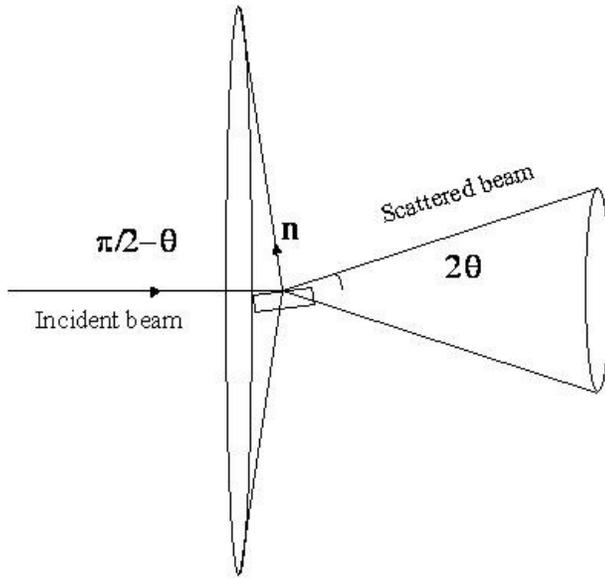


Figure 8: Debye-Scherrer cones and the orientations of the sets of Bragg planes generating them.

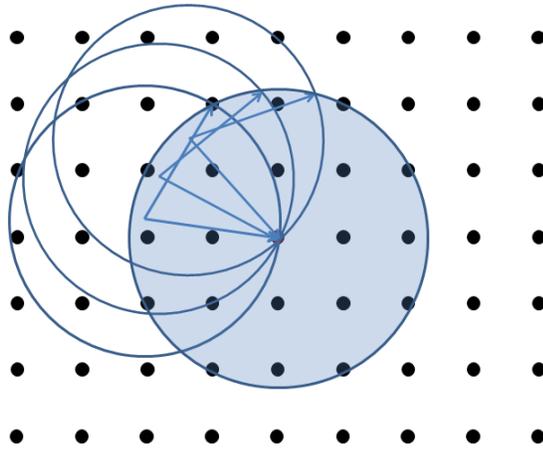


Figure 9: Ewald construction for powder diffraction, to represent the crystal being rotated randomly around the direction of the incident beam (the figure actually shows the opposite, for clarity). Note that many RL nodes are simultaneously in scattering — those that have the same $|q|$. Symmetry-equivalent reflections have the same $|q|$ and also the same structure factor. The powder intensity is therefore multiplied by the number of symmetry-equivalent reflections, known as the *multiplicity*.

corrected for the Lorentz - polarisation (i.e., $\mathcal{P}(\gamma)$), angle-dependent attenuation (typically due to X-ray or neutron absorption) and incident flux terms, but the role these terms may be requested as part of the discussion. The integrated intensity can always be reduced to a dimensionless quantity (counts).

- The general expression for the integrated intensity (number of particles) is

$$P_{\tau} = N_c \left(\frac{d^3}{v_0} \right) m_{\tau} |F(\boldsymbol{\tau})|^2 \mathcal{P}(\gamma) \mathcal{L}(\gamma) \mathcal{A}_{\tau}(\lambda, \gamma) \mathcal{F}_{inc} \quad (44)$$

- N_c is the number of unit cells in the sample.
 - d is the d-spacing of the reflection.
 - v_0 is the unit-cell volume.
 - m_{τ} (powder diffraction only) is the *number of symmetry-equivalent reflections*. This accounts for the fact that in powder diffraction these reflections are not separable, and will always contribute to the same Bragg powder peak (see previous discussion and fig. 9).
 - $\mathcal{P}(\gamma)$ is the *polarisation factor* (dimensionless), which we have already introduced.
 - $\mathcal{L}(\gamma)$ is the so-called *Lorentz factor* (dimensionless), and contains all the experiment-specific geometrical factors arising from the δ -function integration.
 - $\mathcal{A}_{\tau}(\lambda, \gamma)$ (dimensionless) is the *attenuation and extinction coefficient*, which account for the beam absorption and for dynamical effects.
 - \mathcal{F}_{inc} is the incident time-integrated flux term (counts per square metre), which accounts for the strength of the incident beam and for the counting time.
- The product $(d^3/v_0)\mathcal{P}(\gamma)\mathcal{L}(\gamma)\mathcal{A}_{\tau}(\lambda, \gamma)$, is sometimes called the **LPGA factor** (Lorentz-Polarisation-Geometrical-Attenuation), and is used to correct the raw data. When absolute incident flux measurements are not available, one obtains a pattern where the intensities are proportional to the square of the structure factor, the proportionality constant being a *scale factor*.

3.5 Structural solution from diffraction data

3.5.1 The phase problem

- From eq. 20, we can see that **the structure factor is proportional to the Fourier transform of the charge density (or, more in general, scattering density) integrated over the unit cell**.
- By the elementary theory of the Fourier transform over a finite interval (extended to 3 dimensions) we can calculate the charge density given all the structure factors:

$$\rho(\mathbf{x}) = \frac{1}{r_0 v_0} \sum_{\tau} \mathbf{F}(\tau) e^{i\tau \cdot \mathbf{x}} \quad (45)$$

- From eq. 45 follows that *if we were able to measure all the structure factors, we could reconstruct the charge density exactly*. Clearly, it is impossible to measure all the infinite nodes of the reciprocal space, but it can be shown that it would be sufficient to measure up to a value of q_{max} to obtain a **Fourier map** with **resolution** $2\pi/q_{max}$ in *real space*.
- However, direct reconstruction of the charge density from diffraction data is impossible, because only the *amplitudes* of the structure factors are known (through the term $|F|^2$ in the cross section), while the *phases* are unknown. Solving a crystal structure is therefore equivalent to *phasing* the reflections.
- A set of mathematical methods, known as **direct methods**, have been developed to phase reflections without any *a priori* knowledge of the crystal structure. They exploit the fact that the *Fourier maps* are not completely arbitrary, but are *positive* (for X-rays) and *atomic-like*.

3.5.2 The Patterson method

- It is nonetheless possible to obtain some degree of information about scattering densities without any knowledge of the phases. Again, from eq. 20, we obtain:

$$|F(\mathbf{q})|^2 = r_0^2 \iint_{\text{unit cell}} d\mathbf{x} d\mathbf{x}' \rho(\mathbf{x}) \rho(\mathbf{x}') e^{-i\mathbf{q} \cdot (\mathbf{x} - \mathbf{x}')} \quad (46)$$

With some manipulations we obtain:

$$\frac{1}{r_0^2 v_0} \sum_{\tau} |F(\tau)|^2 e^{i\tau \cdot \mathbf{x}} = \int_{\text{unit cell}} d\mathbf{x}' \rho(\mathbf{x}') \rho(\mathbf{x} + \mathbf{x}') = P(\mathbf{x}) \quad (47)$$

- The function defined in eq. 47 is known as the **Patterson function** (from Lindo Patterson, 1934). One can perhaps recognise in eq. 47 that the Patterson is *the autocorrelation function of the scattering density*.
- Patterson functions are 3-dimensional functions defined within one unit cell, and are usually presented in the form of 2-dimensional “slices”.

- Atomic-like scattering densities are *mostly zero*, except at the atomic positions. Therefore the Patterson function will be mostly zero as well, except at the *origin* ($x = 0$) and *for values of x corresponding to vectors joining two atoms*. At these vectors, the Patterson function will have **peaks**.
- The integral of the $x = 0$ peak is easily calculated to be $\sum_i Z_i^2$, where Z_i is the atomic number of atom i and the sum is over all atoms in the unit cell.
- Likewise, the integral of a peak corresponding to the interatomic distance r_{ij} is $Z_i Z_j$.

3.5.3 Structural optimisation: least-square refinements

- Most problems in physical crystallography involve determining subtle structural variations from well-known and rather simple structural motifs. Therefore, structural optimisation is usually the method of choice for the structural condensed-matter physicist.
- If one is reasonably close of the solution, with only a few free parameters left to determine, it is possible to *minimise the agreement between observed and calculated squared structure factors $|F|^2$ as a function of the free parameters*. This is clearly a non-linear optimisation problem, and a number of strategies have been developed to solve it in a variety of cases.
- The best known structural optimisation method is known as the **Rietveld method**, and is applied to powder data.
- In the Rietveld method, one performs a nonlinear least-square fit *of the measured profile*, rather than of the $|F|^2$ as in the single-crystal methods. This could appear more complicated, since one has to fit the microstructural and instrumental parameters controlling peak broadening and the background at the same time, but has the great advantage of *accounting automatically for peak overlap*.

4 Appendix I: more on the theory of scattering

4.1 Scattering from a free electron (extended derivation)

Thomson scattering is a *classical* phenomenon, and can be explained as follows: as electromagnetic radiation impinges on a free electron, the oscillating electric field subjects it to an acceleration. The scattered radiation is the radiation emitted by the accelerated charge. If a charge is accelerated and is observed in a reference frame where its velocity is *small compared to that of light*, the electric field can be written as

$$\mathbf{E}(\mathbf{R}, t) = \frac{(-e)}{4\pi\epsilon_0 c^2} \left[\frac{\mathbf{n} \times (\mathbf{n} \times \mathbf{a})}{R} \right]_{ret} \quad (48)$$

where \mathbf{a} is the acceleration and \mathbf{n} is a **unit vector** along the segment connecting the particle to the observer and pointing towards the latter (fig. 10). The subscript “*ret*” means “**retarded**” (see below).

Note that if we keep rotating the scattered beam in the direction shown in fig. 10, i.e., in the plane *containing* the incident polarisation, the projection a_{\perp} will eventually become zero at 90° . On the other hand, if we rotated *perpendicular* to the incident polarisation, the projection would obviously stay the same. In a nutshell, this is the essence of the polarisation factor.

Before we discuss eq. 48, it is worth reminding the important vector relation (used also later on in the course). For any three vectors:

$$\mathbf{a} \times (\mathbf{b} \times \mathbf{c}) = (\mathbf{a} \cdot \mathbf{c})\mathbf{b} - (\mathbf{a} \cdot \mathbf{b})\mathbf{c} \quad (49)$$

$$\mathbf{n} \times (\mathbf{n} \times \mathbf{a}) = -[\mathbf{a} - (\mathbf{a} \cdot \mathbf{n})\mathbf{n}] \quad (50)$$

The expression in square brackets on the right side of eq. 50 is *the projection of \mathbf{a} on the plane perpendicular to \mathbf{n}*

In eq. 48, the square bracket with subscript “ret” means that the quantity in the bracket is to be evaluated at the “retarded” (i.e., **earlier**) time $t - R/c$. R is the distance between the “retarded” position and the observer (fig. 10). Since we are interested in the radiation at a great distance from the particle and at oscillatory, small-amplitude motions of the latter, we can replace R and \mathbf{n} with constant quantities referring to the average position of the particle.

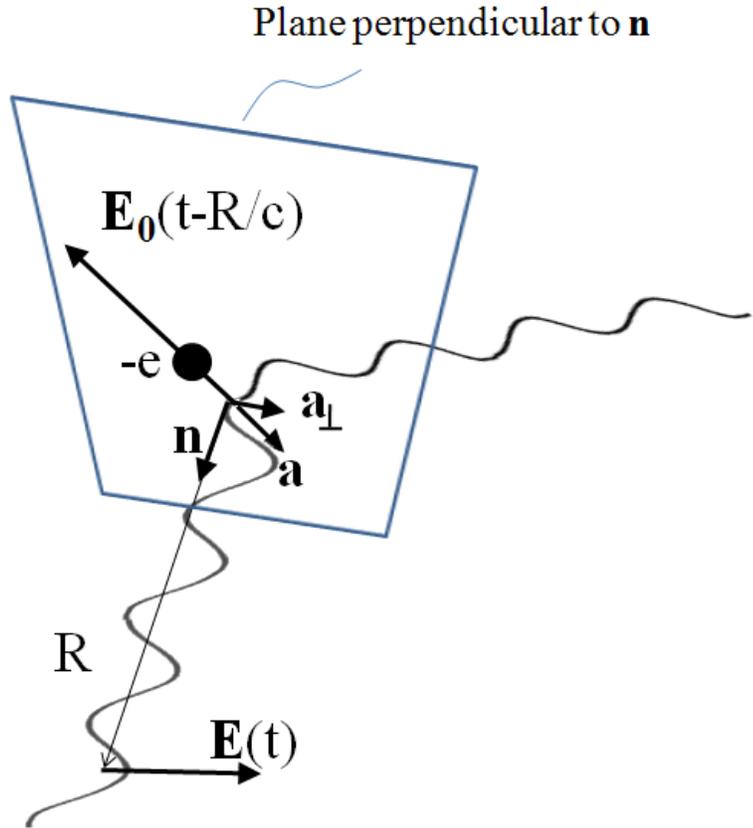


Figure 10: Diagram illustrating the Thomson scattering of X-rays from a free electron. The acceleration due to the incoming wave is a , whereas its *projection perpendicular to the line of sight* is a_{\perp} .

The electric field due to an accelerated particle is proportional to the *projection of the acceleration perpendicular to the line of sight*.

Let us consider a beam of polarised X-rays (i.e., with a well-defined direction of \mathbf{E} , identified by the unit vector ϵ) impinging on a free electron (again, refer to the scheme in fig. 10). The particle will be accelerated by the electric field $\epsilon E_0 e^{-i\omega t}$ of the incoming wave so that

$$\mathbf{a}(t) = \frac{(-e)}{m} \epsilon E_0 e^{-i\omega t} \quad (51)$$

Substituting eq. 51 into eq. 48 we obtain:

$$\mathbf{E}(R, t) = \frac{e^2}{4\pi\epsilon_0 mc^2} E_0 \frac{e^{-i\omega(t-R/c)}}{R} [\mathbf{n} \times (\mathbf{n} \times \boldsymbol{\epsilon})] = \frac{e^2}{4\pi\epsilon_0 mc^2} E_0 \frac{e^{i(kR-\omega t)}}{R} [\mathbf{n} \times (\mathbf{n} \times \boldsymbol{\epsilon})] \quad (52)$$

where $k = \frac{\omega}{c}$ is the wavenumber. The quantity $r_0 = \frac{e^2}{4\pi\epsilon_0 mc^2} = 2.82 \times 10^{-15}$ m is known as the **classical electron radius**. By applying eq. 49 once again we find that the expression in square bracket on the right side of eq. 51 is

$$[\mathbf{n} \times (\mathbf{n} \times \boldsymbol{\epsilon})] = -[\boldsymbol{\epsilon} - (\boldsymbol{\epsilon} \cdot \mathbf{n}) \mathbf{n}] \quad (53)$$

i.e., it is *minus* the component of $\boldsymbol{\epsilon}$ *perpendicular* to \mathbf{n} .

The scattered polarisation $\boldsymbol{\epsilon}'$ is the projection of the incident polarisation perpendicular to the line of sight.

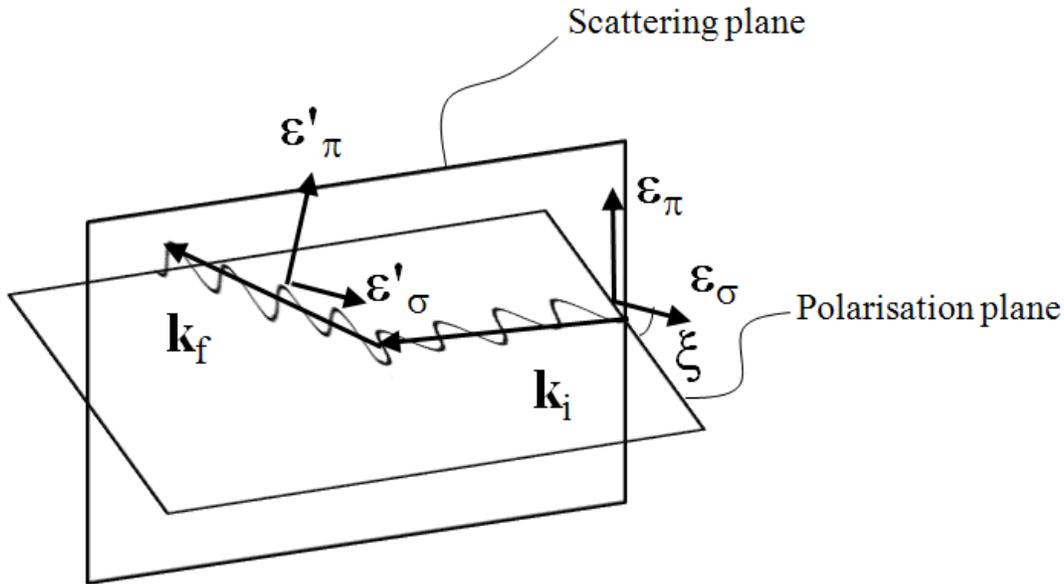


Figure 11: Diagram illustrating the conventional σ and π reference directions for the incident and scattered polarisation. Note that $\boldsymbol{\epsilon}_\sigma \cdot \boldsymbol{\epsilon}'_\sigma = 1$ *always*. Conversely, $\boldsymbol{\epsilon}_\pi \cdot \boldsymbol{\epsilon}'_\pi = \cos \gamma$ **depends on the scattering angle γ** , and **vanishes** for $\gamma = \pi/2$.

It is useful at this point to introduce two orthogonal reference components of $\boldsymbol{\epsilon}$ and of the scattered polarisation $\boldsymbol{\epsilon}'$, according to the scheme shown in fig. 11: $\boldsymbol{\epsilon}_\pi$ and $\boldsymbol{\epsilon}'_\pi$ are in the “scattering plane”, defined by the incident and outgoing directions, whereas $\boldsymbol{\epsilon}_\sigma = \boldsymbol{\epsilon}'_\sigma$ are *perpendicular* to the scattering plane and are equal. We can decompose the incident polarisation as

$$\boldsymbol{\epsilon} = \cos \xi \boldsymbol{\epsilon}_\sigma + \sin \xi \boldsymbol{\epsilon}_\pi \quad (54)$$

so that the incident wave has σ -polarisation for $\xi = 0$ and π -polarisation for $\xi = \frac{\pi}{2}$. The incident polarisation makes an angle ξ with the vector $\boldsymbol{\epsilon}_\sigma$. With a little geometry we conclude

$$\mathbf{E}(R, t) = -r_0 E_0 \frac{e^{i(kR - \omega t)}}{R} [\cos \xi \boldsymbol{\epsilon}'_\sigma + \sin \xi \cos \gamma \boldsymbol{\epsilon}'_\pi] \quad (55)$$

where γ is the angle between the incident and scattered wavevector (this angle is also known, by longstanding diffraction convention, as 2θ). Based on eq. 55, we can make the following observations:

- A plane wave impinging on a quasi-free charge produces a scattered *spherical* wave $\frac{e^{i(kR - \omega t)}}{R}$, with an amplitude that in general depends on the scattering angle γ .
- If the incident wave is σ -polarised, the scattered wave is σ' -polarised, and has amplitude $\frac{r_0}{R} E_0$.
- If the incident wave is π -polarised, the scattered wave is π' -polarised, and has amplitude $\frac{r_0}{R} E_0 \cos \gamma$.
- The intensity of the scattered wave is zero for scattering of π polarisation at 90° .
- The scattered wave has a phase shift of π upon scattering (*minus* sign).

The instantaneous energy flux of the scattered wave is given by the Poynting vector:

$$\mathbf{S} = \mathbf{E} \times \mathbf{H} = \epsilon_0 c |\mathbf{E}|^2 \mathbf{n} \quad (56)$$

The *average* power radiated per unit solid angle in *both* polarisations is therefore

$$\frac{dP}{d\Omega} = R^2 \langle |\mathbf{S}| \rangle = \frac{\epsilon_0 c}{2} R^2 |\mathbf{E}|^2 = \frac{\epsilon_0 c r_0^2}{2} E_0^2 [\cos^2 \xi + \sin^2 \xi \cos^2 \gamma] \quad (57)$$

It can also be shown that the power radiated for an arbitrary final polarisation $\boldsymbol{\epsilon}'$ is

$$\left(\frac{dP}{d\Omega} \right)_{\boldsymbol{\epsilon}'} = \frac{\epsilon_0 c r_0^2}{2} E_0^2 [\boldsymbol{\epsilon} \cdot \boldsymbol{\epsilon}']^2 \quad (58)$$

As appropriate for a scattering process, it is convenient at this point to introduce the *cross section*, defined as the average power radiated per unit solid angle divided by the average incident power per unit area (power flux, Φ), which is

$$\Phi = \frac{\epsilon_0 c}{2} E_0^2 \quad (59)$$

The cross section into both final polarisation channels (i.e., if the scattered beam is measured *without* an analyser) is therefore

$$\frac{d\sigma}{d\Omega} = r_0^2 [\cos^2 \xi + \sin^2 \xi \cos^2 \gamma] \quad (60)$$

whereas for an arbitrary final polarisation ϵ' is

$$\left(\frac{d\sigma}{d\Omega} \right)_{\epsilon'} = r_0^2 [\epsilon \cdot \epsilon']^2 \quad (61)$$

For an *unpolarised* X-ray beam, for which all the angles ξ are equally represented, the cross section becomes

$$\left[\frac{d\sigma}{d\Omega} = r_0^2 \left[\frac{1 + \cos^2 \gamma}{2} \right] \right] \quad (62)$$

NOTE: our discussion on the incident and final polarisations is relevant because different X-ray sources have different characteristics. The beam from a typical lab X-ray machine is unpolarised, and so eq. 62 applies. Synchrotron radiation is naturally polarised in the plane of the electron orbit, so that $\xi = 0$ in eq. 60. Unlike the case of lab machines, synchrotron diffractometers have a *vertical* scattering plane, so that the 90° -cross section does not vanish. Synchrotron beamlines specifically designed for resonant or magnetic scattering often have the ability to change the incident polarisation to the π channel or even to produce circularly-polarised X-rays. In addition, it is possible to *analyse* the scattered polarisation as well.

4.2 Thomson scattering from many quasi-free electrons (extended derivation)

The Thomson formula can be easily extended to the case of multiple scattering centres, provided that the amplitude of the motion of each electron is small with respect to the wavelength. What we aim to achieve is to find an expression for the X-ray scattering amplitude and cross section of a **multi-electron atom**. In this case, the radiation emitted by each electron at position \mathbf{x}_i will be characterised by an approximately *time-independent* phase factor $e^{i\mathbf{k}\cdot\mathbf{x}_i}$, accounting for the fact that the charge is not at the origin, \mathbf{k} being the wavevector of the incident radiation. Also, the radius R in eq. 55 needs to be replaced with individual radii R_i . Here, we can employ the very useful trick of approximating

$$R_i \approx R - \mathbf{n} \cdot \mathbf{x}_i \quad (63)$$

This is equivalent to considering diffraction in the “far field” limit (*Fraunhofer diffraction*). Eq. 63 can be obtained by writing the vector relation;

$$R_i = |\mathbf{R}_i| = |\mathbf{R} - \mathbf{x}_i| = |R\mathbf{n} - \mathbf{x}_i| \quad (64)$$

and expanding it to the quadratic term in x_i/R ; is certainly valid in the case we are interested in, where the distances between scattering centres are comparable to atomic sizes whereas R (the experimental scattering path) is macroscopic. By summing the amplitudes of individual scattering centres we obtain

$$\begin{aligned} \mathbf{E}(R, t) &= -r_0 E_0 \frac{e^{i(kR - \omega t)}}{R} [\boldsymbol{\epsilon} \cdot \boldsymbol{\epsilon}'] \sum_i e^{i(\mathbf{k}_i - \mathbf{k}_f) \cdot \mathbf{x}_i} \\ &= -r_0 E_0 \frac{e^{i(kR - \omega t)}}{R} [\boldsymbol{\epsilon} \cdot \boldsymbol{\epsilon}'] \sum_i e^{-i\mathbf{q} \cdot \mathbf{x}_i} \end{aligned} \quad (65)$$

where \mathbf{k}_i and \mathbf{k}_f are the incident and scattered wavevectors and $\mathbf{q} = \mathbf{k}_f - \mathbf{k}_i$.⁵

⁵Throughout this part of the course, we will employ the convention that \mathbf{q} is the *change of wavevector of the particle or photon*, so $\mathbf{q} = \mathbf{k}_f - \mathbf{k}_i$. the convention $\mathbf{q} = \mathbf{k}_i - \mathbf{k}_f$ identifies \mathbf{q} with the wavevector transferred to the crystal, and is widely employed particularly in the context of inelastic scattering

5 Appendix II: X-ray absorption and resonant scattering

5.1 X-ray absorption: the photo-electric effect and X-ray fluorescence

When the beam of X-rays impinges at normal incidence on a slab of material of thickness L , it suffers both scattering and absorption, and is therefore **attenuated** according to the familiar equation:

$$I = I_0 e^{-\mu L} \quad (66)$$

where μ is the **linear attenuation coefficient**, which is related to the **total cross section** σ_{tot} (scattering plus absorption) by the equation:

$$\mu = \sigma_{tot} N_a \quad (67)$$

where N_a is the number of scattering/absorption centres (here atoms) per unit volume. Fig. 12 shows a comparison of the cross sections of different processes leading to X-ray attenuation in materials.

At X-ray energies used in typical experiments (5–50 KeV), the photo-electric absorption cross section is by far the largest contributor to X-ray attenuation.

Key facts about the photoelectric absorption of X-rays

- In the photo-electric absorption process, a photon is completely absorbed and the energy is transferred to a **core electron** (i.e., an electron in the inner atomic shell), which is excited into unoccupied bound states above the Fermi energy or in the continuum.
- The key parameter controlling this effect is, naturally, the **electron binding energy**, which is typical of each shell and atom or ion. **No photoelectric absorption can take place if the photon energy is lower than the binding energy of the electron.** This is in complete analogy with the more familiar photo-electric effect in semiconductors. As the photon energy is increased through a binding energy “threshold”, **additional absorption can take place**, so absorption increases abruptly. This is known as an **absorption edge** (see fig. 13).
- Binding energy are classified based on the **quantum numbers of the core electron**. A **letter indicates the principal quantum number of the core electron**, so “K” for n=1, “L” for n=2, “M” for n=3 “N” for n=4 and so on. This is followed by a **roman subscript** indicating energy sub-levels. Therefore, the *K* edge indicates a transition from the 1s core state. *L_I*, *L_{II}* and *L_{III}* indicate transitions from the 2s, 2p_{1/2} and 2p_{3/2}, respectively (2p_{1/2} and 2p_{3/2} having distinct values of the *total* angular momentum *J*).

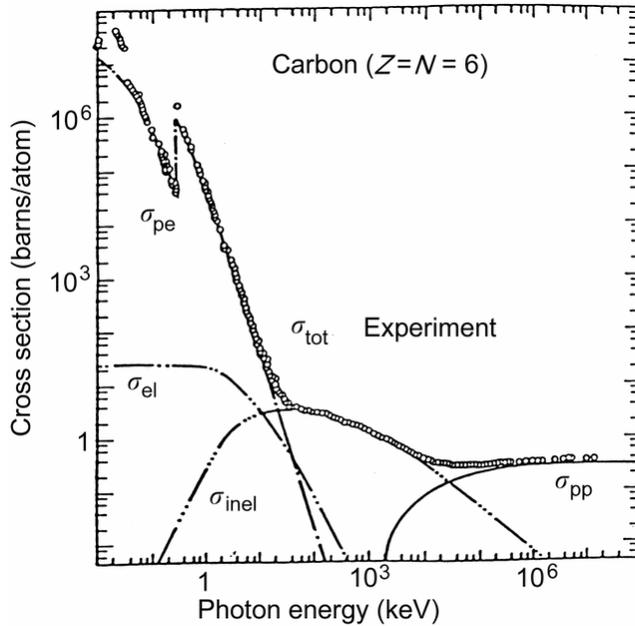


Figure 12: Contributions to the X-ray scattering and absorption cross section for the element carbon (C), from the International Tables for Crystallography, vol. C, p 213. In this figure, σ_{el} is the Thomson cross section, σ_{inel} is the Compton inelastic cross section and σ_{pp} is the pair-production cross section, whereby a high-energy photon produces an electron-positron pair. Note the K absorption edge in the photo-electric cross section at 284.2 eV

- An X-ray photo-electric absorption event is followed by a chain of **X-ray emission (or fluorescence) events** whereby the excited atom gradually relaxes to the ground state. The processes of absorption and subsequent re-emission are shown schematically in fig. 14. Strong emission lines are those that follow the **dipole selection rules**, i.e., $\Delta l = \pm 1$ and $\Delta j = 0, \pm 1$. For example, for transition metals, there are 3 strong emission lines: $K_{\alpha 1}$ and $K_{\alpha 2}$ for transitions from $2p_{1/2}$ and $2p_{3/2}$ to $1s$ and K_{β} for transitions from $3p$ to $1s$. X-ray emission is extensively employed to produce monochromatic X-ray radiation (see below).

- **Far from absorption edges, photo-electric absorption decreases as a function of photon energy**, following the very approximate law:

$$\sigma_{ph} \propto \frac{Z^n}{(\hbar\omega)^3} \quad (68)$$

where Z is the atomic number and the exponent is a number between 4 and 5.

- A list of characteristic absorption and emission X-ray energies can be found in the International Tables for Crystallography, vol. C, starting from p 206.

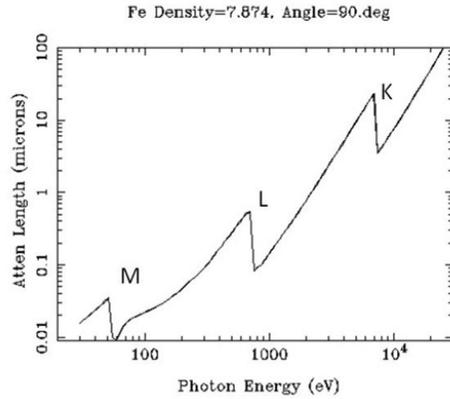


Figure 13: Attenuation length ($1/\mu$) in microns for elemental iron (Fe), in the energy interval between 30 eV and 25 KeV. The figure was generated using the attenuation calculator in http://henke.lbl.gov/optical_constants/atten2.html. Note the three absorption edges: K at 7.112 KeV, L (actually three edges at 845 eV, 720 eV and 707 eV) and M (edges at 90 eV and 50 eV).

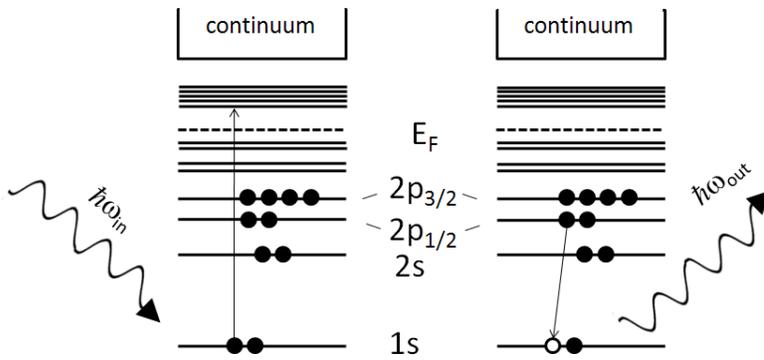


Figure 14: Schematic representation of the absorption and subsequent emission for a K edge event. **Left:** a photon with energy above the K edge is absorbed and an $1s$ electron is ejected above the Fermi energy or into the continuum. **Right:** an electron in the $2p_{1/2}$ shell makes a transition to fill the $1s$ core hole, resulting in the emission of a photon with the characteristic energy $K_{\alpha 2}$.

5.2 X-ray scattering beyond the free-electron approximation

Up to now, we have left the issue of “free” electrons somewhat ambiguous. Truly “free” electrons (e.g., conduction electrons in a metal) hardly contribute to the scattering of X-rays, because their probability distribution extends a long way throughout the crystal, and the form factor decays very rapidly away from forward scattering. Conversely, the largest contribution to X-ray scattering from atoms is given by “core” electrons, which are close to the nucleus and have slowly decaying form factors — but these electrons are certainly

not free! Indeed, there are large departures from the Thomson scattering formula near *atomic resonances*, where the energy of the photon is just sufficient to eject an electron from a core state into the continuum. Away from resonances, the Thomson formula can be corrected to a very good approximation by replacing the form factor by the *complex* quantity

$$f(\mathbf{q}) = \mathbf{f}_{\text{Thom}}(\mathbf{q}) + \mathbf{f}'(\hbar\omega) + i\mathbf{f}''(\hbar\omega) \quad (69)$$

where the so-called *anomalous terms*, f' and f'' , away from atomic resonances do not depend on q and are weak functions of the photon energy.

It can be shown, as a consequence of the so-called optical theorem, that *the imaginary part of the scattering factor is proportional to the linear absorption coefficient due to the photoelectric effect.*

$$f''(\hbar\omega) = \frac{\omega}{4\pi r_0 c N_a} \mu \quad (70)$$

where N_a is the number of atoms per unit volume, and the other symbols have the usual meaning. The quantity μ is the *linear absorption coefficient*, defined in eq. 66.

5.3 Resonant scattering and anomalous corrections to the form factor

Here, we repeat essentially the same derivation that led to the calculation of the Thomson cross section, but replacing the “free-electron” acceleration in eq. 51 with an expression appropriate to a **damped oscillator**.

$$m [\ddot{x} + \gamma\dot{x} + \omega_i^2 x] = (-e)\mathbf{E}(t) \quad (71)$$

$$\mathbf{a}(t) = \frac{(-e)}{m} \epsilon E_0 e^{-i\omega t} \frac{\omega^2}{\omega^2 - \omega_i^2 + i\omega\gamma_i} \quad (72)$$

where ω_i is the resonance frequency of each electron. If we use 72 instead of 51 in the previous derivations, we obtain in general a **complex scattering amplitude**. It is easy to evaluate this in the case $\omega \gg \omega_i$, i.e., for example, for scattering of high-energy X-rays ($> 20\text{KeV}$) from first-period transition-metal ions. In this case

$$f(\mathbf{q}) = \sum_i [f(\mathbf{q})_{Thom}]_i \left(1 - \frac{\omega_i^2}{\omega^2} + i \frac{\gamma_i}{\omega} \right) \quad (73)$$

5.4 Compton scattering

One important issue related to the bound nature of electrons is the fact that no elastic scattering is possible for a truly free electron, but the Compton formula applies instead:

$$\frac{k'}{k} = \frac{1}{1 + \frac{\hbar\omega}{mc^2}(1 - \cos \gamma)} \quad (74)$$

At low photon energy, the photon momentum is transferred to the atom as a whole (much heavier) or to the entire crystal, and the scattering is elastic to a very good approximation. As the energy increases nearing the rest mass energy of the electron ($mc^2 = 511 \text{ KeV}$), the Compton scattering cross section increases.

6 Appendix III: Scattering of particle beams

A plane wave of X-rays impinging on a quasi-free distribution of charges produces a *spherical wave*, the amplitude of which is proportional to the incident amplitude E_0 . The coefficient multiplying the spherical wave is

$$r_0 f(\mathbf{q}) [\cos \xi \epsilon'_\sigma + \sin \xi \cos \gamma \epsilon'_\pi] \quad (75)$$

can be complex. In the general case, for a given wavelength, this coefficient depends on both angular variables of the scattered beam, but for spherically-symmetric atoms it depends only on the scattering angle $\gamma = 2\theta$. Importantly, **the cross section is equal to the square modulus of the spherical wave coefficient**. As we shall see shortly, the same principles applies to the scattering of particle beams, provided that the particle beam is described quantum-mechanically, so that the wave-like nature of the particles is apparent. Indeed, quantum mechanics is essential to obtain exact results, although the essential features are often classical or semi-classical in origin. In addition, it is often convenient to discuss the *stationary* problem rather than the

time-dependent problem of a single particle starting off far away from the scatterer. The stationary problem is equivalent to considering a steady streams of particle coming from infinity, which is partly converted into a current of scattered particles in the form of a spherical wave. Finally, provided that we operate in the non-relativistic limit, we can consider the 2-particle scattering problem to be equivalent to that of scattering from a static potential $V(\mathbf{r})$, provided that the mass of the particle is replaced by the effective mass

$$m_{eff} = \frac{m_1 m_2}{m_1 + m_2} \quad (76)$$

Hereafter, we will simply refer at the effective mass as m .

6.1 Wavefunction equation for the static scattering problem

We are looking for the solutions $\psi(\mathbf{r})$ for the following eigenfunction equation

$$\left(-\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r}) \right) \psi(\mathbf{r}) = E\psi(\mathbf{r}) \quad (77)$$

For the scattering problem, we are not interested in the bound states, so we will focus on the continuous spectrum with positive eigenvalues. We also expect that, at long distances from the origin of the potential, the solution will approximate a plane wave (at least on one side), with energy $E = \frac{\hbar^2 k^2}{2m}$. By defining the new potential $U(\mathbf{r}) = \frac{2m}{\hbar^2} V(\mathbf{r})$ we arrive at the equation:

$$(\nabla^2 + k^2) \psi(\mathbf{r}) = U(\mathbf{r})\psi(\mathbf{r}) \quad (78)$$

The solution of eq: 78 with the right side set to zero is clearly a plane wave

$$\varphi(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} \quad (79)$$

Eq. 79 represent the free-particle limit of the wavefunction, i.e., the **incident** wave. Therefore, we will later employ 79 with $\mathbf{k} = \mathbf{k}_i$.

An important step towards the solution of the general eq. 78 is to solve the point-source equation:

$$(\nabla^2 + k^2) \psi(\mathbf{r}) = \delta(\mathbf{r}) \quad (80)$$

The solutions of equations of the type 80 are known as **Green's functions**. It can be shown rather straightforwardly that the following two functions are solutions of eq: 80

$$\begin{aligned} G^+(\mathbf{r}) &= -\frac{1}{4\pi} \frac{e^{ik|\mathbf{r}|}}{|\mathbf{r}|} \\ G^-(\mathbf{r}) &= -\frac{1}{4\pi} \frac{e^{-ik|\mathbf{r}|}}{|\mathbf{r}|} \end{aligned} \quad (81)$$

To verify that 81 are indeed solutions of eq: 80 it is sufficient to use the relation

$$\nabla^2(ab) = a\nabla^2b + b\nabla^2a + 2\nabla a \cdot \nabla b \quad (82)$$

The two solutions in eq. 81 are expanding and contracting spherical waves, respectively. By selecting the former, we can rewrite eq. 78 in an *integral* form (we only write the solution with the expanding Green function):

$$\psi(\mathbf{r}) = \varphi(\mathbf{r}) + \int d\mathbf{r}' G^+(\mathbf{r} - \mathbf{r}') U(\mathbf{r}') \psi(\mathbf{r}') \quad (83)$$

Since we are primarily interested in solutions far away from the region where the potential is non-zero, we can employ the so-called far-field approximation. The key observation here is that **\mathbf{r}' is small, because the potential is non-zero only near the scatterer**. Also, importantly, $|\mathbf{k}_i| = |\mathbf{k}_f| = k$, since we are dealing with **elastic scattering**. The correspondence between eq. 63 and eq. 84 is clear if we write $\mathbf{k}_f = k\mathbf{n}$

$$k|\mathbf{r} - \mathbf{r}'| \approx kr - \mathbf{k}_f \cdot \mathbf{r}' \quad (84)$$

after some simple algebra we obtain (again, at long distances from the scattering centre):

$$\psi(\mathbf{r}) = e^{i\mathbf{k} \cdot \mathbf{r}} + \left[-\frac{1}{4\pi} \int d\mathbf{r}' e^{-i\mathbf{k}_f \cdot \mathbf{r}'} U(\mathbf{r}') \psi(\mathbf{r}') \right] \frac{e^{ikr}}{r} \quad (85)$$

Eq. 85 has a very pleasing form: it is very similar to eq. 55, and we could surmise that the squared modulus of the expression in square brackets (the “scattering amplitude”) is the cross section (this is proven in most standard quantum mechanics textbooks by introducing the probability current density).

Here, we will take it for granted without further proof. Unfortunately, the scattering amplitude in eq. 85 depends on the wavefunction itself. We can make progress by assuming that potential is in some sense “small”, so that the spherical wave is a small component of the overall wavefunction. We can therefore attempt to expand the integral term in series:

$$-\frac{1}{4\pi} \int d\mathbf{r}' e^{-i\mathbf{k}_f \cdot \mathbf{r}'} U(\mathbf{r}') \psi(\mathbf{r}') \approx -\frac{1}{4\pi} \int d\mathbf{r}' e^{-i\mathbf{k}_f \cdot \mathbf{r}'} U(\mathbf{r}') \varphi(\mathbf{r}') + \left(\frac{1}{4\pi}\right)^2 \int d\mathbf{r} d\mathbf{r}' \varphi(\mathbf{r}') \frac{e^{ik|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|} U(\mathbf{r}) U(\mathbf{r}') \quad (86)$$

The series in eq. 86 is known as the **Born series**; taking the first term alone is known as the **first Born approximation**. It is easy to obtain the expression for the scattering cross section in the first Born approximation; remembering that $\varphi(\mathbf{r}')$ is the plane wave $\exp(i\mathbf{k}_i \cdot \mathbf{r}')$, we obtain:

$$\left(\frac{d\sigma}{d\Omega}\right)_{Born} = \left| \frac{1}{4\pi} \int d\mathbf{r} e^{-i\mathbf{q} \cdot \mathbf{r}} U(\mathbf{r}) \right|^2 \quad (87)$$

where $\mathbf{q} = \mathbf{k}_f - \mathbf{k}_i$. In other words, **in the first Born approximation, the cross section is proportional to the Fourier transform of the potential energy.**

6.2 Elastic scattering of electrons in the 1st Born approximation

As a first example of scattering of a particle beam, we will consider the elastic scattering of electrons from the Coulomb potential produced by the nucleus and by the electrons bound in an atom. For simplicity, we will consider electrons as spinless particles. Based on eq. 87, we need to calculate the *potential*, and for this is useful to recall that

$$\nabla^2 e^{-i\mathbf{q} \cdot \mathbf{r}} = -q^2 e^{-i\mathbf{q} \cdot \mathbf{r}} \quad (88)$$

Recalling that $U(\mathbf{r}) = \frac{2m}{\hbar^2} V(\mathbf{r})$, we can rewrite the integral in eq. 87 as

$$\frac{1}{4\pi} \int d\mathbf{r} e^{-i\mathbf{q} \cdot \mathbf{r}} U(\mathbf{r}) = -\frac{m}{2\pi q^2 \hbar^2} \int d\mathbf{r} V(\mathbf{r}) \nabla^2 e^{-i\mathbf{q} \cdot \mathbf{r}} = -\frac{m}{2\pi q^2 \hbar^2} \int d\mathbf{r} e^{-i\mathbf{q} \cdot \mathbf{r}} \nabla^2 V(\mathbf{r}) \quad (89)$$

where the rightmost expression is obtained by integrating twice by part and assuming that both the potential and its first derivative are zero at infinite distance from the origin. We can now use Poisson's equation and the expression for the charge density of an atom of atomic number Z :

$$\nabla^2\Phi = \frac{\rho}{\epsilon_0} \quad (90)$$

$$V = (-e)\Phi \quad (91)$$

$$\rho(\mathbf{r}) = Ze\delta(\mathbf{r}) + (-e)\rho_{el}(\mathbf{r}) \quad (92)$$

where Φ is here the electrostatic potential and $\rho_{el}(\mathbf{r})$ is the same electron density we have employed for X-rays. To find the expression for the elastic scattering cross section:

$$\frac{d\sigma}{d\Omega} = \left(\frac{e^2}{\epsilon_0} \frac{m}{2\pi q^2 \hbar^2} \right)^2 \left| Z - \int d\mathbf{r} e^{-i\mathbf{q}\cdot\mathbf{r}} \rho_{el}(\mathbf{r}) \right|^2 \quad (93)$$

We can see the immediate analogy with the scattering cross section for X-rays. The integral term is exactly the same as the X-ray form factor, and is referred to as f_X in the text. The term in brackets takes the place of the classical electron radius, and is numerically

$$\frac{e^2}{\epsilon_0} \frac{m}{2\pi \hbar^2} = 3.38 \times 10^{-10} \text{ m } \text{\AA}^{-2} \quad (94)$$

whereas, for comparison, the classical electron radius is $r_0 = \frac{e^2}{4\pi\epsilon_0 mc^2} = 2.82 \times 10^{-15} \text{ m}$. We can see therefore that for all typical values of q ($1-10 \text{ \AA}^{-1}$) employed for electron diffraction experiments, **the scattering amplitudes for electrons is much larger than for X-rays.**

The elastic scattering amplitude for electrons f^B is often expressed in wavelength/angle units as in eq. 95. One can find tabulated values for neutral and ionised atoms in the International Tables for Crystallography, volume C, p 263 (λ is the electron wavelength and both λ and f^B in eq. 95 are expressed in \AA):.

$$f^B(\sin \theta/\lambda) = 0.023934\lambda^2[Z - f_X(\sin \theta/\lambda)]/\sin^2 \theta \quad (95)$$

6.3 Nuclear scattering of “slow” neutrons

The kinetic energies of neutrons employed in typical scattering experiments is much lower than the energies of nuclear reactions, which are typically in the MeV range. In fact, it is established from nuclear physics that the neutron-nuclear interaction can be approximated with a square potential well of depth $V_0 \approx 50$ MeV and range $d = 1.3A^{\frac{1}{3}} \times 10^{-15}$ m, where A is the mass number of the nucleus. It is therefore implausible that the first Born approximation could be applied as such to the scattering of slow neutrons. In fact, a more detailed calculation shows that the first Born approximation is applicable only to neutrons with $E > 25$ MeV.

Nevertheless, Fermi proposed in 1936 that slow neutron scattering could still be satisfactorily treated in the first Born approximation. The general idea here is that the wavelength of the neutrons is so large that one can replace the real potential with a “pseudopotential” (known as the Fermi pseudopotential), which yields the same first Born scattering amplitude and for which the approximation definitely applies. For this, one observes that, over the range of the true potential, the phase of the neutron is essentially constant in eq. 86, and the scattering amplitude can be written as:

$$f = -\frac{m}{2\pi\hbar^2} \int d\mathbf{r} V_0(\mathbf{r}) = -\frac{m}{2\pi\hbar^2} V_0 d^3 \quad (96)$$

We could therefore think of decreasing the depth of the potential well into the thermal ranges by increasing the range of the potential by a factor of, ~ 1000 , while maintaining the same value of the scattering amplitude and, crucially, still keeping the range much smaller than the neutron wavelength — a set of conditions for which the first Born approximation definitely applies. This conjecture led to the development of the **Fermi pseudopotential**, which has the form:

$$V_F(\mathbf{r}) = \frac{2\pi\hbar^2}{m} b_F \delta(\mathbf{r}) \quad (97)$$

where b_F is the scattering length, known as the **Fermi length**. In practice, the Fermi pseudopotential is completely satisfactory to describe nuclear neutron scattering for diffraction experiments, and only need corrections (analogous to the X-ray anomalous corrections) only for energies near neutron-nuclear resonances.

Here are some important facts about neutron scattering lengths and cross

sections:

- Neutron scattering amplitudes **do not depend on q** , i.e., they carry no form factor. For diffraction experiment this is crucially important, because it means that the intensity of the diffraction features **does not decay at high angles as fast as in the case of X-rays** (we will see in the next lecture that thermal motion causes high- q Bragg intensity decay even in the case of neutrons). They are also largely independent on the neutron energy, at least in the regime of interest for neutron diffraction.
- Fermi lengths for typical nuclei are of the order of a few fm (10^{-15} m), which means that they are comparable to the classical electron radius. However, atoms have a single nucleus and many electrons, so X-ray scattering cross sections in the *forward* direction are typically much larger than neutron cross sections. Neutron cross sections are traditionally measured in **barns** (10^{-28} m²).
- **Neutron absorption is also much lower than for X-rays**, which, together with the previous observation, means that attenuation (absorption + scattering) lengths are of the order of **cm for neutrons** and of **μm for X-rays**. This has a profound effect on the design of diffraction experiments exploiting the two types of radiation.
- Fermi lengths vary across the periodic table without any particular regularity. They can be positive or negative depending on the sign of the nuclear potential. They depend on the *isotope*, often very strongly, and also on the direction of the *nuclear spin* with respect to the *neutron spin*. This has two main consequences, one “positive” and one “negative”: the “negative” consequence is the presence of “incoherent” scattering, due to the random mixture of different isotope and spin orientations, which contributes to the experimental background. The “positive” consequence is the possibility to exploit different isotopes of the same element to gain additional contrast.

6.4 The Fermi golden rule and its connection with the first Born approximation

In the previous sections, we have considered the Born series for a spinless particle beam, so that there was no internal degree of freedom to consider. In addition, the internal state of the scatterer (in our case a time-independent potential) was also unchanged during the collision. Consequently, the energy

of the scattered particle remains the same after the collision. It is useful to extend our description of the scattering to cases in which there are internal degrees of freedom which may be altered in the collision. The Fermi golden rule (the development of which is mainly due to Dirac) is widely employed to calculate the transition probability of an eigenstate (in our case, a plane wave), into a continuum of “final” states due to a perturbation. As in the case of the first Born approximation, it is the first term of a perturbative expansion, and is applicable within very similar conditions to the first Born approximation, namely that the final states do not significantly deplete the original eigenstate. Here, we only quote the general result for the scattering cross section between states with wavevectors \mathbf{k}_i and \mathbf{k}_f and an internal transition between states λ_i and λ_f with energies E_i and E_f , respectively.

$$\frac{d\sigma}{d\Omega dE_f} = \frac{k_f}{k_i} \left| (m/2\pi\hbar^2) \langle \mathbf{k}_f, \lambda_f | \hat{V} | \mathbf{k}_i, \lambda_i \rangle \right|^2 \delta(\hbar\omega + E_i - E_f) \quad (98)$$

where we have employed the familiar $\langle bra | - | ket \rangle$ notation, $V(\mathbf{r})$ is the “perturbing” potential and $\hbar\omega = \hbar^2(k_f^2 - k_i^2)/2m$, ensuring energy conservation.

It is a simple exercise to show that, for elastic scattering in the absence of internal degrees of freedom, the “golden rule” cross section in eq. 98 is exactly the same as the first Born approximation result in eq. 87.

6.5 Magnetic scattering of neutrons

We will exemplify the application of the Fermi golden rule by outlining the calculation of the scattering of slow neutron onto a magnetic atom. We will assume that no energy is exchanged in the process. Here, the interaction potential is naturally the dipole interaction between the neutron spin \mathbf{S} and the magnetic field $\mathbf{B}(\mathbf{r})$ generated by the electrons (we will assume zero external magnetic field for simplicity). When dealing with **elastic** magnetic scattering, the initial and final states of the **atoms** are assumed to be the *same*, implying that conservation of linear and angular momenta is ensured by the crystal as a whole. Therefore, the **operator** quantities (here indicated explicitly with a “ $\hat{}$ ”) are **only those acting on the neutron coordinates**.

$$V(\mathbf{r}) = -\gamma_N \mu_N \hat{\mathbf{S}} \cdot \mathbf{B}(\mathbf{r}) \text{ [Joules]} \quad (99)$$

where $\hat{\mathbf{S}}$ is the **neutron spin operator**, γ_N is the neutron gyromagnetic ratio (-1.9130418) and μ_N is the nuclear magneton ($\frac{e\hbar}{2m_p} = 5.05078324(13) \times 10^{-27}$

JT^{-1}). The magnetic field of a single electron moving with velocity \mathbf{v} is

$$\mathbf{B}(\mathbf{r}) = \nabla \times \left[\frac{\mu_0}{4\pi} \frac{\boldsymbol{\mu}_e \times \hat{\mathbf{r}}}{r^3} \right] + \frac{-e\mu_0}{4\pi} \frac{\hat{\mathbf{v}} \times \hat{\mathbf{r}}}{r^3} \quad (100)$$

Where $\boldsymbol{\mu}_e$ is the magnetic moment of the electron, given by (μ_B is the Bohr magneton, \mathbf{s} is the spin of the electron)

$$\boldsymbol{\mu}_e = -2\mu_B \mathbf{s} \quad (101)$$

The two terms in eq. 100 represent the *spin* and *orbital* part of magnetic moment. The “hatted” vector quantities in eq. 100 are meant as operators (so, for instance,

$$\hat{\mathbf{v}} = -i\hbar\nabla \quad (102)$$

The derivation of the cross section in in eq. 98, even in the general case of inelastic scattering and is quite straightforward, and is reported, for example, in Stephen W. Lovesey, “Theory of neutron scattering from condensed matter”, Oxford Science Publications, Clarendon Press, Oxford (1984) — Volume 2. Here, for simplicity, we only report the final result for *elastic scattering of unpolarised neutrons, i.e., we are averaging on the initial and final neutron spins*:

$$\frac{d\sigma}{d\Omega} = \gamma_N^2 r_0^2 \mathbf{Q}_\perp^\dagger \cdot \mathbf{Q}_\perp \quad (103)$$

where

- r_0 is the **classical electron radius**. This means that *the scattering amplitude for a neutron by the magnetic field of a single electron is comparable to the Thomson scattering amplitude of X-rays.*
- \mathbf{Q} is given by the formula (*spin only scattering*)

$$\mathbf{Q} = \sum_i e^{i\mathbf{q}\cdot\mathbf{r}_i} \mathbf{s}_i \quad (104)$$

and, in the general case, is **the Fourier transform of the magnetisation density (spin + orbital) for unpaired electrons**. In simple cases,

$$\mathbf{Q} = f_m(q) \boldsymbol{\mu} \quad (105)$$

μ is the magnetic moment of the atom and $f_m(q)$ — the *magnetic form factor* — takes the place of the X-ray form factor in the analogous expression for Thomson scattering.

- \mathbf{Q}_\perp is the projection of \mathbf{Q} *perpendicular* to the scattering vector \mathbf{q}

$$\mathbf{Q}_\perp = \frac{1}{q^2} \mathbf{q} \times \mathbf{Q} \times \mathbf{q} \quad (106)$$

in practical terms, this means that **neutrons are only sensitive to the components of the magnetic moments *perpendicular* to the scattering vector.**

- If we take into account the direction of the neutron spins, the cross section will contain terms of the kind $\hat{\mathbf{S}} \cdot \mathbf{Q}_\perp$ and depends on the initial and final states of the neutron. **For pure magnetic elastic scattering, the cross section is non-zero only for *opposite* incident and scattered neutron spins — we say that it is “spin flip” only.**

7 Appendix IV: Useful constants

$$\epsilon_0 = 8.854187 \times 10^{-12} \text{ F m}^{-1} \text{ — vacuum permittivity}$$

$$\mu_0 = 4\pi \times 10^{-7} \text{ N A}^{-2} \text{ — vacuum permeability (exact)}$$

$$c = 2.99792458 \times 10^8 \text{ m s}^{-1} \text{ — speed of light in vacuum}$$

$$e = 1.602176487(40) \times 10^{-19} \text{ C — unit charge}$$

$$m_e = 9.10938215(45) \times 10^{-31} \text{ Kg — electron rest mass}$$

$$m_p = 1.672621637(83) \times 10^{-27} \text{ Kg — proton rest mass}$$

$$m_n = 1.674927729(28) \times 10^{-27} \text{ Kg — neutron rest mass}$$

$$r_0 = \frac{e^2}{4\pi\epsilon_0 mc^2} = 2.82 \times 10^{-15} \text{ m — classical electron radius}$$

$$\mu_N = \frac{e\hbar}{2m_p} = 5.05078324(13) \times 10^{-27} \text{ JT}^{-1} \text{ — nuclear magneton}$$

$$\gamma_N = -1.9130418 \text{ — neutron gyromagnetic ratio}$$

$$\mu_B = \frac{e\hbar}{2m_e} = 9.27400915(23) \times 10^{-24} \text{ JT}^{-1} \text{ — Bohr magneton}$$