

Frontiers of Experimental Condensed Matter Physics

Lecturer:

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■ Overview

■ Part A Scattering

- Probes and phenomenology:
 - Scattering of electrons, photons and neutrons. Perfect and distorted lattices.

■ Part B Excitations

- Electronic properties of solids:
 - Ultra-violet and x-ray photoemission. Band-structure determination, core-level shifts.
- Surfaces and interfaces:
 - Surface phenomenology, the effect of a surface on a bulk probe.

Overview, cont..

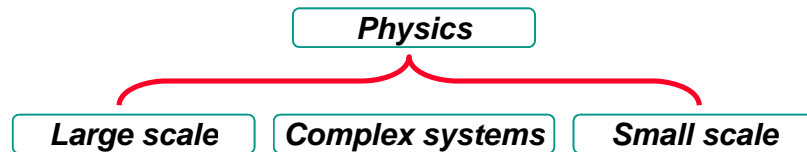
■ Part C Atomic time- and length-scales

- Microscopy:
 - Structure and spectroscopy. Electron microscopy; Scanned probe techniques. Atomic force microscopy and probes of local forces. Atom manipulation.
- Dynamics:
 - Observation of electronic and atomic motion on sub-picosecond time-scales. Pump probe laser methods. Scattering approach for atomic motion - spin-echo technique.

■ Books and sources

- "Diffraction Physics", JM Cowley
- "Structure and Dynamics", MT Dove
- "Modern Techniques in Surface Science", DP Woodruff and TA Delchar
- "Scanning Probe Microscopy and Spectroscopy", R Wiesendanger
- plus recent research papers

Experiments and Condensed Matter Physics



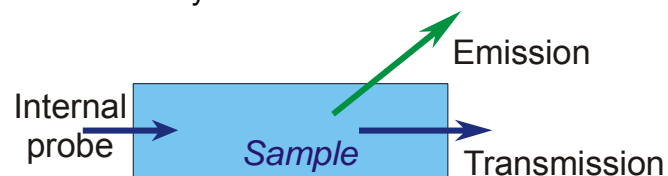
- Complexity does not necessarily imply complication: e.g.: emergence of order in complex systems.

Overall aim:

- Appreciate the experimental approach to characterising and understanding complex systems.

Probes of condensed systems;

- Internal probes:
 - Important, especially for device characterisation.
 - Usually limited to electrons

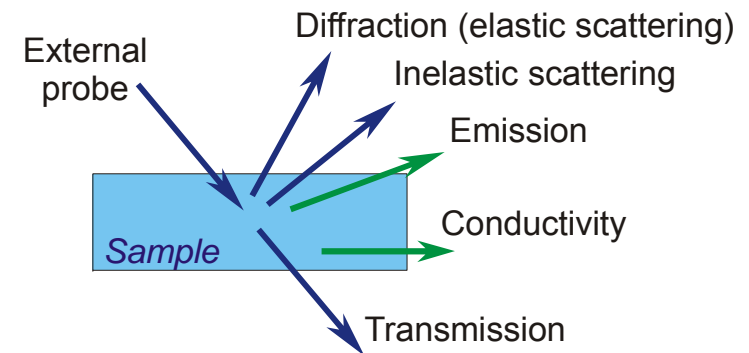


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Internal and external probes

External probes

- Photons, electrons, neutrons etc....



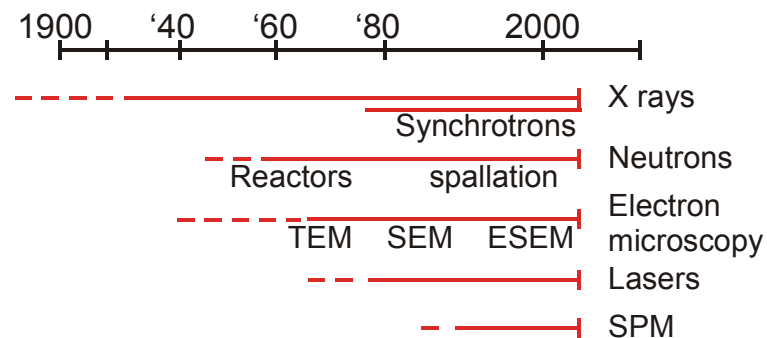
- Huge variety of phenomena
- In the present course we will:
 - Concentrate on external probes
 - Focus on the generality of behaviour.

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Science and technology

- Experiment requires technology. Key technologies include:
 - Liquefaction of gases ~1907: low temperatures.
 - Electronic methods for instrumentation, control and, more recently, experimental design.
 - Vacuum technology: controlled environment for samples (e.g. MBE growth) and measurement.
 - New probes: Lasers, synchrotrons, etc.

Time-line

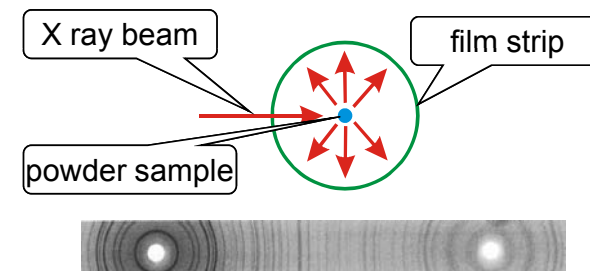


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Instrumental technology

Early diffractometers

- Simple devices, with simple detectors (eg. film for X rays). Debye-Scherrer camera for powder diffraction.



(Photographs, Dove p121)

- Similar devices still used in routine lab-measurements.

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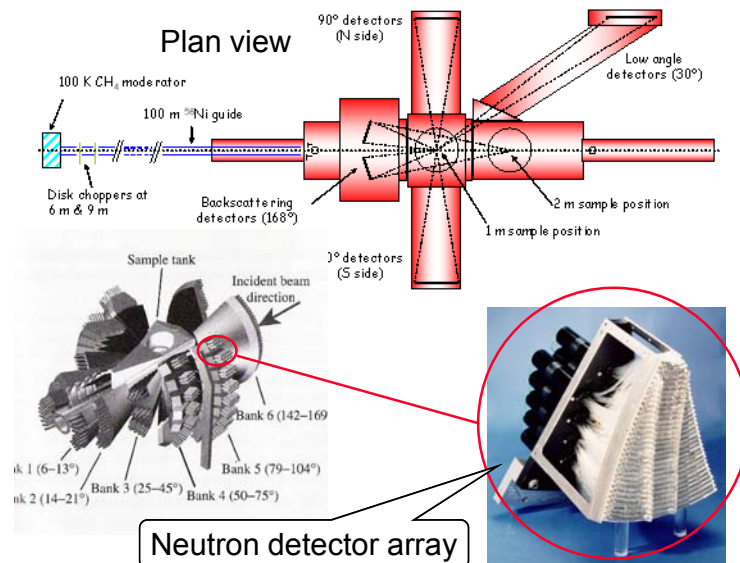
Source technology

Modern diffractometers

- Complex and specialised functionality
- Typically with multiple, electronic detection.
- Usually found at central facilities

Example:

- Powder neutron diffractometer at Rutherford Appleton Lab.



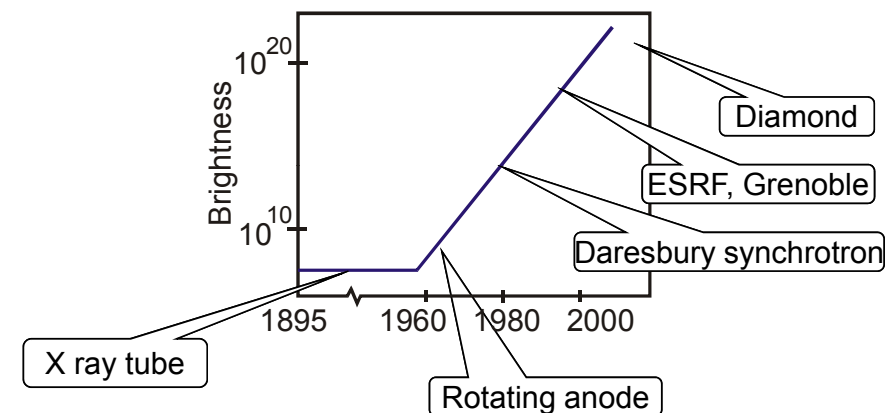
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Early instruments

- small, low power sources. eg. conventional X-ray tube.
- Fixed wavelength, not well monochromated

High power sources

- For x rays, a synchrotron offer greater brightness, together with tuneable wavelength and improved monochromaticity
- Brightness in photons/(s mm² mrad²) into 0.1% bandwidth. (Source Duke, Synchrotron radiation).



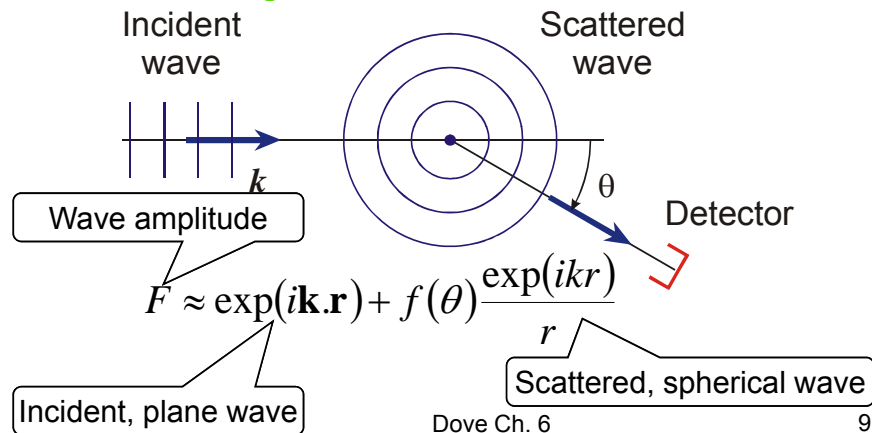
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Part A: Scattering

■ Probes and phenomenology

- Scattering potentials:
 - X rays scatter predominantly from electrons.
 - Electrons from charged particles (Coulomb interaction)
 - Neutrons scatter mainly from the nucleus
- In most cases the scattering can be approximated by an assembly of *point scatterers*. A continuous distribution of scattering density can be constructed by integration over volume elements.

■ Scattering and Diffraction

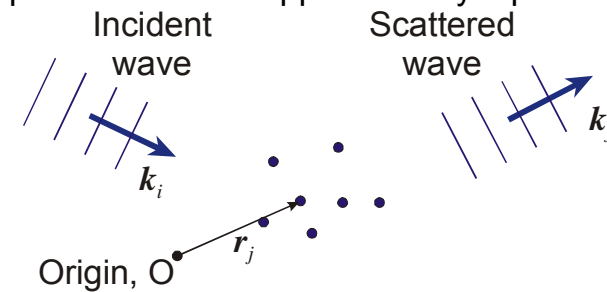


Dove Ch. 6

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Far field

- We assume the scattering is weak (no multiple scattering).
- At the detector, far from the scatterer, the spherical wave is approximately a plane wave.



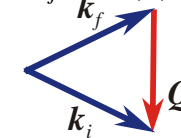
- Taking the phase of incident and scattered wave to be zero at the origin,

Incident wave: $\exp(i\mathbf{k}_i \cdot \mathbf{r}_j)$ (incoming)

Scattered wave: $f_j \exp(-i\mathbf{k}_f \cdot \mathbf{r}_j)$ (outgoing)

- Adding the incoming and outgoing phases, the wave scattered from scatterer, j , is

$$f_j \exp(i(\mathbf{k}_i - \mathbf{k}_f) \cdot \mathbf{r}_j) = f_j \exp(i\mathbf{Q} \cdot \mathbf{r}_j)$$



Scattering vector, \mathbf{Q}

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Assembly of scatterers

- For a single scatterer: $F \sim f_j \exp(i\mathbf{Q}\cdot\mathbf{r}_j)$
- For an assembly: $F \sim \sum_j f_j \exp(i\mathbf{Q}\cdot\mathbf{r}_j)$
- Identical scatterers (all f_j the same) $F \sim f \sum_j \exp(i\mathbf{Q}\cdot\mathbf{r}_j)$

■ Example: Scattering from a lattice

- In general the phase factors, $\mathbf{Q}\cdot\mathbf{r}$, will add randomly unless all are multiples of 2π . For a rectangular lattice, cell (a,b,c)

$$\mathbf{r}_j = la\hat{\mathbf{x}} + mb\hat{\mathbf{y}} + nc\hat{\mathbf{z}}$$

$$F \sim f \sum_{lmn} \exp(i(Q_x la + Q_y mb + Q_z nc))$$

$$= 0 \quad \text{except when} \quad \begin{cases} Q_x = 2\pi/a \\ Q_y = 2\pi/b \\ Q_z = 2\pi/c \end{cases} \quad \text{and multiples thereof}$$

- We recognise **Bragg scattering**. (Note, the result is true generally, not just in the weak scattering limit.)

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Kinematic scattering as a Fourier transform

- Scattered amplitude has two parts:

$$F \sim f \sum_j \exp(i\mathbf{Q}\cdot\mathbf{r}_j)$$

- In the case of a continuous distribution of scatterers, having density, $\rho(\mathbf{r})$, then

$$F \sim \int \rho(\mathbf{r}) \exp(i\mathbf{Q}\cdot\mathbf{r}) d\mathbf{r}$$

- This is known as the **kinematic approximation**. It is useful in the weak scattering limit and is thus good for X rays and neutrons. As electrons scatter more strongly it is usually necessary to consider multiple scattering (Dynamical scattering theory)
- Note the scattered amplitude is the **Fourier Transform** of the distribution of scatterers.

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Friedel's Law

$$F(\mathbf{Q}) = \int \rho(\mathbf{r}) \exp(i\mathbf{Q}\cdot\mathbf{r}_j) d\mathbf{r}$$

- If $\rho(\mathbf{r})$ is real (a good approximation for X rays away from an absorption energy). So, replacing \mathbf{Q} with $-\mathbf{Q}$,

$$F(-\mathbf{Q}) = \int \rho(\mathbf{r}) \exp(i-\mathbf{Q}\cdot\mathbf{r}_j) d\mathbf{r} \\ = F^*(\mathbf{Q})$$

- We measure

$$|F(\mathbf{Q})|^2 = F(\mathbf{Q})F^*(\mathbf{Q}) = |F(-\mathbf{Q})|^2$$

hence the diffraction pattern is symmetric about the origin. The result is known as

Friedel's Law.

- Deviations from Friedel's Law can be exploited to aid the determination of complex, multi-atom structures. For example, by tuning the energy of X rays near to an absorption edge, $\rho(\mathbf{r}) = \rho'(\mathbf{r}) + i\rho''(\mathbf{r})$ for the absorbing atoms. Deviations from symmetry in the scattering intensity clearly relate to these particular atoms.

Dove sections 6.7, 6.8

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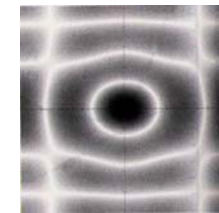
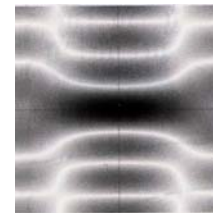
The phase problem

- Since $\rho(\mathbf{r})$ and $F(\mathbf{Q})$ are related by a Fourier transform then knowledge of $F(\mathbf{Q})$, a complex function, would give the scattering density directly. The phase information in $F(\mathbf{Q})$ is not present in the quantity we measure, $|F(\mathbf{Q})|^2$.
- The phase is, however, the more important than the amplitude of $F(\mathbf{Q})$. Example (from Dove. p142).
- Consider two digitised characters, **I** and **O**, as real, 2-D scattering systems.

I

O

- The corresponding measured intensities, $|F(\mathbf{Q})|^2$, are



- Note that there are differences (as expected)

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Phase problem cont..

- Differences in the phases are more important as can be seen by reconstructing the objects by

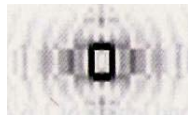
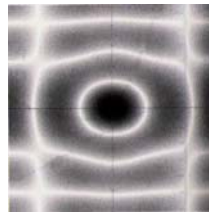
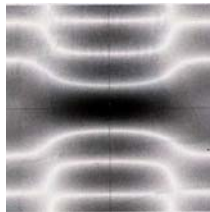
$$F_I(\mathbf{Q}) = |F_I(\mathbf{Q})| \exp(i\angle(F_o(\mathbf{Q})))$$

$$F_o(\mathbf{Q}) = |F_o(\mathbf{Q})| \exp(i\angle(F_I(\mathbf{Q})))$$

- Lower panel, below, shows the result

I

O



- Note the characters are transposed, indicating that the (normally absent) phase information dominates the reconstruction.

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Structure from diffraction

Overcoming the phase problem

- Structure determination is now a routine process and largely an automatic one.
- Probabilistic rules exist giving phase relations, e.g. *Sayre's equation*.
- For a centrosymmetric structure where, $\rho(\mathbf{r}) = \rho(-\mathbf{r}) \Rightarrow F(\mathbf{Q}) = |F_I(\mathbf{Q})|s(\mathbf{Q})$ and $s(\mathbf{Q}) = \pm 1$. It can be shown that, with a high probability strong beams, that $s(\mathbf{q}_1) \times s(\mathbf{q}_2) \times s(\mathbf{q}_3) = 1$ if $\mathbf{q}_1 + \mathbf{q}_2 + \mathbf{q}_3 = 0$. Thus, if some phases can be guessed others can be deduced. Iteration can lead to a Fourier synthesis that solves for all the atoms.
- A final stage of refinement optimises the structure by minimising differences between measured and calculated intensities.
- Older methods include Patterson synthesis. We explore the Patterson function in order to see the connection between scattering and correlations in space and time.

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Correlation functions

■ Nomenclature:

- For the next section we follow the treatment by Cowley (Ch.5 and 12) and use his nomenclature and FT definitions. Specifically:

$$FT[f(x)] = F(u) = \int f(x) \exp[2\pi i u x] dx$$

$$f(x) = FT^{-1}[FT[f(x)]] = \int F(u) \exp[-2\pi i u x] du$$

Including 2π in the exponent avoids constant multipliers in either of the integrals. (see Cowley Ch. 2, definitions and transforms)

- In terms of our usage so far: $\mathbf{Q} = 2 \pi \mathbf{u}$.

■ Inverse transform of Intensity, $|F(\mathbf{u})|^2$

$$FT^{-1}[|F(\mathbf{u})|^2] = FT^{-1}[F(\mathbf{u}) \times F^*(\mathbf{u})]$$

- Using the convolution theorem

$$= \rho(\mathbf{r}) * \rho(-\mathbf{r}) = \int \rho(\mathbf{R}) \rho(\mathbf{r} + \mathbf{R}) d\mathbf{R} \equiv P(\mathbf{r})$$

Spatial correlation function

Patterson Function

Cowley Ch. 5 & 12

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Assemblies of atoms

■ Scattering density for an assembly

- If the j th atom has density, $\rho_j(\mathbf{r})$.

Then the total density is

$$\rho(\mathbf{r}) = \sum \rho_j(\mathbf{r}) * \delta(\mathbf{r} - \mathbf{r}_j)$$

$$\rho(\mathbf{r}) * \rho(-\mathbf{r}) =$$

$$\sum_{ij} \rho_i(\mathbf{r}) * \rho_j(-\mathbf{r}) * \delta(\mathbf{r} - \mathbf{r}_i) * \delta(\mathbf{r} - \mathbf{r}_j)$$

$$= \sum_{ij} [\rho_i(\mathbf{r}) * \rho_j(-\mathbf{r})] * \delta(\mathbf{r} - (\mathbf{r}_i - \mathbf{r}_j))$$

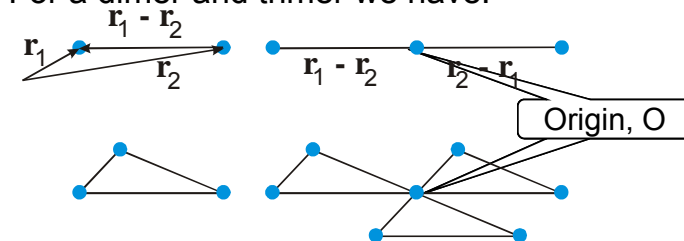
Atom position



- Typically $\rho_j(\mathbf{r})$ is approximately gaussian and so is $\rho_j * \rho_j$ (though a little broader)

- **A** Indicates we have a peak in the correlation function at every interatomic vector $\mathbf{r}_i - \mathbf{r}_j$ and an identical peak at $\mathbf{r}_j - \mathbf{r}_i$.

- For a dimer and trimer we have:



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Time dependent structures

4-D Correlation function

- In general structures are not static so we need to consider correlations in time and space.

$$P(\mathbf{r}, t) = \int \rho(\mathbf{R}, T) \rho(\mathbf{r} + \mathbf{R}, t + T) d\mathbf{R} dT$$

$$= \rho(\mathbf{r}, T) * \rho(-\mathbf{r}, -t)$$

and its Fourier transform

$$|F(\mathbf{u}, \nu)|^2 = \int \int P(\mathbf{r}, t) \exp(2\pi i(\mathbf{u} \cdot \mathbf{r} + \nu t)) d\mathbf{r} dt$$

Change in \mathbf{k} as a result of scattering

Change in frequency as a result of scattering

- \mathbf{u} is determined by the scattering geometry,
 ν is determined by the energy change ($\Delta E = h\nu$)

Diffraction

Relationship between 4-D and 3-D Patterson functions

- Consider purely elastic scattering (strict definition of diffraction), so that $\nu = 0$ in the previous equation

$$|F(\mathbf{u}, 0)|^2 = \int \int P(\mathbf{r}, t) \exp(2\pi i \mathbf{u} \cdot \mathbf{r}) d\mathbf{r} dt$$

$$= \int \left[\int P(\mathbf{r}, t) dt \right] \exp(2\pi i \mathbf{u} \cdot \mathbf{r}) d\mathbf{r}$$

Time average of the 4-D Patterson function

- Diffraction corresponds to scattering from the time average of the structural correlations.

Probes: X rays

■ Scattering strength

- The theory has been general in the sense that we have only assumed weak scattering.
- Different probes have different scattering mechanisms and are therefore sensitive to different aspects of a sample.

■ X rays

- Scattering of X rays is dominated by *electrons*.
- For an electron located at the origin having some restoring force (giving it a resonant frequency, ω_o). An incident wave (with $\omega > \omega_o$)

$$\mathbf{E} = \mathbf{E}_o \exp\{i(\omega t - \mathbf{k} \cdot \mathbf{r})\}$$

undergoes Thomson scattering giving radiation at observation point \mathbf{R} as

$$\mathbf{E}_s = \mathbf{E}_o \frac{e^2}{mc^2} \frac{1}{R} \sin \psi \exp\{i(\omega t - \mathbf{k} \cdot \mathbf{R})\}$$

ψ = angle between observation and direction of acceleration of the electron

“Scattering strength” of one electron

- $1/m$ ensures nuclear charge does not contribute.
- Total scattering comes from e^- density $\rho(\mathbf{r})$.

Probes: Electrons

■ Electrons

- To a good approximation for elastic scattering, electrons scatter from the electrostatic potential.

Poisson's equation

$$\nabla^2 \phi = -\frac{\rho}{\epsilon_o} = -\frac{1}{\epsilon_o} \{Z\delta(\mathbf{r}) - \rho(\mathbf{r})\}$$

nucleus electrons

- Scattering form factor is a FT of the scattering density (p. 9). i.e. FT of $\phi(\mathbf{r})$ in the present case.
Note:

$$FT(\nabla^2 \phi) = 2\pi i |u|^2 FT(\phi)$$

Hence we can take the “scattering density”, in earlier equations, roughly as the charge in the system (electrons and nucleus) remembering that there is an additional factor $1/u^2$.

- Different spatial extent of the nuclear and electronic charge means that:
- Electron charge:
 - decays slowly with \mathbf{r} → scattering localised in \mathbf{u} .
- Nuclear charge:
 - localised in \mathbf{r} → scattering decays slowly with \mathbf{u} .

Probes: Neutrons

Neutrons

- The scattering of neutrons is dominated by the nuclear forces, hence the main interaction is with the nucleus.
- Range of the interaction $\sim 10^{-15}\text{m}$ is much smaller than a typical wavelength $\sim 10^{-10}\text{m}$. The scattering is isotropic (s-wave scattering) and the scattered wave is

$$\psi_s = -\frac{b}{r} \exp(ikr)$$

scattering length

The minus sign is a convention so that b is +ve for a repulsive potential.

- The scattering length is directly related to the scattering probability (no. of scattered neutrons)
- If the velocity is v , no. passing through areas dS per second is

$$v \, dS |\psi_s|^2 = v \, dS \frac{b^2}{r^2} = v b^2 \, d\Omega$$

➤ Incident flux

$$\Phi = v |\psi_{inc}|^2 = v$$

- Cross section is

$$\frac{d\sigma}{d\Omega} = \frac{v b^2 \, d\Omega}{\Phi \, d\Omega} = b^2$$

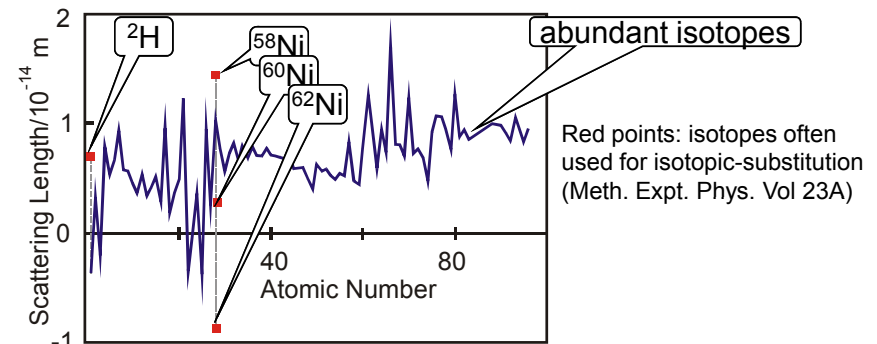
➤ Total scattering

$$\sigma_{tot} = 4\pi b^2$$

Neutron scattering

Fermi pseudopotential

- The scattering can be approximated by an effective potential
- $$V(\mathbf{r}) = a \delta(\mathbf{r}) \quad a \propto b$$
- b varies strongly from one element to the next and can be either +ve or -ve.



- The neutron spin must also be considered.
 - If the scatterer consists of a single isotope, spin I , the neutron-nucleus system has the values $I+1/2$, $I-1/2$, with scattering lengths b^+ , b^- . In general the scattering lengths are different and the scattering is some kind of average over all possibilities (Unless the nuclear spins and/or neutron are polarised)

Coherent and incoherent scattering

- Randomness in the distribution of scattering lengths is conventionally dealt with by considering the scattering to be composed of a coherent fraction and an incoherent fraction.

■ Coherent scattering

- This is the scattering from a system consisting of identical scatterers having the average scattering length, \bar{b} . The strength of the scattering (cross-section) is $\sigma_{coh} = 4\pi(\bar{b})^2$ and includes all interference effects arising from the different nuclear positions.

■ Incoherent scattering

- This term is the difference between the ideal coherent scattering and the scattering from the real system with disorder in the scattering lengths. In fact it can be shown that the corresponding cross-section is $\sigma_{incoh} = 4\pi\{\bar{b}^2 - (\bar{b})^2\}$. Equivalent to a sum of intensities from all the nuclei, without phase information (no interference).

■ Example: Hydrogen and Deuterium

- Hydrogen ($I=1/2$):

- $s=I+1/2=1$: $(2s+1)=3$: $b^+ = 1.04 \times 10^{-14} \text{m}$:

- $s=I-1/2=0$: $(2s+1)=1$: $b^- = -4.74 \times 10^{-14} \text{m}$:

$$\bar{b} = \frac{3}{4}b^+ + \frac{1}{4}b^- = 0.38 \times 10^{-14} \text{m}$$

$$(\bar{b}^2) = \frac{3}{4}|b^+|^2 + \frac{1}{4}|b^-|^2 = 6.43 \times 10^{-28} \text{m}^2$$

- coherent $\sigma_{coh} = 4\pi(\bar{b})^2 = 1.81 \times 10^{-28} \text{m}^2$

- incoherent $\sigma_{incoh} = 4\pi\{b^2 - (\bar{b})^2\} = 58 \times 10^{-28} \text{m}^2$

σ_{incoh} dominant

- Deuterium ($I=1$):

- $s=I+1/2=3/2$: $(2s+1)=4$: $b^+ = 0.95 \times 10^{-14} \text{m}$:

- $s=I-1/2=1/2$: $(2s+1)=2$: $b^- = 0.10 \times 10^{-14} \text{m}$:

$$\bar{b} = \frac{4}{6}b^+ + \frac{2}{6}b^- = 0.67 \times 10^{-14} \text{m}$$

$$(\bar{b}^2) = \frac{4}{6}|b^+|^2 + \frac{2}{6}|b^-|^2 = 0.61 \times 10^{-28} \text{m}^2$$

- coherent $\sigma_{coh} = 4\pi(\bar{b})^2 = 5.6 \times 10^{-28} \text{m}^2$

- incoherent $\sigma_{incoh} = 4\pi\{b^2 - (\bar{b})^2\} = 1.96 \times 10^{-28} \text{m}^2$

σ_{coh} dominant

- Deuterated samples show coherent scattering; non-deuterated show only incoherent scattering.

Absorption and resonant scattering

Scattering density

- In most of the discussion so far we have taken the scattering strength to be a real function.
- Reality is more complicated. For example:
 - X rays and electrons can excite atoms resulting in absorption.
 - Neutrons can scatter resonantly and form a compound nucleus.
- All these phenomena can be treated by allowing the scattering density (or scattering length) to become complex.
- Usually the complex part is only non-zero in a small range of energy (or, equivalently, k).
- Provided these regions are avoided in experiment the assumption of a real scattering density (scattering length) is valid.
- Conversely, the effects can be exploited to introduce atom-specific information in the data.

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Diffraction geometry

Experimental geometry is determined by the probe characteristics.

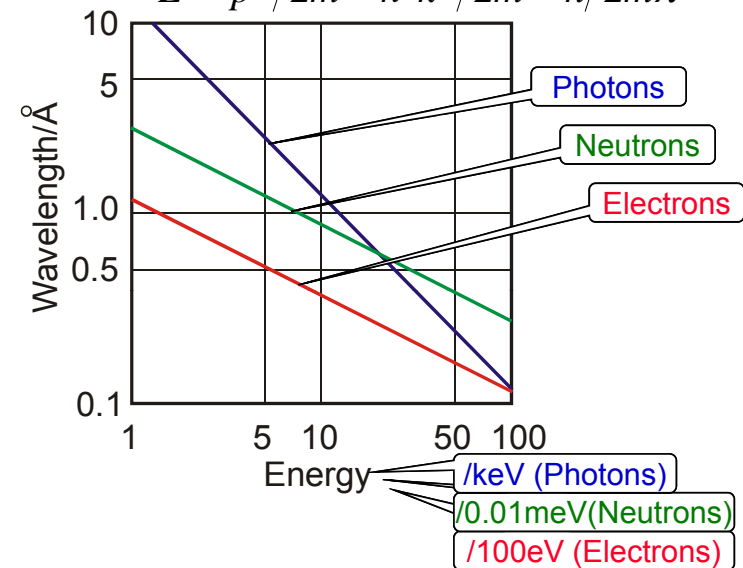
- The wavelength/energy relationship depends on the particle:

- Photons:

$$E = \hbar\omega = \hbar ck = hc/\lambda \quad \sim 1/\lambda$$

- Massive particles:

$$E = p^2/2m = \hbar^2 k^2/2m = h/2m\lambda^2 \quad \sim 1/\lambda^2$$



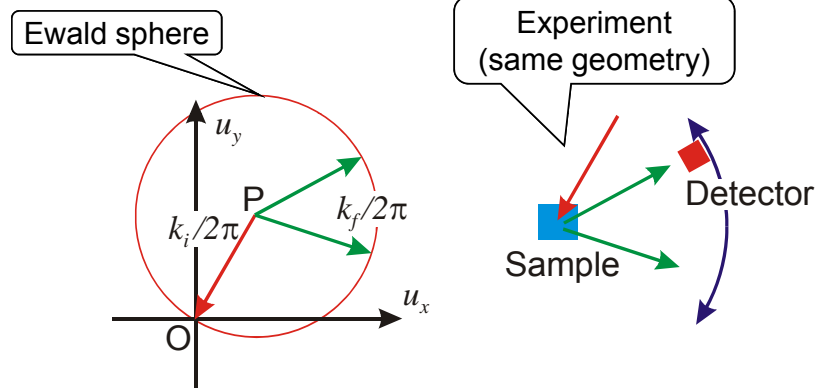
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Probes of matter

- The energy ranges shown correspond to:
Photons: x-rays region
Neutron: Thermal neutron regime
Electrons: Low energy regime.
- Note that electron microscopy generally uses much higher energies ($\sim 100\text{keV}$) and hence shorter wavelengths.

Ewald construction

- Scattering geometry is visualised easily by the Ewald construction.
 - Start by drawing k_i to origin (defines the point P).
 - k_f lies on circle centred at P. (Eg. shown green.)



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Diffraction geometry

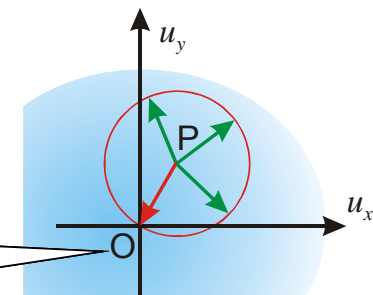
Scattering angles

- The size of the Ewald sphere, in relation to the scattering function $F(u)$ determines the scattering geometry

Neutrons, X rays, low energy electrons

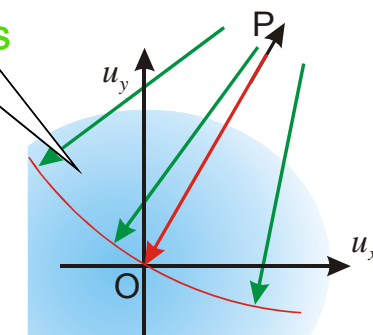
- The scale of $k/2\pi$ and $F(u)$ are similar. So, all scattering angles observed.

Shading indicates region where $F(u)$ is significant



High energy electrons

- As in a microscope
- The scale of $k/2\pi$ is much greater than $F(u)$. So, only small scattering angles occur.



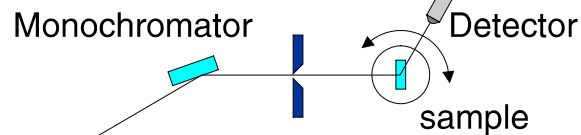
Cowley section 5.6

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Schematic experiments

X rays

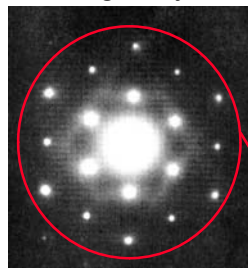
- Large angle scattering; typically multi-detector



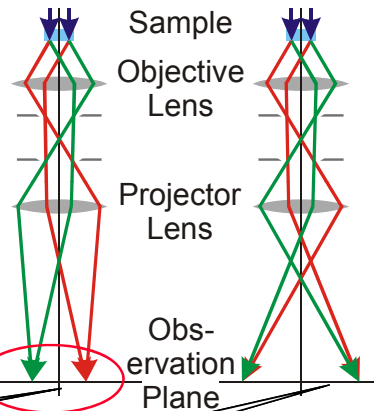
Synchrotron

High energy electrons: Transmission electron microscope (TEM)

- Forward scattering (angles greatly magnified on the diagram), detection on phosphor screen
- Al single crystal



(source Williams and Carter "TEM")



diffraction pattern

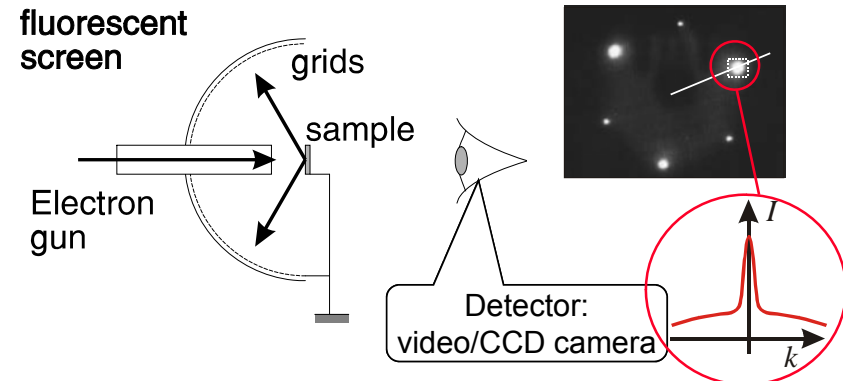
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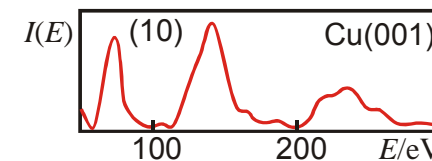
Illustration: electrons

Low energy electron diffraction (LEED)

- Energies of 100-500eV give wavelengths $\leq 1\text{\AA}$.
- scattering through large angles is possible
- Energies correspond to short mean-free paths in a solid, hence used as a surface structure tool.



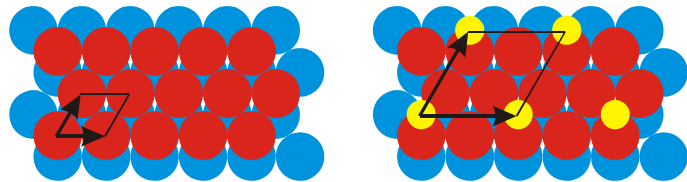
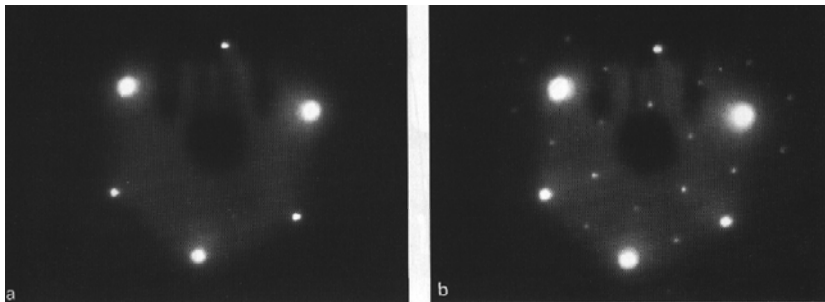
- Energy dependence of the scattered intensity relates to the structure.



- Electrons scatter strongly, the kinematic approximation fails, and a "dynamical" analysis is needed

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- Example: f.c.c. (111) surface with and without adsorbates



- Note:
- 3-fold symmetry in pattern (bulk)
 - Change in periodicity due to adsorbate unit cell
 - Strong diffraction from high-z substrate
 - Weaker features from the lighter adsorbate