Elements of Modern X-ray Physics

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About this course

“To explain the physics underlying the production and exploitation of X-rays with emphasis on application in condensed matter and materials physics”

1. Sources of X-rays
2. X-rays and their interaction with matter: scattering
3. Refraction and absorption of X-rays
4. X-ray imaging
X-rays and their interaction with matter

About this lecture

1. Cross-sections and scattering lengths
2. Semi-classical description of elastic scattering
   • Thomson scattering
   • Resonant scattering
   • Relationship between scattering, refraction and absorption
3. Compton scattering
   • Kinematics
   • Klein-Nishina cross-section
4. Quantum mechanical treatment
   • Non-resonant magnetic scattering
   • Resonant scattering from multipoles

Scattering amplitude is a tensor

\[ A = e' \cdot f \cdot \epsilon, \]

\[ f = \sum_n T_n \exp(iQ \cdot r). \]
X-ray Magnetic Scattering

(1972) X-ray Magnetic Scattering

Tube source: Counts per 4 hours!

NiO, de Bergevin and Brunel (1972)

(1985) First Synchrotron Studies

Holmium, Gibbs et al. (1985)

”Modern” Era?!?

(1985) First Resonant Scattering

Nickel, Namikawa (1985)
Scattering Cross-sections

$I_{sc}$ scattered beam intensity [particles/s]

Incident beam flux

$\Phi_0 = \frac{I_0}{\text{Beam Area}}$

$\Delta\Omega$ element of solid angle $[(\text{Area})/(\text{distance})^2]$

Quite generally we expect

$$I_{sc} = \Phi_0 \times \Delta\Omega \times \text{Scattering efficiency factor} = \Phi_0 \times \Delta\Omega \times \left( \frac{d\sigma}{d\Omega} \right)$$

This defines the **Differential Cross-section**

$$\left( \frac{d\sigma}{d\Omega} \right) = \frac{\text{Number of particles scattered per second into detector}}{\text{Incident Flux} \times \text{Detector solid Angle}} = \frac{I_{sc}}{\Phi_0 \Delta\Omega}$$

The **Total Cross-section** is obtained by integrating over all solid angle

$$\sigma = \int \left( \frac{d\sigma}{d\Omega} \right) d\Omega$$

This **Partial Differential Cross-section**

$$\left( \frac{d\sigma}{d\Omega dE_f} \right) = \frac{\text{Particles scattered per second into detector in energy window } dE_f}{\text{Incident Flux} \times \text{Detector solid Angle} \times dE_f}$$
# Photons: Basic Properties and Interactions

<table>
<thead>
<tr>
<th></th>
<th>Photon</th>
<th>Neutron</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Charge</strong></td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td><strong>Mass</strong></td>
<td>0</td>
<td>1.675 x 10^{-27} Kg</td>
</tr>
<tr>
<td><strong>Spin</strong></td>
<td>1</td>
<td>1/2</td>
</tr>
<tr>
<td><strong>Magnetic Moment</strong></td>
<td>0</td>
<td>-1.913 μ_N</td>
</tr>
</tbody>
</table>

## Scattering lengths:

<table>
<thead>
<tr>
<th><strong>Sensitivity to</strong></th>
<th><strong>Structure</strong>: (E field photon and e)</th>
<th><strong>Sensitivity to</strong>: b\sim r_0 (Short range nuclear forces)</th>
</tr>
</thead>
<tbody>
<tr>
<td>r_0=2.82 x 10^{-5} Å</td>
<td></td>
<td></td>
</tr>
<tr>
<td>r_0(\hbar\omega/mc^2)</td>
<td>(E, H field photon and e and \mu_B )</td>
<td>b_{mag} \sim r_0 (\mu_n \cdot B_{dipp})</td>
</tr>
</tbody>
</table>

**Resonant Scattering:**

\[ r_0 = \frac{1}{4\pi\varepsilon_0} \frac{e^2}{mc^2} = 2.82 \times 10^{-15} m \]

\[ r_0 = 100 \times r_0! \]
Scattering of an electromagnetic wave

Semi-classical treatment

Poynting Vector: \[ S = \frac{1}{\mu_0} \mathbf{E} \times \mathbf{B} \Rightarrow S = c \varepsilon_0 E^2 \]

Units: Energy/s/unit area
Radiation from an accelerating charge

Electric dipole radiation

\[ E_{\text{rad}} \propto -\frac{e}{R} a_x(t') \sin \Psi \propto \frac{e}{R} a_x(t')(\hat{e} \cdot \hat{e}') \quad \text{where } t' = t - R/c \]

The acceleration of the charge is given by

\[ a_x(t') = -\frac{eE_0 e^{-i\omega t'}}{m} = -\frac{e}{m} E_{\text{in}} e^{i\omega (R/c)} = -\frac{e}{m} E_{\text{in}} e^{ikR} \quad \text{where } E_{\text{in}} = E_0 e^{-i\omega t} \]

\[ \therefore \quad \frac{E_{\text{rad}}(R,t)}{E_{\text{in}}} \propto \left( \frac{e^2}{m} \right) \frac{e^{ikR}}{R} (\hat{e} \cdot \hat{e}') \]

\[ = -r_0 \frac{e^{ikR}}{R} |\hat{e} \cdot \hat{e}'| \quad \text{from exact treatment} \]

\[ r_0 = \left( \frac{e^2}{4\pi\varepsilon_0 mc^2} \right) = 2.82 \times 10^{-15} \text{ m} \]

\[ \frac{d\sigma}{d\Omega} = \frac{|E_{\text{rad}}|^2 R^2}{|E_{\text{in}}|^2} = r_0^2 |\hat{e} \cdot \hat{e}'|^2 \]
Thomson cross-section

Scattering from the charge of a single, unbound electron

Scattering length:

\[-r_0\]

phase shift of $\pi$ on scattering (refractive index, $n < 1$)

Polarization dependence:

\[
\frac{d\sigma}{d\Omega} = r_0^2 |\hat{\epsilon} \cdot \hat{\epsilon}'|^2 = r_0^2 P
\]

with

\[
P = |\hat{\epsilon} \cdot \hat{\epsilon}'|^2 = \begin{cases} 
|\hat{\sigma} \cdot \hat{\sigma}'|^2 = 1 & \text{Synchrotron: vertical scattering} \\
|\hat{\pi} \cdot \hat{\pi}'|^2 = \cos^2(2\theta) & \text{Synchrotron: horizontal scattering} \\
\frac{1}{2}(1 + \cos^2(2\theta)) & \text{Unpolarised source}
\end{cases}
\]

Total scattering cross-section:

\[
\sigma_r = \int \frac{d\sigma}{d\Omega} d\Omega = 4\pi r_0^2 \left\langle |\hat{\epsilon} \cdot \hat{\epsilon}'|^2 \right\rangle = 4\pi r_0^2 \frac{2}{3}
\]

\[
\sigma_r = \left( \frac{8\pi}{3} \right) r_0^2
\]
**Diffraction: Two point scatterers**

**Definition of the scattering vector**

**Elastic scattering**

$k = k'$

**incident plane wave**

$k = \frac{2\pi}{\lambda}$

**scattered plane wave**

$k' = \frac{2\pi}{\lambda}$

$l_1 = \frac{k \cdot r}{k} = \frac{\lambda}{2\pi} k \cdot r$

$l_2 = \frac{-k' \cdot r}{k} = -\frac{\lambda}{2\pi} k' \cdot r$

Total path length difference: $l_1 + l_2$

Total phase difference: \( \frac{2\pi}{\lambda} (l_1 + l_2) = (k - k') \cdot r = Q \cdot r \)

**Scattering vector**

$Q = k - k'$
Diffraction: Two point scatterers

Amplitude and intensity of scattered beam

Scattered wave from origin: \[ \psi_1(x) = Ae^{ik' \cdot x} \]

Scattered wave from \( r \): \[ \psi_2(x) = Ae^{ik' \cdot x} e^{iQ \cdot r} \]

Total amplitude: \[ \psi_t = \psi_1(x) + \psi_2(x) = Ae^{ik' \cdot x} + Ae^{ik' \cdot x} e^{iQ \cdot r} \]

Intensity: \[ I = |\psi_t|^2 = \psi_t \psi_t^* = 2A^2 (1 + \cos(Q \cdot r)) \]

Scattering triangle

incident plane wave \( k = \frac{2\pi}{\lambda} \)

scattered plane wave \( k' = \frac{2\pi}{\lambda} \)

\[ Q = \frac{4\pi}{\lambda} \sin(\phi / 2) \]
Scattering from an atom
unbound electrons

Discrete system: scattering amplitude \( A(Q) = -r_0 \sum_{j} e^{iQr_j} \)

Continuous system: \( A(Q) = -r_0 \int \rho(r) dr \ e^{iQ \cdot r} \) \( \rho(r) \): number density of scatterers

**X-rays**

Atomic form factor defined by \( f^0(Q) = \int \rho(r) dr \ e^{iQ \cdot r} \)

\( f^0(Q) \to Z \) as \( Q \to 0 \)

\( f^0(Q) \to 0 \) as \( Q \to \infty \)

Formally, the atomic form factor is the Fourier transform of the atomic electron density

Example: 1s hydrogenic wave function

\[ \psi_{1s}(r) = \frac{1}{\sqrt{\pi a^3}} e^{-r/a} \Rightarrow f_{1s}^0(Q) = \frac{1}{(1 + (Qa/2)^2)^2} \] with \( a = a_0 / Z \)

**Neutrons**

For neutrons \( \rho(r) = \delta(r) \) and \( \int \delta(r) dr \ e^{iQ \cdot r} = 1 \)

**X-ray charge scattering:** decrease of scattering intensity with increasing \( Q \)

**Neutron nuclear scattering:** no decrease
Atomic form factor of Hydrogen-Like Atom

1s Wavefunction

Form factor

\[ \psi_{1s}(r) \]

\[ f^0_{1s}(Q) \]
Scattering cross-section from a crystal

Laue condition

For lattice sum: \( \sum_{R_n} e^{iQ \cdot R_n} \) large number of terms means cancellation unless special condition is fulfilled where they all add up. This condition requires that \( Q \cdot R_n = 2\pi \times \text{integer} \)

This condition is met if \( Q = G \) a reciprocal lattice vector since \( R_n = n_1a_1 + n_2a_2 + n_3a_3 \) and \( G = ha_1^* + ka_2^* + la_3^* \) where the primitive reciprocal lattice vectors are defined by \( a_i \cdot a_j^* = 2\pi \delta_{ij} \Rightarrow G \cdot R_n = 2\pi (hn_1 + kn_2 + ln_3) \)

All unit cells therefore scatter in phase when \( Q = G \) Laue condition

Can show that

\[
\left| \sum_{R_n} e^{iQ \cdot R_n} \right|^2 = N_v \sum_G \delta(Q - G)
\]

Thus

\[
\left( \frac{d\sigma}{d\Omega} \right)^\text{Crystal} = N_v \sum_G |F(Q)|^2 \delta(Q - G)
\]

Unit cell structure factor

For x-rays \( F_{\text{x-rays}}(Q) = r_0 \sum_{r_j} Pf_j(Q) e^{iQ \cdot r_j} \)

For neutrons \( F_{\text{neutrons}}(Q) = \sum_{r_j} b_j e^{iQ \cdot r_j} \)
X-ray Resonant Scattering

Dispersion corrections

From electrons bound in atoms expect:

\[ f(Q, \omega) = f^0(Q) + f'(\omega) + i f''(\omega) \]

Forced, damped oscillator model

\[
\ddot{x} + \Gamma \dot{x} + \omega^2 x = -\left( \frac{eE_0}{m} \right) e^{-i\omega t} \Rightarrow x(t) = \left( -\frac{e}{m} \right) \frac{E_0 e^{-i\omega t}}{(\omega_0^2 - \omega^2 - i\omega\Gamma)}
\]

\[
f_s' = \frac{\omega_0^2 (\omega^2 - \omega_0^2)}{(\omega^2 - \omega_0^2)^2 + (\omega\Gamma)^2} \quad f_s'' = -\frac{-\omega_0^2 \omega \Gamma}{(\omega^2 - \omega_0^2)^2 + (\omega\Gamma)^2}
\]
Resonant scattering in crystallography
Breakdown of Friedel’s Law

Non-resonant

\[ A(Q) = f_1^0 + f_2^0 e^{iQx} \]
\[ \Rightarrow I(Q) = (f_1^0)^2 + (f_2^0)^2 + 2 f_1^0 f_2^0 \cos(Qx) \]
\[ \therefore I(Q) = I(-Q) \]

Resonant

\[ f_1 = f_1^0 + f_1' + i f_1'' \equiv r_1 e^{i\phi_1} \]
\[ A(Q) = r_1 e^{i\phi_1} + r_2 e^{i\phi_2} e^{iQx} \]
\[ \Rightarrow I(Q) = r_1^2 + r_2^2 + 2 f_1^0 f_2^0 \cos(Qx - \phi_1 + \phi_2) \]
\[ \cos(Qx - \phi_1 + \phi_2) \neq \cos(-Qx - \phi_1 + \phi_2) \]
\[ \therefore I(Q) \neq I(-Q) \]

Dispersion corrections reveal absolute atomic configurations:
route to solution of phase problem, enables MAD, SAD, etc.
**Relationship between scattering and refraction**

Electric field $\mathbf{E}(t) \Rightarrow \mathbf{P}(t)$ (electric dipole/V)

$$\mathbf{P}(t) = \varepsilon_0 \chi \mathbf{E}(t) = (\varepsilon - \varepsilon_0) \mathbf{E}(t)$$

where

$$P(t) = -\frac{N e x(t)}{V} = -\rho e x(t) = -\rho e \left( -\frac{e}{m} \right) \frac{E_0 e^{-i\omega t}}{(\omega_0^2 - \omega^2 - i\omega\Gamma)}$$

$$\Rightarrow \frac{P(t)}{E(t)} = \varepsilon - \varepsilon_0 = \left( \frac{e^2 \rho}{m} \right) \frac{1}{(\omega_0^2 - \omega^2 - i\omega\Gamma)}$$

The refractive index is defined by

$$n^2 = \frac{c^2}{v^2} = \frac{\varepsilon}{\varepsilon_0}$$

$$\Rightarrow n^2 = 1 + \left( \frac{e^2 \rho}{\varepsilon_0 m} \right) \frac{1}{(\omega_0^2 - \omega^2 - i\omega\Gamma)}$$

For X-rays, $\omega \gg \omega_0 \gg \Gamma$

$$n \approx 1 - \frac{1}{2} \left( \frac{e^2 \rho}{\varepsilon_0 m \omega^2} \right) = 1 - \frac{2\pi \rho r_0}{k^2}$$

$$n \approx 1 - \delta + i\beta$$

Since $\rho = \rho_a f(0)$

$$\delta = \frac{2\pi \rho_a r_0 (f^0(0) + f'(h\omega))}{k^2}$$

$$\beta = -\frac{2\pi \rho_a r_0 f''(h\omega)}{k^2}$$
Relationship between scattering and refraction

Resonant scattering

\[ f(Q, \hbar \omega) = f^0(Q) + f'(\hbar \omega) + if''(\hbar \omega) \]

Rayleigh scattering

Visible light

Refractive index

\[ n = 1 - \delta + i\beta \]

\[ \delta = (f^0(0) + f') \frac{2\pi \rho a r_0}{k^2} \]

\[ \beta = -f'' \left( \frac{2\pi \rho a r_0}{k^2} \right) \]

Scattering and refraction: different ways of understanding the same phenomena
Absorption coefficient $\mu$ defined by $I = I_0 e^{-\mu z}$ and absorption cross-section $\sigma_a = \mu / \rho_a$

Absorption is proportional to the imaginary part of the forward scattering amplitude (Optical Theorem)
**Compton scattering**

**Kinematics**

Consider a photon incident along the $x$ direction scattering off of a stationary electron. After the scattering event the photon is deflected by an angle $\psi$ in the $x-y$ plane, while the electron moves at an angle $\phi$. The momenta and energy before and after the scattering event may be written as:

<table>
<thead>
<tr>
<th>Initial</th>
<th>Final</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\chi_i + 1$</td>
<td>$\chi_f + \gamma_f$</td>
</tr>
</tbody>
</table>

where $\gamma_{i(f)} = h\nu_{i(f)}/mc^2$, etc.

Conservation of momentum implies that:

\[
\begin{align*}
\chi_i &= \chi_f \cos \psi - \gamma_f \beta_f \cos \phi \\
0 &= \chi_f \sin \psi - \gamma_f \beta_f \sin \phi
\end{align*}
\]

where $\chi_{i(f)} = h\nu_{i(f)}/mc^2$, etc.

Squaring and adding the above equations to eliminate the scattering angle $\phi$ of the electron yields

\[
\gamma_f^2 = 1 + (\chi_i - \chi_f)^2 + 2\chi_i \chi_f (1 - \cos \psi)
\]

while from the conservation of energy we have

\[
\gamma_f^2 = 1 + (\chi_i - \chi_f)^2 + 2(\chi_i - \chi_f)
\]

By comparing the two expressions for $\gamma_f^2$ we obtain

\[
\frac{\chi_i}{\chi_f} = 1 + \chi_i (1 - \cos \psi)
\]

or using the fact that $\chi = \lambda_i k$

\[
\frac{k_i}{k_f} = 1 + \lambda_i k_i (1 - \cos \psi) = \frac{E_i}{E_f} = \frac{\lambda_f}{\lambda_i}
\] (1)
Compton scattering
Klein-Nishina Cross-section

\[ \frac{d\sigma}{d\Omega} = \frac{r_0^2}{2} \left( \frac{\mathcal{E}'}{\mathcal{E}} \right)^2 \left[ (1 + \cos^2 \psi) + \frac{\mathcal{E} - \mathcal{E}'}{mc^2} (1 - \cos \psi) \right] \]

unpolarized source

When \( \mathcal{E} \ll mc^2 \) (\( \Rightarrow \mathcal{E}' \rightarrow \mathcal{E} \)) or \( \psi \rightarrow 0 \) we recover the Thomson scattering formula

\[ \frac{d\sigma}{d\Omega} = \frac{r_0^2}{2} (1 + \cos^2 \psi) \]
X-rays and their interaction with matter

Adapted from de Bergevin and Brunel, 1981
Quantum mechanical description of scattering

**Theoretical Framework**

Task is to determine the differential cross-section:

\[
\left( \frac{d\sigma}{d\Omega} \right) = \frac{\text{Number of particles scattered per second into detector}}{\text{Incident Flux} \times \text{Detector solid Angle}}
\]

\[
= \frac{W}{\Phi_0(\Delta\Omega)}
\]

The transition rate probability \( W \) to 2nd order

\[
W = \frac{2\pi}{\hbar} \left| \langle f | H_I | i \rangle + \sum_n \frac{\langle f | H_I | n \rangle \langle n | H_I | i \rangle}{\varepsilon_i - \varepsilon_n} \right|^2 \rho(E_f)
\]

**Interaction Hamiltonian** \( H_I \): describes interaction between radiation and target

**Density of final states**

\[
\rho(E_f) dE_f = \rho(k_f) dk_f
\]

Box normalisation implies

\[
\rho(E_f) dE_f = \rho(k_f) k_f^2 \Delta\Omega dk_f
\]

\[
\therefore \rho(E_f) = \frac{V}{(2\pi)^3} k_f^2 \Delta\Omega \frac{dk_f}{dE_f}
\]

To first order

\[
\left( \frac{d\sigma}{d\Omega} \right) = \frac{1}{\Phi_0} \frac{2\pi}{\hbar} \left| \langle f | H_I | i \rangle \right|^2 \frac{V}{(2\pi)^3} k_f^2 \frac{dk_f}{dE_f}
\]
Quantum mechanical description of scattering

Theoretical Framework

\[
\left( \frac{d\sigma}{d\Omega} \right) = \frac{1}{\Phi_0} \frac{2\pi}{\hbar} \left| \langle f | H_I | i \rangle \right|^2 \frac{V}{(2\pi)^3} k_f^2 \frac{dk_f}{dE_f}
\]

For photons, \( \Phi_0 = c / V \) and \( E = \hbar ck \)

\[
\left( \frac{d\sigma}{d\Omega} \right) = \frac{V}{c} \frac{2\pi}{\hbar} \left| \langle f | H_I | i \rangle \right|^2 \frac{V}{(2\pi)^3} \frac{E_f^2}{(\hbar c)^2} \frac{1}{\hbar c}
\]

\[
\left( \frac{d\sigma}{d\Omega} \right) = \left( \frac{V}{2\pi} \right)^2 \frac{E_f^2}{\hbar^4 c^4} \left| \langle f | H_I | i \rangle \right|^2
\]

which for elastic scattering becomes

\[
\left( \frac{d\sigma}{d\Omega} \right)_{\text{elastic}} = \left( \frac{V}{2\pi} \right)^2 \frac{1}{\hbar^4 c^4} \int E_f^2 \left| \langle f | H_I | i \rangle \right|^2 \delta(E_f - E) dE
\]
Quantizing the Radiation Field

Classical energy of electromagnetic field (free space)

\[ E_{\text{rad}} = \varepsilon_0 \int_V E \cdot E \, dr \quad \text{with} \quad E = -\frac{\partial A}{\partial t} \]

Most general form for Vector potential \( A \) is as a Fourier series, of which one term is:

\[ A(r,t) = A_0 \hat{\varepsilon} \left[ a_k e^{i(k \cdot r - \omega t)} + a_k^* e^{-i(k \cdot r - \omega t)} \right] \]

Therefore

\[ E_{\text{rad}} = 2\varepsilon_0 \omega^2 A_0^2 a_k^* a_k V = \hbar \omega a_k^* a_k \quad \text{if} \quad A_0 = \sqrt{\frac{\hbar}{2\varepsilon_0 \omega V}} \]

c.f. Harmonic Oscillator

\[ E_{\text{sho}} = \hbar \omega (a_k^* a_k + \frac{1}{2}) \]

Suggests radiation field is quantised like an harmonic oscillator with

\[ a_k |n\rangle = \sqrt{n} |n-1\rangle \quad \text{and} \quad a_k^* |n\rangle = \sqrt{n+1} |n+1\rangle \]

\[ A(r,t) = \sum_u \sum_k \sqrt{\frac{\hbar}{2\varepsilon_0 \omega V}} \hat{\varepsilon}_u \left[ a_{u,k} e^{i(k \cdot r - \omega t)} + a_{u,k}^* e^{-i(k \cdot r - \omega t)} \right] \]

Vector potential is LINEAR in photon annihilation and creation operators
**X-ray Scattering: Interaction Hamiltonian**

*Single Electron in an electromagnetic field (ignore magnetic degrees of freedom to start with)*:

\[ H_0 = \frac{p^2}{2m} + V \]

Canonical momentum \( p \rightarrow p + eA \) with \( B = \nabla \times A \) and \( E = -\nabla \phi - \dot{A} \)

\[ H_0 \rightarrow H_0 + \frac{eA \cdot p}{m} + \frac{e^2 A^2}{2m} \]

\[ H_I = \left( \frac{e^2}{2m} \right) A^2 + \left( \frac{e}{m} \right) A \cdot p \]

Non-magnetic, Non-resonant scattering

**1st order**:

\[ W = \frac{2\pi}{\hbar} \left| \langle f | H_I | i \rangle \right|^2 \rho(\mathcal{E}_f) \]

\[ H_I = \left( \frac{e^2}{2m} \right) A^2 + \left( \frac{e}{m} \right) A \cdot p \]
## Thomson (Charge) Scattering

\[ \langle a; k', \beta \mid \left( \frac{e^2}{2m} \right) A^2 \mid a; k, \alpha \rangle = \langle k', \beta \mid \left( \frac{e^2}{2m} \right) A^2 \mid k, \alpha \rangle = \left( \frac{e^2 \hbar}{2m e_0 V \omega} \right) \hat{e}_{\alpha,k} \hat{e}_{\beta,k} \]

\[
\left( \frac{d\sigma}{d\Omega} \right)^{\text{Charg} e} = \frac{W}{\Phi_0(\Delta\Omega)} = r_0^2 |\hat{\epsilon}' \cdot \hat{\epsilon}|^2
\]

### Differential cross-section for an array of atoms

\[
\left( \frac{d\sigma}{d\Omega} \right) = r_0^2 (\hat{\epsilon}' \cdot \hat{\epsilon}) \left| \sum_s f_s^0 (Q) e^{iQ \cdot r_s} \right|^2
\]

- \( f_s^0 (Q) \) is the atomic form factor and \( r_0 = \left( \frac{e^2}{4\pi \epsilon_0 m c^2} \right) = 2.82 \times 10^{-5} \text{Å} \)

### Polarization factor refers to E field may be written as

\[
(\hat{\epsilon}' \cdot \hat{\epsilon}) \quad \rightarrow \quad \begin{array}{c|cc}
\hat{\epsilon}_\perp & \hat{\epsilon} & \hat{\epsilon}_\parallel \\
\hline
\hat{\epsilon}_\perp & 1 & 0 \\
\hat{\epsilon}_\parallel & 0 & \cos 2\theta \\
\end{array}
\]
Interaction Hamiltonian
X-ray Magnetic Scattering

Single Electron in an electromagnetic field:
\[ H_0 = \frac{p^2}{2m} + V \]

Canonical momentum \( p \rightarrow p + eA \) with \( B = \nabla \times A \) and \( E = -\nabla \phi - \dot{A} \)

Zeeman Interaction:
\[ H_Z = g \mu_B s \cdot B = \frac{e\hbar}{m} s \cdot \nabla \times A \]

Spin - Orbit Interaction:
\[ H_{so} = -\frac{1}{2} m \cdot B = \frac{1}{2} g \mu_B s \cdot \frac{E \times v}{c^2} = \frac{e\hbar}{2m^2c^2} s \cdot E \times p = \left( \frac{e\hbar}{2m^2c^2} \right) s \cdot \left( -\nabla \phi - \dot{A} \right) \times \left( p + eA \right) \]
\[ \approx -\left( \frac{e^2\hbar}{2m^2c^2} \right) s \cdot \left( \dot{A} \times A \right) \]

\[ H_1 = \left( \frac{e^2}{2m} \right) A^2 + \left( \frac{e}{m} \right) A \cdot p + \left( \frac{e\hbar}{m} \right) s \cdot \nabla \times A - \left( \frac{e^2\hbar}{2m^2c^2} \right) s \cdot \left( \dot{A} \times A \right) \]
\[ H_2 = \left( \frac{e}{m} \right) A \cdot p + \left( \frac{e\hbar}{m} \right) s \cdot \nabla \times A \]
\[ H_3 = \left( \frac{e\hbar}{m} \right) s \cdot \nabla \times A \]
\[ H_4 = -\left( \frac{e^2\hbar}{2m^2c^2} \right) s \cdot \left( \dot{A} \times A \right) \]
Non-resonant Magnetic Scattering

1st order: \[ W = \frac{2\pi}{\hbar} |\langle f | H_i | i \rangle|^2 \rho(\mathcal{E}_f) \]

2nd order: \[ W = \frac{2\pi}{\hbar} \left| \sum_n \frac{\langle f | H_I | n \rangle \langle n | H_I | i \rangle}{\mathcal{E}_i - \mathcal{E}_n} \right|^2 \rho(\mathcal{E}_f) \]

1st order:
\[ H_I = \left( \frac{e^2}{2m} \right) A^2 + \left( \frac{e}{m} \right) A \cdot p + \left( \frac{e\hbar}{m} \right) s \cdot \nabla \times A - \left( \frac{e^2\hbar}{2m^2c^2} \right) s \cdot (\hat{A} \times A) \]

2nd order:
\[ H_I = \left( \frac{e^2}{2m} \right) A^2 + \left( \frac{e}{m} \right) A \cdot p + \left( \frac{e\hbar}{m} \right) s \cdot \nabla \times A - \left( \frac{e^2\hbar}{2m^2c^2} \right) s \cdot (\hat{A} \times A) \]
Summary: 1st Order Scattering Processes

\[ H_I = \left( \frac{e^2}{2m} \right) A^2 - \left( \frac{e^2 \hbar}{2m^2 c^2} \right) s \cdot (\hat{A} \times \hat{A}) \]

**Thomson scattering**

\[ \langle a; k', \beta \left| \left( \frac{e^2}{2m} \right) A^2 \right| a; k, \alpha \rangle = \langle k', \beta \left| \left( \frac{e^2}{2m} \right) A^2 \right| k, \alpha \rangle = \left( \frac{e^2 \hbar}{2me_0 V \omega} \right) \hat{e}_{\alpha, k} \cdot \hat{e}_{\beta, k'} \]

\[ \frac{d\sigma}{d\Omega}^{\text{Charge}} = \frac{W}{\Phi_0 (\Delta \Omega)} = r_0^2 |\hat{e}' \cdot \hat{e}|^2 \]

**Magnetic scattering**

\[ \langle a; k', \beta \left| - \left( \frac{e^2 \hbar}{2m^2 c^2} \right) s \cdot (\hat{A} \times \hat{A}) \right| a; k, \alpha \rangle = i \left( \frac{e^2 \hbar^2}{2m^2 Vc^2 \epsilon_0} \right) \langle s \rangle (\hat{e}_{\alpha, k} \times \hat{e}_{\beta, k'}) \]

\[ \frac{d\sigma}{d\Omega}^{\text{Magnetic}} = r_0^2 \left( \frac{\hbar \omega}{mc^2} \right)^2 |\hat{e}' \times \hat{e}|^2 \langle s \rangle^2 \]

- Magnetic scattering is weaker than charge by \((\hbar \omega / mc^2)^2 \sim 0.0001\) at 10 keV
- Scattering cross-section is proportional to <s>^2 => Magnetic crystallography
- Magnetic scattering has a distinctive polarization dependence
Total non-resonant magnetic cross-section
Unique ability to separate spin and orbital moments

**Magnetic scattering length**

\[ f^{\text{mag}}(Q) = i \, r_0 \left( \frac{\hbar \omega}{mc^2} \right) \left[ \frac{1}{2} L(Q) \cdot A'' + S(Q) \cdot B \right] \]

\(L(Q)\) and \(S(Q)\) are Fourier transforms of the atomic and spin magnetization densities. \(A''\) and \(B\) contain the dependence on \(k, k', \hat{\epsilon}\) and \(\hat{\epsilon}'\)

\[ f^{\text{mag}}(Q) = i \, r_0 \left( \frac{\hbar \omega}{mc^2} \right) \times \]

\[ \begin{array}{c|cc}
\hat{\epsilon}_\perp \equiv \sigma & \hat{\epsilon}_\parallel \equiv \pi \\
\hat{\epsilon}'_\perp & \sin 2\theta S_2 & -2 \sin^2 \theta \left[ (L_1 + S_1) \cos \theta - S_3 \sin \theta \right] \\
\hat{\epsilon}'_\parallel & 2 \sin^2 \theta \left[ (L_1 + S_1) \cos \theta - S_3 \sin \theta \right] & \sin 2\theta \left[ 2 \sin^2 \theta L_2 + S_2 \right]
\end{array} \]

Blume and Gibbs, PRB 1988
Example: scattering from a magnetic spiral

Assume for clarity that

\[ \langle L \rangle = 0 \text{ and } S = S(\cos(qa \ell), \sin(qa \ell)) \]

and that experiment is done with \( \sigma \) polarized light and no analyser

\[
f^{\text{mag}}(Q) = \iota r_0 \left( \frac{\hbar \omega}{mc^2} \right) S \frac{\hbar}{2} \sum_{\ell} e^{i(Q \pm q) a \ell} \times
\]

\[
\begin{array}{c|c|c}
\hat{\epsilon}_\perp & \hat{\epsilon}_\parallel & \hat{\epsilon}'_\perp & \hat{\epsilon}'_\parallel
\end{array}
\]

\[
\begin{align*}
\hat{\epsilon}_\perp & \equiv \sigma & \hat{\epsilon}_\parallel & \equiv \pi \\
\pm i \sin 2\theta & -2 \sin^2 \theta \cos \theta & 2 \sin^2 \theta \cos \theta & \pm i \sin 2\theta
\end{align*}
\]

\[
\left( \frac{d\sigma}{d\Omega} \right)^{\text{Magnetic}} = r_0^2 \left( \frac{\hbar \omega}{mc^2} \right)^2 S^2 \sin^2 2\theta (1 + \sin^2 \theta) \left( \frac{2\pi}{a} \right) \sum_G \delta(Q - G \pm q)
\]
Experimental considerations

- High flux beamline
- Tunable photon energy, 1-15 keV
- Well defined incident polarization
- Versatile diffractometer
- Azimuthal degree of freedom
- Polarization analysis
First Synchrotron Radiation Studies of Magnetism

Non-Resonant Magnetic scattering from Holmium
Gibbs, Moncton, D’Amico, Bohr and Grier (1985)

Synchrotron Source: Counts per 20s

Advantages of Non-resonant X-ray Magnetic Scattering

• High-resolution technique (Phase transitions)
• Separation of orbital and spin magnetization densities
• Highly focussed beams (Small samples)
Non-resonant X-ray magnetic scattering study of non-collinear order using circularly polarized X-rays

Imaging the electric field control of magnetism in multiferroic TbMnO$_3$

Circularly Polarized X Rays as a Probe of Noncollinear Magnetic Order in Multiferroic TbMnO$_3$

Magnetic Control of Ferroelectric Polarization

TbMnO$_3$

Pbmn
Mn: bar 1
Tb: m
Magnetic inversion symmetry breaking and ferroelectricity in TbMnO$_3$

Kenzelmann et al. PRL (2005)

Neutron Scattering

$q_{\text{Mn}} = (0 \ q \ 1)$  A-type Fourier components

$\Gamma_3$: $m_3[\text{Mn}] = (0.0 \ 2.9 \ 0.0) \mu_B$

$m_3[\text{Tb}] = (0.0 \ 0.0 \ 0.0) \mu_B$

$\Gamma_2$: $m_2[\text{Mn}] = (0 \ 0 \ 2.8) \mu_B$

$m_3[\text{Tb}] = (0 \ 0 \ 0) \mu_B$

$m_2[\text{Tb}] = (1.2 \ 0 \ 0) \mu_B$

Phase between $b$ and $c$ components not fixed by experiment

Ferroelectricity from magnetic Frustration!
Production of circularly polarized X-rays

Perfect diamond crystals can act as 1/4 wave phase retarder producing circularly polarised light

\( e = 7.5 \text{ keV}: \) diamond thickness = 1200 \( \mu \text{m}, \) Circular polarisation \( \sim 98\% \)

\( e = 6.15 \text{ keV}: \) diamond thickness = 700 \( \mu \text{m}, \) Circular polarisation \( \sim 99\% \)

Batterman PRB (1992)

Handedness of circularly polarised light couples to handedness of chiral spin structures
Diffraction in Applied E&H fields

Non-resonant magnetic scattering length:

\[ f_{\sigma'} \propto S_b^M + \epsilon \alpha \gamma S_c^M \] - \[ \beta \gamma S_b^T \]

\[ f_{\pi'} \propto (\epsilon \beta \gamma)(S_b^T + L_b^T) + i(\epsilon S_b^M + \alpha \gamma S_c^M) \]

\( \alpha = \pm 1 \): selects sign of \( \tau \)

\( \beta = \pm 1 \): selects sign of \( l \)

\( \gamma = \pm 1 \): selects rcp or lcp
Polarization analysis of the scattered beam

Beam polarization characterised by Stokes Parameters ($P_1$, $P_2$, $P_3$)

Experiment determines linear parameters $P_1$ and $P_2$

\[ I(\eta) = 1 + P_1 \cos(2\eta) + P_2 \sin(2\eta) = 1 + P' \cos(2(\eta - \eta_0)) \]
Circularly polarized light and cycloidal domains

**LINEAR LIGHT**: Same scattering cross-section for the two cycloidal domains

**CIRCULAR LIGHT**: Coupling between chirality of the magnetic structure and handedness of the circular light $\rightarrow$ possible to discriminate

ex. : simple magnetic structure ; non resonant scattering

Circular right, monochiral domain

$\eta_0 \rightarrow \eta_0 + 90^\circ$

Circular left, monochiral domain

Reversing the polarisation $=$ exchanging domains
Domain populations - A-type peak

- $T=15$ K i.e. in FE phase, field cooling $-700$ V
- $E=7.5$ keV
- A-type star of wave-vectors
- Measured in $\pi'$ channel

- All 4 intensities similar for linear polarization ($\pi-\pi'$)
- $I(\varepsilon_c^+-\pi') \neq I(\varepsilon_c^-+\pi')$, complementary behaviour depending on $\pm \tau$
- Demonstrates imbalance of cycloidal domains
Stokes scans to demonstrate domain reversibility for ±E

Comparison with Kenzelmann model

- Dashed lines for Kenzelmann model – IC structure with cycloidal ordering of Mn spins rotating in bc plane + Tb moment along a
- Unsatisfactory agreement with data
New magnetic structure model

- Additional Tb spin moment component along $b$
- Plus Tb orbital moment equal in size to spin component
Cycloidal domains

- Projection of domains in \( bc \) plane with newly determined longitudinal component of Tb moment
- \( E>0 \) field cooling \( \rightarrow 96\pm3 \% \) Domain 1
- \( E<0 \) field cooling \( \rightarrow 93\pm2 \% \) Domain 2
- Absolute measurement of sense of rotation (chirality)
X-ray absorption edges

Absorption cross-section scales as

\[ \sigma_{abs} \propto (\hbar \omega)^{3} Z^{4} \]

Absorption coefficient \( \mu \) defined by

\[ I = I_{0}e^{-\mu z} \]

In general x-ray scattering length is

\[ f(Q, \hbar \omega) = f_{0}(Q) + f' + if'' \]

\[ f'' = -\left( \frac{k^{2}}{2\pi \rho_{a} r_{0}} \right) \frac{\mu}{2k} \]

Absorption is proportional to imaginary part of the forward scattering amplitude.
X-ray Resonant Magnetic Scattering

"Interesting magnetic effects might occur near an absorption edge" Blume (1985)

X-ray Resonant Magnetic Scattering from Nickel
Namikawa (1985)

(1985) First Resonant Scattering from a Ferromagnet
Large enhancement of XMRS at L edges of Holmium

• 100 fold increase when tuned to the L₃ edge

• Two distinct types of transition are observed: one above and one below the edge

• Higher order satellites up to 4th order

• Polarization state changes with order
  1⁺: rotated, σ→π'
  1⁻: unrotated, σ→σ'

• Signal disappears at Tₙ

• Peaks arise from transitions to bound states
  1⁺: 2p → 5d Dipole
  1⁻: 2p → 4f Quadrupole

XRMS is Born: A New Element and Electron Shell Sensitive Probe!

Gibbs, Harshman, Isaacs, McWhan, Mills and Vettier (1988)
XRMS from Actinides

Resonant Scattering Study of UAs
McWhan, Vettier, Isaacs et al., (1990)

- 10^7 fold increase when tuned to the M_4 edge of U
- Magnetic peak ~1% of Charge peak!
- Fit to sum of three coherent dipole oscillators
- Single Dipole transition at each edge: 3d->5f
- Polarization analysis: rotated \( \sigma \rightarrow \pi' \)
X-ray Dichroism

Preferential absorption of one of two orthogonal photon polarization state

(a) Simplified energy level diagram

2p, $\ell = 1$

2s, $\ell = 0$

$\Delta m = 1$

1s, $\ell = 0$

Right Circular Polarised: $J_z = +1$

|0, 0$\rangle$

$\Delta m = -1$

|1, 0$\rangle$

|1, -1$\rangle$

(b) Normal XMCD geometry

Photon

Atom

parallel

antiparallel

Iron thin films, Chen et al. PRL (1995)