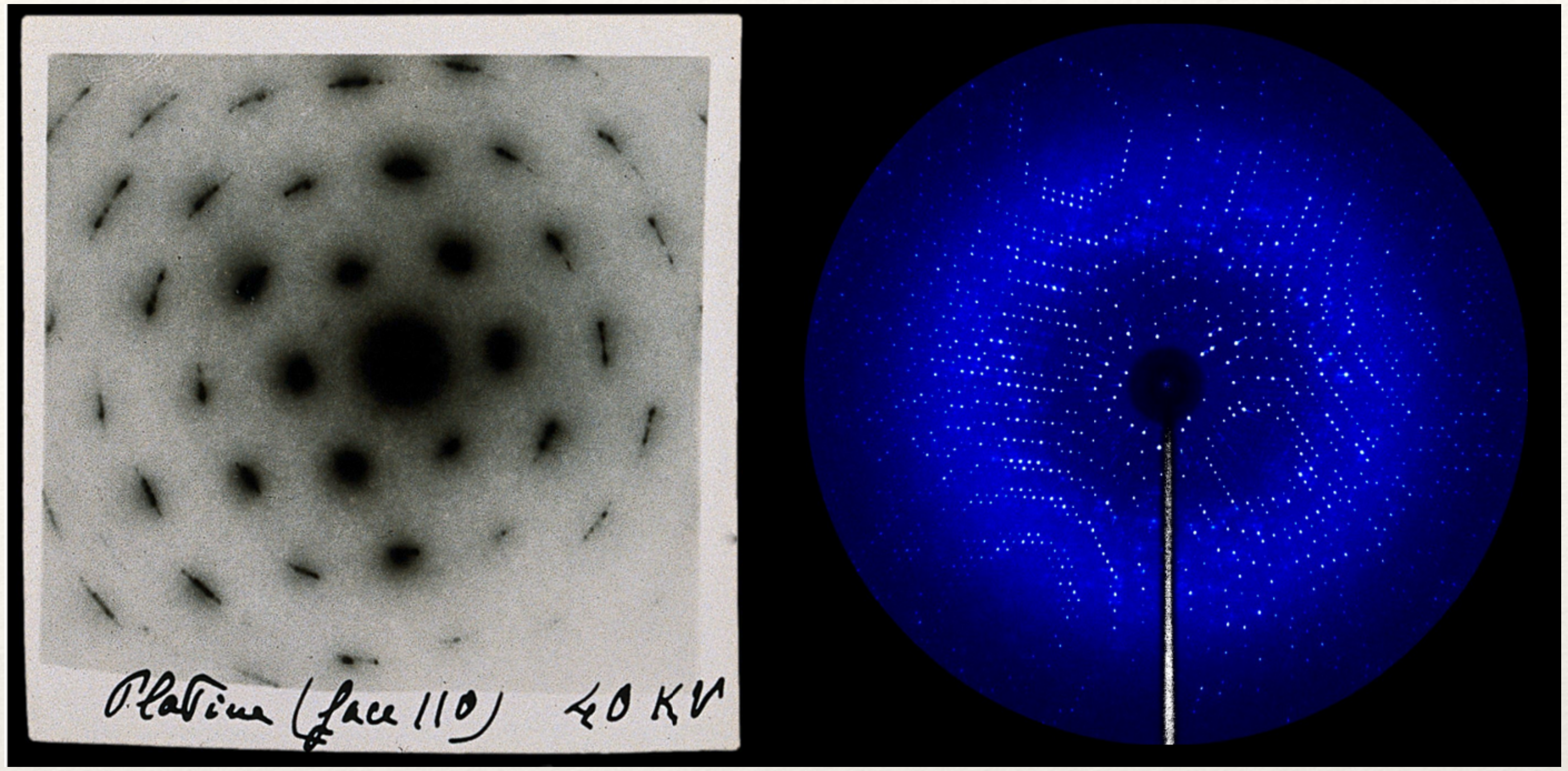

Structure of Solids - X-ray diffraction Studies

Lecture 4

CHM 637
Chemistry & Physics of Materials

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Lecture Plan

- Introduction to X-rays and diffraction
- Basics of Elastic Scattering
- Interaction of an electron with X-rays
- Bragg’s formulation of X-ray diffraction by crystals

Introduction to X-rays and diffraction

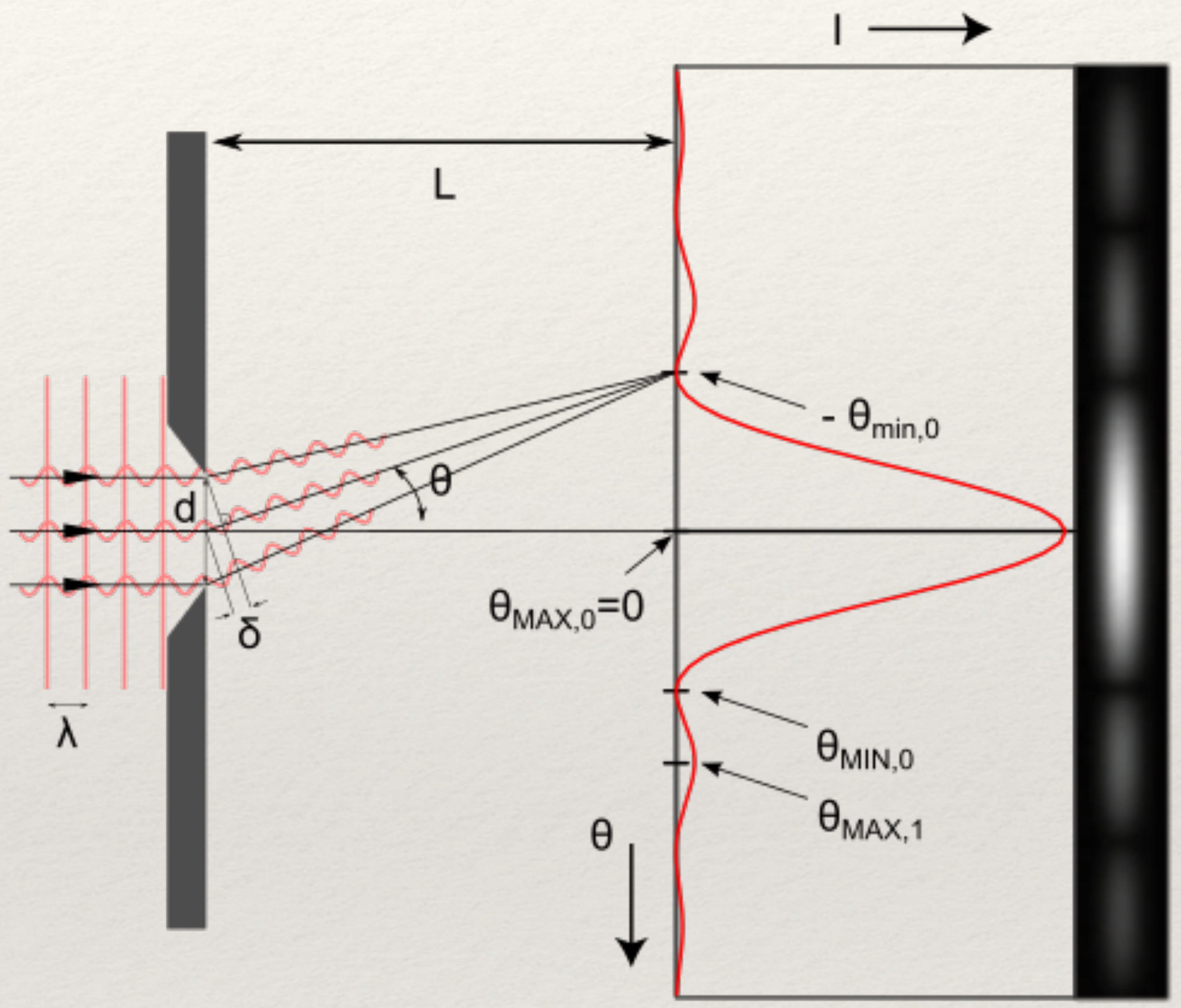
Diffraction

Phenomenon in which light waves bend at obstacles or slits.

Can be understood using the Huygens-Fresnel principle (secondary wavelets originating from each point along the obstacle/slit.

The secondary wavelets superpose to yield interference patterns on a screen.

Location of first minimum $\quad d \sin \theta_{min} = \lambda$



Source: Wikipedia

Introduction to X-rays and diffraction

Diffraction

If there is a regular array of slits then the diffracted waves at each slit superpose with each other to yield an interference pattern.

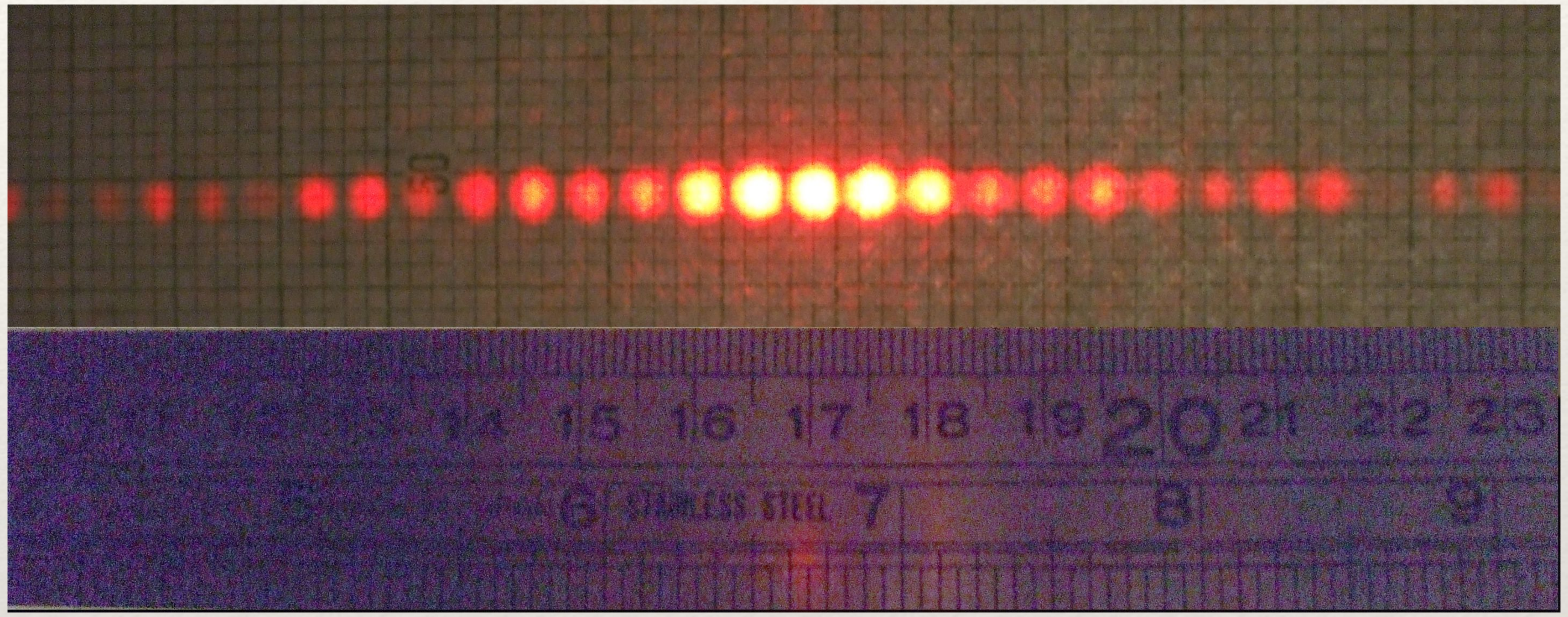
Location of maxima
(at normal incidence)

$$d \sin \theta_m = m\lambda$$

Where m is any integer

Intensity of the maxima is highest at the central peak.

Observation of diffraction effects require $d \approx \lambda$



Source: Wikipedia

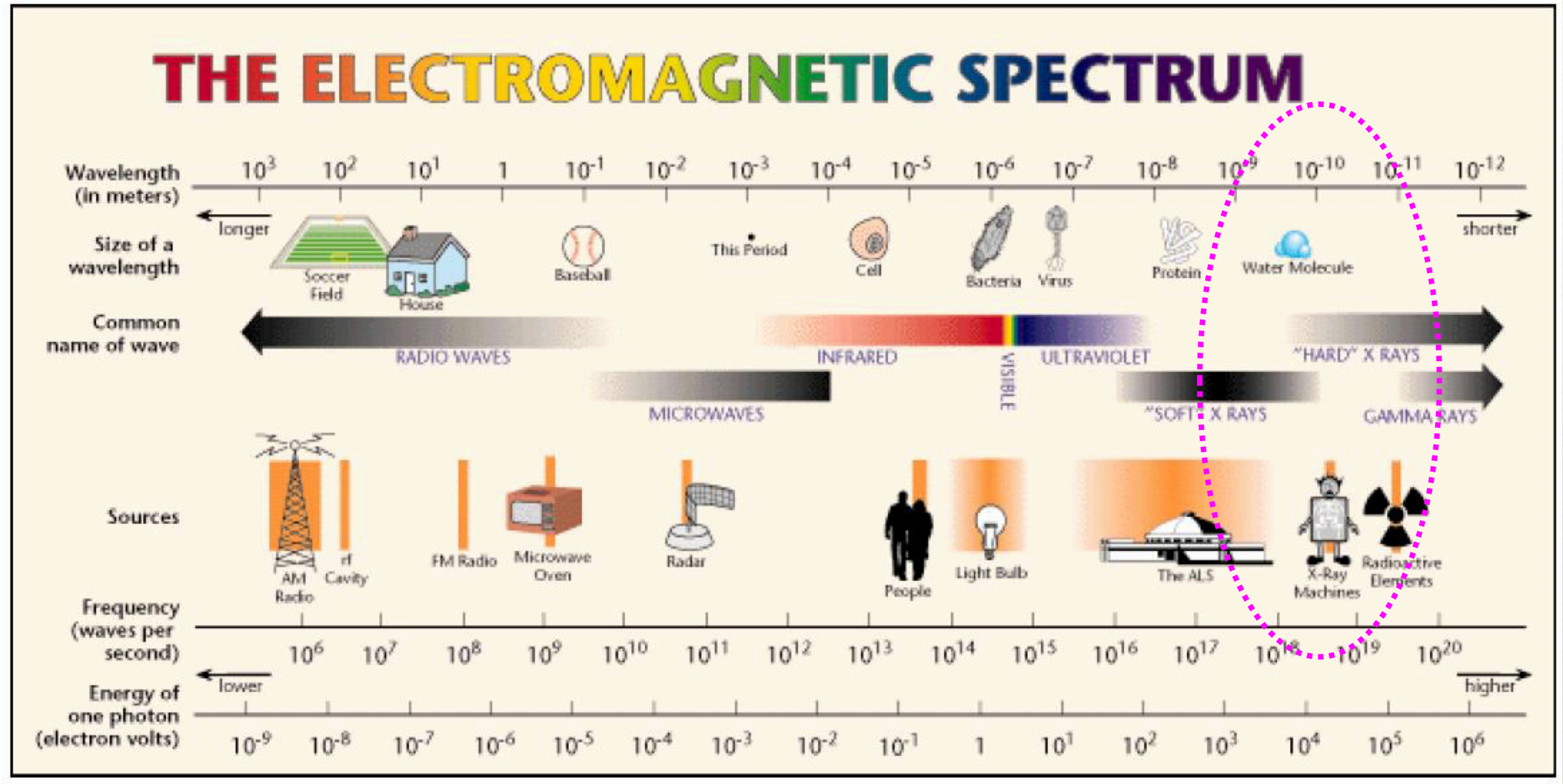
Introduction to X-rays and diffraction

X-rays

Electromagnetic radiation with wavelength in the range 100 to 0.01 Å (100 eV - 1 MeV).

For XRD we are interested in X-rays with wavelengths ~ 1 Å (around 10 KeV).

X-rays can ionise matter, photo-excite core electrons, inelastically scatter from loosely bound electrons (Compton effect) and get diffracted from crystals.



Source: Elena Willinger' Lectures (FHI)

X-rays can penetrate bulk of crystals and hence can probe crystal structure.

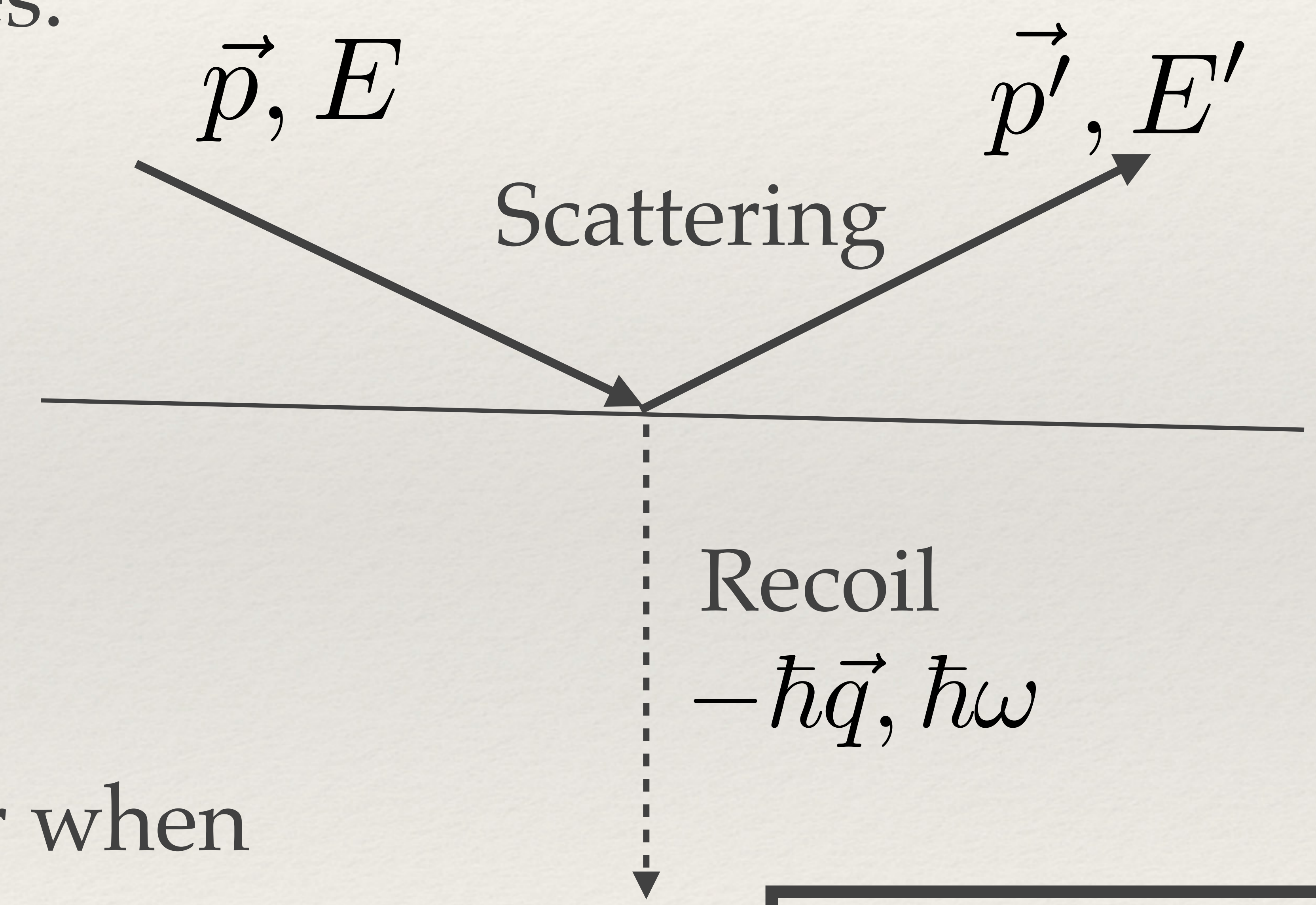
Introduction to X-rays and diffraction

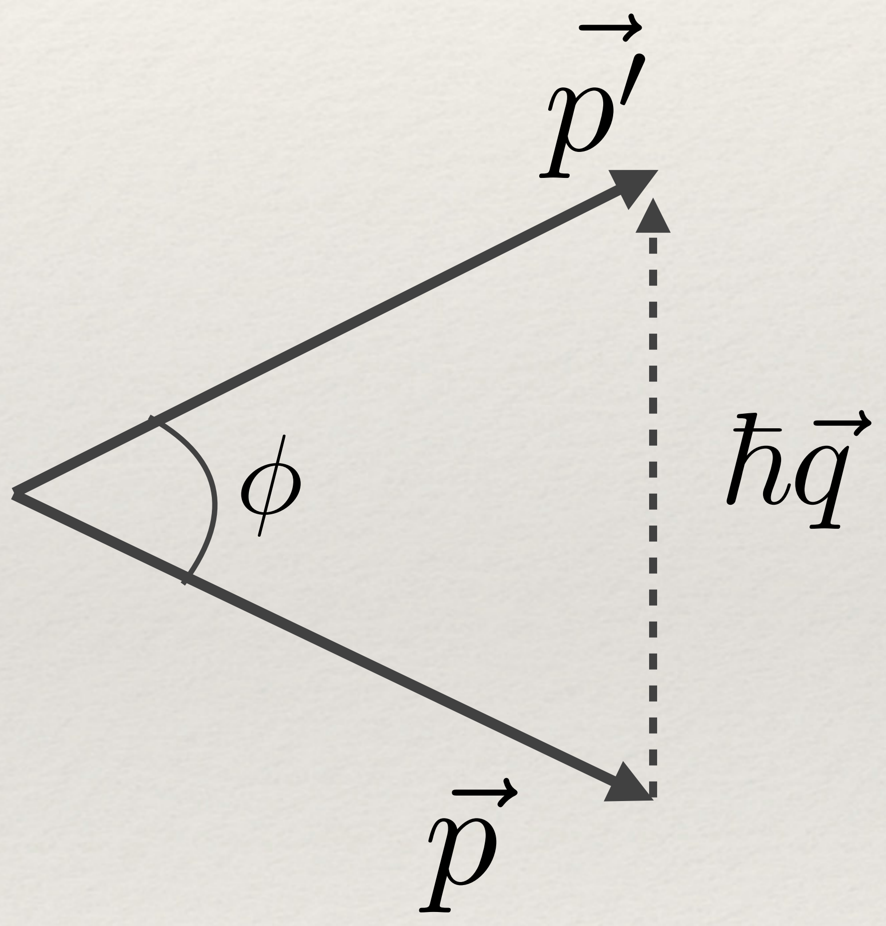
Elastic scattering of X-rays

A general scattering event between a projectile and a scatterer can affect the momentum and energy of the projectile particles.

$$\vec{p'} - \vec{p} = \hbar\vec{q}$$

$$E' - E = \hbar\omega$$





Elastic scattering is said to occur when

$$E' - E = 0$$

It is straightforward to show that in this condition

$$\boxed{q = \frac{2p}{\hbar}\sin\left(\frac{\phi}{2}\right)}$$

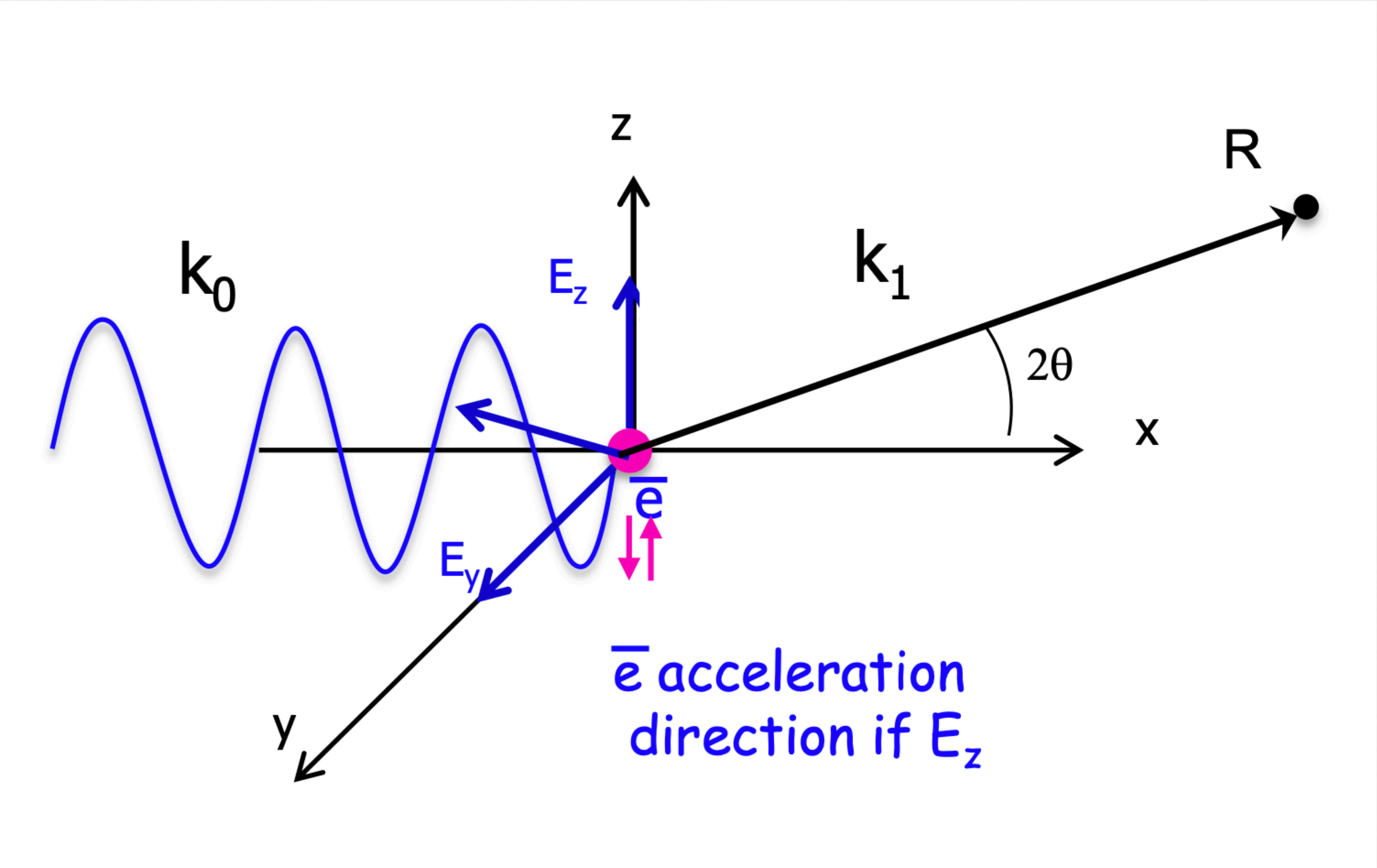
Interaction of electrons with X-rays

Elastic scattering of X-rays

X-rays interact with electrons in crystals and get scattered. The elastically scattered part (i.e. with no change in wavelength) is measured to yield crystal structure

The oscillating electric field of X-rays induces oscillations in bound electrons of same frequency.

This oscillation charge then radiates to yield the scattered X-rays.



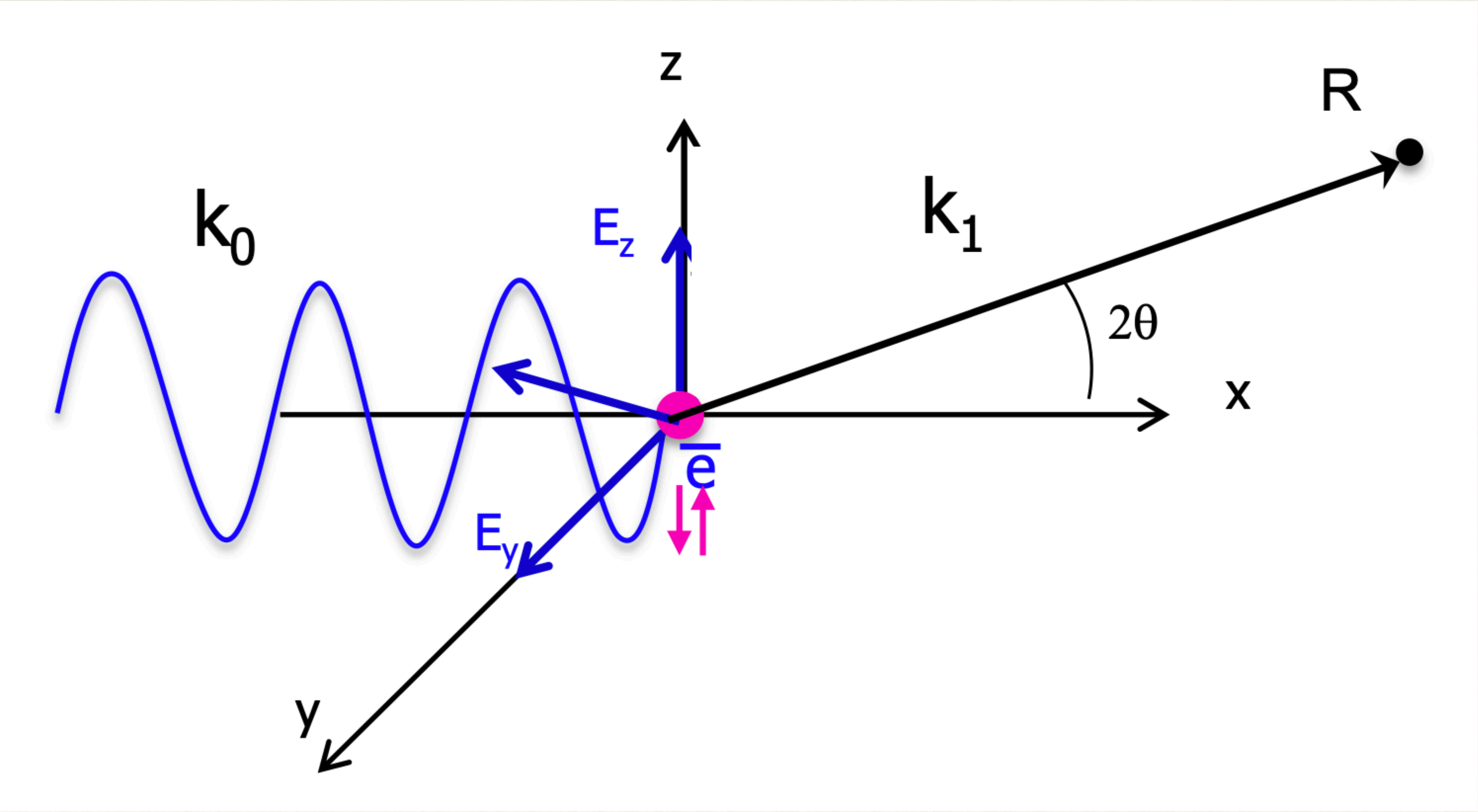
Source: Elena Willinger' Lectures (FHI)

Assuming a classical picture, we can work out a relation for the scattered intensity.

Interaction of electrons with X-rays

Thomson scattering formula

Consider an electron subject to e-m wave interacting with it through its electric field.



Source: Elena Willinger' Lectures (FHI)

Assuming linearly polarised field

$$-e\ E_z\hat{k}\ \sin(\omega t) = m\vec{a}(t)$$

$$\Longrightarrow\ \vec{a}(t) = -\frac{e}{m}E_z \sin(\omega t)\hat{k}$$

An accelerating charge emits radiation. The electric field strength is given by the Larmor formula.

Interaction of electrons with X-rays

Larmor's (Radiation) Formula

The total energy radiated per unit time per unit solid angle by an accelerating charge is given by

$$\frac{dP}{d\Omega} = \frac{e^2 a^2(t)}{16\pi^2 \epsilon_0 c^3} \sin^2\theta$$

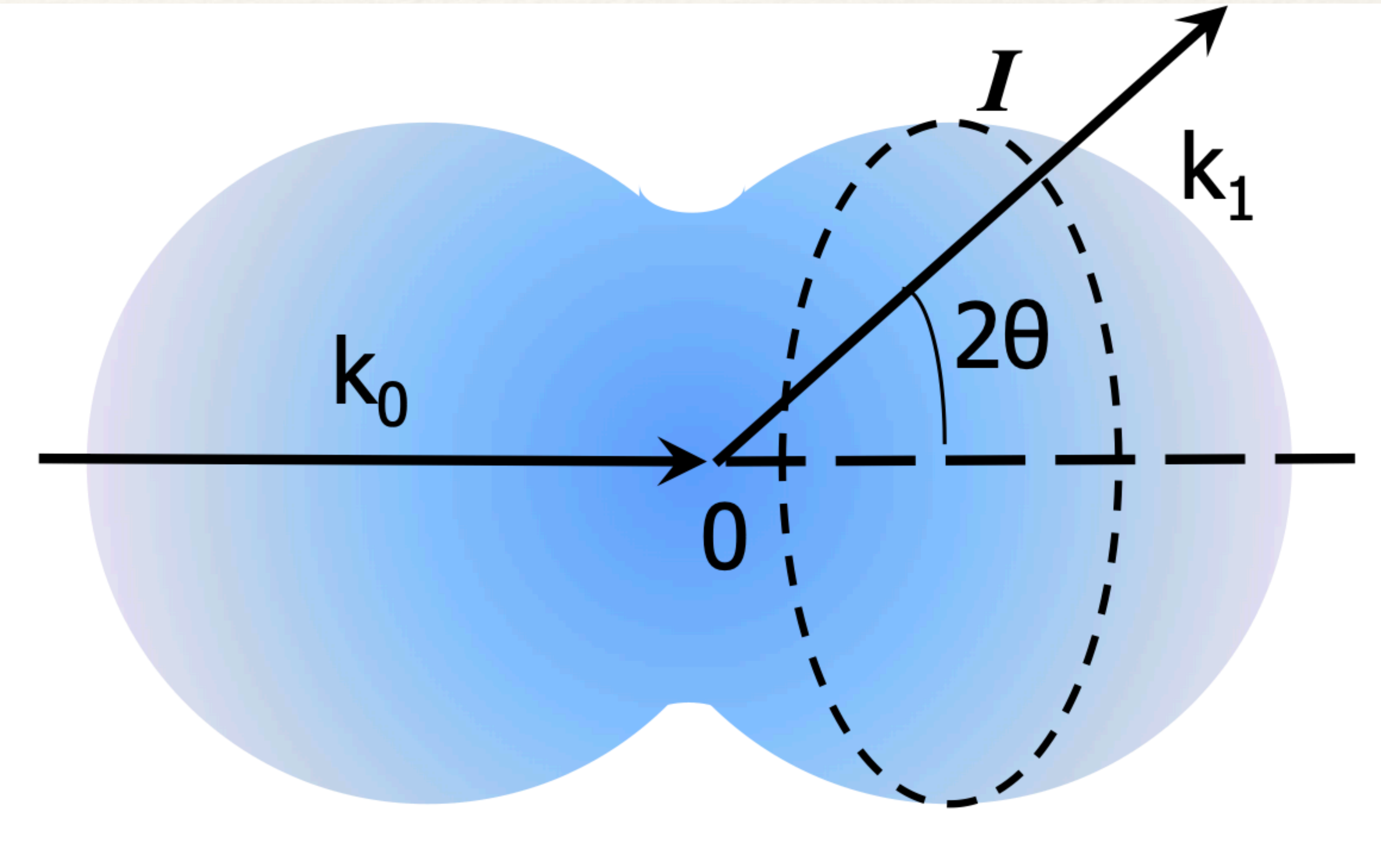
Where $a(t)$ is the acceleration and the angle between the incident polarisation and re-radiated beam is θ

Interaction of electrons with X-rays

Thomson scattering formula

The ratio of the time-averaged (over a time period of e-m wave) scattered power and the incident intensity is defined as the **scattering cross section**.

$$\boxed{\sigma = \frac{\langle P \rangle}{\langle I_0 \rangle} = \frac{8\pi}{3} r_0^2} \qquad r_0 = \frac{e^2}{4\pi\epsilon_0 mc^2}$$



Source: Elena Willinger' Lectures (FHI)

Bringing back the directional dependence of the emitted radiation and averaging over incident polarisation we can also define the differential cross section as

$$\boxed{\frac{d\sigma}{d\Omega} = \frac{r_0^2}{2}\left(1 + \cos^2 2\theta\right)}$$

Note: Here the angle here refers to the scattering geometry

References

Physics and Chemistry of Materials (Textbook for course)

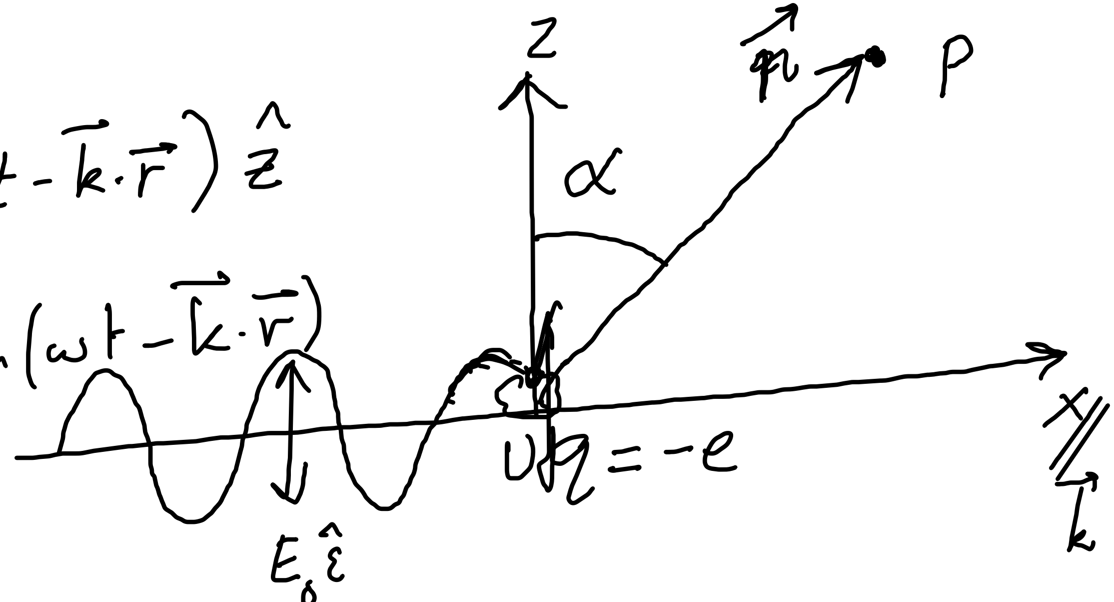
Introduction to Electrodynamics D. J. Griffiths

Elena Willinger's Lectures at FHI (*Fundamentals of X-ray Diffraction*, 2014-15 Winter)

Other links … please check course website

Derivation of the Thomson Scattering formula

$$\vec{E}(\vec{r}, t) = E_0 \sin(\omega t - \vec{k}\cdot\vec{r})\,\hat{z}$$



Generally: $\vec{E} = E_0 \hat{\varepsilon} \sin(\omega t - \vec{k}\cdot\vec{r})$

$\hat{\varepsilon} = \hat{z}$, $\vec{k} = k\,\hat{x}$

$$\boxed{\vec{F}(t) \simeq q\vec{E}(t) = m\vec{a}(t)} \quad \text{— (1)}$$

$\hat{\varepsilon}\cdot\vec{k} = 0$ for an e.m. wave

$$\vec{a}(t) = \frac{q E_0 \hat{z} \sin(\omega t)}{m} \quad \text{— (2)}$$

$\ddot{}$

Larmor formula:

$$\frac{dP}{d\Omega} = \frac{q^2 \langle a^2(t) \rangle}{16\pi^2 \epsilon_0 c^3} \sin^2\alpha \quad \text{--- (3)}$$

$\alpha \rightarrow$ angle between the out-going radiation & the direction of acceleration of the particle

For our case $\therefore$ $\vec{a} \parallel \vec{E}$ ie $\vec{a} \parallel \hat{z}$

$\langle \ldots \rangle \longrightarrow$ time average over a period of the e-m wave T

$$= \frac{1}{T} \int_0^T dt \ldots$$

$$\langle a^2(t)\rangle = \frac{q^2}{m^2} E_0^2 \langle \sin^2(\omega t)\rangle$$

$$\langle \sin^2(\omega t)\rangle = \frac{1}{T}\int_0^T dt\, \sin^2(\omega t) \qquad \omega = 2\pi/T$$

$$= \frac{q^2 E_0^2}{2m^2} \qquad (4)$$

Substitute (4) in (3)

The time-averaged scattered power per unit solid angle is:

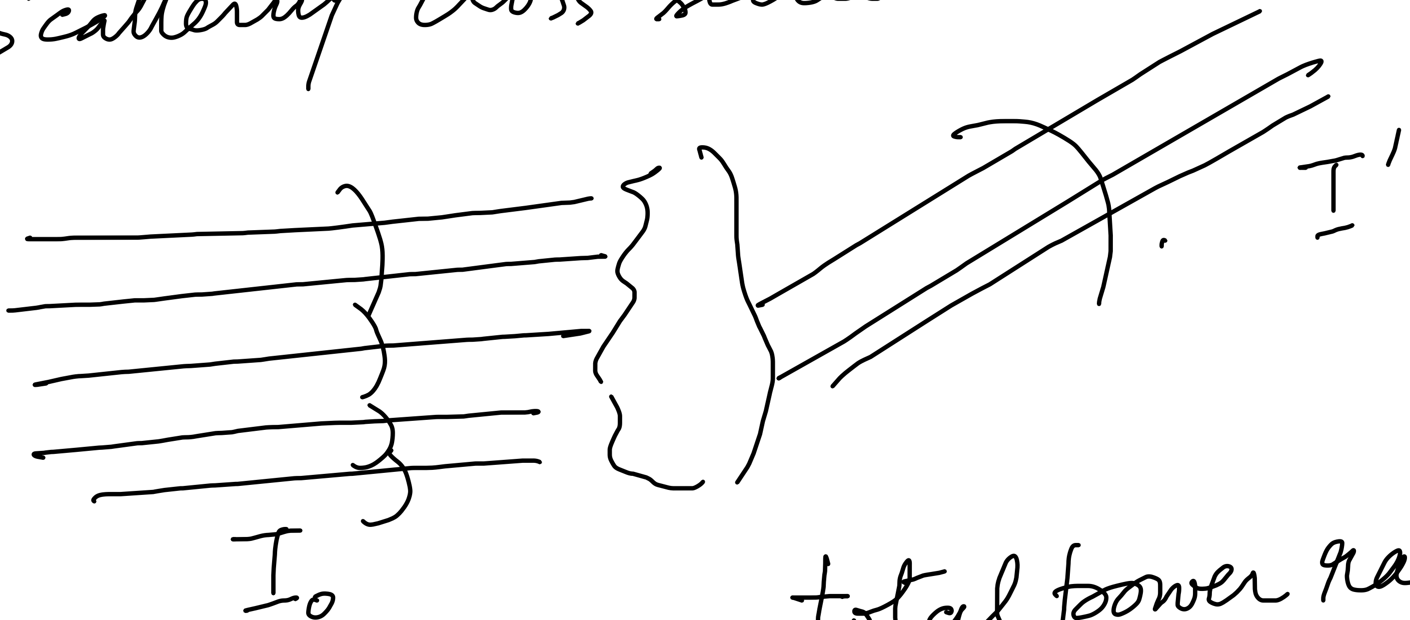
$$\boxed{\frac{dP}{d\Omega} = \left(\frac{q^2}{4\pi\epsilon_0 mc^2}\right)^2 \frac{\epsilon_0 c E_0^2}{2}\left(\sin^2\alpha\right)} \qquad (5)$$

Time-averaged intensity of X-rays incident on the electron:

$$\langle I \rangle = \langle u \rangle \times c \qquad \left(\sim W/m^2\right)$$

$$= \frac{\epsilon_0 c E_0^2}{2} \quad \text{—} \quad (6)$$

Scattering cross section



$$\sigma = \frac{\text{total power radiated}}{\text{time-averaged incident intensity}}$$

$$= \langle P \rangle / \langle I \rangle . \quad \text{--- (7)}$$

$\frac{d\sigma}{d\Omega}$ = differential cross section

$$= \frac{\langle dP/d\Omega \rangle}{\langle I \rangle}$$

$$= \frac{\left(\frac{q^2}{4\pi\epsilon_0 m c^2}\right)^2 \left(\frac{\epsilon_0 c \cancel{E_0^2}}{\cancel{2}}\right)^2 \sin^2\alpha}{\left(\frac{\epsilon_0 c \cancel{E_0^2}}{\cancel{2}}\right)}$$

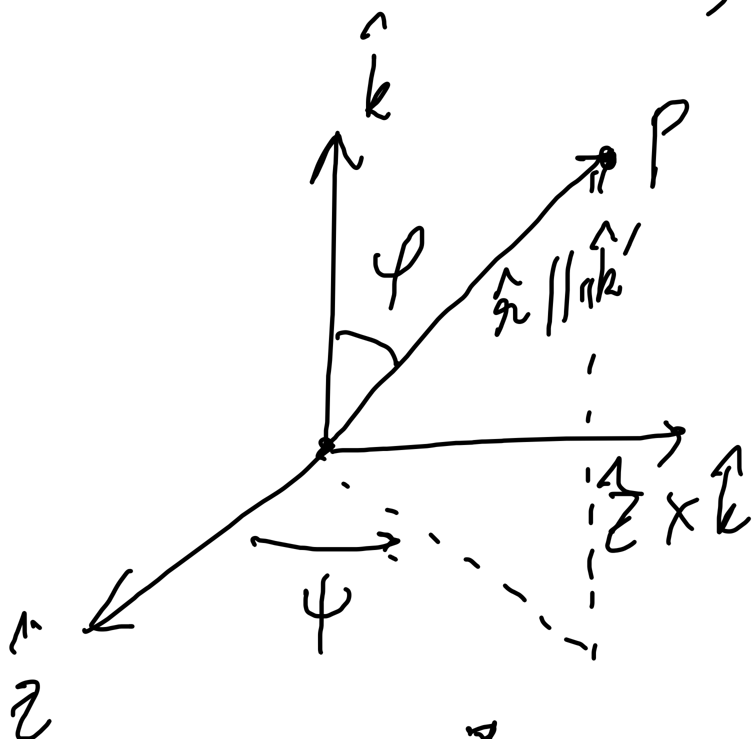
$$= \left(\frac{q^2}{4\pi\epsilon_0 m c^2}\right)^2 \sin^2\alpha \quad \text{— } 8$$

$$\sigma = \int_0^{2\pi} d\varphi \int_0^{\pi} \frac{d\sigma}{d\Omega} \times 2\pi \times \sin\alpha \, d\alpha$$

$$= \frac{8\pi}{3} \left(\underbrace{\frac{q^2}{4\pi\epsilon_0 m c^2}}_{\to\, r_0} \right)^2 \tag{9}$$

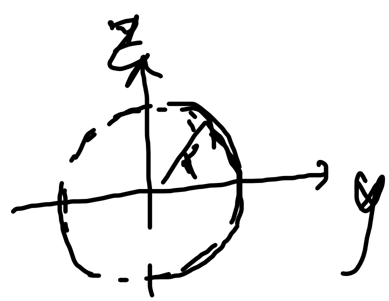
$$\cos\alpha = \hat{r} \cdot \hat{z} \tag{10}$$

Assume a right-handed system of axes along $\hat{z}$, $\hat{z}\times\hat{k}$ & $\hat{k}$,



$\hat{r}$ is also the scattered direction & therefore $\parallel$ to $\hat{k}'$

$\psi \rightarrow$ orientation of the incident polarizn. in the plane $\perp$ to $\hat{k}$



$$\hat{n} = \sin\varphi\cos\psi\,\hat{z} + \sin\varphi\sin\psi\,(\hat{z}\times\hat{k}) + \cos\varphi\,\hat{z} \quad \text{--- } (11)$$

$$\cos\alpha = \hat{n}\cdot\hat{z}$$

$$= \sin\varphi\cos\psi \quad \text{--- } (12)$$

$$\left(\frac{d\sigma}{d\Omega}\right)_{\substack{\text{non-}\\ \text{polarized}}} = \left(\frac{q^2}{4\pi\epsilon_0 mc^2}\right)^2 \overline{\sin^2\alpha}$$

$$= \left(\frac{q^2}{4\pi\epsilon_0 mc^2}\right)^2 \overline{\left(1-\cos^2\alpha\right)} \quad \text{--- } (13)$$

$$\overline{1 - \cos^2\alpha} = 1 - \overline{\sin^2\varphi \cos^2\psi}$$

$$= 1 - \sin^2\varphi \int_0^{2\pi} \cos^2\psi \, d\psi$$

$$= 1 - \frac{\sin^2\varphi}{2}$$

$$= \left(\frac{1 + \cos^2\varphi}{2}\right) \quad \text{—} \quad (14)$$

$$\therefore \left(\frac{d\sigma}{d\Omega}\right)_{non-pol} = \left(\frac{q^2}{4\pi\epsilon_0 mc^2}\right)^2 \left(\frac{1+\cos^2\varphi}{2}\right)$$

$\varphi \longrightarrow$ scattering angle

$$\cos\varphi = \hat{k}\cdot\hat{r} = \hat{k}\cdot\hat{k}'$$

$$\underline{\underline{\varphi = 2\theta}}$$