

Summary : First Lecture

- When a polarized X-ray strikes an electron, the time dependent electric field associated with that wave creates a time dependent electric force which forces the electron into oscillation. The acceleration/deceleration of the electron induces an electromagnetic wave (the scattered wave). This scattered wave is spherical and has the same wavelength as the incident wave. This is what is called Thompson scattering. The amplitude of the scattered wave at a distance r from the electron is given by:

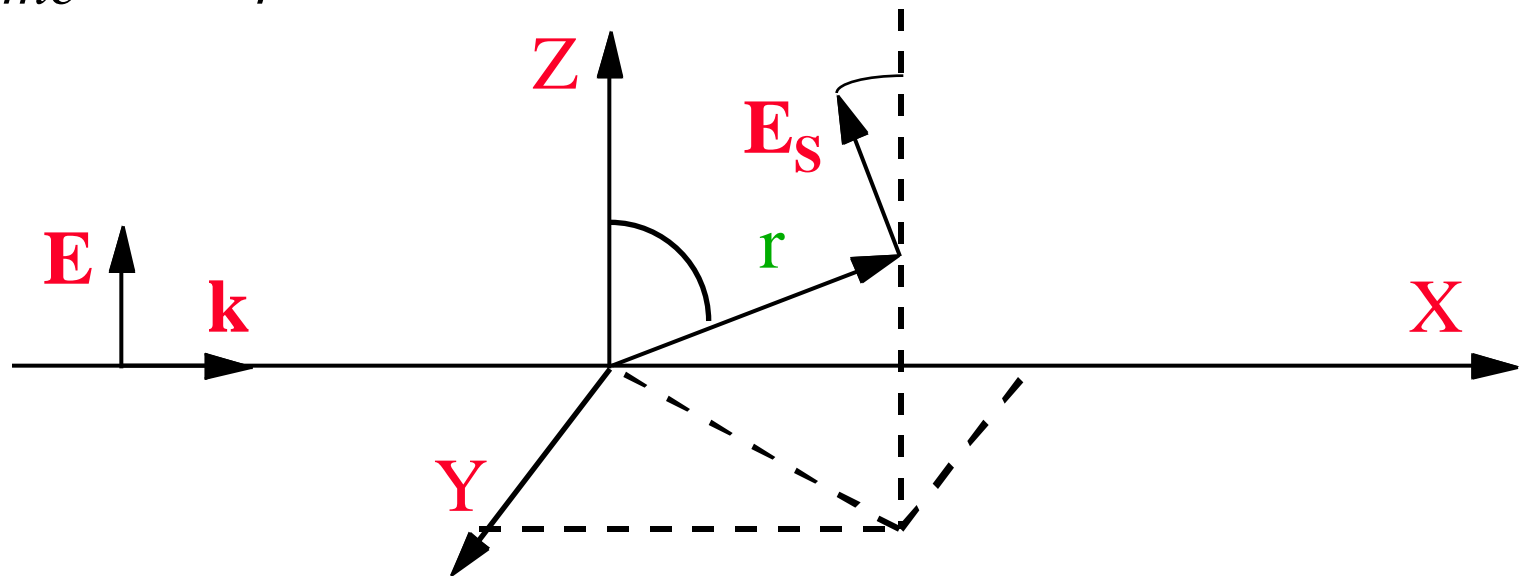
$$|\vec{E}_s| = |\vec{E}_0| \frac{e^2}{mc^2} \frac{1}{r}$$

The intensity of the wave (i.e. the energy passing through a unit area per unit time) is proportional to the square of the amplitude of the wave:

$$I_s = I_0 \frac{e^2}{mc^2}^2 \frac{1}{r^2}$$

- Since the scattered waves are spherical, the electric field vectors for the incident and scattered waves \mathbf{E} and \mathbf{E}_S are only parallel when the point at which the scattered intensity measured by a detector parallel to the z-axis, lies in the (XY) plane. The component of the wave amplitude measured by a detector is then generally $\vec{E}_S = |\vec{E}_S| \cos\psi = |\vec{E}_S| \sin\phi$ and the measured scattering intensity is given by:

$$I_S = I_0 \frac{e^2}{mc^2} \frac{\sin^2 \phi}{r^2}$$



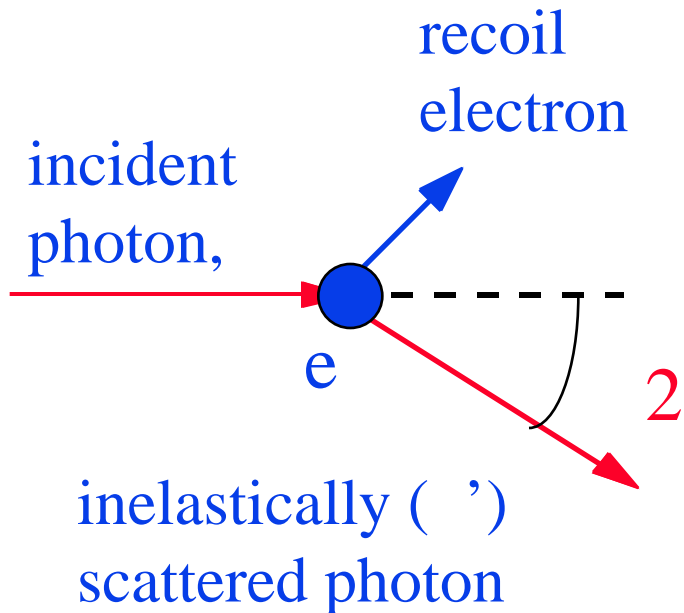
- We usually deal with unpolarized x-ray radiation and must therefore consider that the incident waves have an equal probability of being polarized in the Z and Y directions. This leads us to the following expression for the intensity scattered by one electron and measured at a distance r of the electron:

$$I_S = I_0 \frac{e^2}{mc^2} \frac{\sin^2 \phi + \sin^2 \phi'}{r^2}$$

where 2θ is the scattering angle (angle between the directions of the incident and scattered waves).

The above treatment only corresponds to the **Tompson scattering**.

- The **Compton scattering** arises from the “particle” nature of the X-ray photons (momentum: h/c). Momentum is transferred from the photon to the electron during the inelastic collision and part of the incident radiation is converted to lower energy (i.e. longer wavelength) radiation.



$$\lambda' - \lambda = \frac{2h}{mc} \sin^2 \theta$$

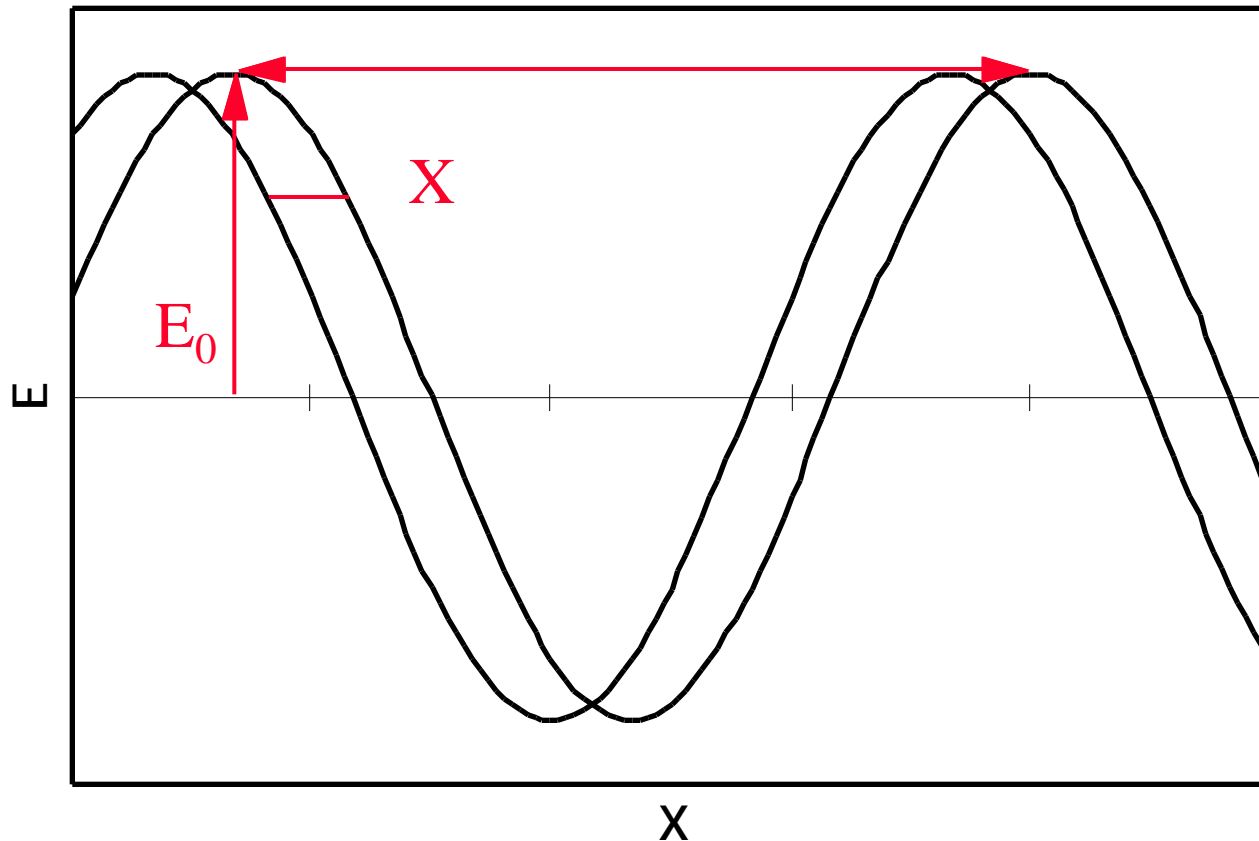
$$\lambda' - \lambda = 0.024(1 - \cos 2\theta)$$

The **Compton** scattering accounts for only a few percents of the **Tompson** scattering. Also note that at $2\theta = 0$, there is no Compton scattering.

Tompson scattering: the incident radiation behaves as a broad-fronted wave stimulating oscillations in many widely separated electrons, inducing many secondary waves. Since these secondary waves are all produced by the same primary wave, there is a relationship between the phases of the secondary waves and interference can occur which leads to the diffraction effect.

Compton Scattering: Independent collisions between photons and electrons implies no phase relationship between them, thus no interference effect and no diffraction. When analyzing X-ray intensities for structural purpose, the contribution from Compton effect must be removed.

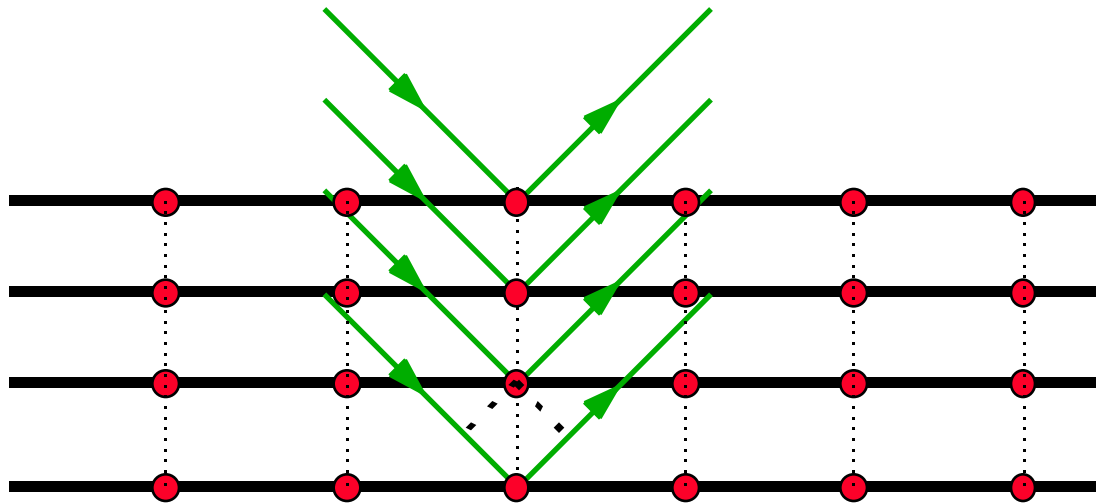
Phase Difference Between Waves



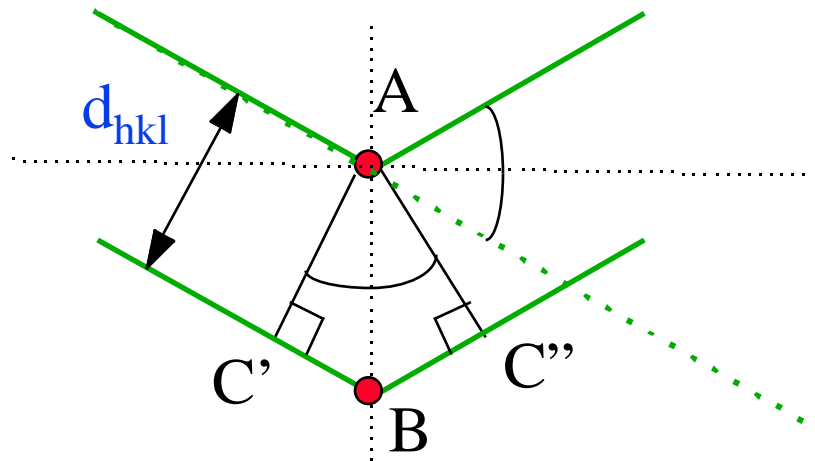
wave given by:
 $\cos(2\pi (X/\lambda))$ or
 $\cos(\mathbf{k}\cdot\mathbf{X})$ or
 $\exp(i\mathbf{k}\cdot\mathbf{X})$

X is the wave displacement, E_0 the amplitude, λ the wavelength
 $2\pi (X/\lambda)$ is the phase difference between the waves

Bragg's Law of Reflection



The path difference between waves reflected by successive planes is $2d\sin\theta$. If this is a multiple of the wavelength of the wave then constructive interference occurs which leads to diffraction



$$\sin\theta = BC' / d_{hkl} = BC'' / d_{hkl}$$

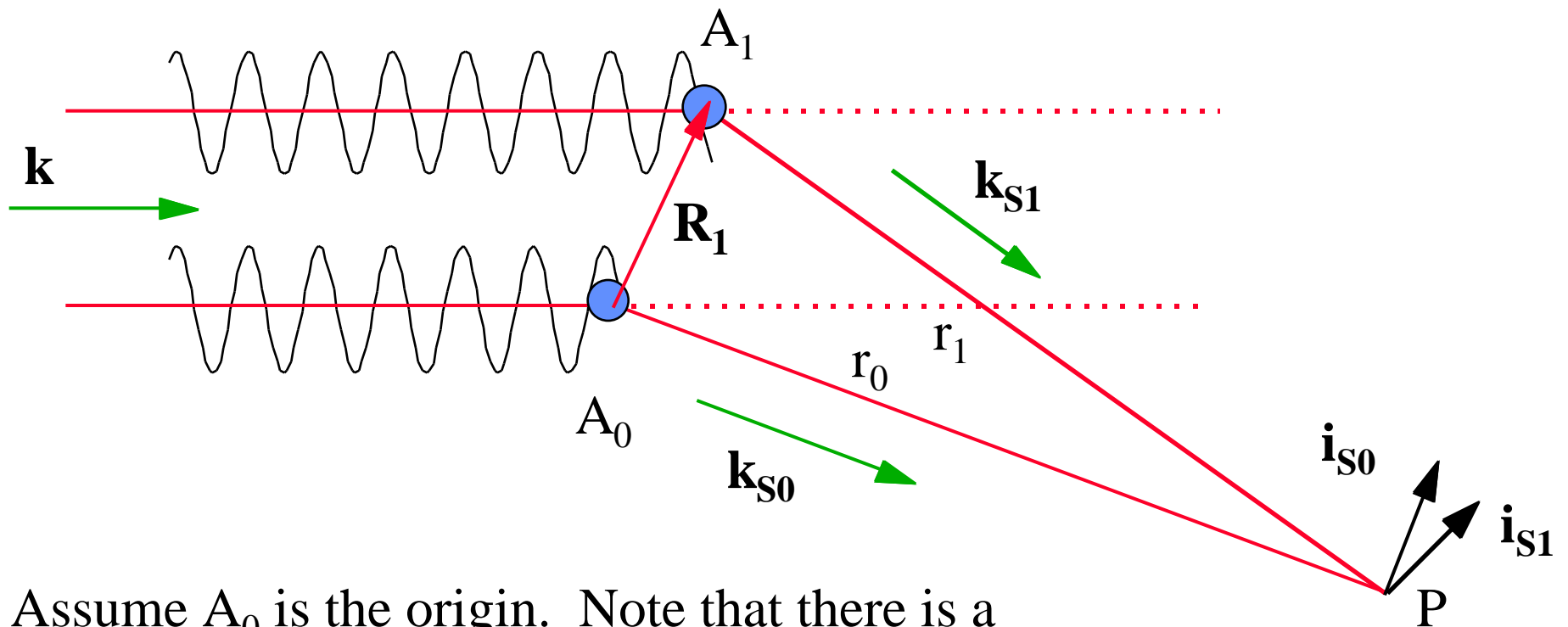
$$\text{path difference} = BC' + BC''$$

$$2 d_{hkl} \sin\theta = n$$

Interference Between Two Scattered Waves

Incident wave: $\vec{E} = \vec{E}_0 e^{i(\vec{k} \cdot \vec{r}_0)}$

Scattered wave from electron at A_0 : $\vec{E}_{s0} = |\vec{E}_0| \frac{e^2}{mc^2} \frac{1}{r_0} e^{i((\vec{k}_{s0} \cdot \vec{r}_0) + \pi)} \vec{i}_{s0}$



Assume A_0 is the origin. Note that there is a 180° phase change between incident and scattered waves at each scattering event

where the net scattering is measured

Scattered wave from electron at A_1 : $\vec{E}_{S1} \equiv |\vec{E}_0| \frac{e^2}{mc^2} \frac{1}{r_1} e^{i((\vec{k}_{S1} \cdot \vec{r}_1) + \pi + \delta_1)} \vec{i}_{S1}$

where: δ_1 accounts for the phase change at the time of scattering
 r_1 accounts for the fact that the incident wave arrives at A_1 later than at A_0 . (the phase difference between the incident wave at A_0 and A_1 is: $\frac{2\pi}{\lambda} |A_1 - A_0| = \vec{k} \cdot \vec{R}_1 = \vec{k} \cdot (\vec{r}_0 - \vec{r}_1)$)

Since the sample to detector distance (r in centimeters) is much larger than the distance between electrons (Angstroms) then:

$$\vec{E}_{S1} \parallel \vec{E}_{S0} \text{ and } \vec{i}_{S1} \parallel \vec{i}_{S0} \quad |\vec{E}_{S1}| + |\vec{E}_{S0}| = |\vec{E}_{ST}|$$

$$\frac{1}{r_1} \quad \frac{1}{r_0} \quad \frac{1}{r}$$

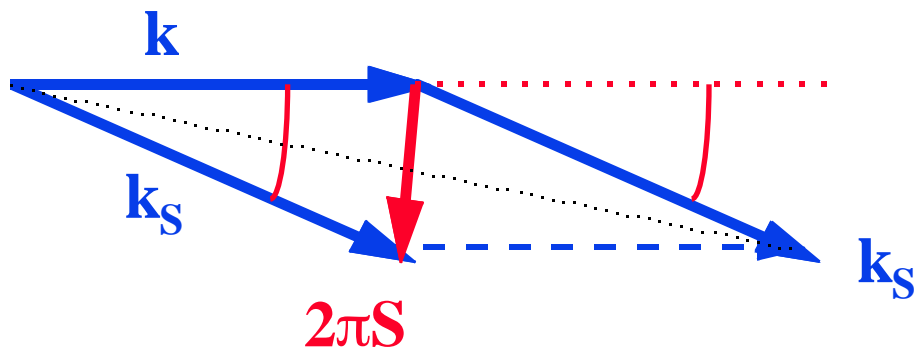
Thus:
$$\vec{E}_{ST} = |\vec{E}_0| \frac{e^2}{mc^2} \frac{1}{r} \left[e^{i((\vec{k}_{S0} \cdot \vec{r}_0) + \pi)} + e^{i((\vec{k}_{S1} \cdot \vec{r}_1) + \pi + \vec{k} \cdot (\vec{r}_1 - \vec{r}_0))} \right] \vec{i}_S$$

$$\vec{E}_{ST} = -|\vec{E}_0| \frac{e^2}{mc^2} \frac{1}{r} \left[e^{i(\vec{k}_S \cdot \vec{r}_0)} \right] \left[1 + e^{-2\pi i \vec{S} \cdot \vec{R}_1} \right] \vec{i}_S$$

where: $2\pi\vec{S} = \vec{k}_S - \vec{k}$ the scattering vector

is of magnitude $|\vec{S}| = \frac{2}{\lambda} \sin\theta$

$$\sin \frac{2\theta}{2} = \frac{\left| \frac{2\pi\vec{S}}{2} \right|}{|\vec{k}|} \quad |\vec{S}| = \frac{2}{\lambda} \sin\theta$$



For a set of N+1 electrons located at positions $A_0, A_1, A_2, \dots, A_N$, the net electric field \mathbf{E}_{ST} resulting from interference of the N+1 waves will be:

$$\vec{E}_{ST} = -|\vec{E}_0| \frac{e^2}{mc^2} \frac{1}{r} \left[e^{i(\vec{k}_S \cdot \vec{r}_0)} \right]_{j=0}^{j=N} e^{-2\pi i \vec{S} \cdot \vec{R}_j} \vec{i}_S$$

\vec{R}_j is the vector linking points A_0 and A_j

Note that the path difference between waves passing through A_0 and A_j is $2 \mathbf{S} \cdot \mathbf{R}_j$. The resulting intensity measured at the scattering angle 2θ from the transmitted beam will be:

$$I_{ST} = I_0 \frac{e^2}{mc^2}^2 \frac{1}{r^2} \left[e^{-2\pi i \vec{S} \cdot \vec{R}_j} \right]_{j=0}^{j=N} \left[e^{-2\pi i \vec{S} \cdot \vec{R}_k} \right]_{k=0}^{k=N}$$

Note that scattered waves originating from different electrons have the same scattering vector \mathbf{S} (same \mathbf{k} and \mathbf{k}_s) but have different phases ($2\mathbf{S}\cdot\mathbf{R}_j$). When they overlap, they will give rise to different kinds of interferences (some constructive, some destructive). The net wave amplitude will depend on:

- The direction in which the scattering intensity is recorded (\mathbf{S} , θ)
- The relative location of the scattering centers
- The distance between scattering centers and the detector

Application of the above concept to the scattering from the individual electrons in a given atom is then straightforward: The electron position is defined through quantum mechanics by the probability distribution function $\rho_a(\mathbf{r})$ or what we will call the electron density in the atom $\rho_a(x,y,z)$.

We replace the discrete sum by , a continuous sum.

We then denote the scattering by the electrons from one atom as the atomic structure factor (also called the atomic scattering power, the atomic scattering amplitude or the atomic form factor).

$$f_a = \int_{\text{atomic volume}} \rho_a(x, y, z) \exp(-2\pi i \vec{S} \cdot \vec{R}) dx dy dz$$

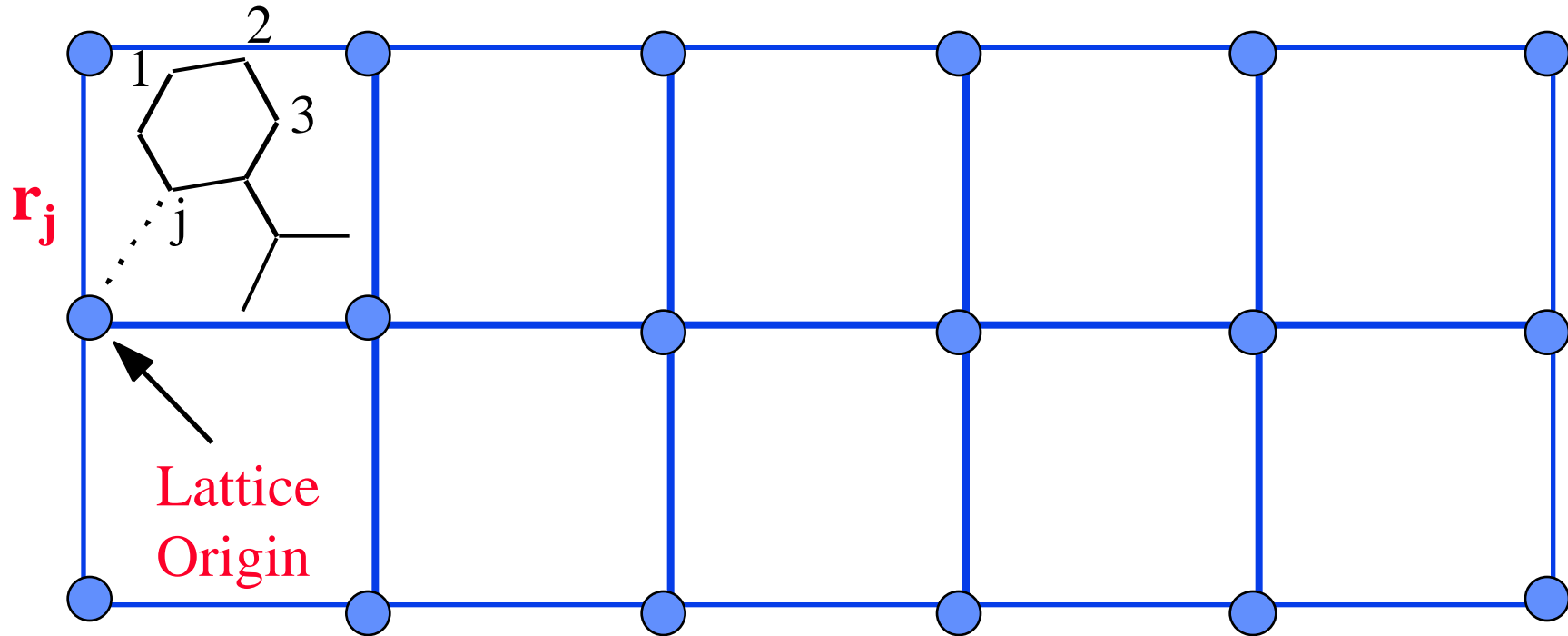
Usually, one approximates the time-independent wave functions of the various orbitals by spherically symmetrical functions to calculate the electron density. These atomic scattering factors are given in the International Tables of Crystallography as a function of $\sin \theta / \lambda$.

Note that the largest value of f_a is the number of electrons in the atom and that this value is obtained for $2\theta = 0$, where all the interferences are constructive (phase difference = 0).

Under these conditions one can define the intensity scattered by one atom as: $I_a = I_e f_a^2$ where I_e is the scattering intensity from one electron.

Scattering of X-Rays by Crystals

- Scattering from one Unit Cell:



The unit cell structure factor is denoted A_{cell} and is the amplitude of the net wave scattered by one unit cell.

$$A_{\text{cell}} = \sum_{j=1}^{N_{\text{cell}}} f_j \exp(-2\pi i \vec{S} \cdot \vec{r}_j)$$

where N_{cell} is the number of atoms in the unit cell.

- Scattering from a crystal having N_1 , N_2 , N_3 , unit cells along the **a-**, **b-**, **c-**axes:

- Since all atoms in the crystal can be located in terms of a three-dimensional parallel translation of the unit cell and since the value of A_{cell} is the same for all unit cells, the scattering of a crystal as a whole is the same as if there were a hypothetical atom with a scattering amplitude A_{cell} located at each lattice point in the crystal.

- Lattice points can be defined by:

$$\vec{R}_n = n_1 \vec{a} + n_2 \vec{b} + n_3 \vec{c} \text{ where } n_1 \ n_2 \ n_3 \in \mathbb{Z}$$

- The crystal structure factor is then given by:

$$A_{\text{crystal}} = \sum_{n_1=1}^{N_1} \sum_{n_2=1}^{N_2} \sum_{n_3=1}^{N_3} A_{\text{cell}} \exp\left(-2\pi i \vec{S} \cdot (n_1 \vec{a} + n_2 \vec{b} + n_3 \vec{c})\right)$$

$$A_{\text{crystal}} = \sum_{n_1=1}^{N_1} \sum_{n_2=1}^{N_2} \sum_{n_3=1}^{N_3} A_{\text{cell}} \exp\left(-i(2\pi \vec{S} \cdot \vec{a})^{n_1}\right) \exp\left(-i(2\pi \vec{S} \cdot \vec{b})^{n_2}\right) \exp\left(-i(2\pi \vec{S} \cdot \vec{c})^{n_3}\right)$$

$$A_{crystal} = A_{cell} \prod_{n_1=1}^{N_1} \exp(iA^{n_1}) \prod_{n_2=1}^{N_2} \exp(iB^{n_2}) \prod_{n_3=1}^{N_3} \exp(iC^{n_3})$$

$$|\vec{A}_{crystal}|^2 = |\vec{A}_{cell}|^2 \prod_{n_1=1}^{N_1} \exp\left(-i(2\pi\vec{S}\cdot\vec{a})^{n_1}\right) \prod_{n_1=1}^{N_1} \exp\left(i(2\pi\vec{S}\cdot\vec{a})^{n_1}\right) \\ \prod_{n_2=1}^{N_2} \exp\left(-i(2\pi\vec{S}\cdot\vec{b})^{n_2}\right) \prod_{n_2=1}^{N_2} \exp\left(i(2\pi\vec{S}\cdot\vec{b})^{n_2}\right) \\ \prod_{n_3=1}^{N_3} \exp\left(-i(2\pi\vec{S}\cdot\vec{c})^{n_3}\right) \prod_{n_3=1}^{N_3} \exp\left(i(2\pi\vec{S}\cdot\vec{c})^{n_3}\right)$$

Using:

$$\prod_{n=1}^N X^{n-1} = \frac{1 - X^N}{1 - X}$$

We obtain:

$$|\vec{A}_{crystal}|^2 = |\vec{A}_{cell}|^2 \frac{1 - \cos(2N_1\pi(\vec{S}\cdot\vec{a}))}{1 - \cos(2\pi(\vec{S}\cdot\vec{a}))} \\ \frac{1 - \cos(2N_2\pi(\vec{S}\cdot\vec{b}))}{1 - \cos(2\pi(\vec{S}\cdot\vec{b}))} \frac{1 - \cos(2N_3\pi(\vec{S}\cdot\vec{c}))}{1 - \cos(2\pi(\vec{S}\cdot\vec{c}))}$$

$|\vec{A}_{crystal}|^2 = |\vec{A}_{cell}|^2 L^2$ where L^2 is the Laue function defined by:

$$L^2 = \frac{\sin^2(N_1\pi(\vec{S}\cdot\vec{a}))}{\sin^2(\pi(\vec{S}\cdot\vec{a}))} \frac{\sin^2(N_2\pi(\vec{S}\cdot\vec{b}))}{\sin^2(\pi(\vec{S}\cdot\vec{b}))} \frac{\sin^2(N_3\pi(\vec{S}\cdot\vec{c}))}{\sin^2(\pi(\vec{S}\cdot\vec{c}))}$$

The Laue function is therefore a function of the crystal size (N_1, N_2, N_3) and of the orientation of the scattering vector with respect to the crystal lattice. Strong diffraction effects will be observed when the $A_{crystal}^2$ is large. This will require a large value for A_{cell}^2 and a non-zero value for L^2 . $A_{crystal}^2$ is maximum when the argument of each sine function have the following values:

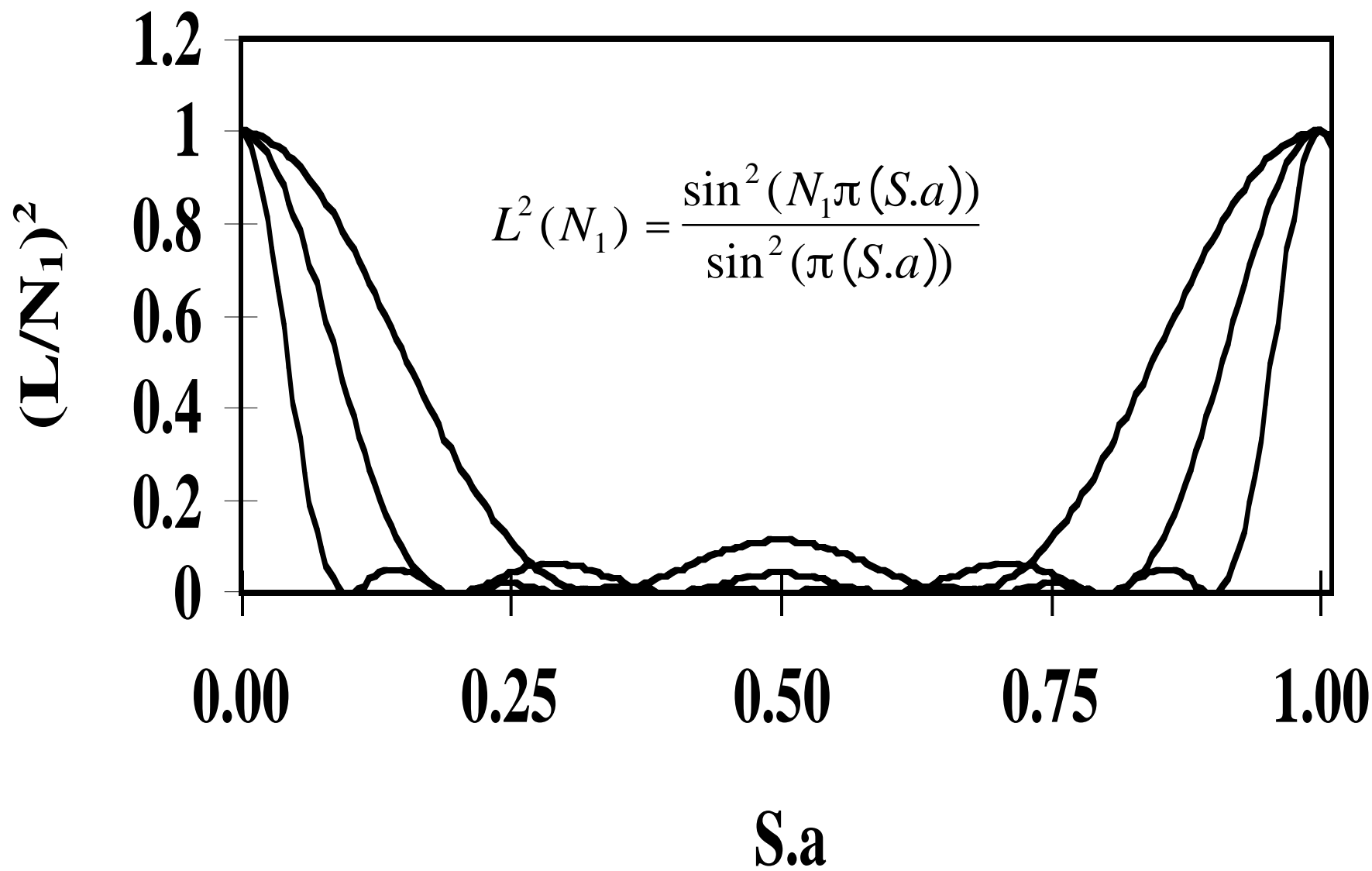
$$\vec{S}\cdot\vec{a} = 0, \pm 1, \pm 2, \dots \quad \vec{S}\cdot\vec{b} = 0, \pm 1, \pm 2, \dots \quad \vec{S}\cdot\vec{c} = 0, \pm 1, \pm 2, \dots$$

If we define h, k and l by: $h = \vec{S}\cdot\vec{a}$ $k = \vec{S}\cdot\vec{b}$ $l = \vec{S}\cdot\vec{c}$

Then: $\vec{S} = h\vec{a}^* + k\vec{b}^* + l\vec{c}^*$ Since: $\vec{S}\cdot\vec{a} = h\vec{a}^*\cdot\vec{a} + k\vec{b}^*\cdot\vec{a} + l\vec{c}^*\cdot\vec{a} = h$

When the Laue Conditions are satisfied, diffraction occurs and the scattering vector \mathbf{S} is perpendicular to a lattice plane having Miller indices $h=\mathbf{S}\cdot\mathbf{a}$, $k=\mathbf{S}\cdot\mathbf{b}$, and $l=\mathbf{S}\cdot\mathbf{c}$

Laue Function (1-dimensional)



- Laue Conditions imply the Bragg's Law

$$|\vec{S}| = \frac{1}{d_{hkl}} \quad \text{and} \quad |\vec{S}| = \frac{2\sin\theta_{hkl}}{\lambda} \quad 2d_{hkl} \sin\theta_{hkl} = \lambda$$

- In conclusion:

$$I_S = I_0 \frac{e^2}{mc^2} \frac{1}{r^2} \frac{1 + \cos^2 \theta}{2} L^2 F_{hkl} F_{hkl}^*$$

where: $F_{hkl} = \sum_j f_j \exp(-2\pi i(hx_j + ky_j + lz_j))$ is called

the Lattice Structure Factor

x_j, y_j, z_j are the coordinates of the j -th atom in the unit cell expressed as fractions of the unit cell dimensions

Other Topics to be Reviewed

- Ewald Sphere and Its use
- Temperature Factor: How thermal vibrations affect the diffraction pattern
- Diffraction Methods (photographic and diffractometers)
- Neutrons and Electrons