Chapter 1

Resonant X-ray Electric Field Intensity

1.1 Experimental Setup

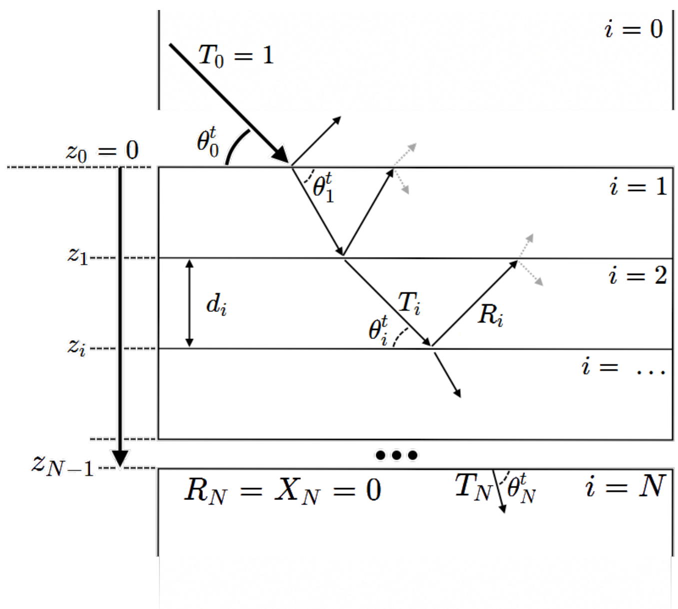

Figure 1.1: Experimental setup for measuring the X-ray electric field intensity. The X-ray beam is incident on a sample, and the reflected beam is analyzed to determine the electric field intensity. Here there are N+1 layers, including the first layer (i.e. vacuum/air) and the substrate both of which are semi-infinite. The interfaces are indexed between two layers i and $i+1$, such that interface is positioned at z_i. This same indexing is used for any interface calculations, such as the Fresnel coefficients.

1.1.1 Electric field

The total electric field of the X-ray beam in any given layer is given by the summation of two propogating waves.

$$\vec{E}_i(\vec{r}) = \vec{T}_i(\vec{r}) + \vec{R}_i(\vec{r}) \tag{1.1}$$

where

$$\vec{T}_i(\vec{r}) = T_i \cdot \exp\left(-\mathbf{i}\vec{k_i} \cdot \vec{r}\right) \tag{1.2}$$

$$\vec{R}_i(\vec{r}) = R_i \cdot \exp\left(+\mathbf{i}\vec{k_i} \cdot \vec{r}\right) \tag{1.3}$$

and $\vec{k_i}$ is the wavevector of the X-ray beam in layer i, at position $\vec{r}$.

Here the transmission and reflection components represent the sum of all multiple-scattering events in the layer. The complex constants T_i and R_i result of the requirement for continuity of the electric field vector at the boundary - more specifically, through a recursive solution using the Fresnel coefficients for each interface.

Typically, especially for non-resonant X-ray scattering, the x-component wavevector k_x is ignored and the attenuation is treated as negligible.

1.1.2 Angle of incidence and wavevector

For any radiation of wavelength λ, and incident angle θ_0 coming from vacuum or a medium of complex refractive index N, the corresponding wavevector $\vec{k}$ is given by

$$\vec{k_0} = \frac{2\pi}{\lambda}\left(\cos(\theta_0)\hat{x} + \sin(\theta_0)\hat{z}\right) \tag{1.4}$$

As the X-ray propogates through the sample, the dielectric constant modifies the (now complex) angle of incidence and the complex wavevector, as per Snell's law (for grazing incidence).

$$\theta_i = \arccos\left(\frac{\cos(\theta_0) \times N_0}{N_i}\right) \tag{1.5}$$

$$\vec{k_i} = \left(|k_0|\cos\theta_0\hat{x} + |k_0|\sqrt{n_i^2 - \cos^2\theta_i}\hat{z}\right) \tag{1.6}$$

Notice here that the attenuation of the X-ray beam in the x-direction has a constant wavevector component that is real

1.1.2.1 Critical angle

For any given refractive index $N_i < N_0$ [1], the critical angle occurs when $\cos(\theta_0) < \frac{N_i}{N_0}$. In the case where $N_0 \approxeq 1$ is air/vacuum, this critical angle corresponds to

$$\theta_0 = \sqrt{2\delta_i} \tag{1.7}$$

[1]This is usually the case for X-rays where $N_i = 1 - \delta_i + \mathbf{i}\beta_i$

1.2 Interface Calculation

To calculate the effect of refraction and reflection at each interface, a boundary condition is applied that the tangential component of the electric field must be continuous across the interface (both in $\hat{x}$ and $\hat{y}$ directions). This requires knowledge of the polarisation of the X-ray beam, as well as the refractive index of the medium.

For convention, we define positive $\hat{z}$ out of the film; z is negative as it penetrates into the film. $\hat{x}$ is positive along the beam path, and monotonically increases. As the x-ray propogates some space in the film (i.e., -ve z and +ve x), the phase contribution is $\exp\left[\mathbf{i}\vec{k}\cdot\vec{r}\right]$. Hence the sign of the wavevector components also match the direction of the beam: negative k_z and positive k_x, such that the imaginary component of the wavevector leads to a decaying wave in the film.

1.2.1 Polarisation Dependence

An x-ray can be S-polarised (parallel to the planar surface, i.e. in the $\hat{y}$ or $\hat{x}$ direction) or P-polarised (parallel to the planar normal, i.e. in the $\hat{z}$ plane). These are also known as transverse electric (TE) and transverse magnetic (TM) polarisations, respectively.

Usually, the polarisation angle α can be defined as the angle between the electric field vector and the plane of incidence, with $\alpha = 0$ for S-polarised waves and $\alpha = \frac{\pi}{2}$ for P-polarised waves. Then the perpendicular and parallel components of the electric field vector can be defined as

$$E_{i,\perp} = E_i \cos(\alpha) \tag{1.8}$$

$$E_{i,\parallel} = E_i \sin(\alpha) \tag{1.9}$$

In the context of grazing incidence experiments, the X-ray beam is typically highly aligned and polarised. It will be routine to perform measurements with both S- and P-polarised X-rays.

1.2.2 Fresnel Coefficients

Fresnel coefficients describe the amplitude of reflected and transmitted waves at an interface between two media with different refractive indices. For S-polarised waves, the Fresnel coefficients are given by

$$t^s_{i,i+1} = \frac{2k_{i,z}}{k_{i,z} + k_{i+1,z}} \tag{1.10}$$

$$r^s_{i,i+1} = \frac{k_{i,z} - k_{i+1,z}}{k_{i,z} + k_{i+1,z}} = t_{s,i} - 1 \tag{1.11}$$

For P-polarised waves, the Fresnel coefficients are given by

$$t^p_{i,i+1} = \frac{2k_{i,z}}{n^2 k_{i,z} + k_{i+1,z}} \tag{1.12}$$

$$r^p_{i,i+1} = \frac{n^2 k_{i+1,z} - k_{i,z}}{n^2 k_{i+1,z} + k_{i,z}} \tag{1.13}$$

At resonance, the refractive index n can be modified by a significant amount. Consider the imaginary component in Polystyrene (CH) at the carbon K edge changing magnitude from 1e-4 to 6e-3.

For P3MEEET ($C_{11}H_{16}O_3S$) at the resonant sulfur K edge, the magnitude changes from 9e-7 to 5.7e-6.

The polarisation dependence for the Fresnel coefficients is not significantly changed by n^2, so we approximate using the s-polarisation case.

1.3 Taylor series result for the reflected electric field between multiple interfaces

Following the derivation of Borne & Wolf (1985) and Savakhin et al. (2020), we derive the electric field in a multi-layer system, accounting for decaying x-propogation of waves.

In any layer, the total electric field is the sum of many reflections.

$$E_j = E_{j,1} + E_{j,2} + E_{j,3} + ... + E_{j,N} + ... \tag{1.14}$$

Considering an interface with a transmitted wave E_j^t into layer j and the corresponding total incident wave E_{j-1} from the previous layer.

$$E_{j,1} = E_j^t \exp\left[\mathbf{i}\left(\vec{k_j}\cdot\vec{r}\right)\right] \tag{1.15}$$

$$= E_{j-1}t_{j-1,j}\exp\left[\mathbf{i}\left(\vec{k_j}\cdot\vec{r}\right)\right] \tag{1.16}$$

$$= E_{j-1}\left(1 + r_{j-1,j}\right)\exp\left[\mathbf{i}\left(\vec{k_j}\cdot\vec{r}\right)\right] \tag{1.17}$$

Secondly, we follow a reflection from the bottom interface between layers $j, j+1$, with reflection coefficient $r_{j,j+1}$. The wave has now travelled additional vertical distance between the two interfaces, so we relabel the z-components d_j for the thickness between interfaces z_i and z_{i+1}.

This section is incorrect - it forgets that the x-component wavevector is constant due to boundary conditions hahahaha. Such are the mistakes of trying new things.

Importantly, and deviating from previous results, we also track the horizontal distance travelled in terms of d_j, as $\tan(\theta_j) = d_j/c_j$, where θ_j is the angle of incidence in layer j between interfaces $i, i+1$. While this distance is continuously increasing (i.e. there's no phase subtraction), we need to observe the decay of the wave is propogates forwards. We therefore write $x \rightarrow \delta x$, where $\delta x < c_j$. Considering only the z position abstracts decaying reflections, and therefore leads to incorrect results.

$$E_{j,2} = E_{j-1}\left(1 + r_{j-1,j}\right) \times r_{j,j+1} \exp\left[\mathbf{i}\left((2d_j - z)k_{j,z} + xk_{j,x}\right)\right] \tag{1.18}$$

$$= E_{j-1}\left(1 + r_{j-1,j}\right) \times r_{j,j+1} \exp\left[\mathbf{i}\left((2d_j - z)k_{j,z}\right)\right]\exp\left[\mathbf{i}\left((c_j + \delta x)k_{j,x}\right)\right] \tag{1.19}$$

The third component is a surface reflection from the top interface, noting that $r_{j,j-1} = -r_{j-1,j}$, corresponding to a phase shift of π.

$$E_{j,3} = E_{j-1}\left(1 + r_{j-1,j}\right) \times r_{j,j+1} \times \left(-r_{j-1,j}\right) \exp\left[\mathbf{i}\left((2d_j + z)k_{j,z}\right)\right]\exp\left[\mathbf{i}\left((2c_j + \delta x)k_{j,x}\right)\right] \tag{1.20}$$

The fourth component is another surface reflection from the bottom surface.

$$\begin{aligned} E_{j,4} &= E_{j-1}\left(1+r_{j-1,j}\right)\times r_{j,j+1}\times\left(-r_{j-1,j}\right)\times\left(r_{j,j+1}\right) && (1.21)\\ &\quad \exp\left[\mathbf{i}\left((4d_j-z)k_{j,z}\right)\right]\exp\left[\mathbf{i}\left((3c_j+\delta x)k_{j,x}\right)\right]\\ &= E_{j-1}\left(1+r_{j-1,j}\right)\times r_{j,j+1}^2\times\left(-r_{j-1,j}\right) && (1.22)\\ &\quad \exp\left[\mathbf{i}\left((4d_j-z)k_{j,z}\right)\right]\exp\left[\mathbf{i}\left((3c_j+\delta x)k_{j,x}\right)\right] \end{aligned}$$

The fifth component is another surface reflection from the top surface.

$$\begin{aligned} E_{j,5} &= E_{j-1}\left(1+r_{j-1,j}\right)\times r_{j,j+1}^2\times\left(-r_{j-1,j}\right)^2 && (1.23)\\ &\quad \exp\left[\mathbf{i}\left((4d_j+z)k_{j,z}\right)\right]\exp\left[\mathbf{i}\left((4c_j+\delta x)k_{j,x}\right)\right] \end{aligned}$$

And so on. Considering the remaining δx as a function of z, we can parametrise this as:

$$\delta x = \begin{cases} (z)\tan{\theta_j}^{-1} & N\in 2\mathbb{Z}+1 \quad \text{(odd)} \\ (d-z)\tan{\theta_j}^{-1} & N\in 2\mathbb{Z} \quad \text{(even)} \end{cases} \tag{1.24}$$

This leads to the following sets of expressions for forward and backward propogating waves corresponding to odd and even N.

$$E_{j,N} = E_{j-1}\left(1+r_{j-1,j}\right)\times\begin{cases} r_{j,j+1}^{(N-1)/2}\times\left(-r_{j-1,j}\right)^{(N-1)/2} & \\ \times\exp\left[\mathbf{i}k_{j,z}\left((N-1)d_j+z\right)\right] & N\in 2\mathbb{Z}+1 \quad \text{(odd)}\\ \times\exp\left[\mathbf{i}k_{j,x}\left((N-1)\,c_j+z\tan{\theta_j}^{-1}\right)\right] & \\ & \\ r_{j,j+1}^{N/2}\times\left(-r_{j-1,j}\right)^{N/2-1} & \\ \times\exp\left[\mathbf{i}k_{j,z}\left(Nd_j-z\right)\right] & N\in 2\mathbb{Z} \quad \text{(even)}\\ \times\exp\left[\mathbf{i}k_{j,x}\left((N-1)c_j+(d_j-z)\tan{\theta_j}^{-1}\right)\right] & \end{cases} \tag{1.25}$$

Also note $\left((N-1)c_j+(d_j-z)\tan{\theta_j}^{-1}\right)\equiv Nc_j - z\tan{\theta_j}^{-1}$, simplifying the even expression.

The total sum of all reflections can then be written as a geometric series where the common component of the odd/even terms is factored in ζ:

$$\begin{aligned} E_j &= E_{j-1}(1+r_{j-1,j})\times\zeta && (1.26)\\ &\quad\times\begin{pmatrix} \exp\left[\mathbf{i}\left(k_{j,z}+k_{j,x}\tan{\theta_j}^{-1}\right)z\right] \\ +r_{j,j+1}\exp\left[\mathbf{i}\left(k_{j,z}+k_{j,x}\tan{\theta_j}^{-1}\right)(2d_j-z)\right] \end{pmatrix}\\ \zeta &= 1 - r_{j-1,j}r_{j,j+1}\exp\left[\mathbf{i}(2(k_{j,z}+k_{j,x}\tan{\theta_j}^{-1})d_j)\right] && (1.27)\\ &\quad + r_{j-1,j}^2 r_{j,j+1}^2\exp\left[\mathbf{i}(4(k_{j,z}+k_{j,x}\tan{\theta_j}^{-1})d_j)\right]\\ &\quad - \ldots \end{aligned}$$

We recognise the Taylor expansion form of $1/(1+x)$, with the expression for x being $x =$

$r_{j-1,j} r_{j,j+1} \exp\left[\mathbf{i}(2(k_{j,z} + k_{j,x} \tan{\theta_j}^{-1}) d_j)\right]$. Thus the series can be written as:

$$\begin{aligned} E_j = E_{j-1}\left(1 + r_{j-1,j}\right) & \\ \times \frac{\exp\left[-\mathbf{i}(k_{j,z} + k_{j,x} \tan{\theta_j}^{-1}) z\right] + r_{j,j+1} \exp\left[\mathbf{i}(k_{j,z} + k_{j,x} \tan{\theta_j}^{-1})(2d_j - z)\right]}{1 + r_{j-1,j} r_{j,j+1} \exp\left[\mathbf{i}(2(k_{j,z} + k_{j,x} \tan{\theta_j}^{-1}) d_j)\right]} & \end{aligned} \tag{1.28}$$

1.3.1 Separating the reflection and transmission summation coefficients similar to Dev et al. (2020) and

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