

## Electron Density and Structure Factors

Relationship between the structure factor and the electron density

The structure factor  $F$  can be described as sum of the wavelets scattered from all the infinitesimal elements of the electron density in the unit cell ( $\rho$ ).  $\rho$  ( $\rho$ ) is defined as the number of electrons per unit volume then the number of electrons in any volume element will be  $\rho(xyz)dV$  and the wavelet scattered by this element will be

$$\rho(xyz)e^{2\pi(hx+ky+lz)} dV$$

The resultant is the sum of all of the elements in the unit cell (the integral over all of the unit cell's volume)

$$F_{hkl} = \iiint \rho(xyz)e^{2\pi(hx+ky+lz)} dV$$

Solving this integral affords

$$F_{hkl} = \rho(xyz) \iiint_{hkl} e^{2\pi(hx+ky+lz)} dV$$

$$\sum_{hkl} F_{hkl} = \rho(xyz)V \sum_{hkl} e^{2\pi(hx+ky+lz)}$$

$$\frac{\sum_{hkl} F_{hkl} e^{-2\pi(hx+ky+lz)}}{V} = \rho(xyz)$$

$$\rho(xyz) = \frac{1}{V} \sum_{hkl} F_{hkl} e^{-2\pi(hx+ky+lz)}$$

Let  $\hbar = (hx + ky + lz)$

From the periodic function

$$\rho(xyz) = \frac{1}{V} \sum_h \sum_{k=-\infty}^{\infty} \sum_l F_{hkl} e^{-2i\pi\hbar}$$

let  $F_{hkl} = |F_{hkl}| e^{i\alpha_{hkl}}$

substituting for  $F_{hkl}$

$$\rho(xyz) = \frac{1}{V} \sum_h \sum_{k=-\infty}^{\infty} \sum_l^{\infty} |F_{hkl}| e^{i\alpha_{hkl}} e^{-2i\pi\hbar}$$

Rearranging

$$\rho(xyz) = \frac{1}{V} \sum_h \sum_{k=-\infty}^{\infty} \sum_l^{\infty} |F_{hkl}| e^{-i(2\pi\hbar - \alpha_{hkl})}$$

let  $2\pi\alpha'_{hkl} = \alpha_{hkl}$  then

$$\rho(xyz) = \frac{1}{V} \sum_h \sum_{k=-\infty}^{\infty} \sum_l^{\infty} |F_{hkl}| e^{-i2\pi(\hbar - \alpha'_{hkl})}$$

Given that  $e^{-iax} = \cos ax - i \sin ax$  then

$$\rho(xyz) = \frac{1}{V} \sum_h \sum_{k=-\infty}^{\infty} \sum_l^{\infty} |F_{hkl}| \left[ \cos 2\pi(\hbar - \alpha'_{hkl}) - i \sin 2\pi(\hbar - \alpha'_{hkl}) \right]$$

Friedel's law states  $F_{hkl} = F_{\bar{h}\bar{k}\bar{l}}$  ( for  $\hbar$  and  $-\hbar$  ) and summing  $h = 0$  to  $h = -\infty$

$$\rho(xyz) = \frac{1}{V} \sum_{h=0}^{\infty} \sum_{k=-\infty}^{\infty} \sum_l^{\infty} |F_{hkl}| \left[ \cos 2\pi(\hbar - \alpha'_{hkl}) - i \sin 2\pi(\hbar - \alpha'_{hkl}) \right] + |F_{\bar{h}\bar{k}\bar{l}}| \left[ \cos 2\pi(-\hbar - \alpha'_{hkl}) - i \sin 2\pi(-\hbar - \alpha'_{hkl}) \right]$$

Given that  $\cos(x) = \cos(-x)$  and  $\sin(x) = -\sin(-x)$  and  $F_{\bar{h}\bar{k}\bar{l}} = F_{hkl}$  then

$$\rho(xyz) = \frac{1}{V} \sum_{h=0}^{\infty} \sum_{k=-\infty}^{\infty} \sum_l^{\infty} \left\{ |F_{hkl}| \left[ \cos 2\pi(\hbar - \alpha'_{hkl}) - i \sin 2\pi(\hbar - \alpha'_{hkl}) \right] + |F_{hkl}| \left[ \cos 2\pi(\hbar - \alpha'_{hkl}) + i \sin 2\pi(\hbar - \alpha'_{hkl}) \right] \right\}$$

rearranging

$$\rho(xyz) = \frac{1}{V} \sum_{h=0}^{\infty} \sum_{k=-\infty}^{\infty} \sum_l^{\infty} |F_{hkl}| \left[ \cos 2\pi(\hbar - \alpha'_{hkl}) + \cos 2\pi(\hbar - \alpha'_{hkl}) - i \sin 2\pi(\hbar - \alpha'_{hkl}) + i \sin 2\pi(\hbar - \alpha'_{hkl}) \right]$$

Cancelling sin terms and summing cosine terms leaves:

$$\rho(xyz) = \frac{1}{V} \sum_{h=0}^{\infty} \sum_{k=-\infty}^{\infty} \sum_l^{\infty} |F_{hkl}| \left[ 2 \cos 2\pi(\hbar - \alpha'_{hkl}) \right]$$

Multiplying and substituting  $\hbar = (hx + ky + lz)$  affords:

$$\rho(xyz) = \frac{2}{V} \sum_{h=0}^{\infty} \sum_{k=-\infty}^{\infty} \sum_l^{\infty} |F_{hkl}| \cos 2\pi(hx + ky + lz - \alpha'_{hkl})$$

Summing from  $h = -\infty$  to  $h = +\infty$  leaves

$$\rho(xyz) = \frac{1}{V} \sum_h^{\infty} \sum_{k=-\infty}^{\infty} \sum_l^{\infty} |F_{hkl}| \cos 2\pi(hx + ky + lz - \alpha'_{hkl})$$

where  $\alpha'_{hkl} = \frac{\alpha_{hkl}}{2\pi}$

If  $|F_{hkl}|$  **and** the phase angle  $\alpha_{hkl}$  are known one can calculate  $\rho$  electron density map

the X-ray experiment provides the  $|F_{hkl}|$  **however** the phase angles  $\alpha_{hkl}$  are **unknown**

"To get the Answer, you need the Answer"