Introduction to X-ray diffraction

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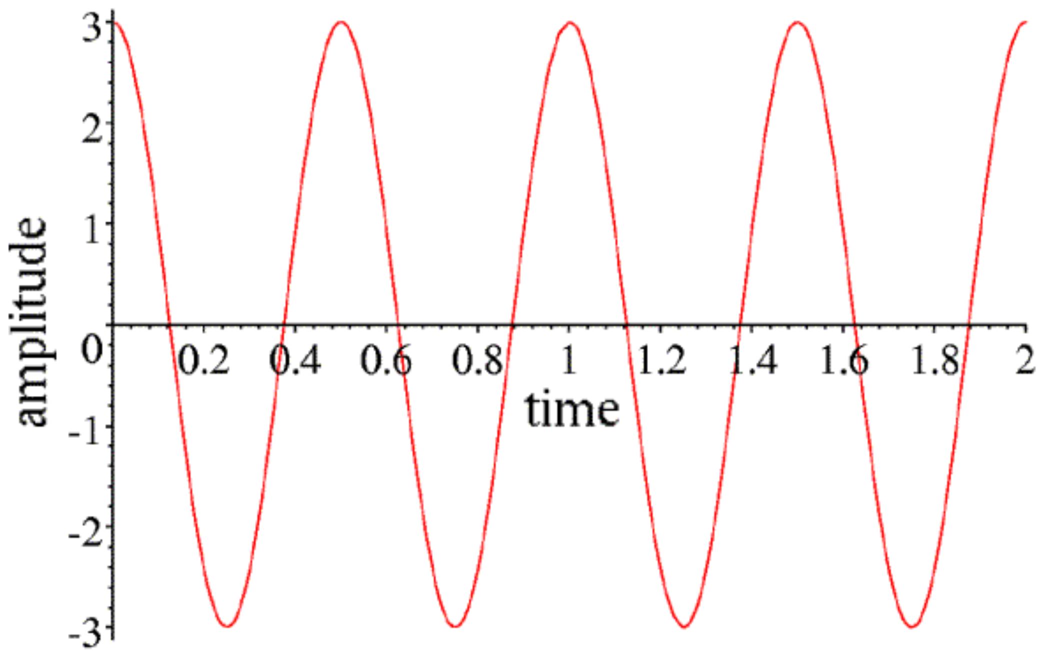
- Waves
- Diffraction
- Structure factors
- Reciprocal space

- http://www-structmed.cimr.cam.ac.uk/Course

Describing waves

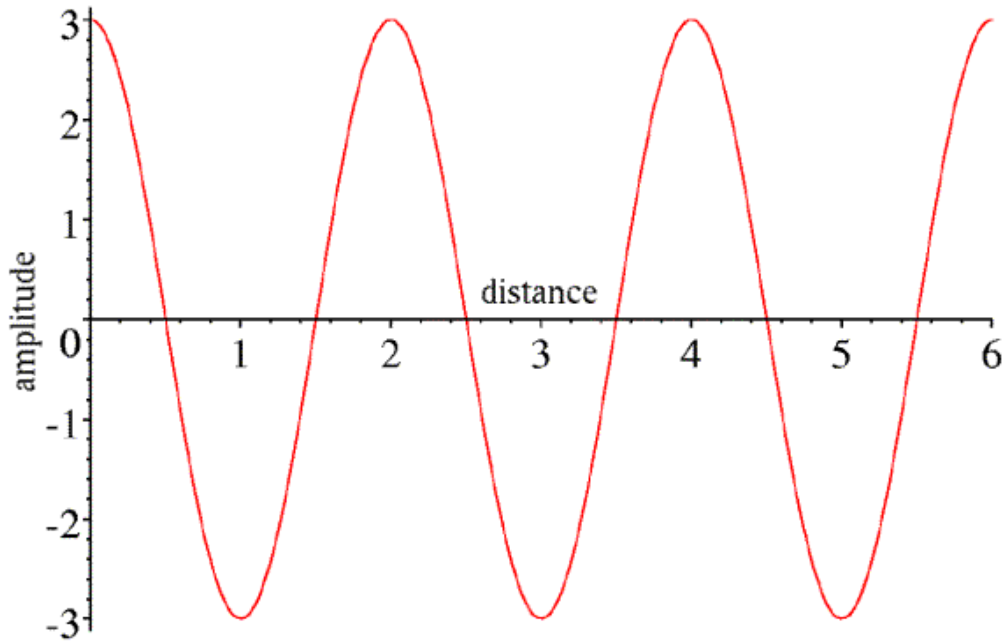
- Wave as function of time



$$A\cos(2\pi \nu t)$$

Describing waves

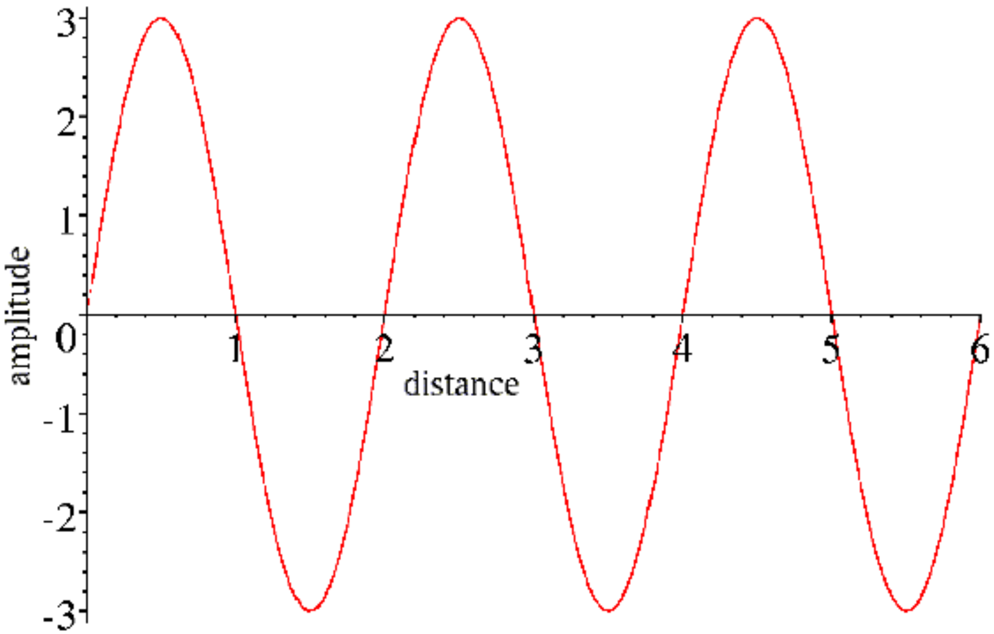
- Wave as function of position in space



$$A\cos(2\pi x/\lambda) = A\cos(-2\pi x/\lambda)$$

Describing waves

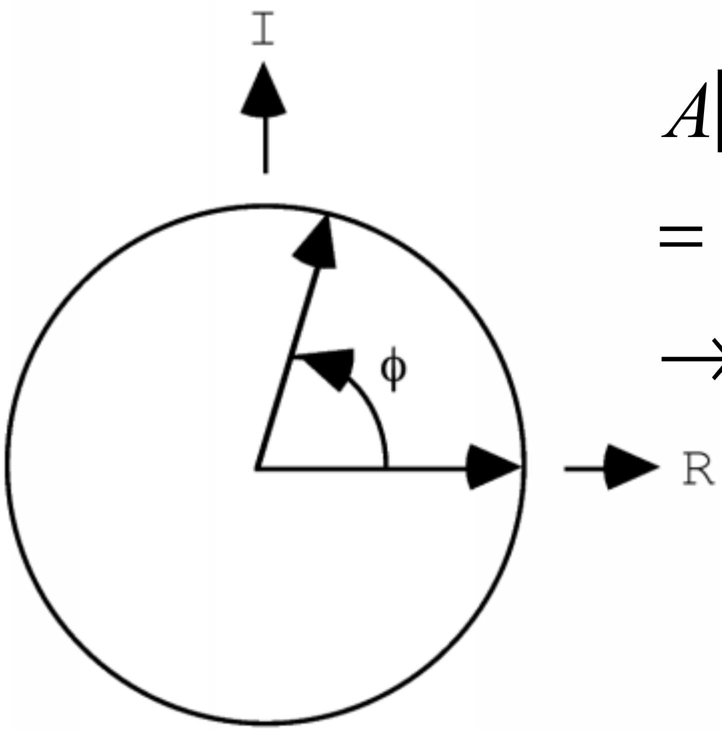
- Wave as function of time and space



$$A\cos[2\pi(\nu t - x/\lambda)]$$

Wave as vector (or complex number)

- Wave is x-component of rotating vector
- Initial rotation gives initial phase shift

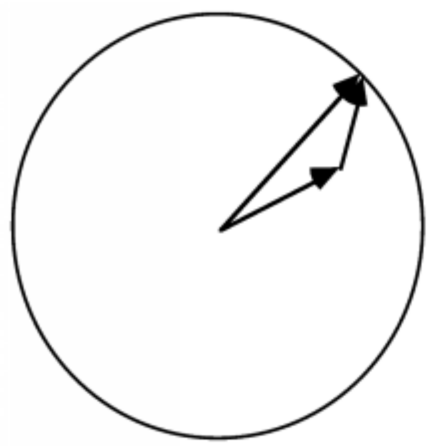


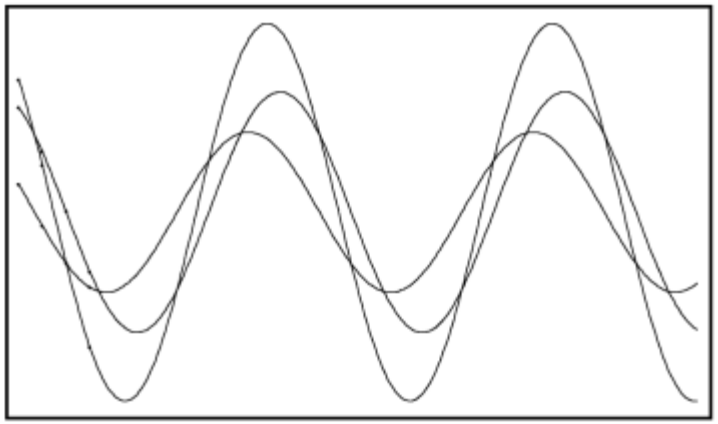
$$A[\cos(\phi + 2\pi\nu t) + i\sin(\phi + 2\pi\nu t)]$$
$$= A\exp[i(\phi + 2\pi\nu t)]$$
$$\to A\exp(i\phi)$$

Adding waves as vectors

- Adding waves is equivalent to adding vectors
  - easier than trigonometry

$$A\cos(\alpha+\varphi_1)+B\cos(\alpha+\varphi_2)$$



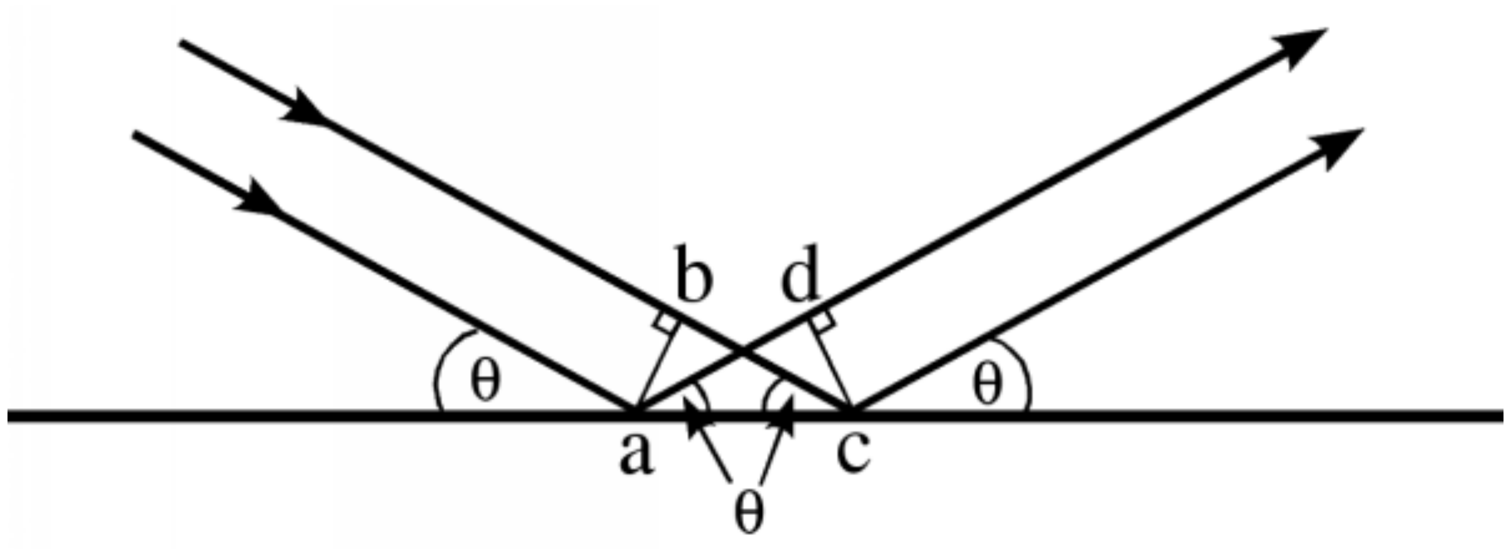


Interaction between X-rays and matter

- X-rays interact with electrons
  - classical view: fluctuating electric field accelerates charged particles, leading to emission of electromagnetic radiation
  - intensity proportional to $(\text{charge}/\text{mass})^2$
    - proton is 2000 times as massive as electron
- Think of electrons scattering X-rays in all directions
  - waves from different electrons interfere

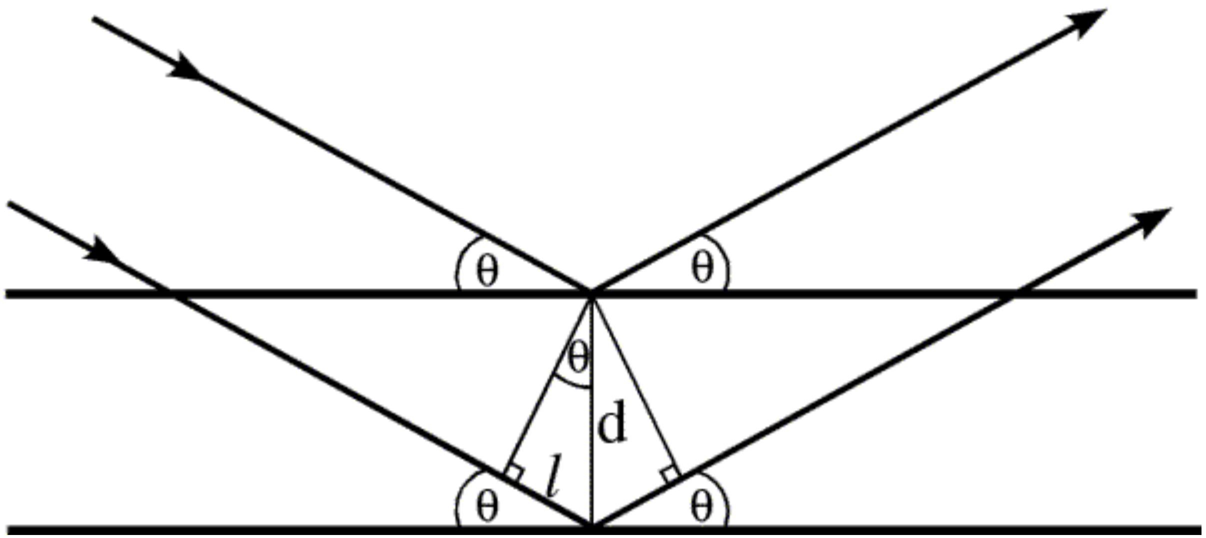
Diffraction: waves in phase

- When do waves add up in phase?
  - when they have exactly the same pathlength
    - scattered from plane where angle of incidence equals angle of reflection



Diffraction: waves in phase

- When do waves add up in phase?
  - when their pathlengths differ by a multiple of the wavelength
  - Bragg's law: $\lambda = 2d\sin\theta$



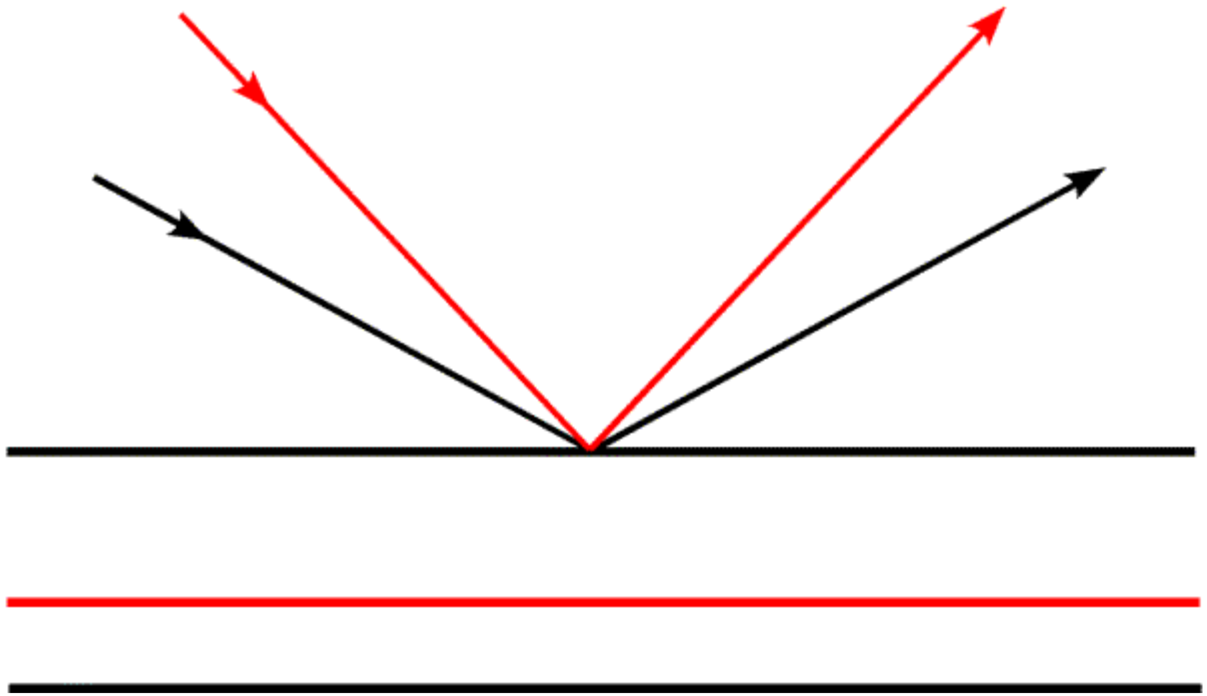
Reciprocal space in Bragg's law

- Bragg planes are closer at higher angles

$$\lambda = 2d\sin\theta$$

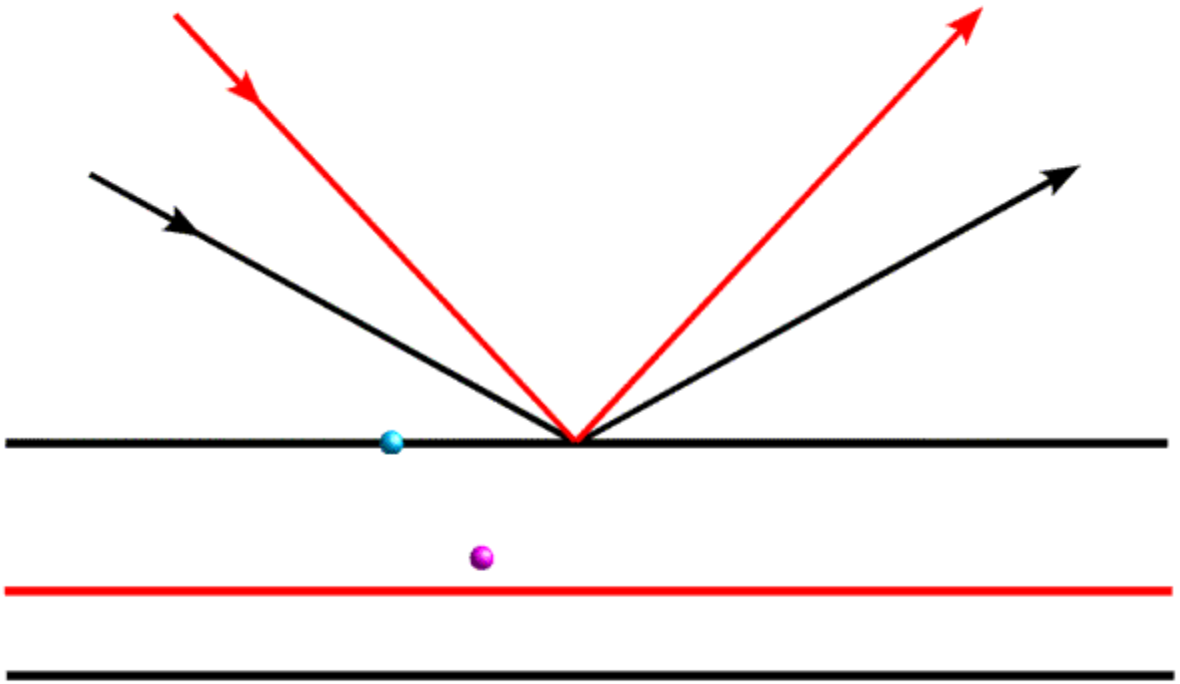
$$\sin\theta/\lambda = 1/2d$$

$$d = \lambda/(2\sin\theta)$$



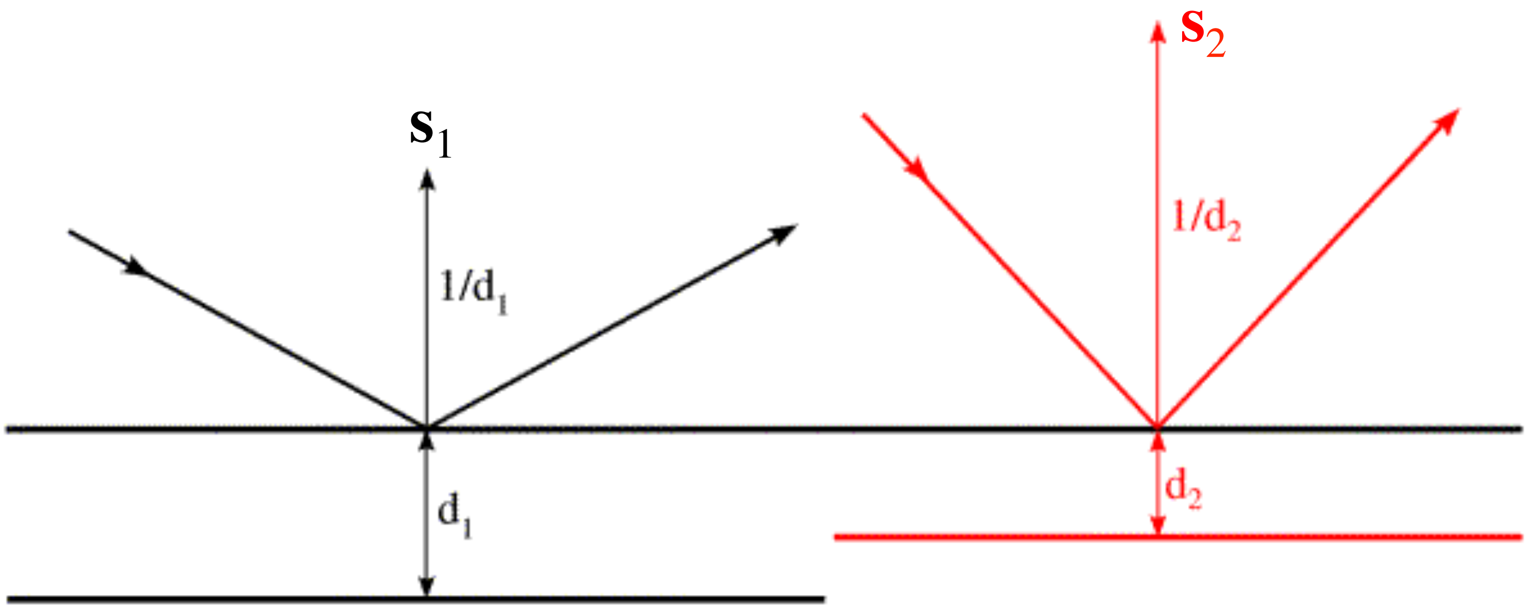
Interference changes with scattering angle

- Add up waves scattered from two electrons
  - out of phase for low angle, nearly in phase for high



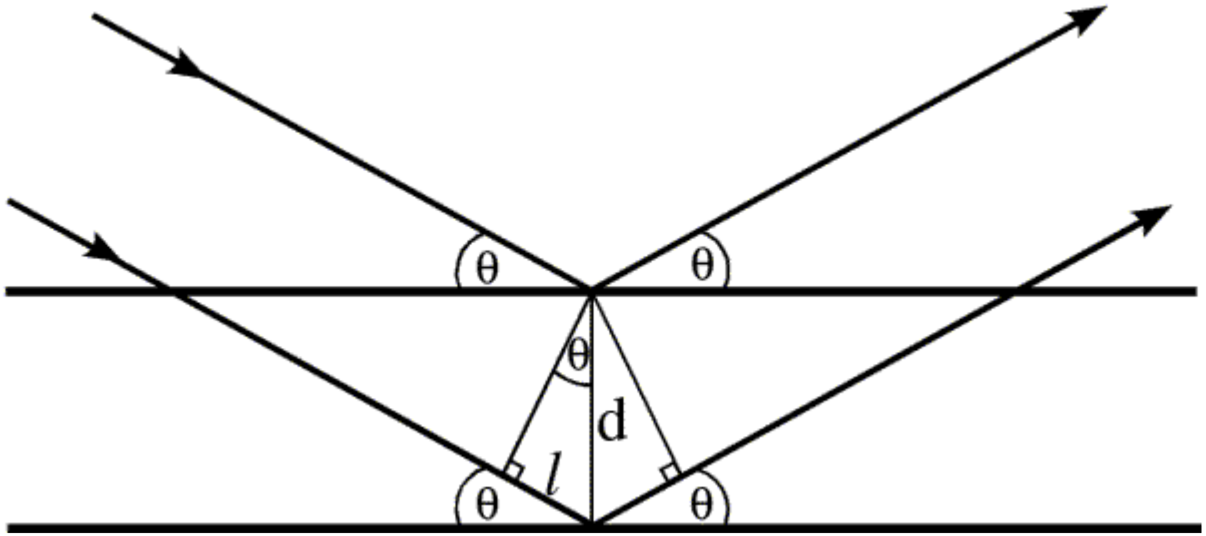
Reciprocal space: the diffraction vector

- Diffraction vector
  - perpendicular to Bragg plane
  - length is reciprocal of distance between planes



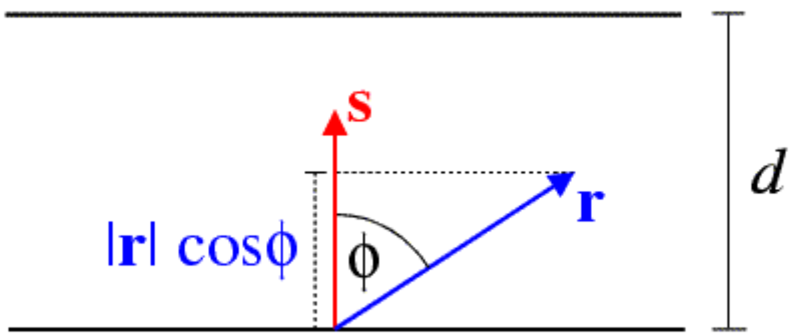
Diffraction from one electron

- Define diffraction from one electron at origin as wave with amplitude 1e and phase of zero
- Diffraction from any point on any Bragg plane also has phase of zero (modulo 2π)



Diffraction from one electron

- Phase depends on position relative to Bragg planes
  - **s** is diffraction vector (measured in reciprocal Å)
  - **r** is position of electron (in Å)
  - fraction of interplanar distance is $\mathbf{s}\cdot\mathbf{r}$ ($=|\mathbf{r}|\cos\phi/d$)
  - phase is $2\pi\mathbf{s}\cdot\mathbf{r}$
  - wave is $\exp(2\pi i\,\mathbf{s}\cdot\mathbf{r})$
    - wavelength is *d* for fixed **s**!



Diffraction from more than one electron

- Add waves from different electrons
  - total amplitude depends on interference effects
    - gives information on relative positions

$$\mathbf{F}(\mathbf{s}) = \sum_j \exp\left(2\pi i \mathbf{s} \cdot \mathbf{r}_j\right)$$

- For continuous electron density, replace sum by integral

$$\mathbf{F}(\mathbf{s}) = \int_{space} \rho(\mathbf{r}) \exp(2\pi i \mathbf{s} \cdot \mathbf{r}) d\mathbf{r}$$

Structure factors and Fourier transforms

- The structure factor is the Fourier transform of the electron density

$$\mathbf{F}(\mathbf{s}) = \int_{space} \rho(\mathbf{r}) \exp(2\pi i \mathbf{s} \cdot \mathbf{r}) d\mathbf{r}$$

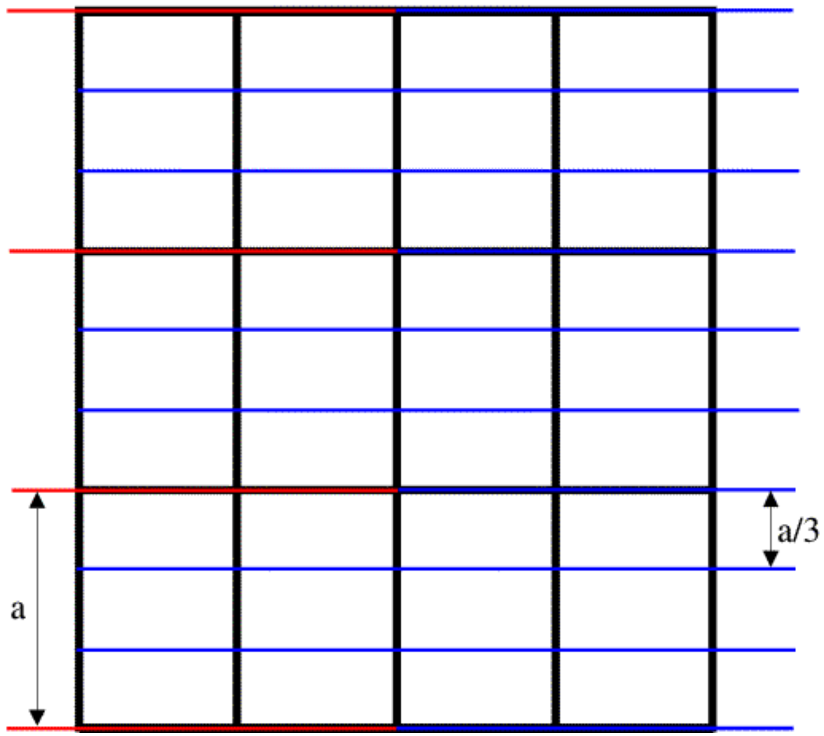
- Fourier transforms can be inverted
  - electron density equation turns structure factors back into electron density

When do we see diffraction from a crystal?

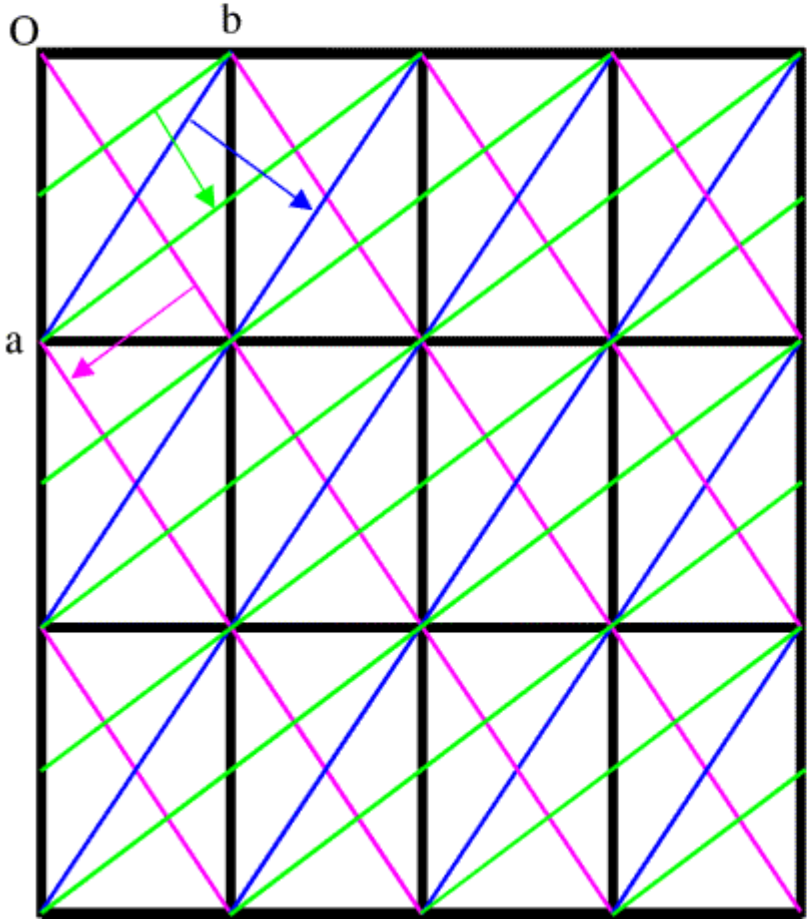
- When the Bragg planes pass through the same points in all unit cells
  - Bragg planes separated by integral fractions of cell edge
  - describe by Miller indices *hkl*

(1 0 0)

(3 0 0)



Bragg planes dividing more than one cell edge



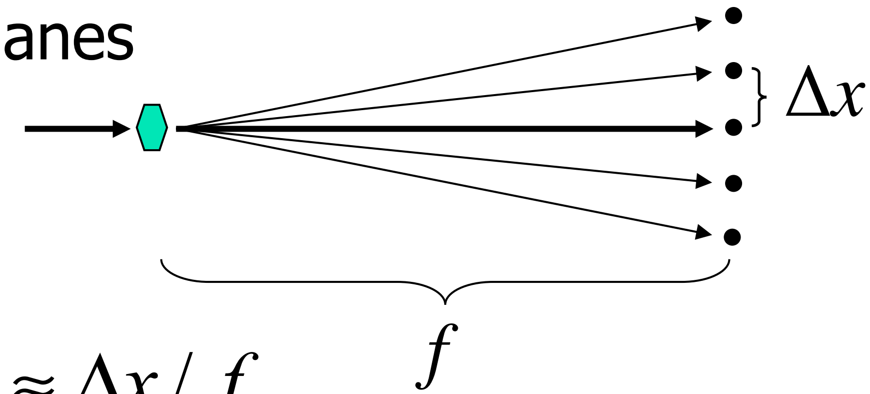
(1 1 0)

(2 1 0)

(1 -1 0)

Bragg's law for crystal diffraction

- Diffraction is only seen for planes defined by Miller indices
- Real lattice becomes reciprocal lattice
  - *e.g h00* reflections separated by inverse of distance between **bc** planes



$$\lambda = 2d \sin\theta$$

$$\sin\theta / \lambda = 1/2d$$

$$d = \lambda / (2 \sin\theta)$$

$$\sin 2\theta \approx \Delta x / f$$

$$2 \sin\theta \approx \Delta x / f, d \approx \lambda(f / \Delta x)$$

Structure factor equation for crystal

- Use **h** (Miller indices *hkl*) instead of **s** to describe diffraction vector
- Use **x** (fractional coordinates *xyz*) instead of **r** to describe position in real space
- It turns out that **s·r** is equal to **h·x** (*hx*+*ky*+*lz*)
  - see web page for details

$$\mathbf{F}(\mathbf{h}) = \int_{cell} \rho(\mathbf{x}) \exp(2\pi i \mathbf{h} \cdot \mathbf{x}) d\mathbf{x}$$

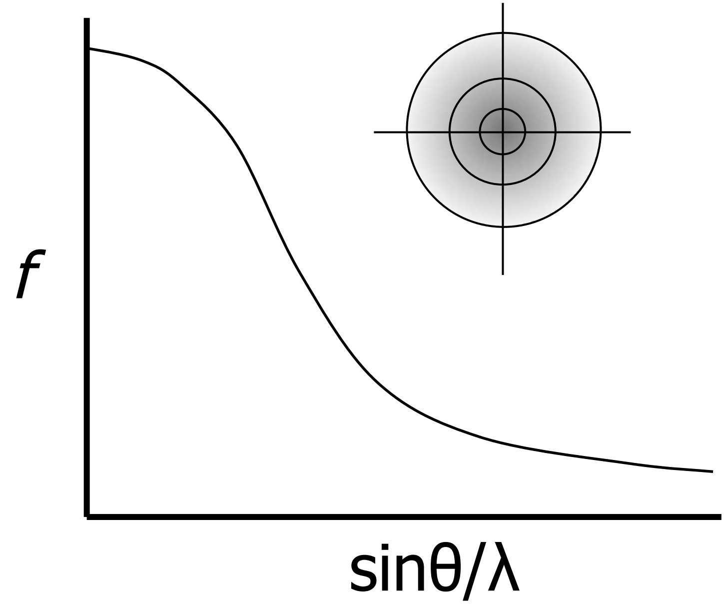
Structure factors and electron density

- Turn structure factors back into electron density by inverting Fourier transform
  - same equation, opposite sign in exponential
  - normalisation factor of $1/V$

$$\mathbf{F}(\mathbf{h}) = \int_{cell} \rho(\mathbf{x}) \exp(2\pi i \mathbf{h} \cdot \mathbf{x}) d\mathbf{x}$$

$$\rho(\mathbf{x}) = \frac{1}{V} \sum_{\mathbf{h}} \mathbf{F}(\mathbf{h}) \exp(-2\pi i \mathbf{h} \cdot \mathbf{x})$$

Structure factor equation with atoms

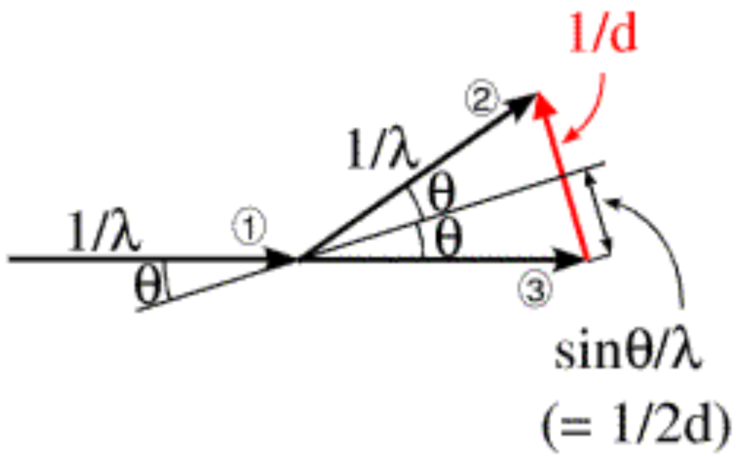


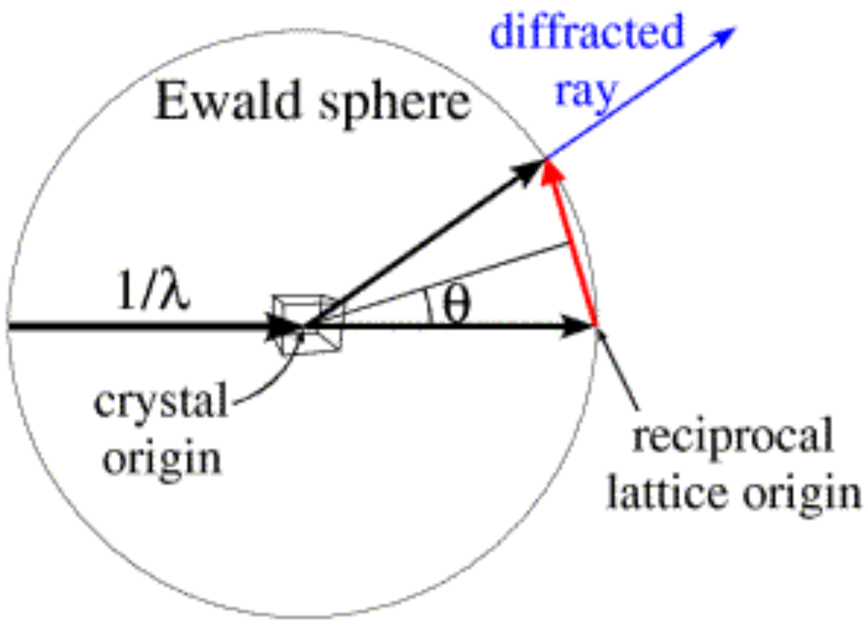
- Define structure factor for atom at origin as *f*
- Moving an electron from origin to **x** changes its phase by $2\pi\mathbf{h}\cdot\mathbf{x}$
  - same applies to atom
- Structure factor equation can then be defined as sum over atoms

$$\mathbf{F}(\mathbf{h}) = \sum_j f_j \exp\left(2\pi i \mathbf{h} \cdot \mathbf{x}_j\right)$$

The Ewald sphere

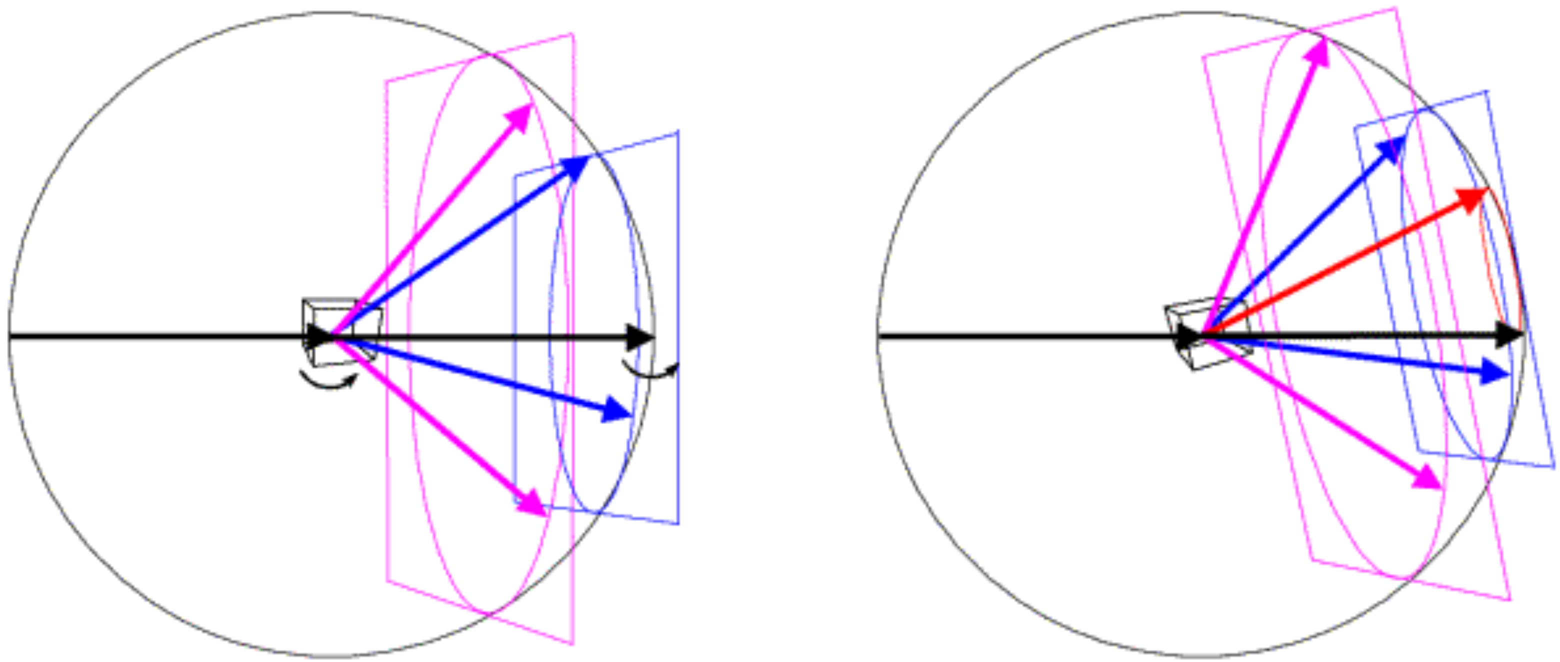
- Useful construction to visualise reciprocal space
  - which Bragg planes are in the diffracting condition





Rotating real and reciprocal space

- Reciprocal space rotates with real space
  - but origin of reciprocal lattice is edge of Ewald sphere!



Rotating reciprocal space for a crystal

- www-structmed.cimr.cam.ac.uk/Course/Basic_diffraction/data_animation.html