



1.3 The structure factor and some diffraction basics

Scattering
Block Course
12.-13.02.2024

The structure factor

Structure from atoms works in reciprocal space too!

- Generally: the FT of the sum of functions is equal to the sum of the FTs of each function

$$\mathcal{F}[g_1(r) + g_2(r) + \dots] = \mathcal{F}[g_1(r)] + \mathcal{F}[g_2(r)] + \dots$$

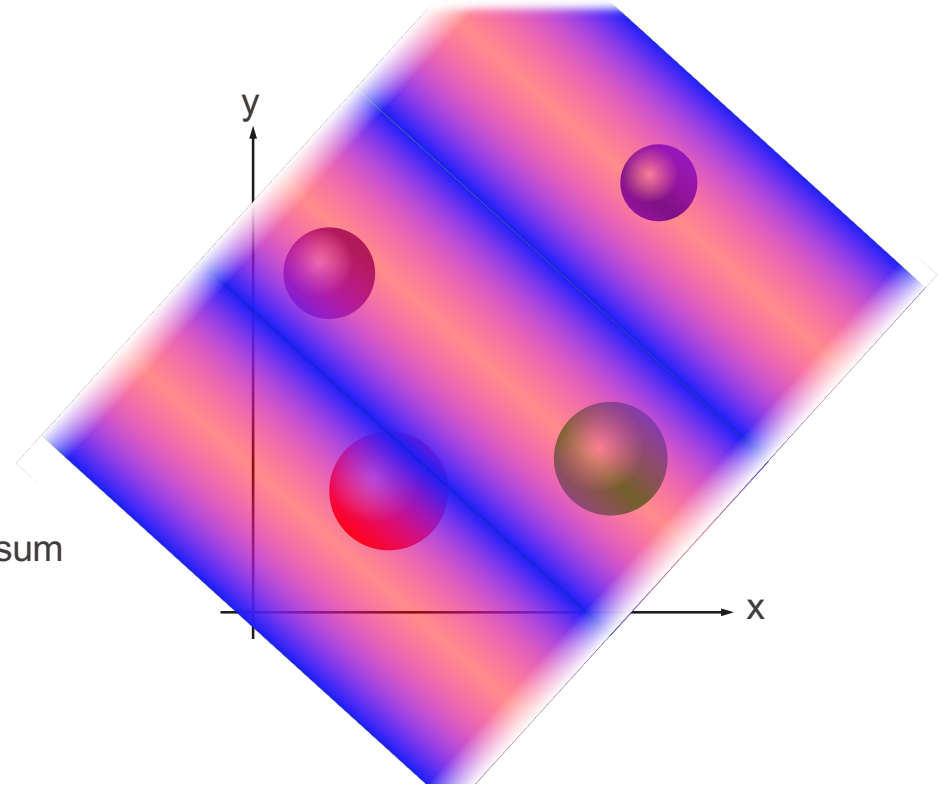
- Molecules or unit cells are simply ensembles of atoms in a particular configuration

Mathematically:

$$M = \sum_{j=1}^n \rho_j(r)$$

$$\Rightarrow \mathcal{F}[M] = \sum_{j=1}^n \mathcal{F}[\rho_j(r)] = \sum_{j=1}^n f_j(Q)$$

Vector sum



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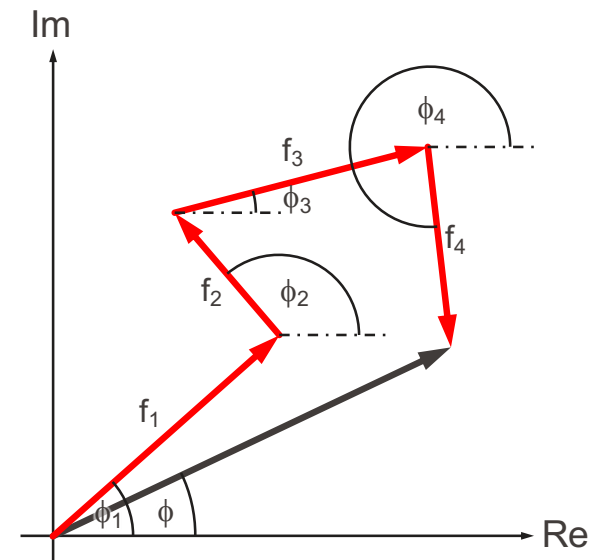
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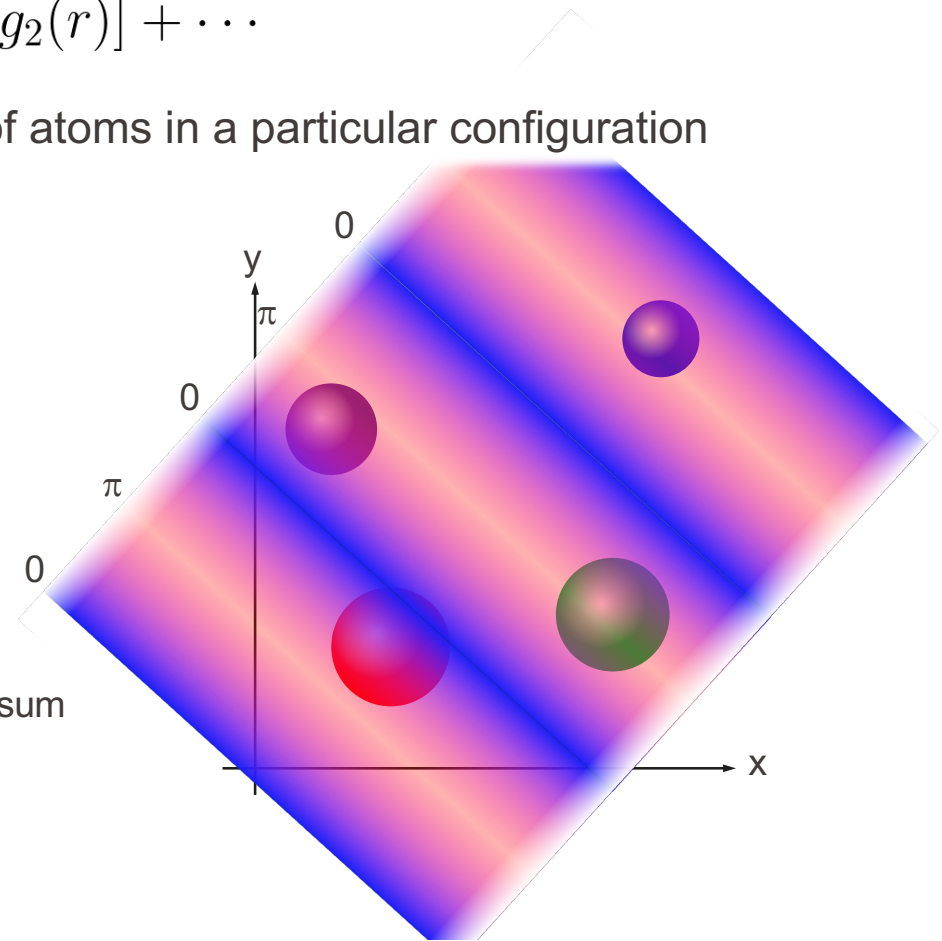
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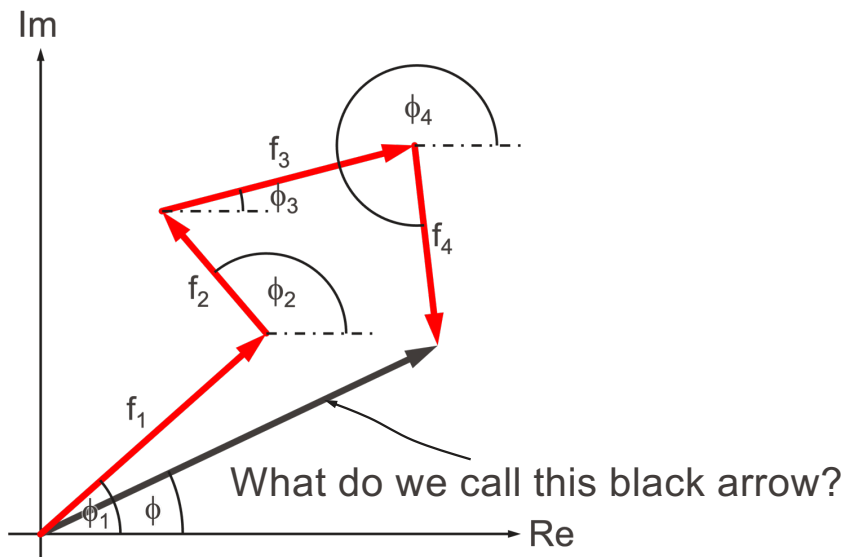
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Vector sum



Time out – source of confusion in nomenclature!!



- If considering the scattering from a single molecule, the square of the magnitude of the black arrow is referred to as the structure factor,

$$S(Q) = \left| \sum_{j=1}^n f_j(Q) \right|^2$$

- If considering a crystalline structure, then the black arrow itself is also called the structure factor,

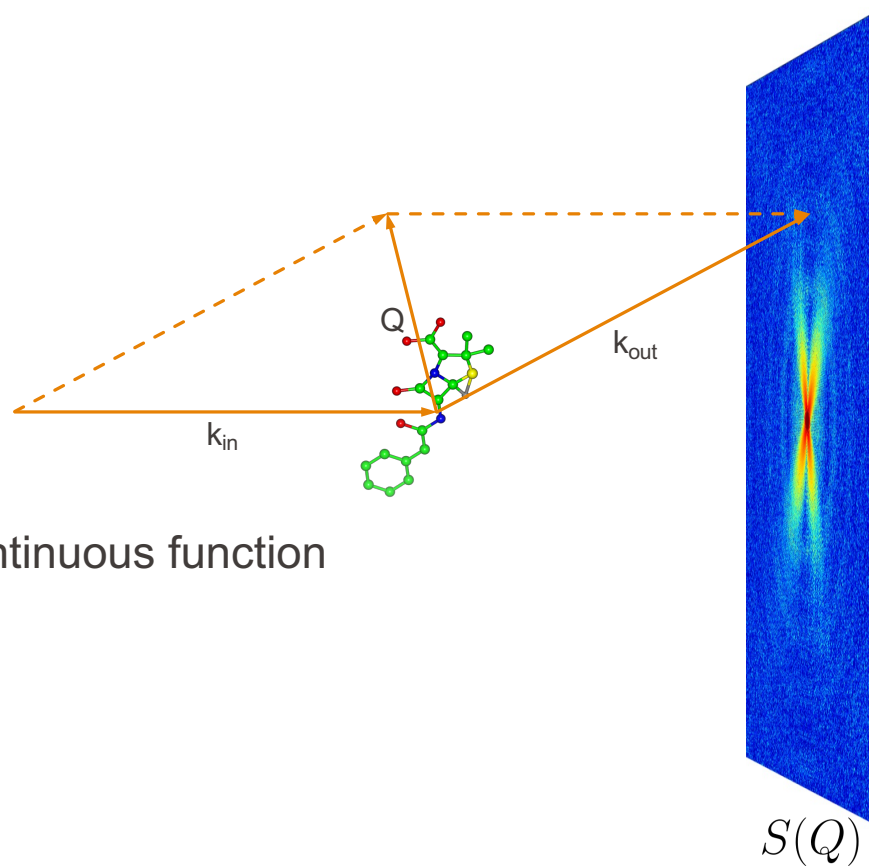
$$F(Q) = \sum_{j=1}^n f_j(Q)$$

which has a magnitude AND phase ϕ

Scattering from crystals

The structure factor of a single molecule

- For a single molecule, the structure factor $S(Q)$ is simply the $|FT|^2$ of that molecule's structure parallel to, and projected perpendicular to, the scattering vector



- This is a continuous function

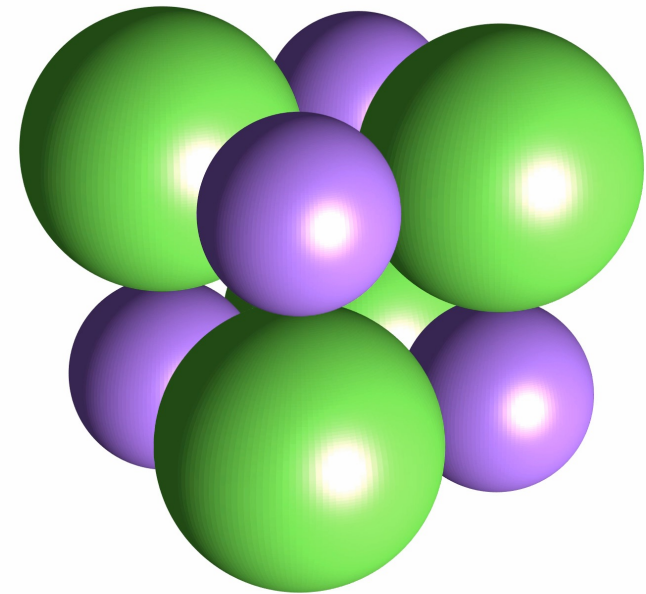
Definition of a crystal



- Repeat of motif in regular distances in 3D space
 - ‘Anchor points’ = ‘Bravais lattice’
 - Each anchor point has a motif: the ‘basis’
- Unit cell
 - Lattice constants a, b, c
 - Angles between lattice constants α, β, γ
 - Unit-cell volume

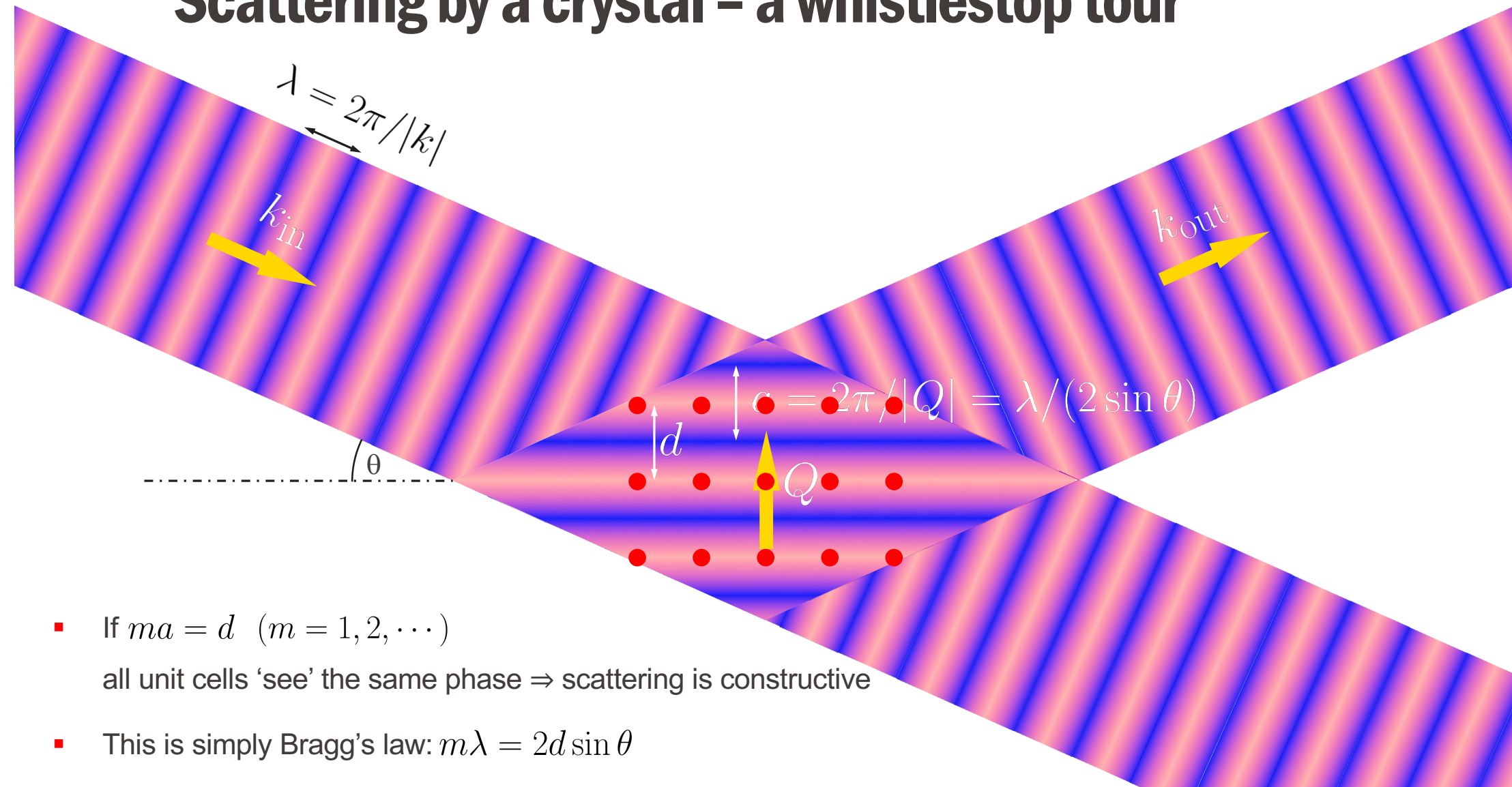
$$V_c = |\mathbf{a} \cdot \mathbf{b} \times \mathbf{c}|$$

$$V_c = abc \left(1 + 2 \cos \alpha \cos \beta \cos \gamma - \cos^2 \alpha - \cos^2 \beta - \cos^2 \gamma \right)^{1/2}$$



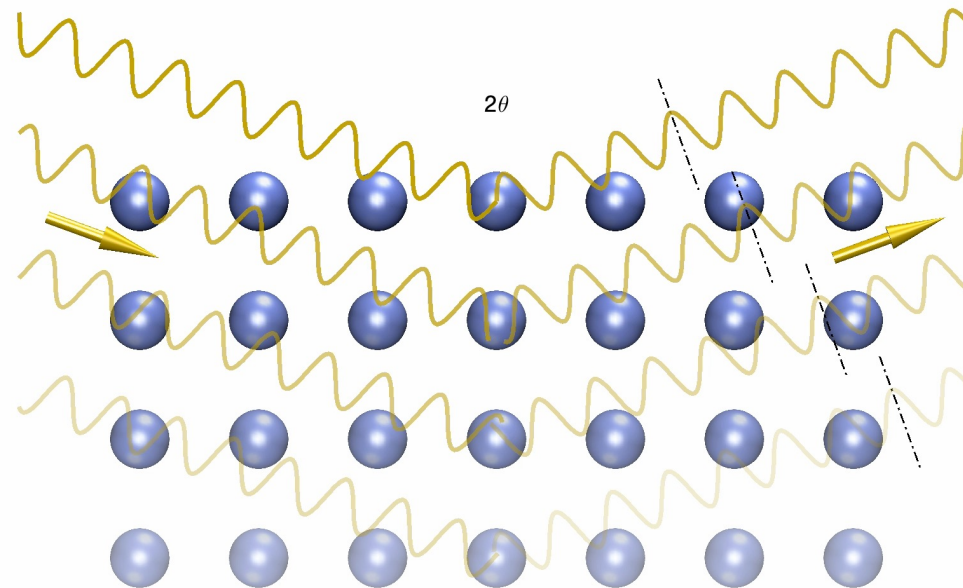
Face-centered cubic
rocksalt (NaCl)

Scattering by a crystal – a whistlestop tour



- If $ma = d$ ($m = 1, 2, \dots$)
all unit cells 'see' the same phase \Rightarrow scattering is constructive
- This is simply Bragg's law: $m\lambda = 2d \sin \theta$

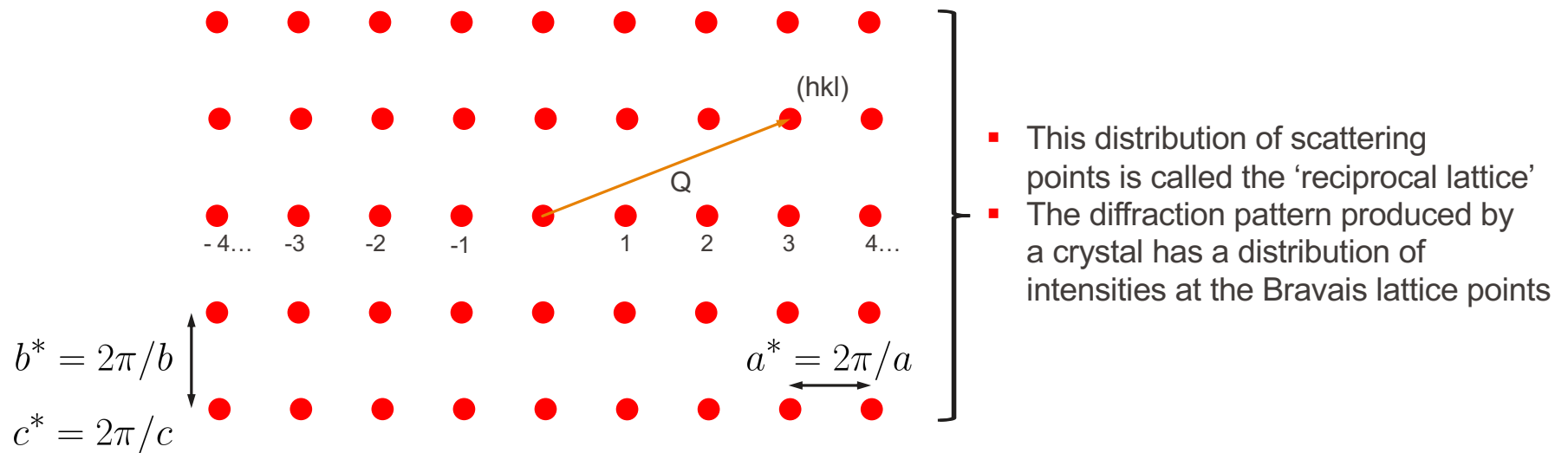
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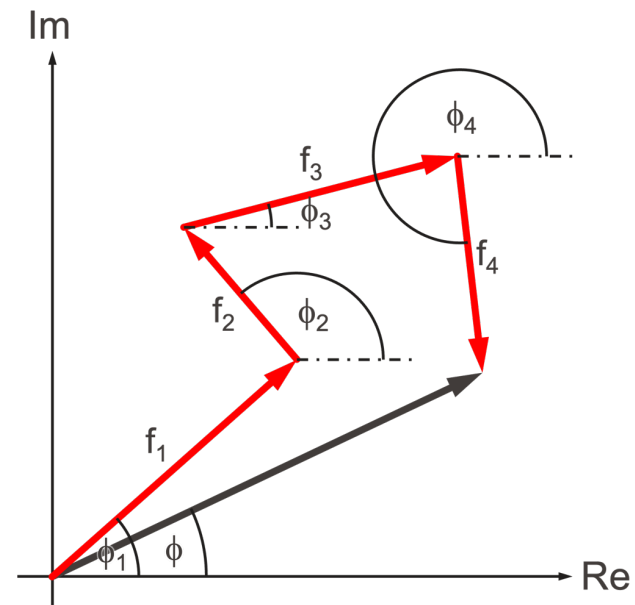
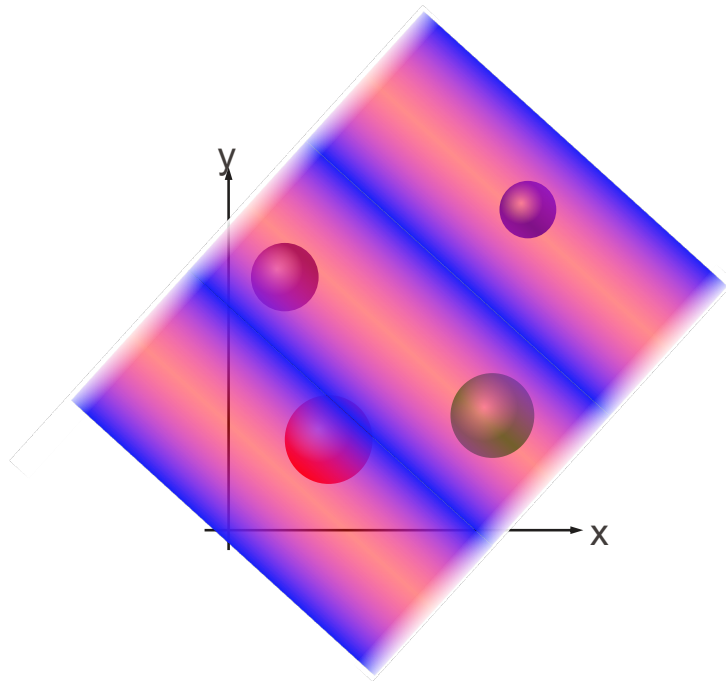
- Reciprocal space: mapping out momenta (Q) values
- 1D: whenever $Q = 2\pi/a = 2m\pi/d$, unit cells scatter in phase, and we get an intensity maximum



- (hkl) = 'Miller indices' = m-values for each crystallographic direction in reciprocal space

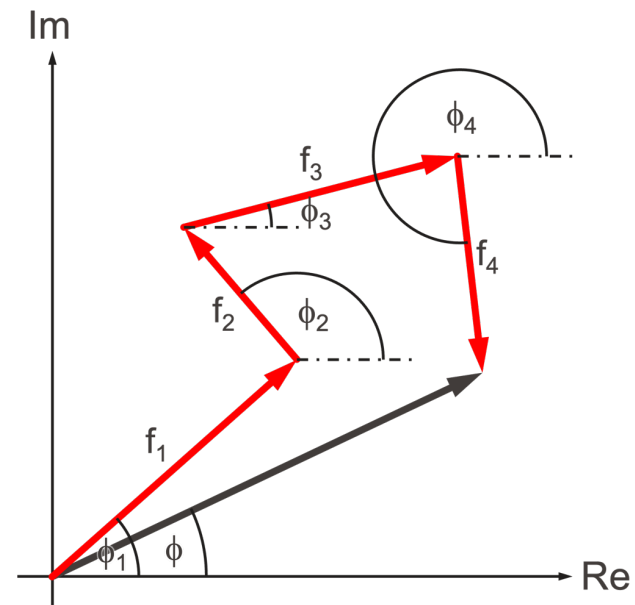
Scattering by a crystal – a whistlestop tour

- We now know where we can expect to find intensity in a crystal diffraction pattern
- But until now we have not thought about the diffraction-peak intensities
- Let's return to our description of the structure factor summarized again here:



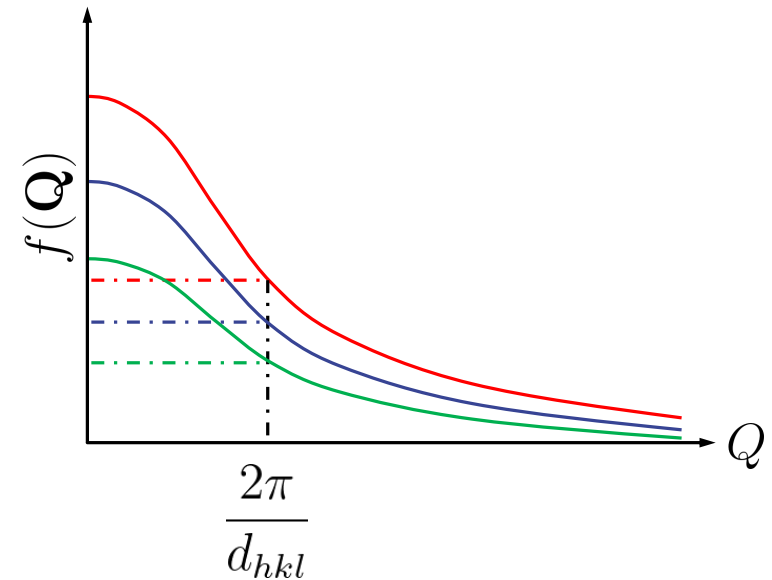
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- We want to find an expression that describes the magnitude and angle of the sum of the atomic form factors (the black arrow)
- We need
 - $f_j(Q)$
 - ϕ_j

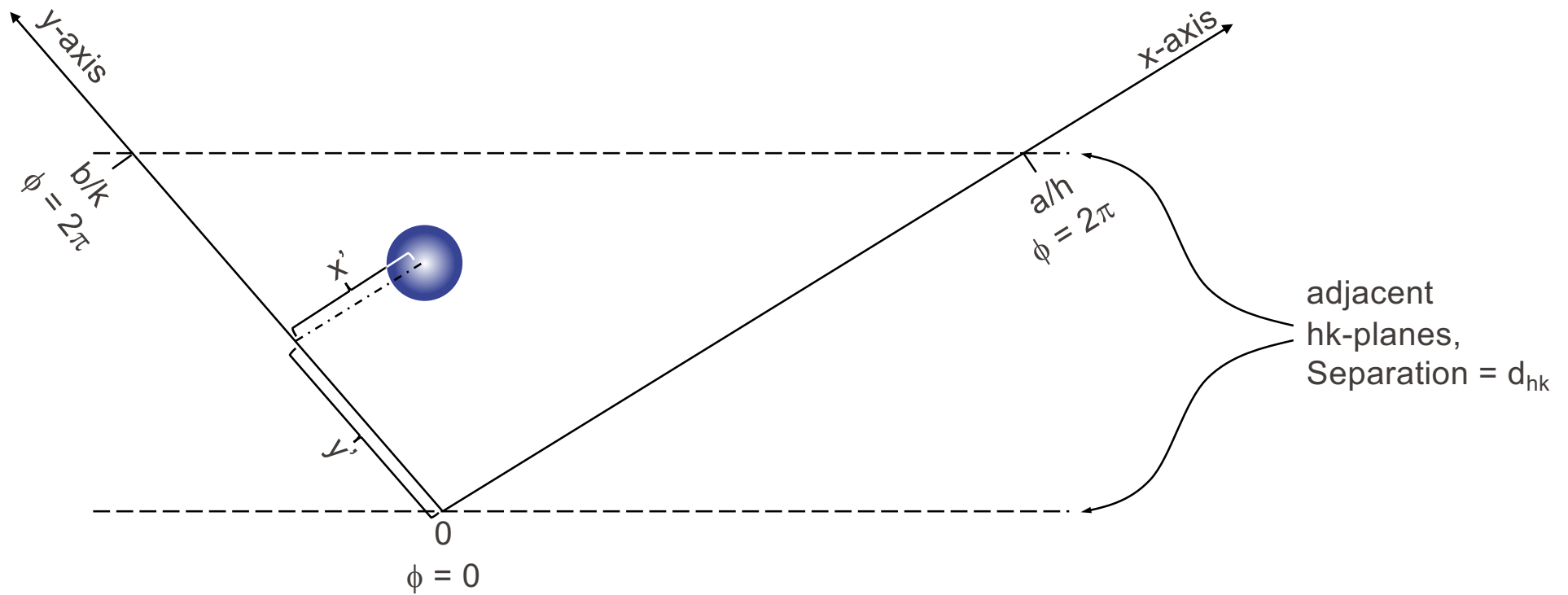


Scattering by a crystal – a whistlestop tour

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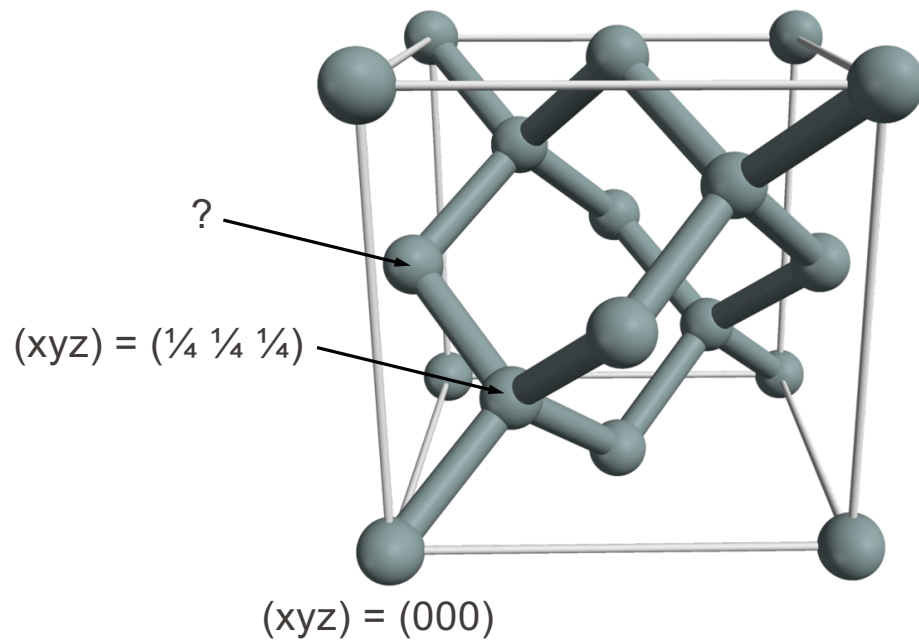
The phases of the atoms



$$\phi = 2\pi \left(\frac{x'}{a/h} + \frac{y'}{b/k} \right) \quad \text{or} \quad \phi = 2\pi (hx + ky)$$

whereby
 $x = x'/a, y = y'/b$

The phases of the atoms

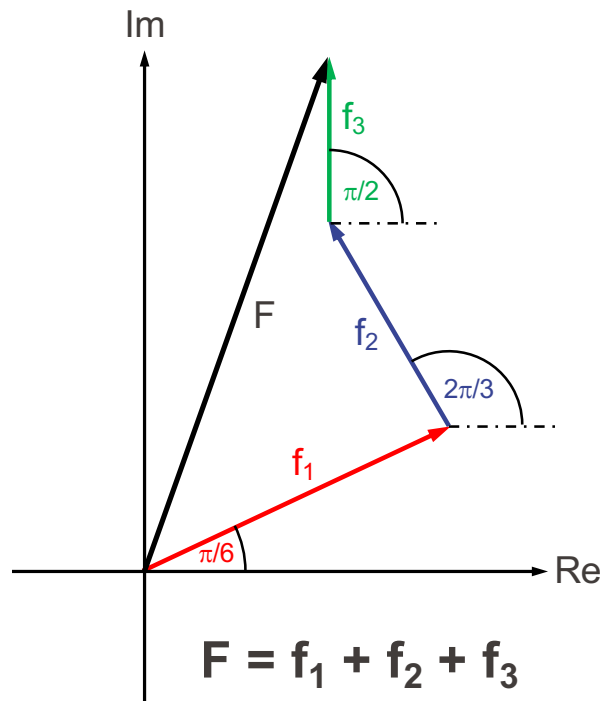


$$\phi = 2\pi(hx + ky + lz)$$

$$(hkl) = (220)$$

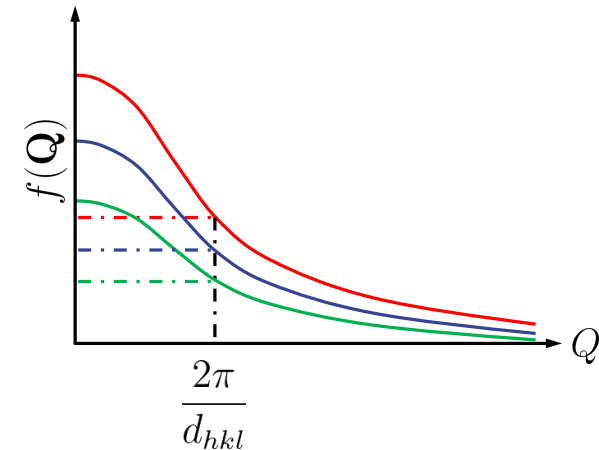
$$\begin{aligned}\phi &= 2\pi(2 \cdot \frac{1}{4} + 2 \cdot \frac{1}{4} + 0 \cdot \frac{1}{4}) \\ &= 2\pi\end{aligned}$$

The structure factor, F , for crystals



- Amplitudes of scattered waves

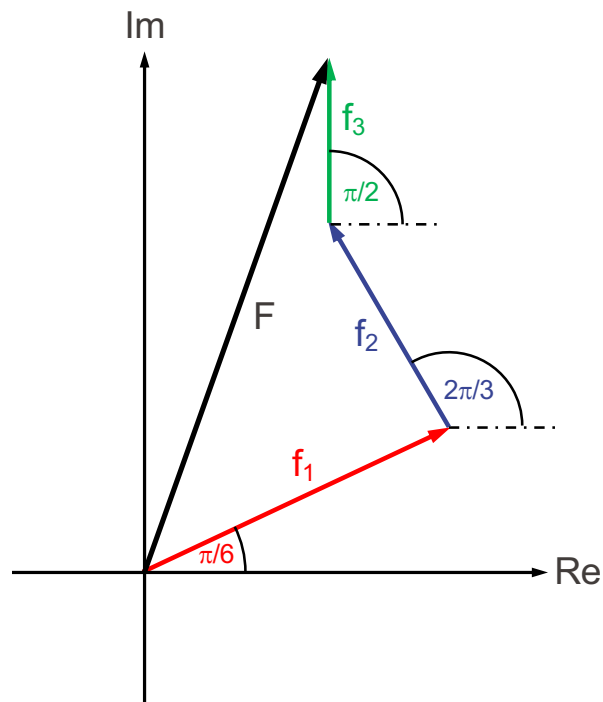
- Atomic form factors for $Q = 4\pi/\lambda \sin \theta$



- e.g., phases of scattered waves

- Atom 1: $\phi_1 \simeq \pi/6$ (30°)
- Atom 2: $\phi_2 \simeq 2\pi/3$ (120°)
- Atom 3: $\phi_3 \simeq \pi/2$ (90°)

The structure factor, F , for crystals

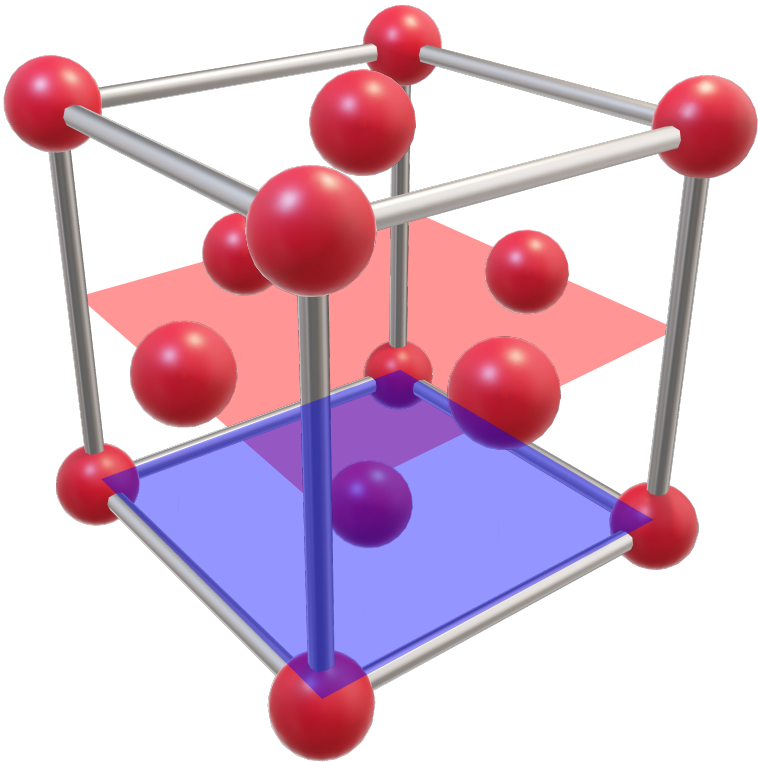


- F = vector sum of atomic form factors

$$F_{hkl} = \sum_j f_j \exp \left[-i2\pi \underbrace{(hx_j + ky_j + lz_j)}_{\phi_j} \right]$$

- Intensity of Bragg peak @ (hkl) is proportional to $|F_{hkl}|^2$
- All phase information ϕ_j is lost!
- This is the “phase problem”

The structure factor for some high-symmetry examples

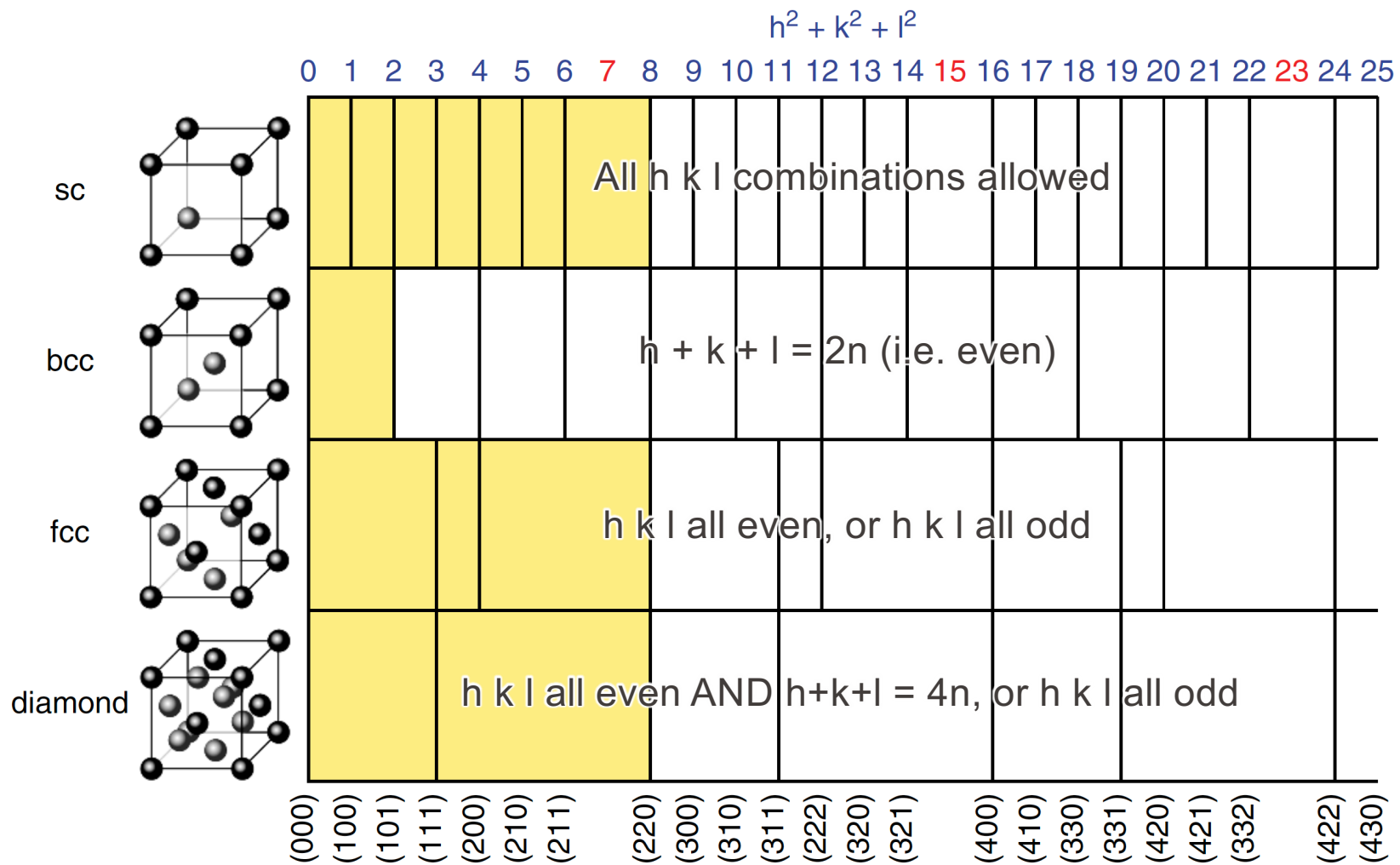


- Face-centered cubic (fcc): 4 identical atoms/unit cell
- x_j, y_j, z_j
 - 0, 0, 0 (corner)
 - $\frac{1}{2} \frac{1}{2} 0$ (face centre)
 - $\frac{1}{2} 0 \frac{1}{2}$ (face centre)
 - $0 \frac{1}{2} \frac{1}{2}$ (face centre)
- F_{001} ?
 - $$F_{001} = f_{\text{atom}}[\exp(0) + \exp(0) + \exp(-i\pi) + \exp(-i\pi)]$$

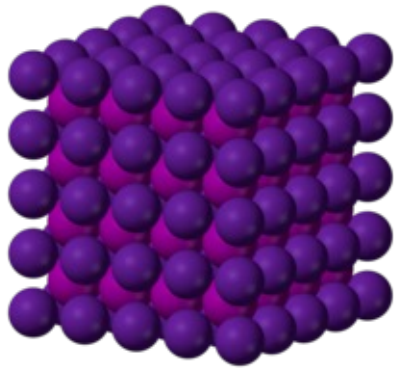
$$= f_{\text{atom}}[1 + 1 - 1 - 1] = 0!!$$
- Bragg's law tells you that you will see a Bragg peak at $(hkl) = (001)$
- But structure factor here = 0... **“systematic absence”**
- General rule for fcc crystals: only BP intensity if h, k, l all odd, or h, k, l all even

See also Supplementary material “Systematic absences”

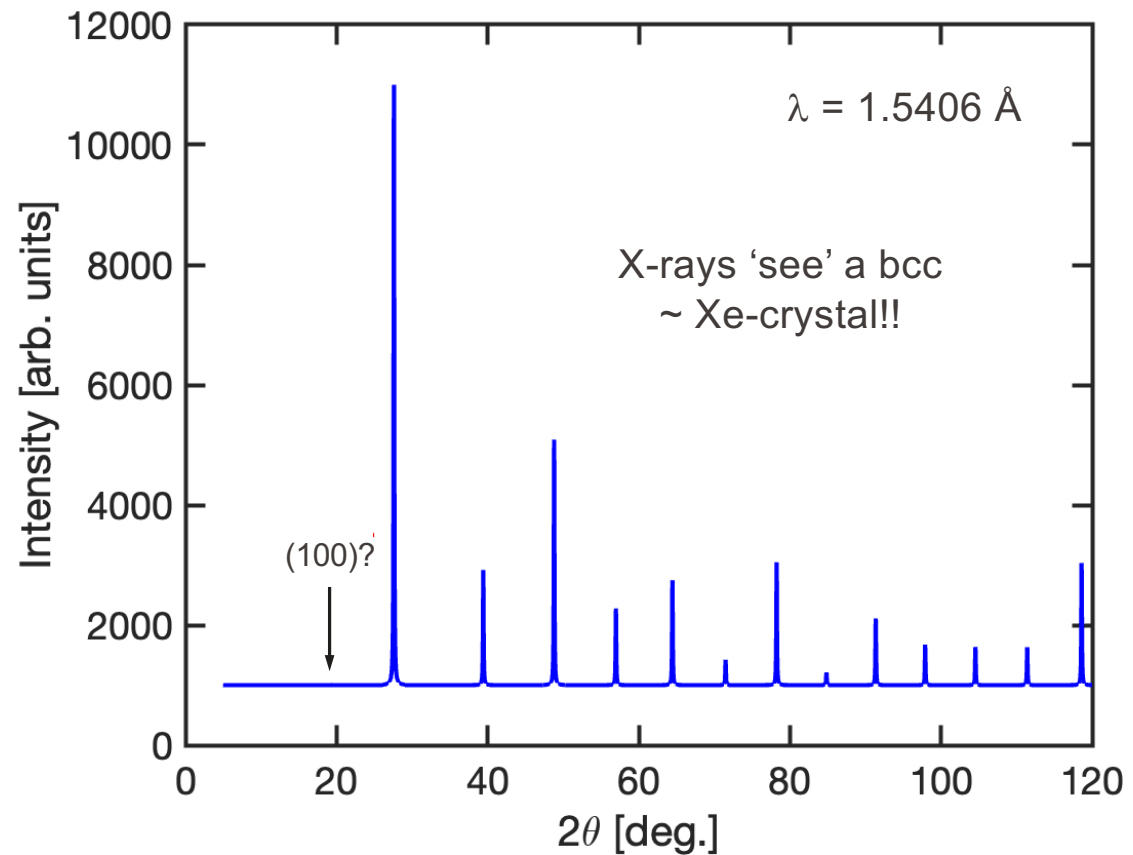
The structure factor for some high-symmetry examples



Example: Caesium Iodide



CsI
 $a = 4.567 \text{ \AA}$
Simple cubic
1 Cs-ion at (0,0,0)
1 I-ion @ $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$
 $Z_{\text{Cs}} = 55$
 $Z_{\text{I}} = 53$



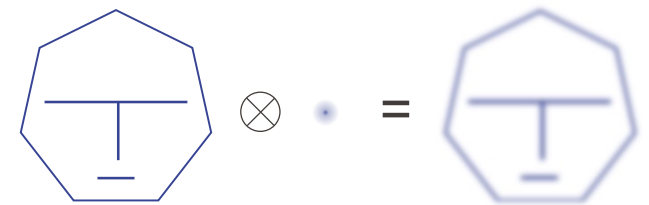
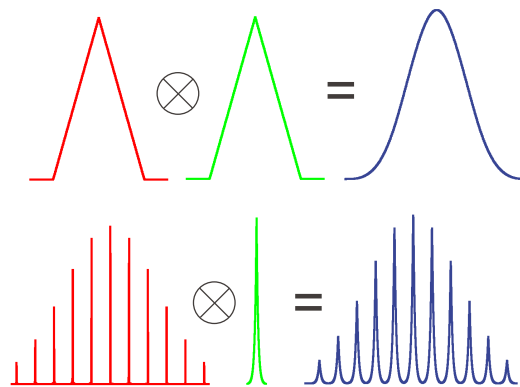
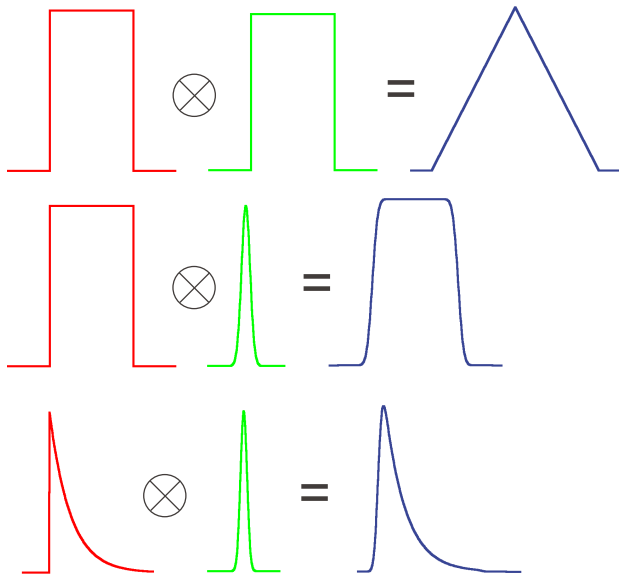
Another interpretation of crystal diffraction patterns

“The Fourier transform of the convolution of two functions equals the FT of the first function multiplied by the FT of the second”

or

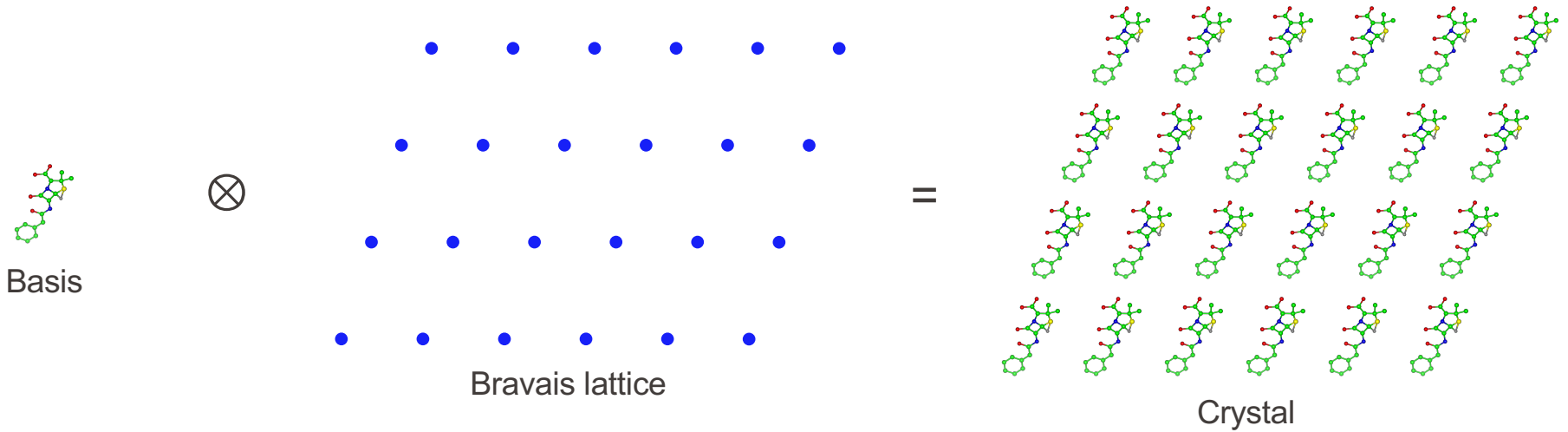
“The Fourier transform of the product of two functions equals the FT of the first function convoluted with the FT of the second”

$$\mathcal{F}[f \times g] = \mathcal{F}[f] \otimes \mathcal{F}[g] \quad \text{or} \quad \mathcal{F}[f \otimes g] = \mathcal{F}[f] \times \mathcal{F}[g]$$

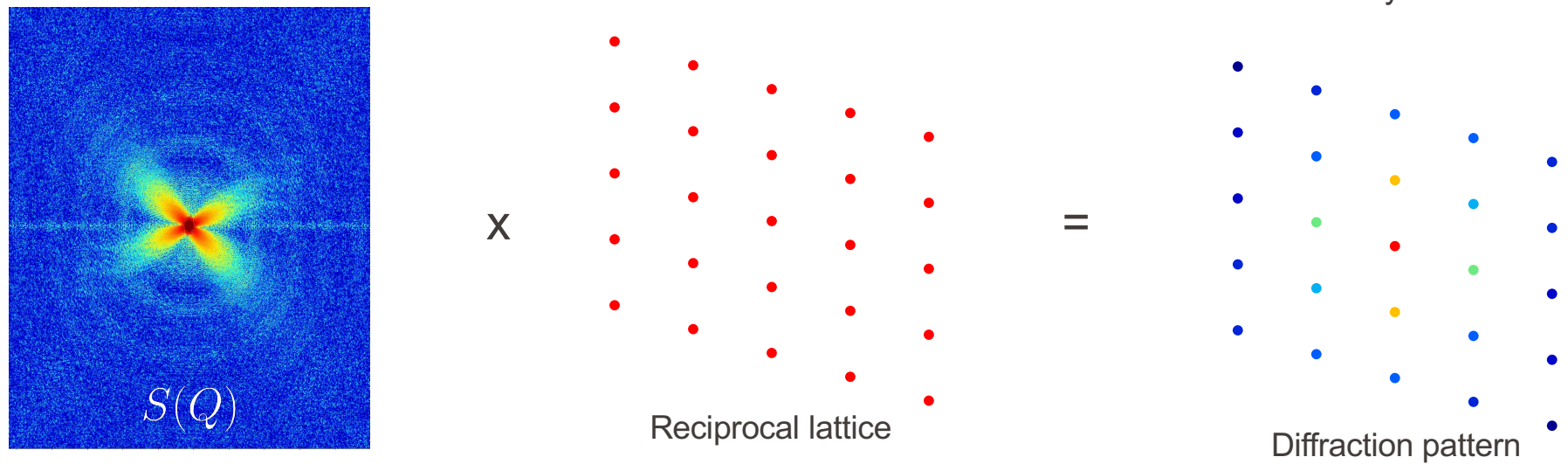


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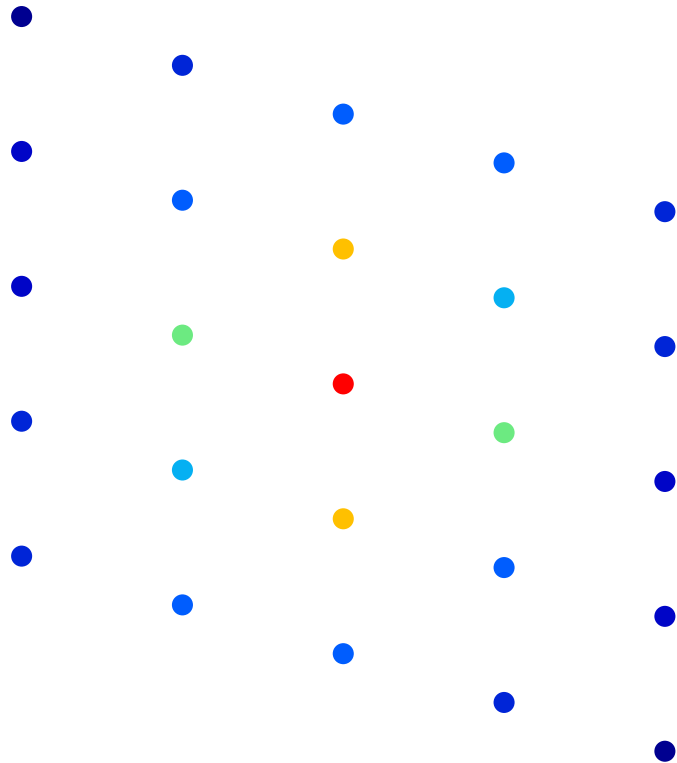
Real space



Reciprocal space

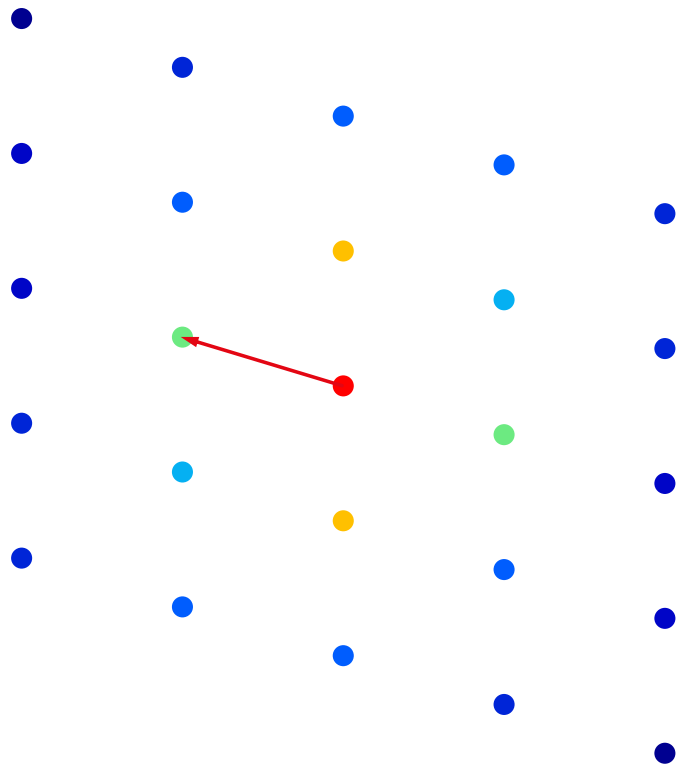


Information gained from diffraction patterns



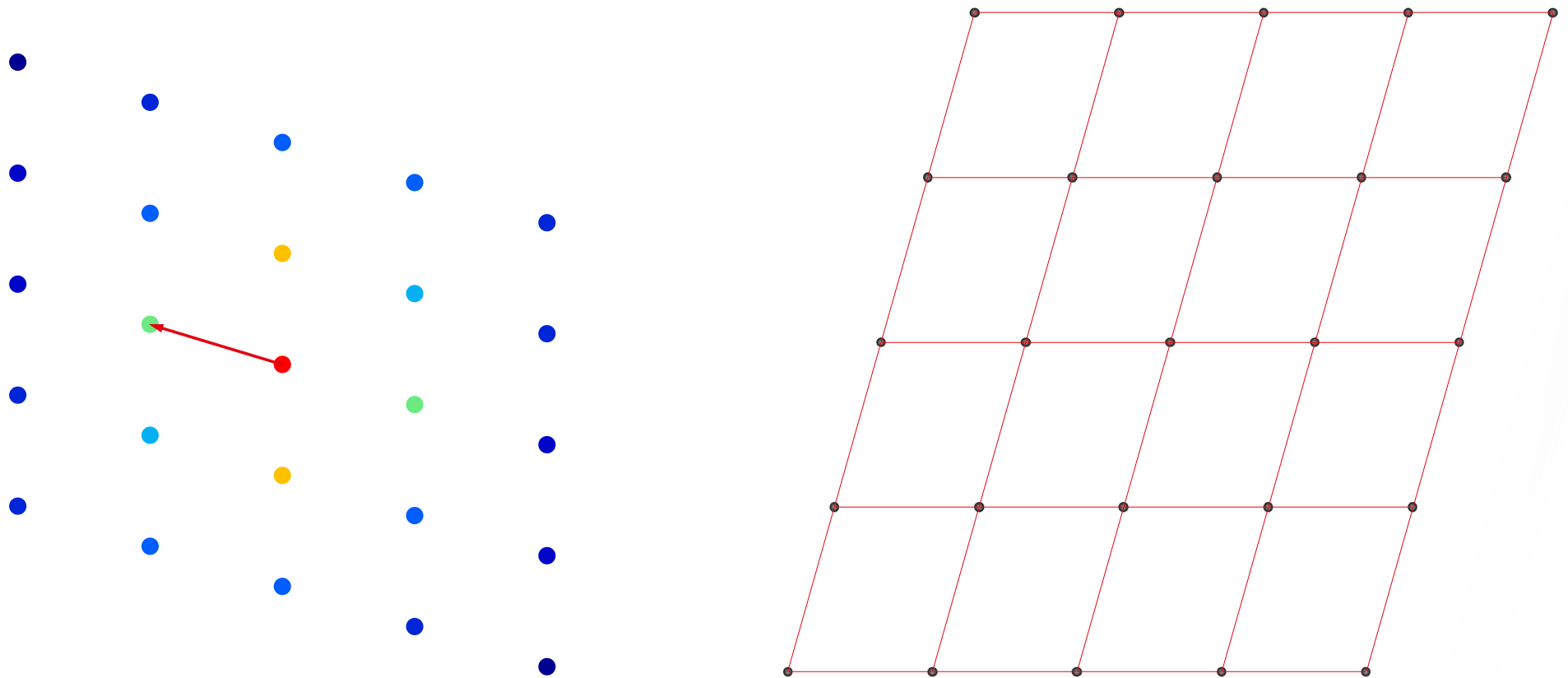
- Remember: a diffraction pattern is the FT of the object that produces it
 - Each point in the RL is therefore a “Fourier component” of the diffraction pattern
 - The position of each point in the RL defines the frequency and direction of a sinusoidal wave of electron density
 - The intensity at each point defines the amplitude of the wave
 - The phase ϕ of that wave is fixed for that wave relative to all the other waves but cannot be measured directly

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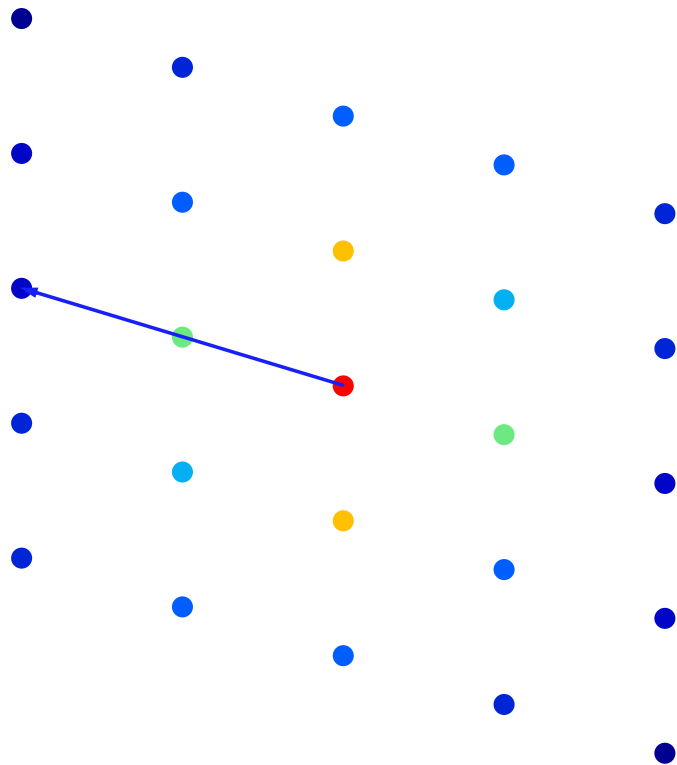


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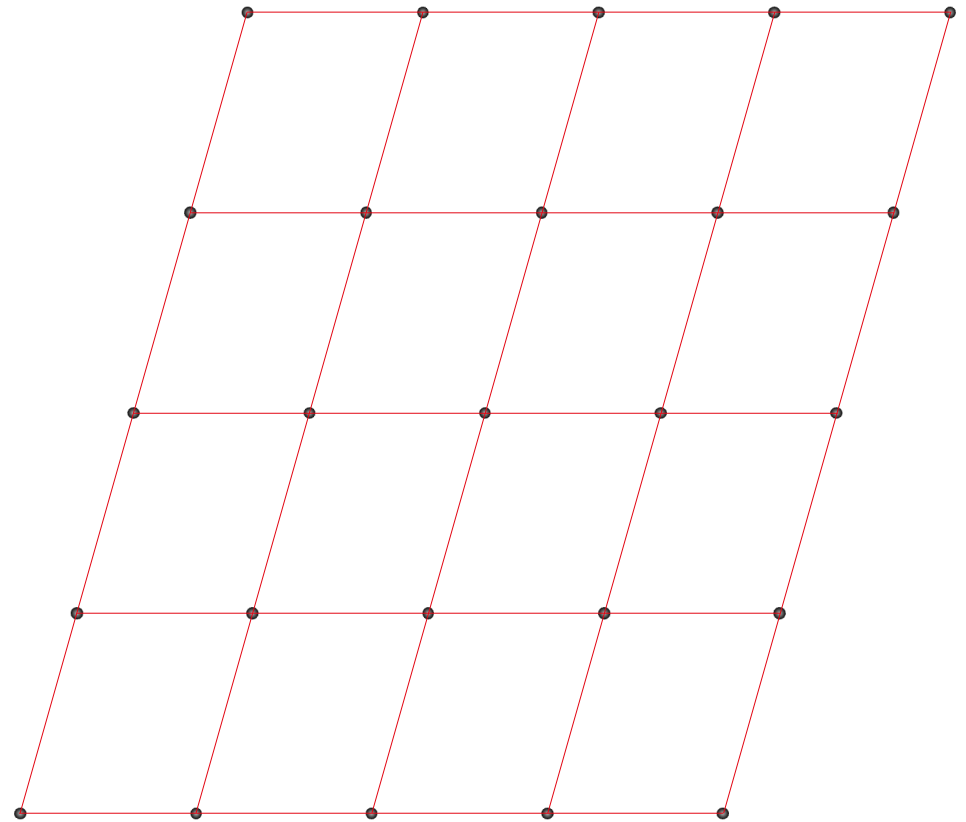
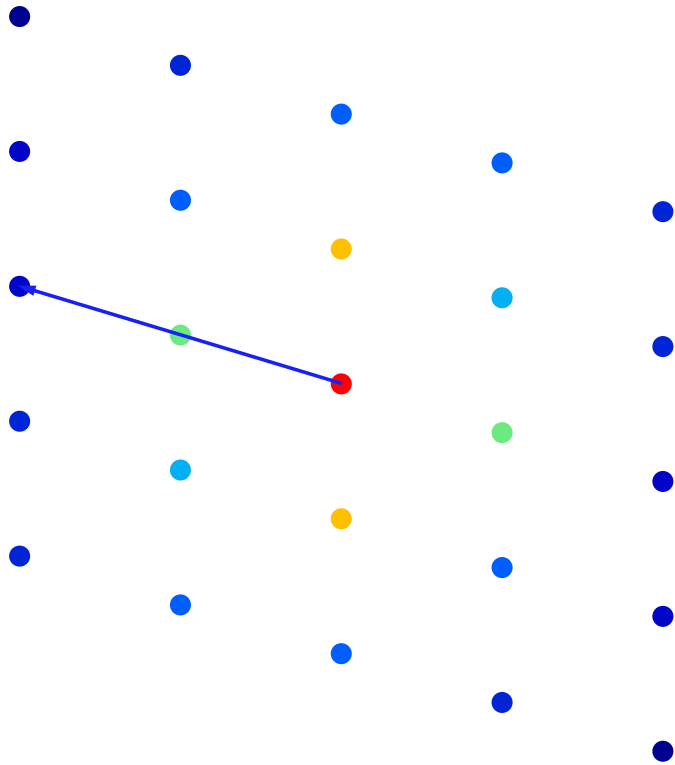


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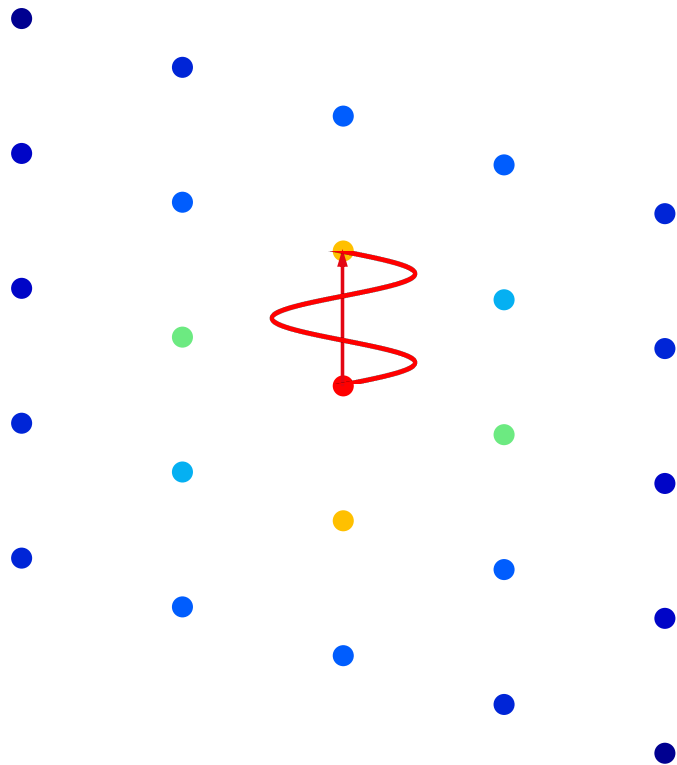


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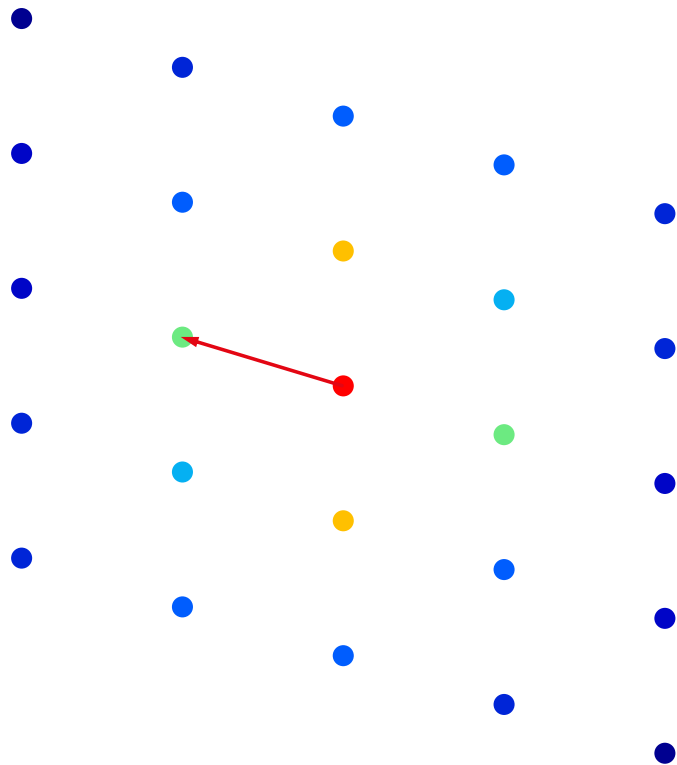


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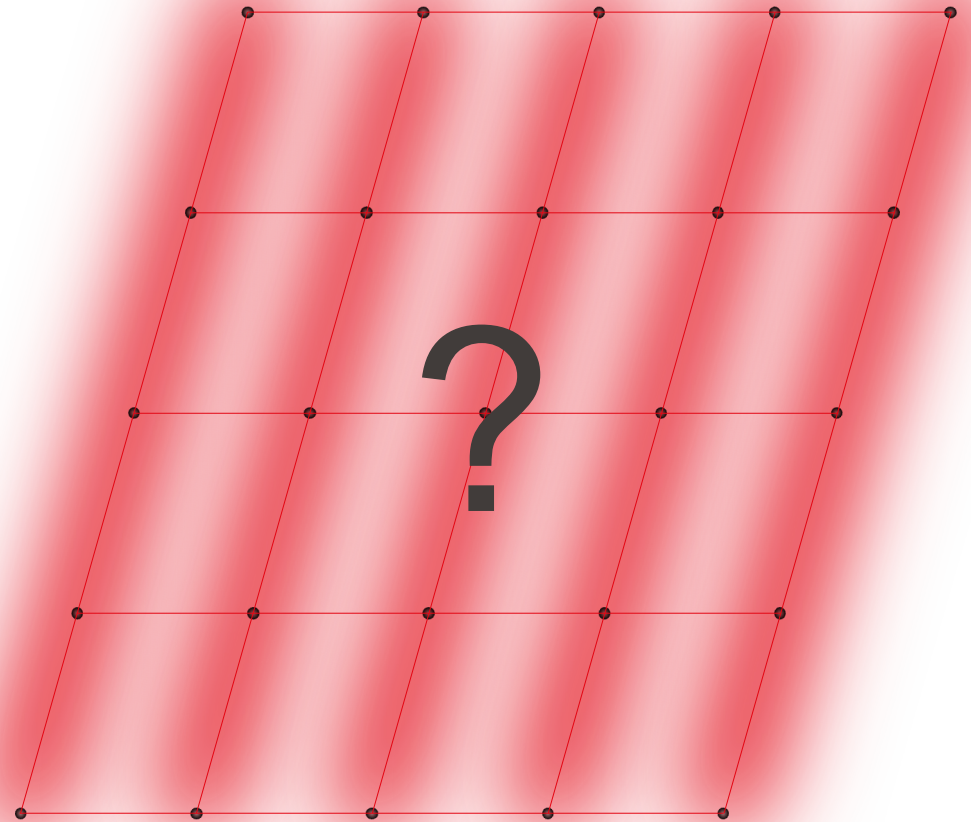
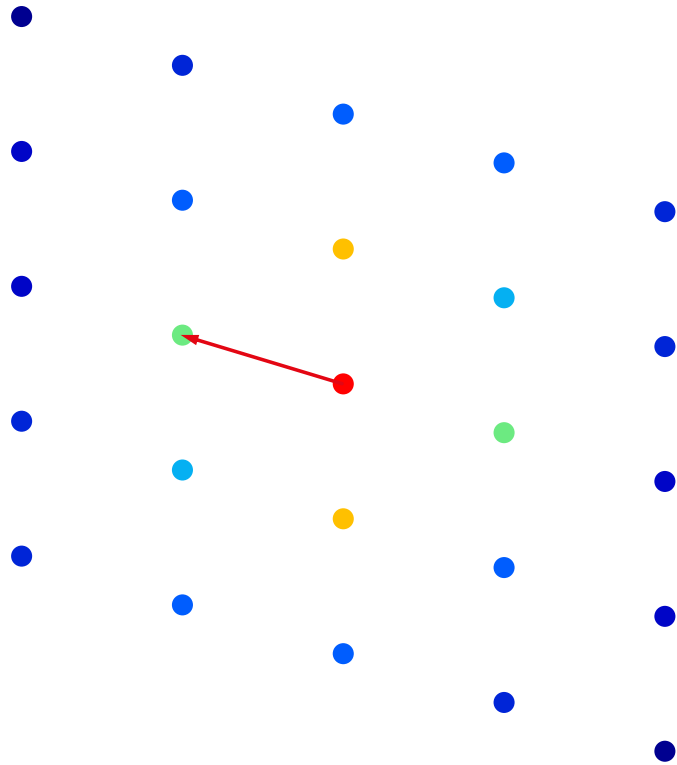
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 - **The intensity at each point defines the amplitude of the wave (\sqrt{I})**
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Information gained from diffraction patterns



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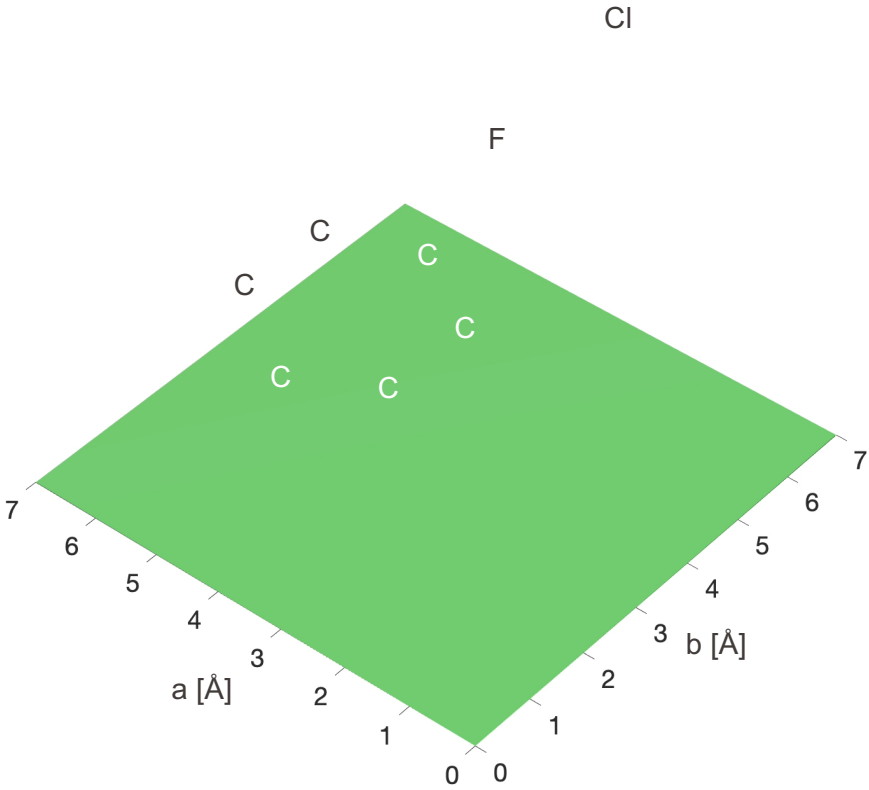
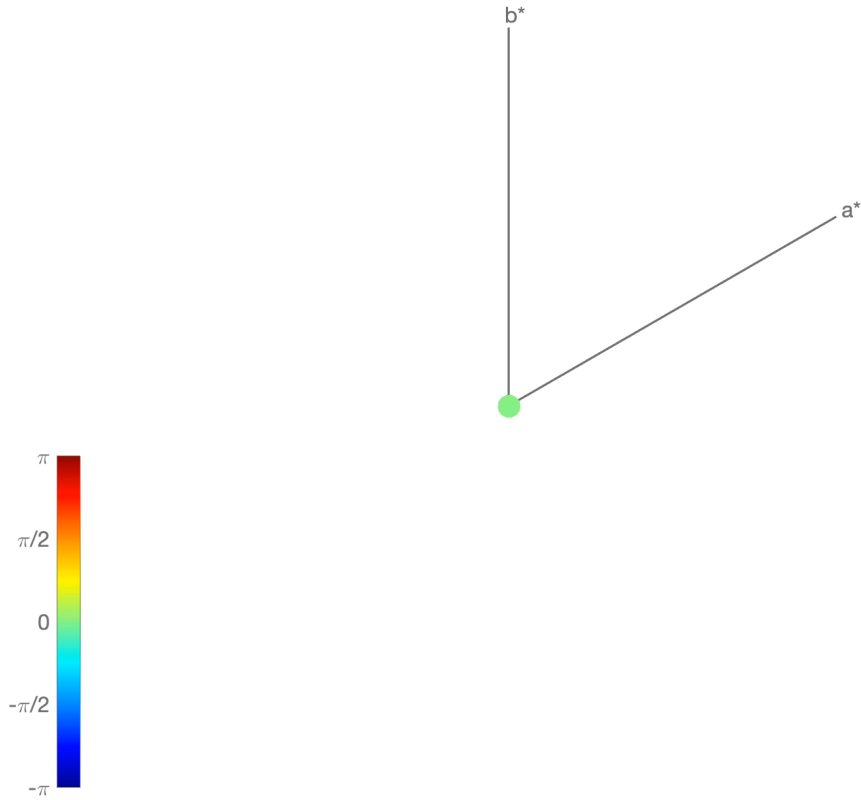
Information gained from diffraction patterns



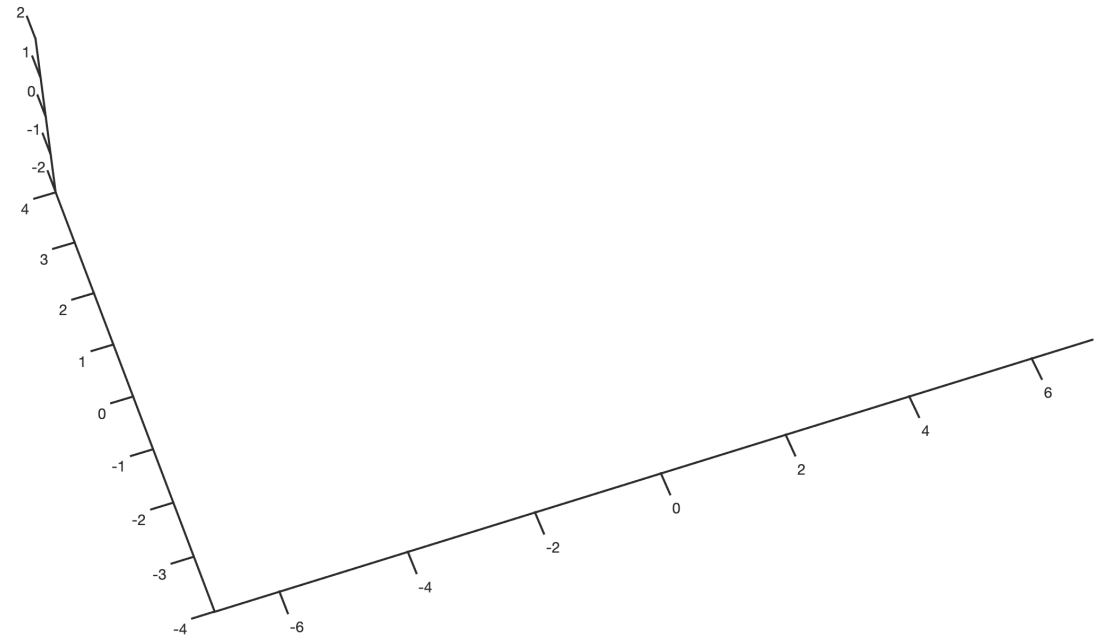
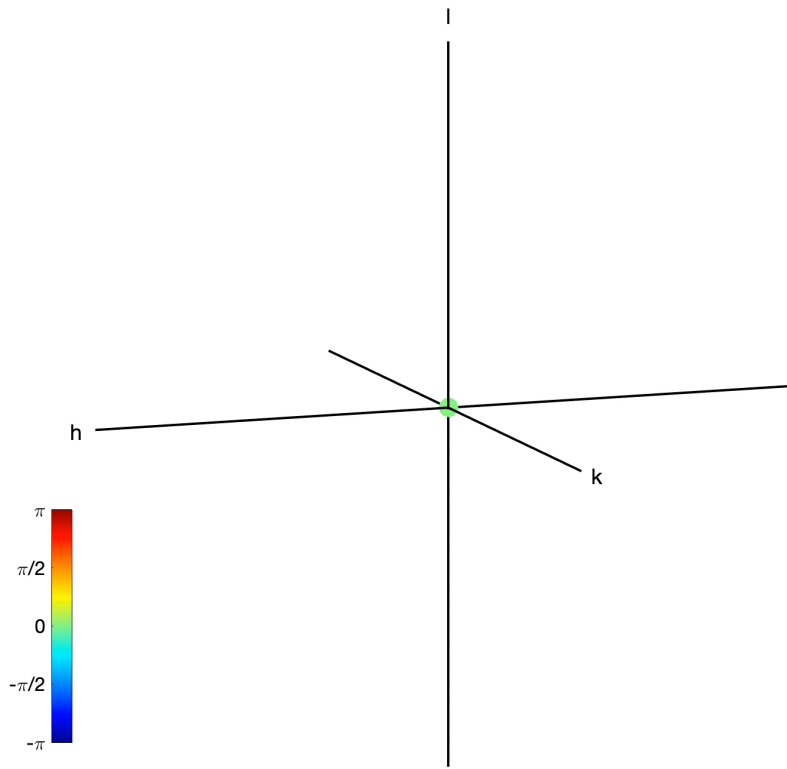
Information gained from diffraction patterns

- So, what happens if you...
 - ... take the information provided by each diffraction point in the RL
 - The direction (angle) of the wave relative to the origin of the RL
 - The frequency (given by the distance from origin of the RL, proportional to $1/\lambda$)
 - The amplitude of the wave, given by the square root of the intensity
 - ... by some clever trick, work out the phase ϕ associated with each of these points (more on this in a moment!!)
 - ... draw the corresponding wave $W(A,\lambda,\phi)$ in real space
 - ... and add them all together?

Let's see...



... and in 3D

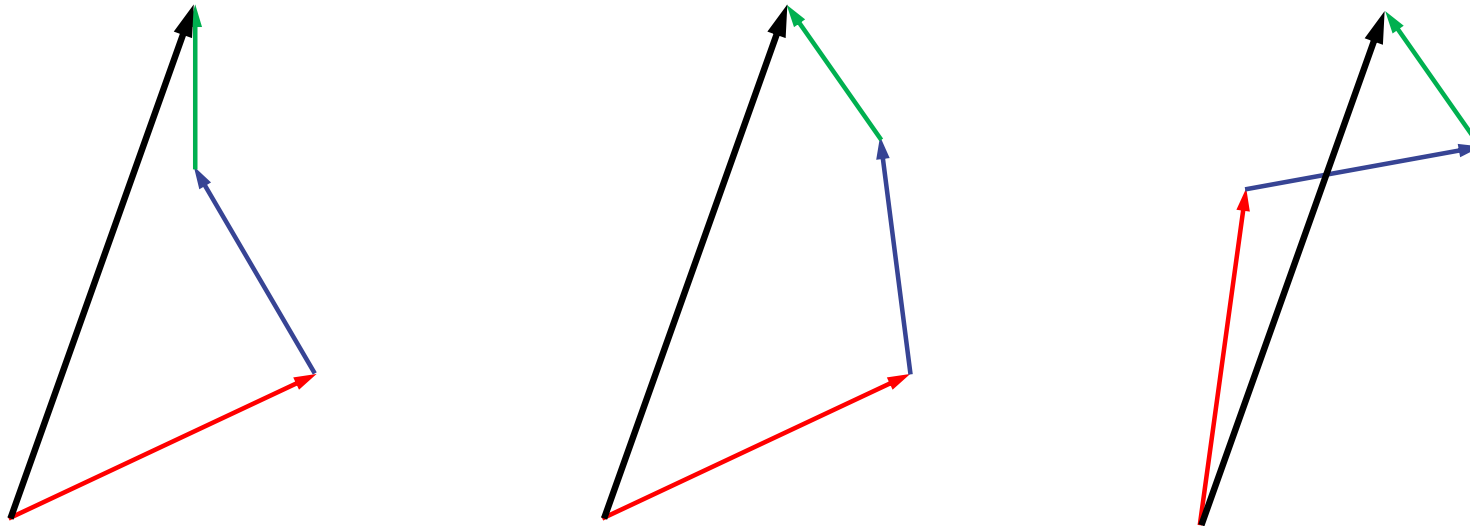


The phase problem

Amplitude v intensity

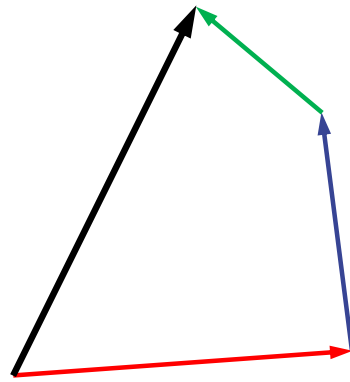
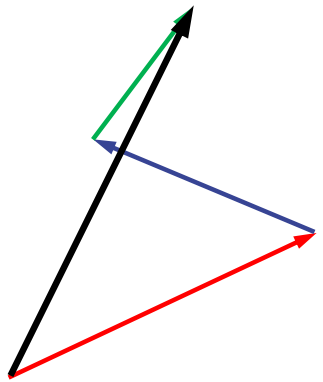
- Measured diffraction pattern – intensities
- Intensity \propto |amplitude|²
 - Amplitude: $a + bi \equiv A \exp(i\phi)$; $A = \sqrt{a^2 + b^2}$; $\tan \phi = b/a$
 - Intensity: $I \propto |A|^2$
 - Phase information (ϕ) is lost!!
 - But not just the phase of structure factor, but the phases of the component atomic form factors (ϕ_j)!!

Structure-factor construction

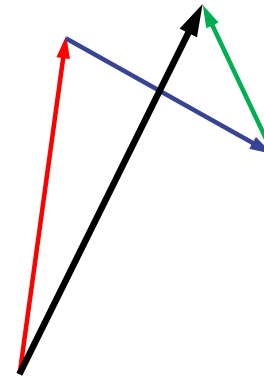


(hkl)

Structure-factor construction

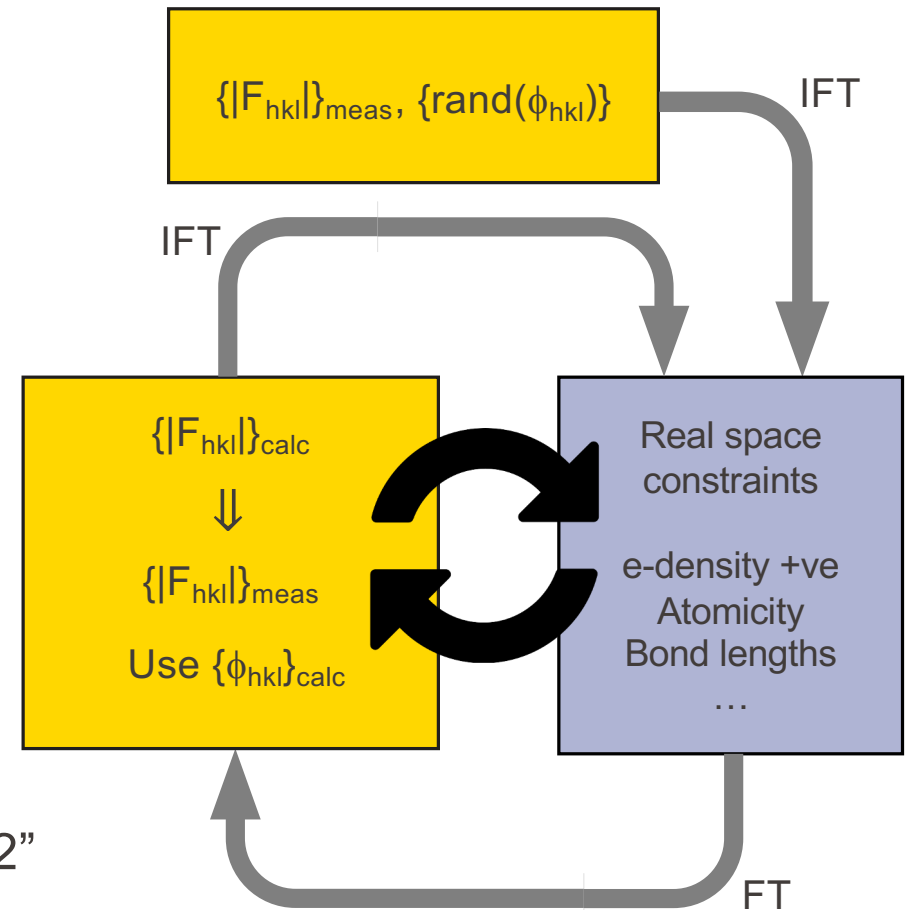


$(h'k'l')$



Phase-retrieval strategies

- Chemical constraints
 - Bonding types, chemical affinities
 - Bond lengths
 - Moieties
- Iterative methods
 - Cycle between real- and reciprocal space
- Machine learning/AI
 - Macromolecular crystallography: “AlphaFold2”

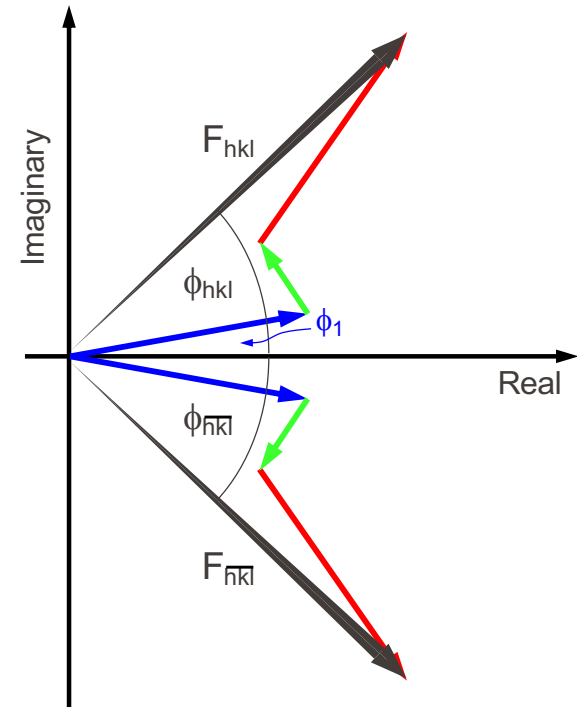
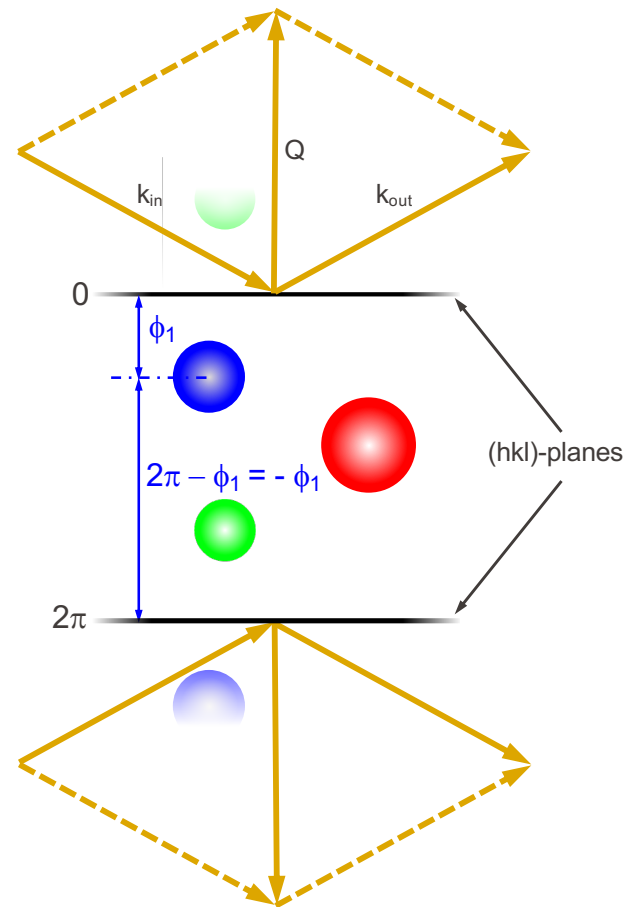
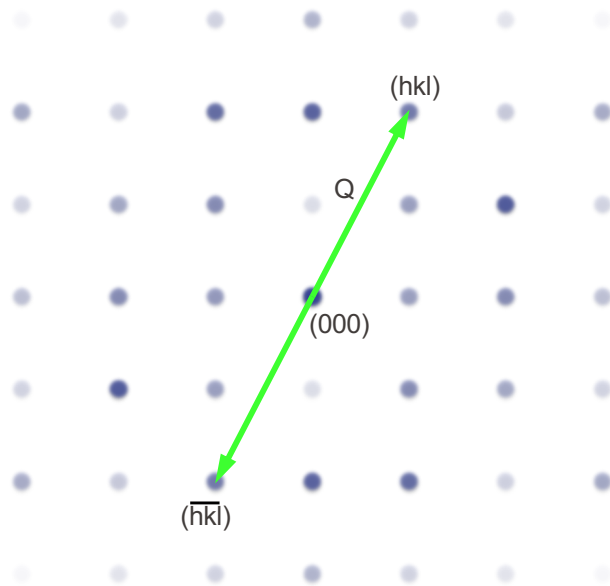


Phase-retrieval strategies – anomalous diffraction

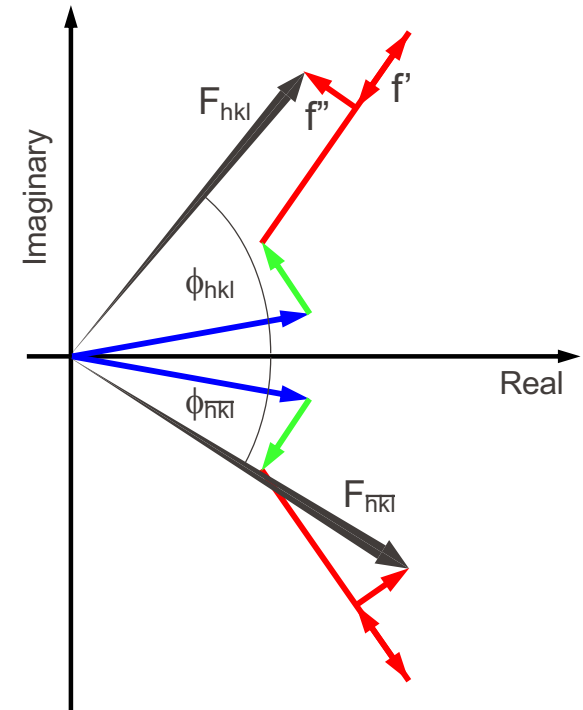
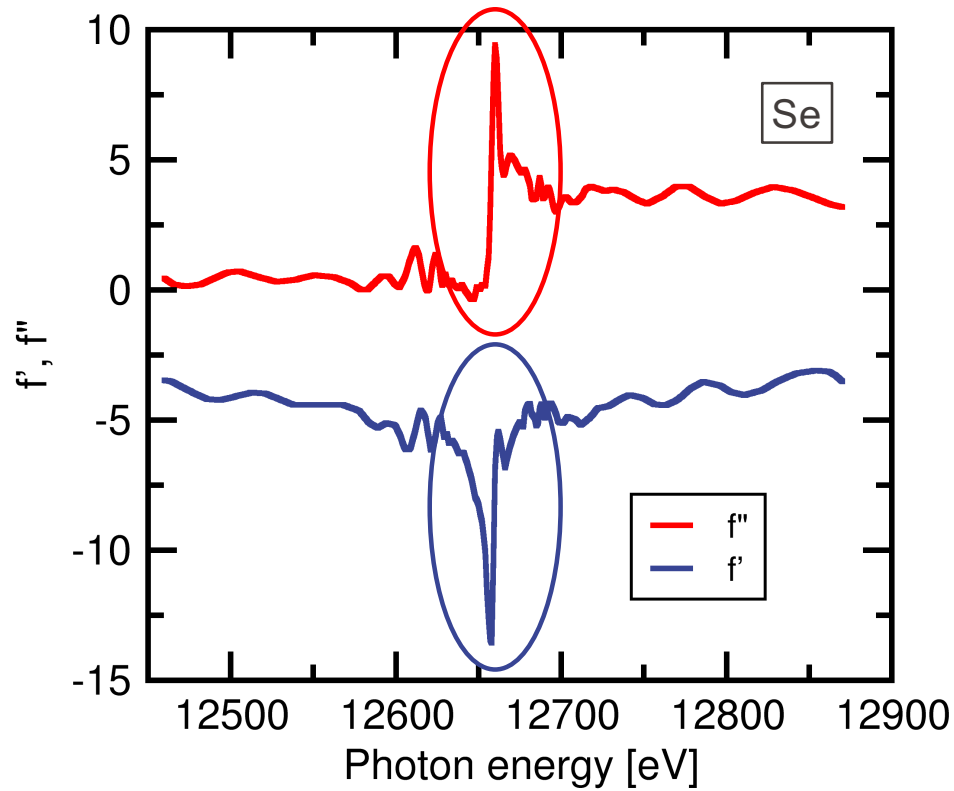
- Anomalous diffraction
 - Away from absorption edges

$$F_{hkl} = F_{\overline{h}\overline{k}\overline{l}}$$

$$\phi_{hkl} = -\phi_{\overline{h}\overline{k}\overline{l}}$$



Close to an absorption edge

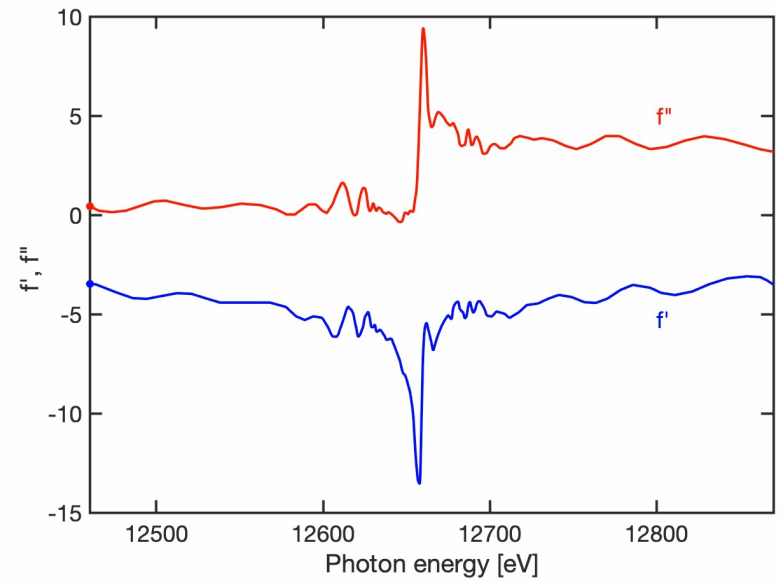
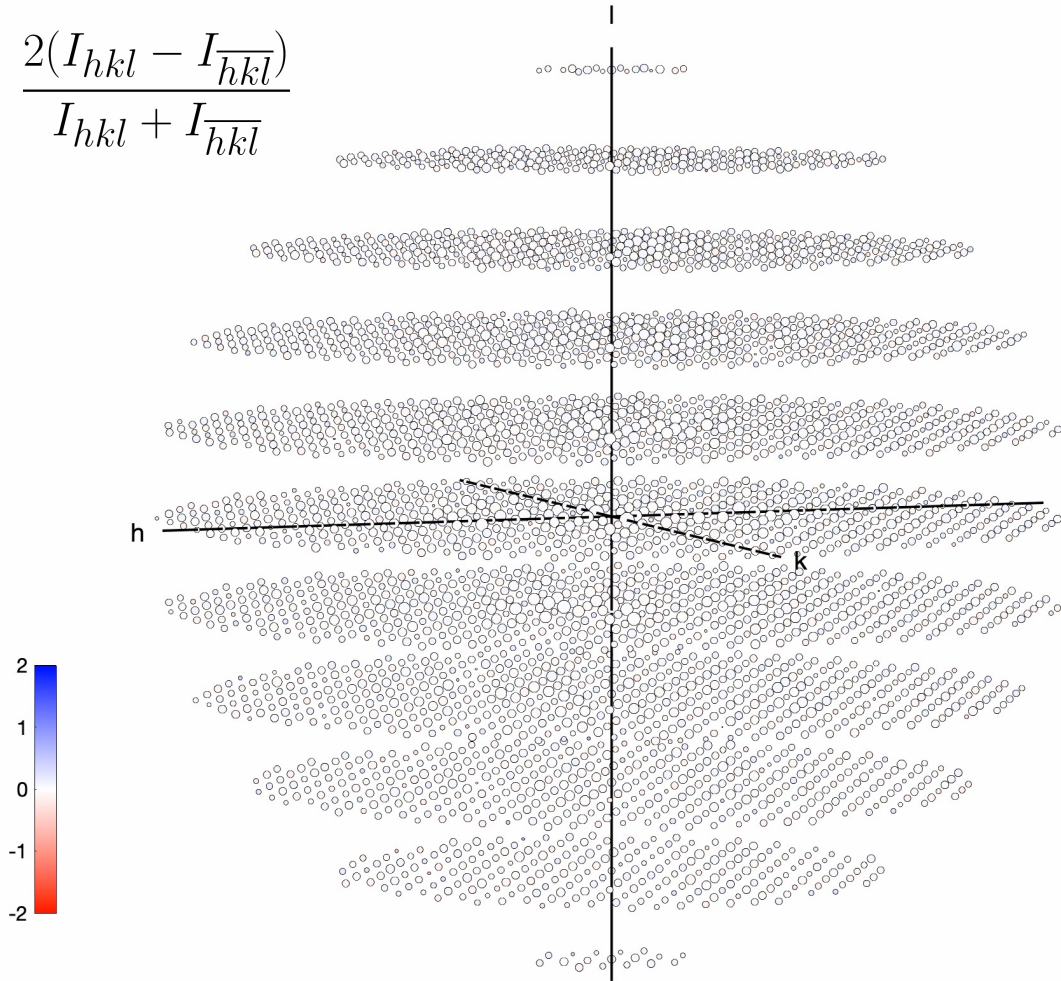


$$f(\hbar\omega, Q) = f^0(Q) + f'(\hbar\omega) + i f''(\hbar\omega)$$

$$|F_{hkl}|^2 \neq |F_{\bar{h}kl}|^2 \quad \phi_{hkl} \neq -\phi_{\bar{h}kl}$$

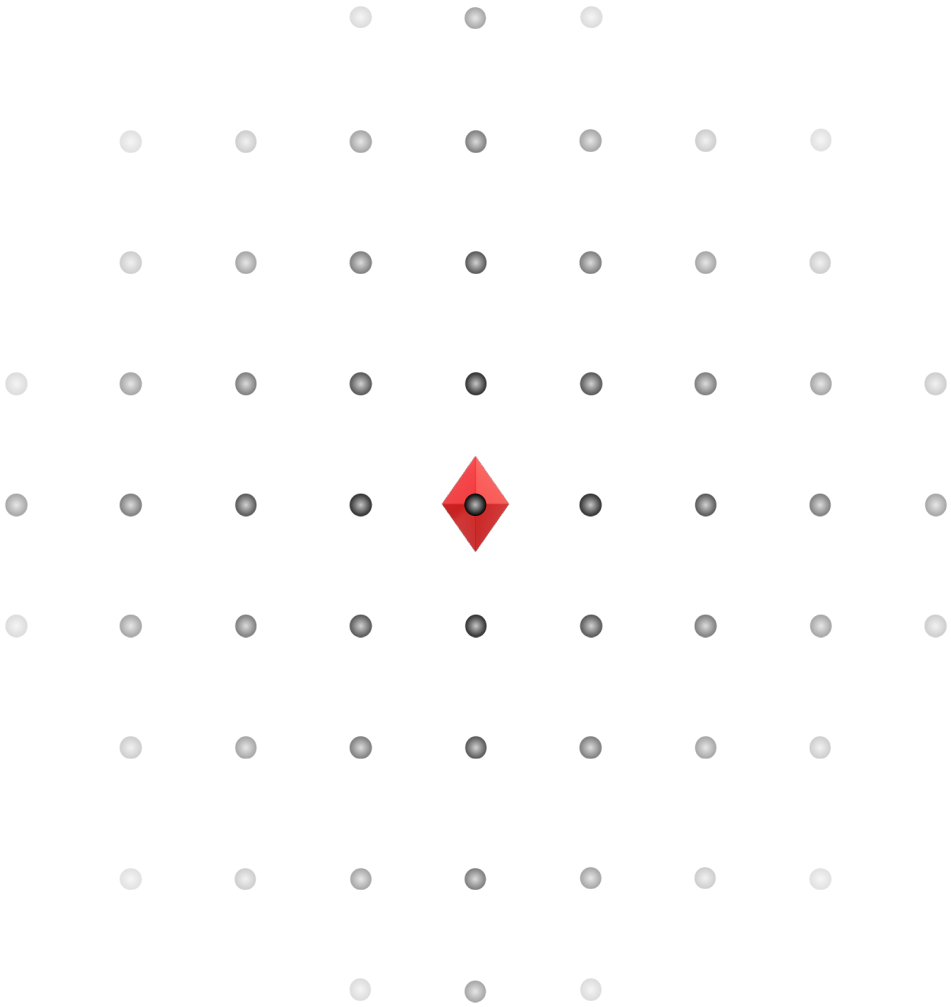
Close to an absorption edge

$$\frac{2(I_{hkl} - I_{\overline{hkl}})}{I_{hkl} + I_{\overline{hkl}}}$$

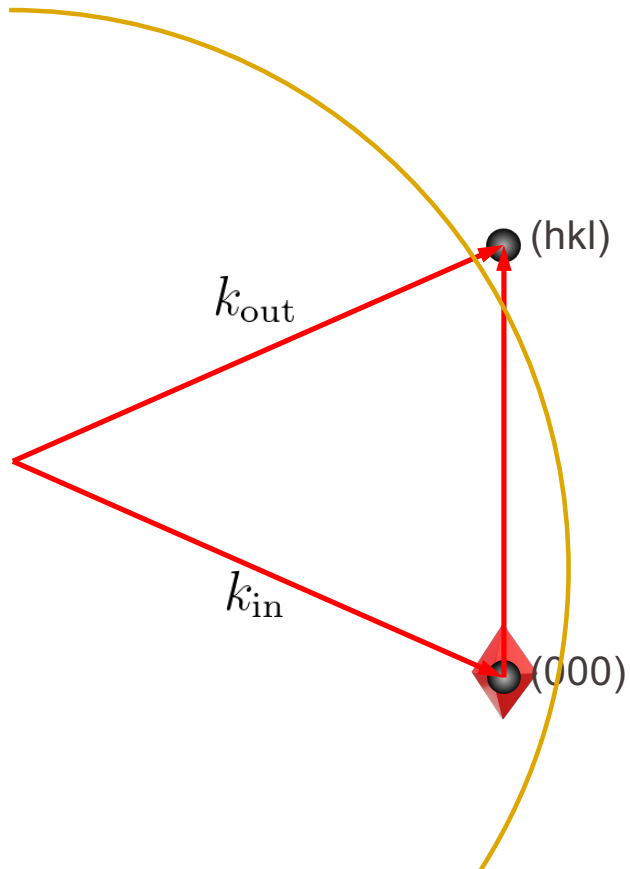


The Ewald sphere

Rotations in real- and reciprocal space

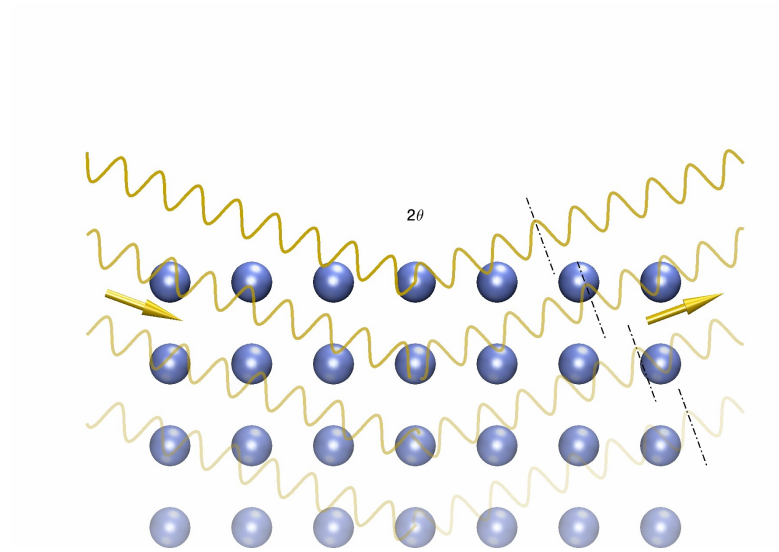
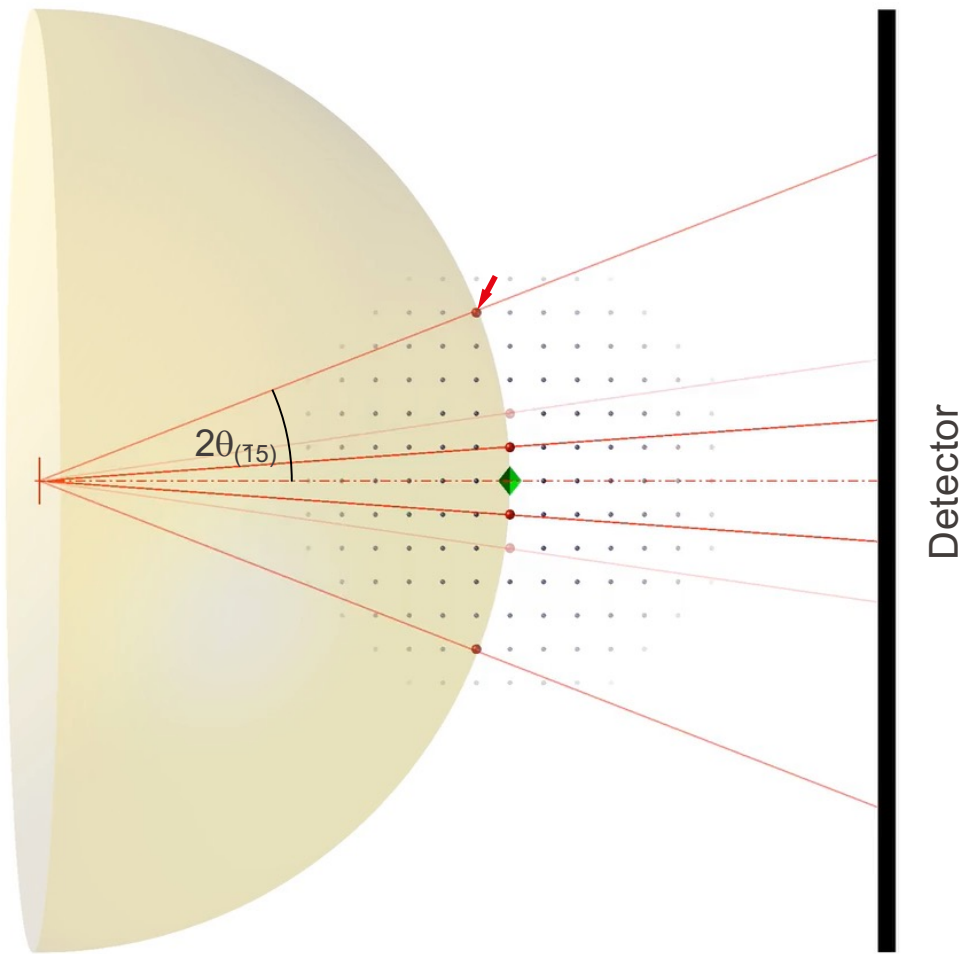


The Ewald sphere

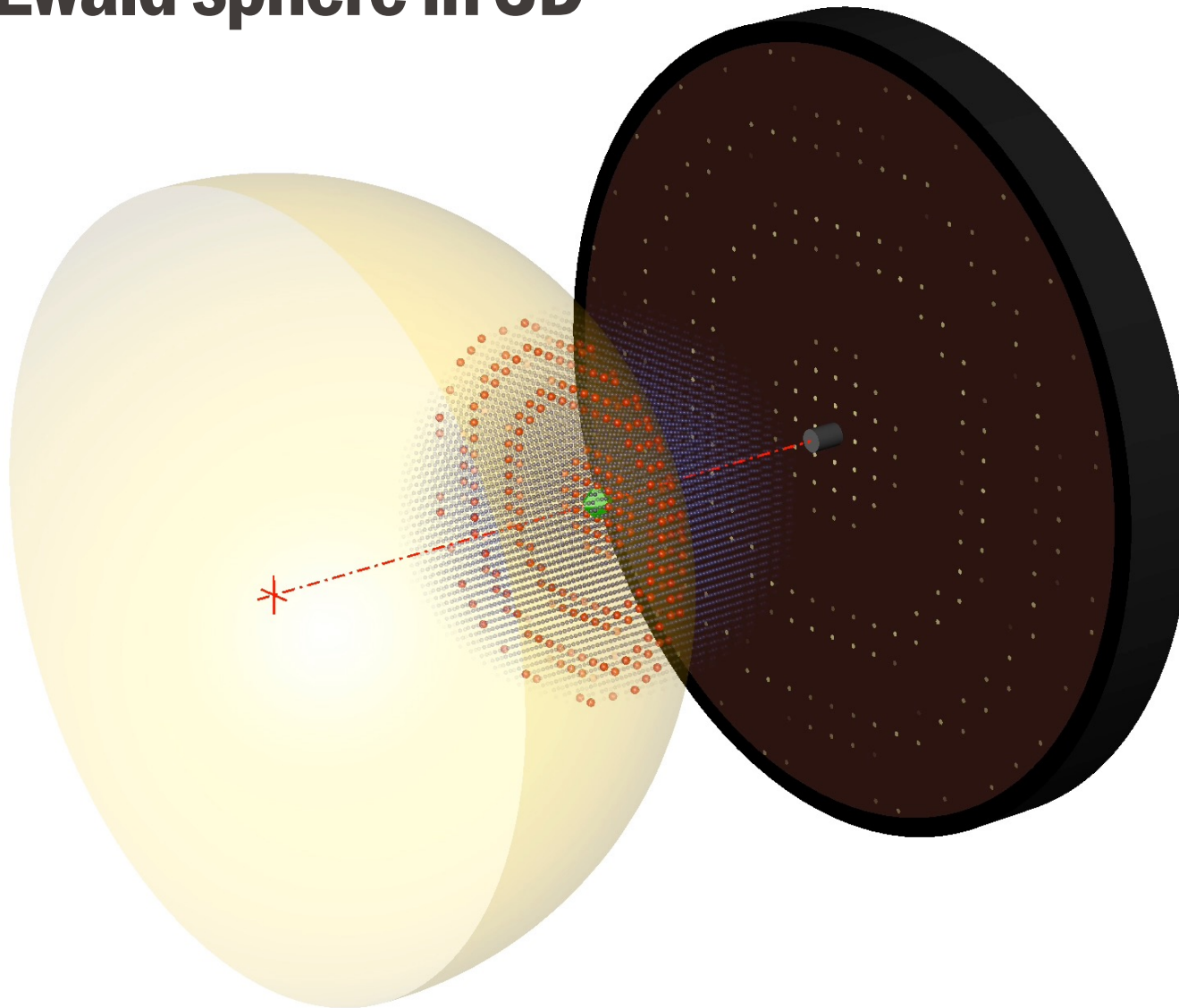


- To see a diffraction peak @ (hkl), the Bragg points (000) and (hkl) must lie on a sphere of radius $|k| = 2\pi/\lambda$ in reciprocal space (RS) – the Ewald sphere
- To achieve this “Bragg condition”, rotate the crystal appropriately

The Ewald sphere



The Ewald sphere in 3D



Tomorrow

