La Matematica della cristallografia:

Una breve descrizione

Andrea Ilari
IBPM (CNR)

L’osservabile finale della cristallografia ai Raggi X che si ottiene a partire
Dalla diffrazione dei raggi X da parte dei cristalli proteici è la MAPPA DI DENSITA’ ELETTRONICA della proteina.

LA MAPPA DI DENSITA’ ELETTRONICA è la trasformata di Fourier dei FATTORI DI STRUTTURA

Con l’ausilio delle prossime diapositive cercheremo di capire cos’è la trasformata di Fourier

The conceptual idea of the **Fourier transform**

$$F(v) = \int_{-\infty}^{\infty} f(x) e^{-2\pi i v x} dx$$

The conceptual idea of the **Fourier transform**

$$F(v) = \int_{-\infty}^{\infty} f(x) e^{-2\pi i v x} dx$$

Forward Fourier transform

$$f(x) = \int_{-\infty}^{\infty} F(v) e^{-2\pi i v x} dv$$

Inverse Fourier transform

The conceptual idea of the **Fourier transform**

transform

$$F(\nu) = \int_{-\infty}^{\infty} f(x) e^{-2\pi i \nu x} dx \qquad f(x) = \int_{-\infty}^{\infty} F(\nu) e^{-2\pi i \nu x} d\nu$$

Forward Fourier transform   Inverse Fourier transform

The conceptual idea of the **Fourier transform**

transform

$$F(v) = \int_{-\infty}^{\infty} f(x) e^{-2\pi i v x} dx \qquad f(x) = \int_{-\infty}^{\infty} F(v) e^{-2\pi i v x} dv$$

Forward Fourier transform — Inverse Fourier transform

Transform = mapping between different domains

$$F(v) \lll = \ggg f(x)$$

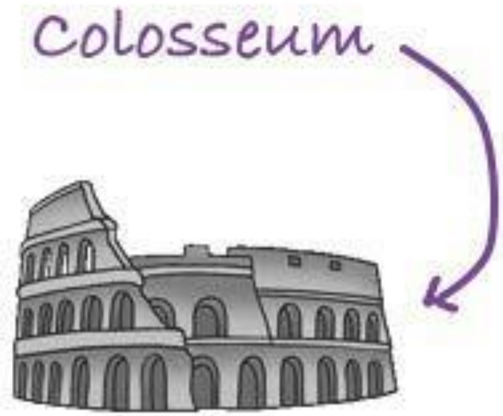
Both domains represent exact same information

The conceptual idea of the **Fourier transform**

Transform = mapping between different domains

$$F(\nu) \lll = \ggg f(x)$$

Both domains represent **exact same information**



The conceptual idea of the **Fourier transform**

Transform = mapping between different domains

$$F(v) \ll=\gg f(x)$$

Both domains represent **exact same information**

Piazza del Colosseo
00184 Roma RM
Italia

The conceptual idea of the **Fourier transform**

Transform = mapping between different domains

$$F(v) \lll = \ggg f(x)$$

Both domains represent **exact same information**

GPS

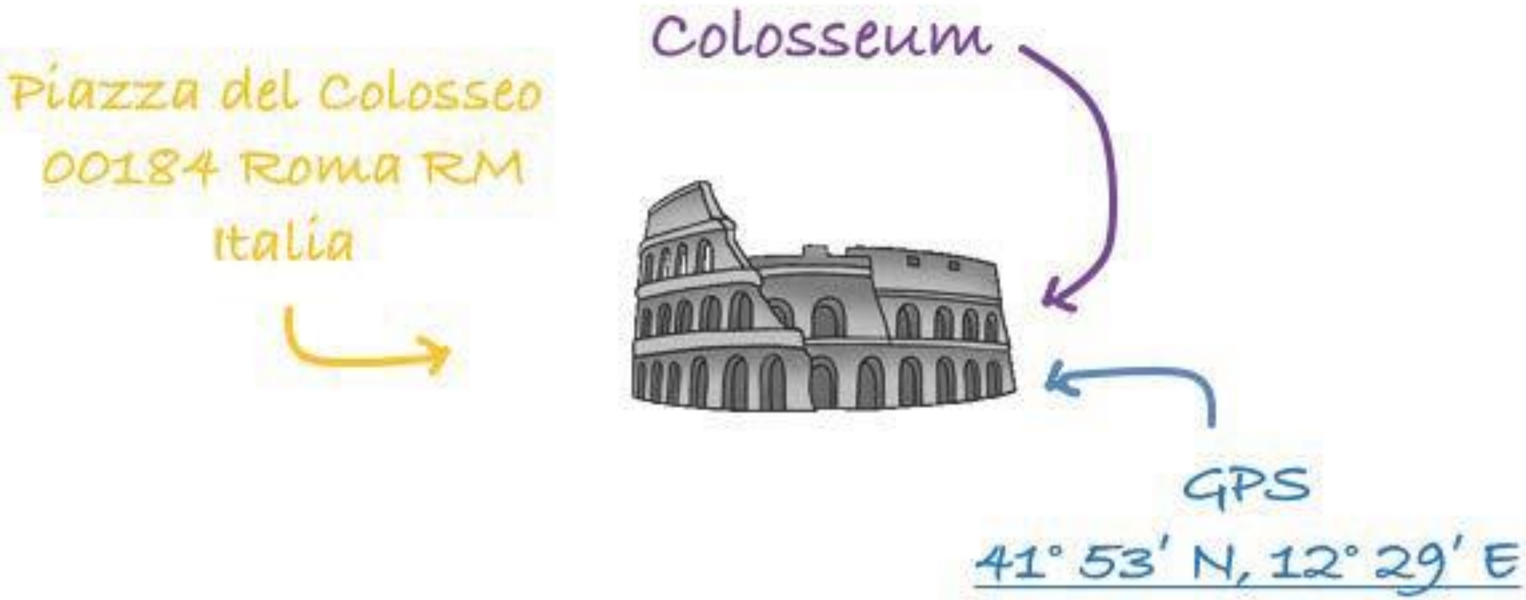
41° 53′ N, 12° 29′ E

The conceptual idea of the **Fourier transform**

Transform = mapping between different domains

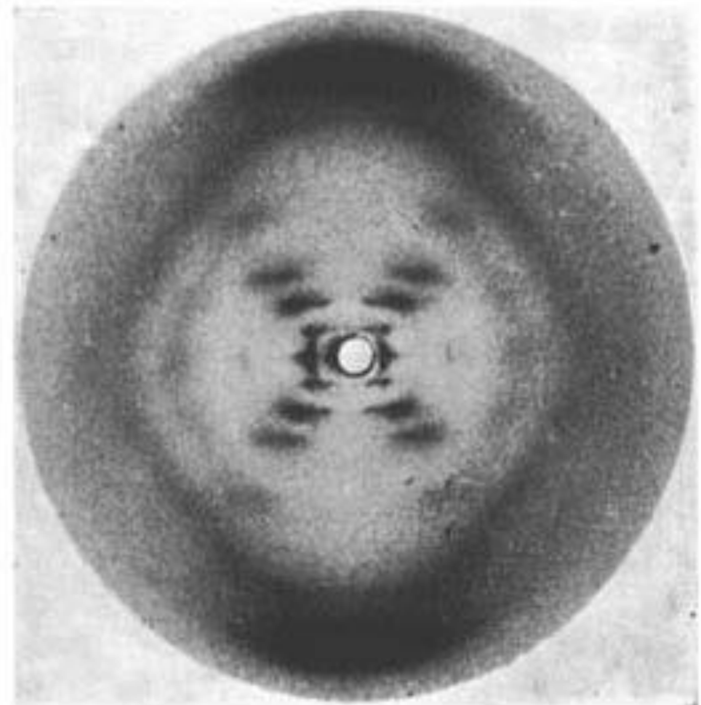
$$F(v) \lll = \ggg f(x)$$

Both domains represent exact same information



A prominent example

Watson-Crick model of B-DNA



Rosalind Franklin, 1952

$f(x)$ ≪=≫ $F(\nu)$

Fourier transform

Fourier series: *Periodic functions as sums simple waves*

Jean-Baptiste Joseph Fourier
Théorie analytique de la chaleur

1822

Any arbitrary periodic signal can be represented by a sum of sinusoids

Fourier series: *Periodic functions as sums simple waves*

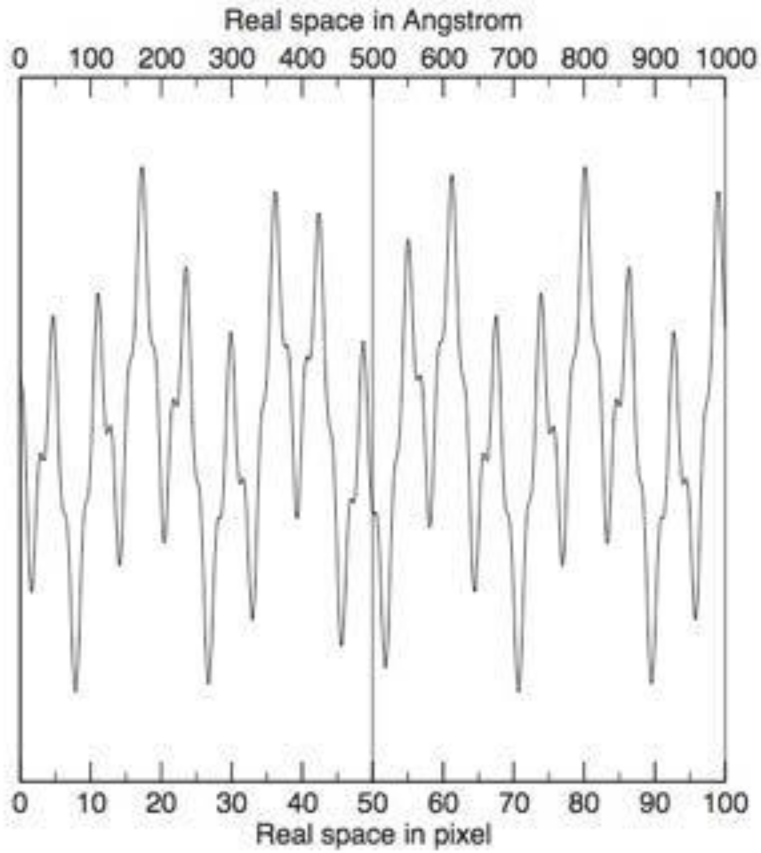
Jean-Baptiste Joseph Fourier

Théorie analytique de la chaleur

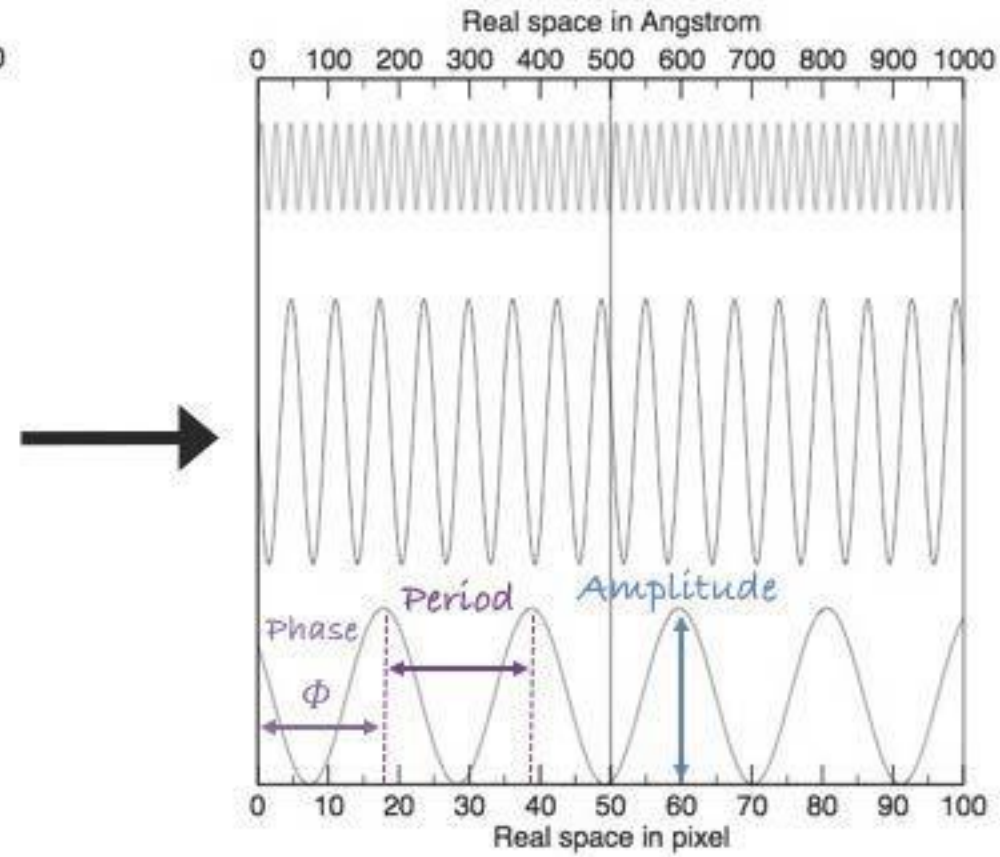
1822

Any arbitrary periodic signal can be represented by a sum of sinusoids

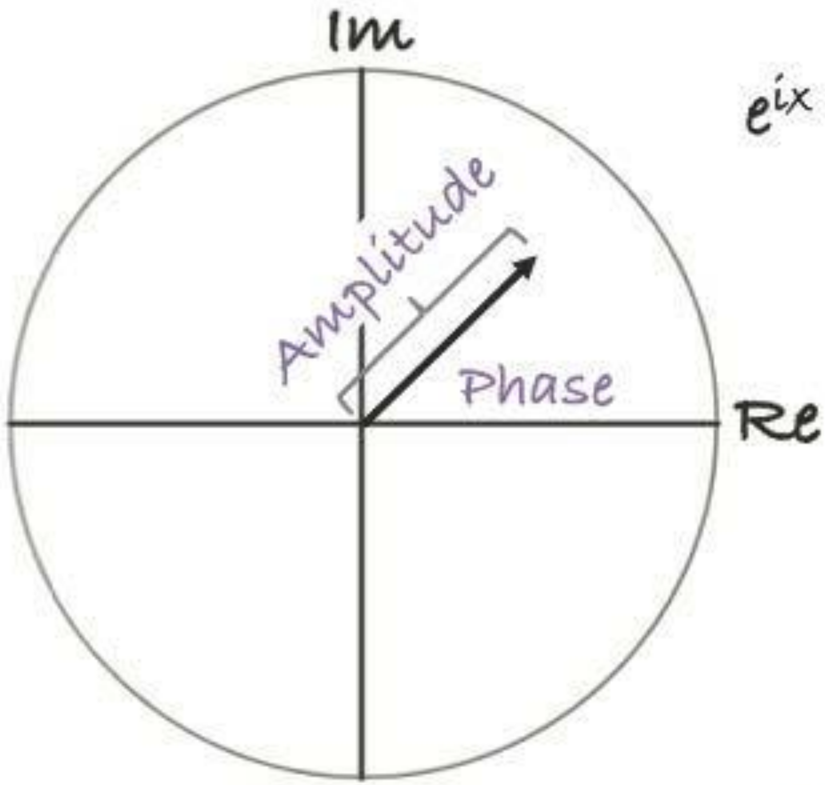
Superposition of cosine functions



Component cosine functions



Euler's formula: *Expressing waves as complex numbers*



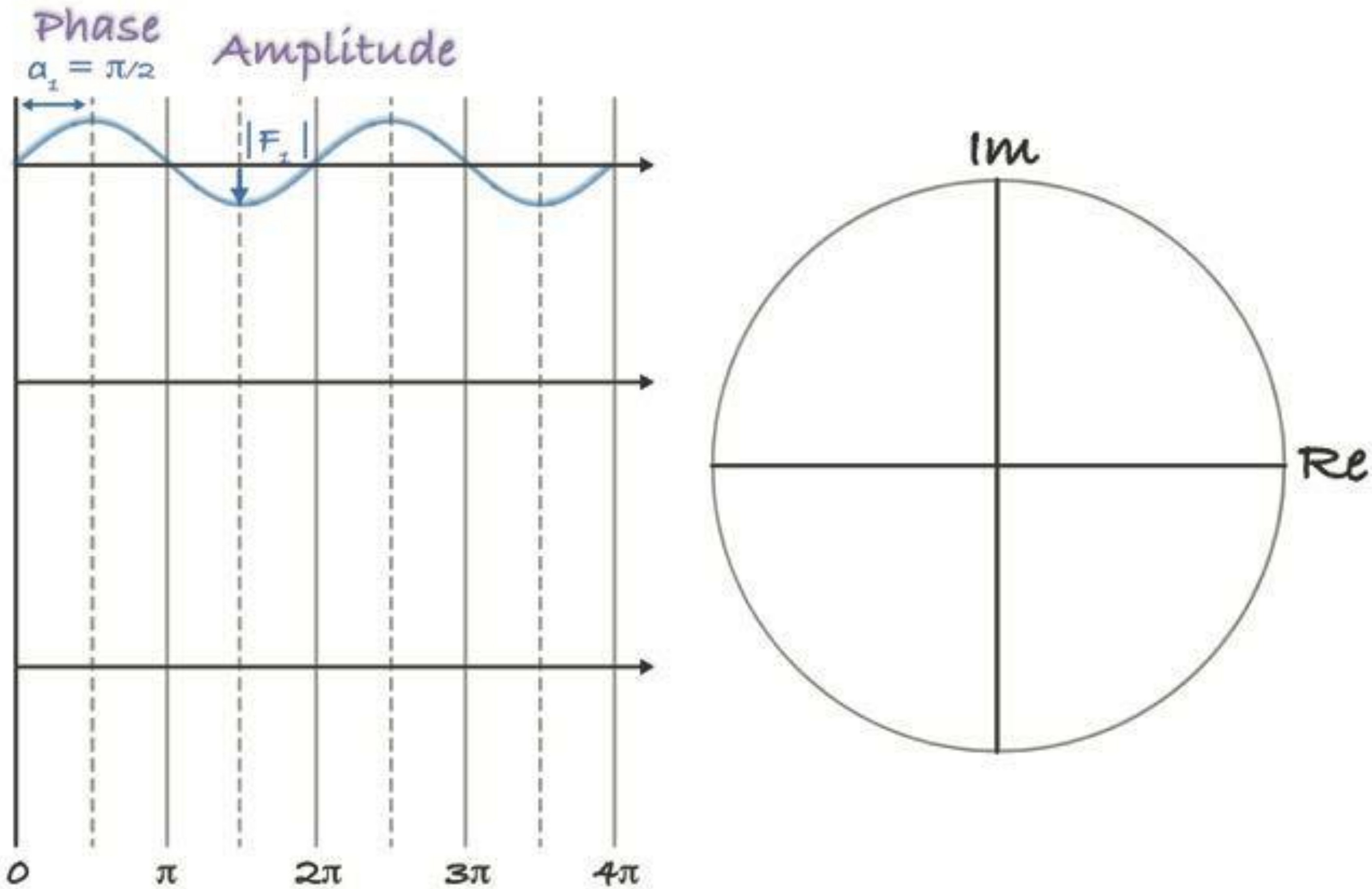
$$e^{ix} = \cos(2\pi\nu x) + i\sin(2\pi\nu x)$$

$F(\nu)=A(\nu)\ e^{ix}$

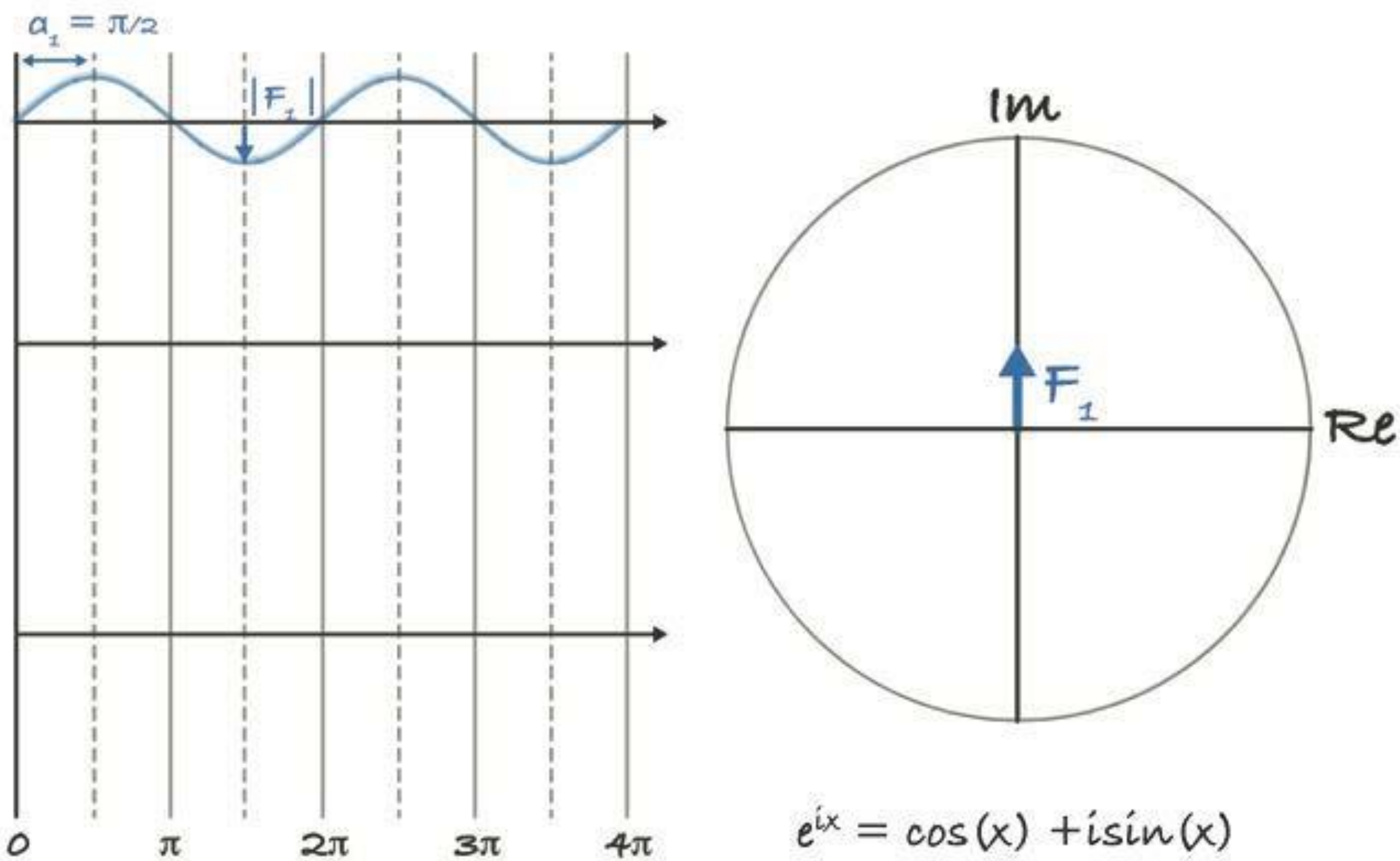
$X=\alpha$ (FASE)

$$F(\nu) = A(\nu)\,(\cos(x) + i\sin(x))$$

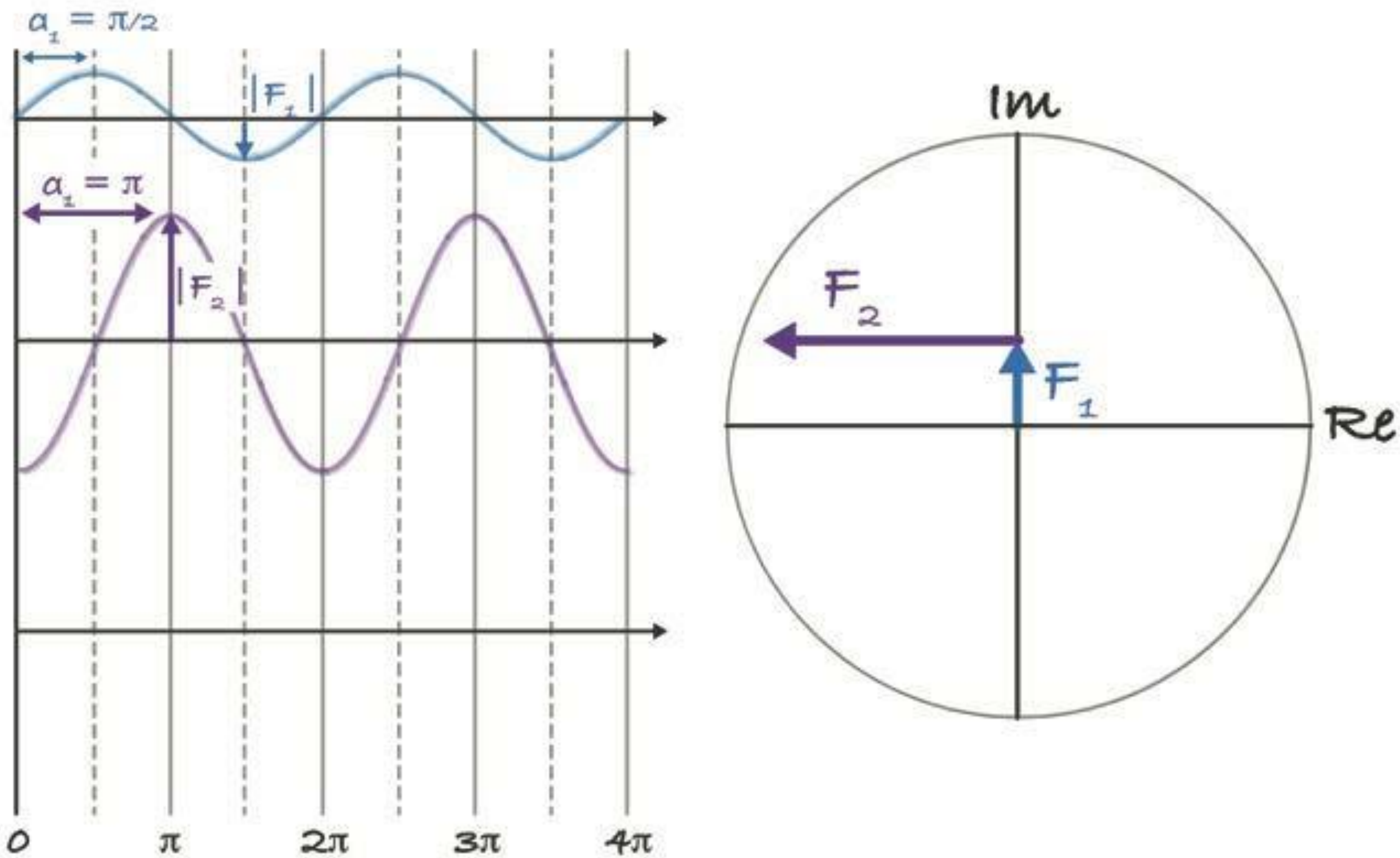
Euler's formula: *Expressing waves as complex numbers*



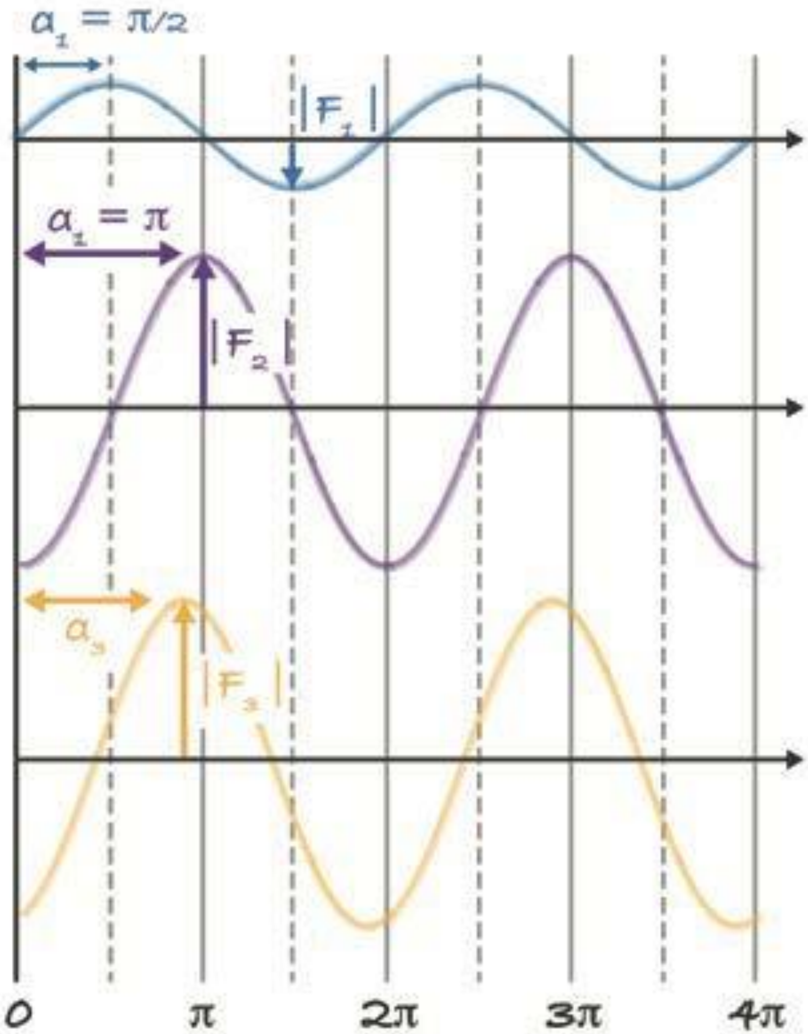
Euler's formula: *Expressing waves as complex numbers*

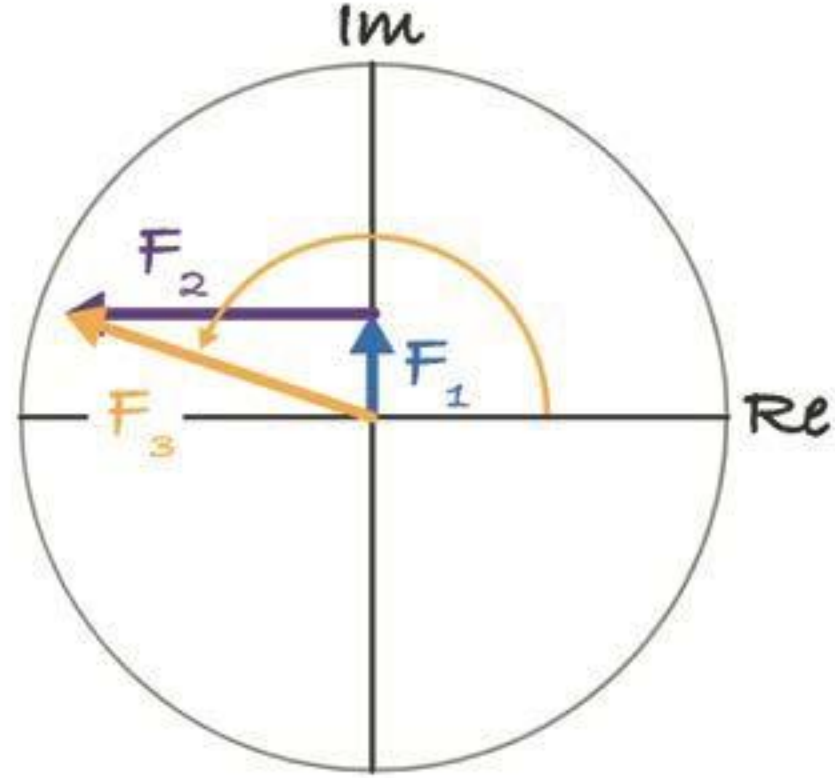


Euler’s formula: *Expressing waves as complex numbers*



Euler's formula: *Expressing waves as complex numbers*



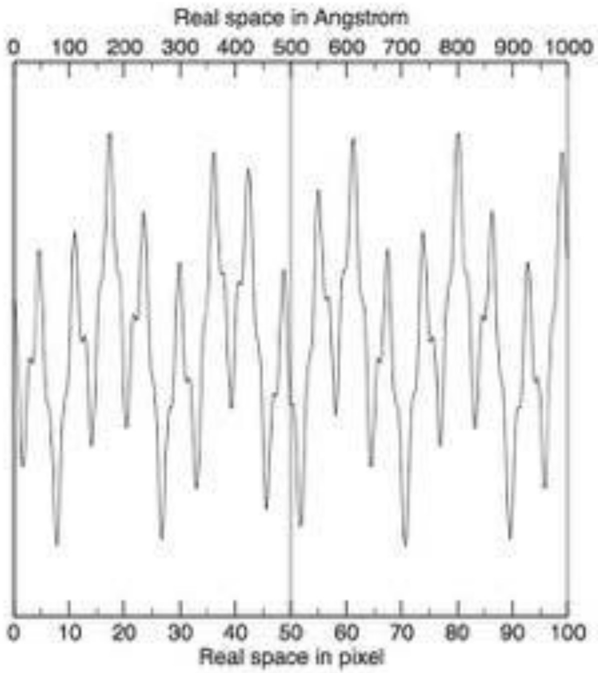


$$f(x) = \sum_{h=1}^{N} F(v)\, e^{-2\pi i v x} dv$$

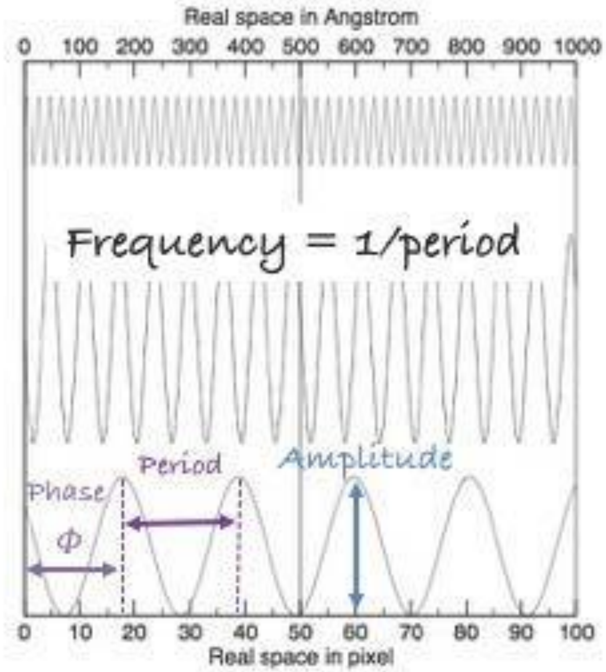
Deconstructing periodic functions

Spatial domain

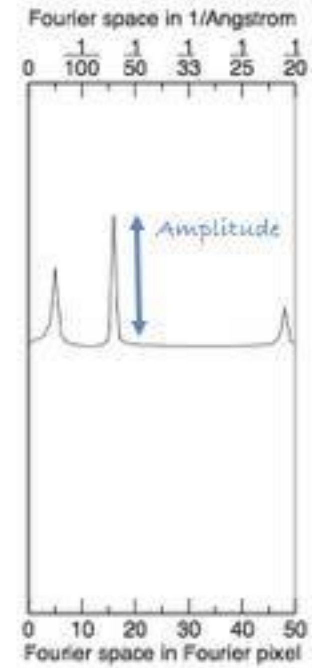
Frequency domain



Signal



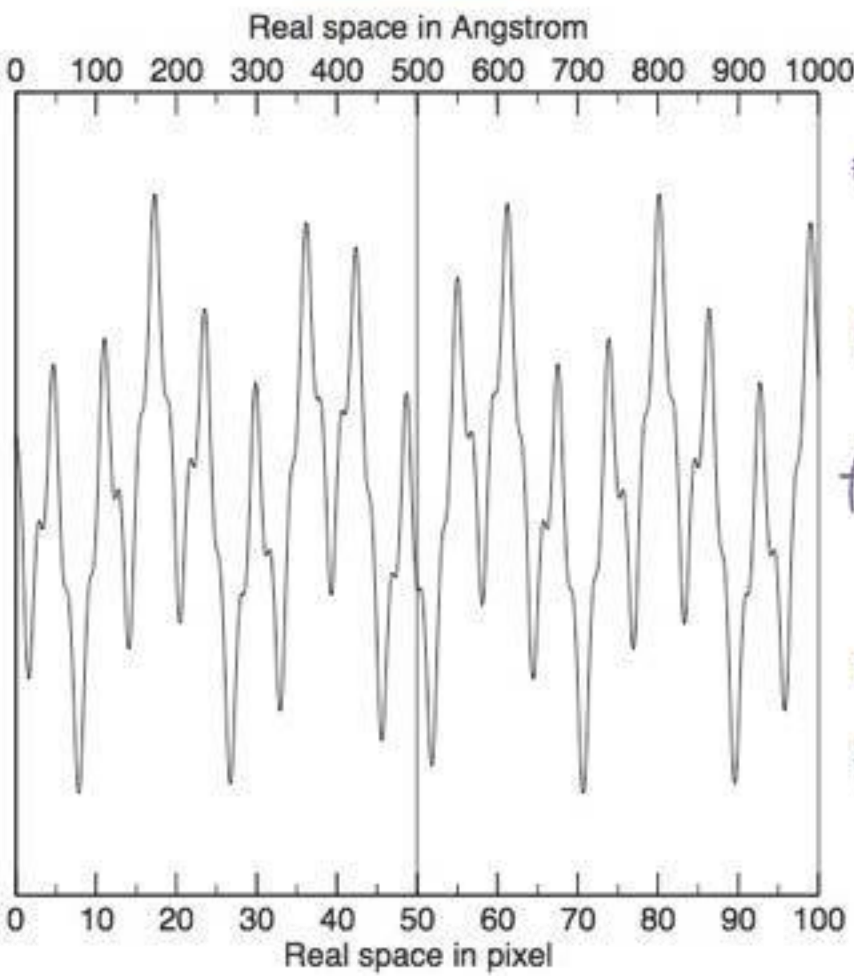
Wave components



Fourier components

Deconstructing periodic functions

Real space



$$F(v) = \int_{-\infty}^{\infty} f(x) e^{-2\pi i v x} dx$$

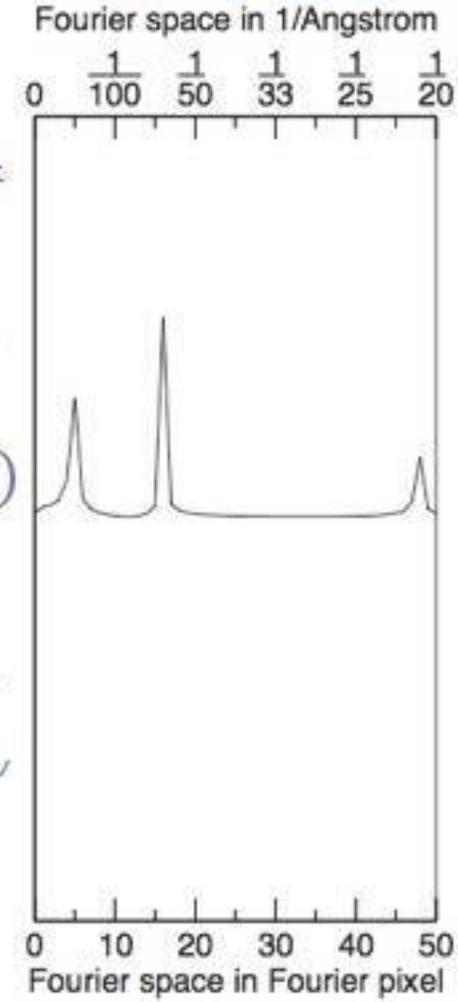
<u>Forward</u>
Fourier transform

$$f(x) \lll\!=\!\ggg F(v)$$

<u>Inverse</u>
Fourier transform

$$f(x) = \int_{-\infty}^{\infty} F(v) e^{-2\pi i v x} dv$$

Frequency space



The Fourier transform demystified

Sinusoids

$$f(x) = \int_{-\infty}^{\infty} F(v) e^{-2\pi i v x} dv$$

Form sum

Amplitudes and phases

- The Fourier allows to switch representation of a function from one domain to another
- Simple instruction how to perform addition and multiplications of sinusoid terms
- Frequency representation can be very useful to perform operations on signal

I FATTORI DI STRUTTURA

- Quando i raggi X colpiscono il detector producono un segnale con una certa intensità **I**
- Quel segnale dipende dalla somma dei segnali

di tutti gli atomi presenti nella cella unitaria.

La sommatoria di tutte le onde diffratte che danno luogo al segnale in uno specifico punto dello spazio reciproco (che corrisponde alla diffrazione di una famiglia di piani hkl) è il fattore di struttura F(hkl)

$$F_{hkl} = \sum_{j=1}^{n} f_j e^{2\pi i (hx_j + ky_j + lz_j)}.$$

Relazione tra fattori di struttura e densità elettronica

$$F_{hkl} = \int_x \int_y \int_z \rho(x, y, z) e^{2\pi i (hx+ky+lz)} \, dx \, dy \, dz,$$

o anche

$$F_{hkl} = \int_V \rho(x, y, z) e^{2\pi i (hx+ky+lz)} \, dV$$

Poiché come abbiamo visto la trasformata di Fourier è un'operazione
Matematica reversibile abbiamo anche

$$\rho(x, y, z) = \frac{1}{V} \sum_h \sum_k \sum_l F_{hkl} e^{-2\pi i (hx+ky+lz)},$$

Abbiamo che in questo caso l'integrale è sostituito da una sommatoria
Perché i fattori di struttura sono rappresentati da grandezze discrete nello spazio
Reciproco (spot di una certa intensità)

In pratica la trasformata di Fourier mette in relazione la funzione Densità elettronica
Nello spazio reale con i Fattori di struttura nello spazio reciproco

Per approfondire il concetto che ogni oggetto può essere descritto come una sommatoria di onde prendetevi il tempo di guardare questi 2 video.

Ricordate che secondo Eulero un onda può essere descritta come **un vettore** con un certo raggio (**ampiezza**) **che ruota** sul piano immaginario ad una certa velocità (**frequenza**) partendo da un certo angolo (**fase**):

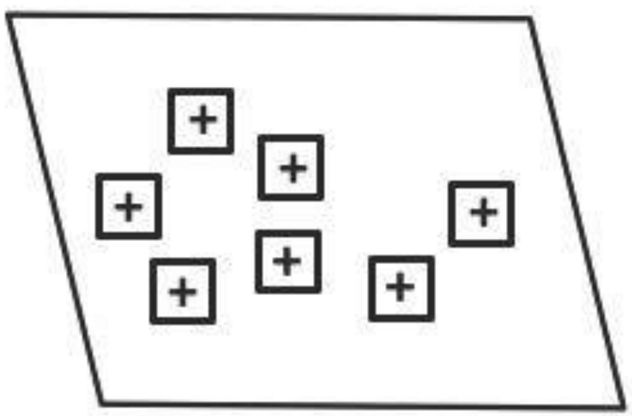
Epicycles, complex Fourier series and Homer Simpson's orbit
(25 min)
https://youtu.be/qS4H6PEcCCA

But what is a Fourier series? From heat flow to circle drawings
(24 min)
https://youtu.be/r6sGWTCMz2k

Reconstruction of electron density

Immaginiamo di avere un cristallo bidimensionale, con la cella unitaria come in figura.

Come sarà il «pattern» di diffrazione
Degli oggetti contenuti nella cella unitaria ?

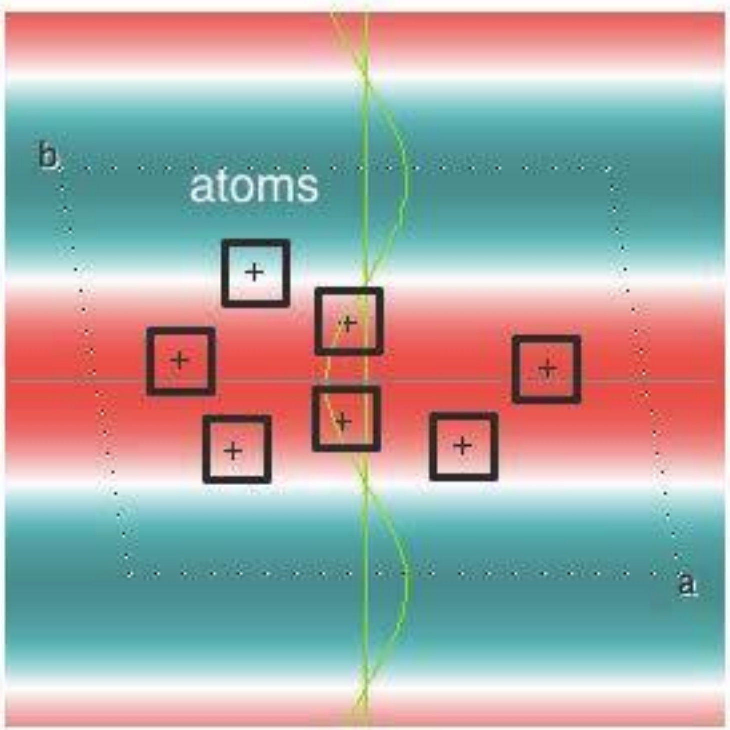


Reconstruction of electron density in X-ray crystallography

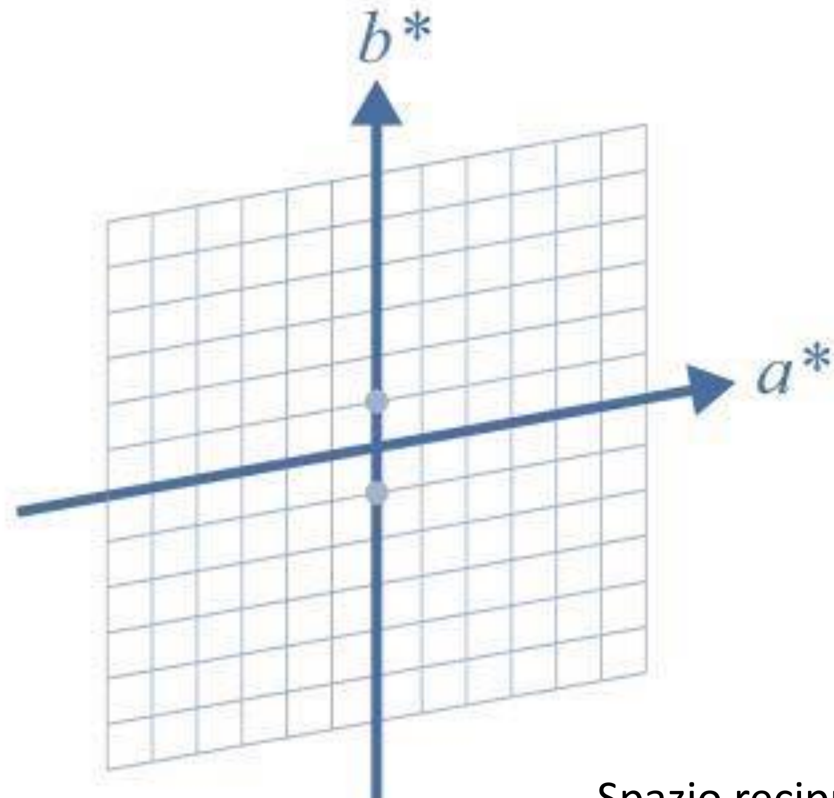
$$\rho(x,y) = \frac{1}{A}\sum_{h=-\infty}^{\infty}\sum_{k=-\infty}^{\infty} \mathbf{F}_{hk} \exp[-2\pi i(hx+ky)$$

La trasformata di fourier del riflesso 0 1 è semplicemente una funzione sinusoidale con la densità elettronica nel piano 0 1 con picchi positivi (rosso) e picchi negativi (blu)

Spazio reale



h=0,k=1
$\mathbf{F}_{01}$

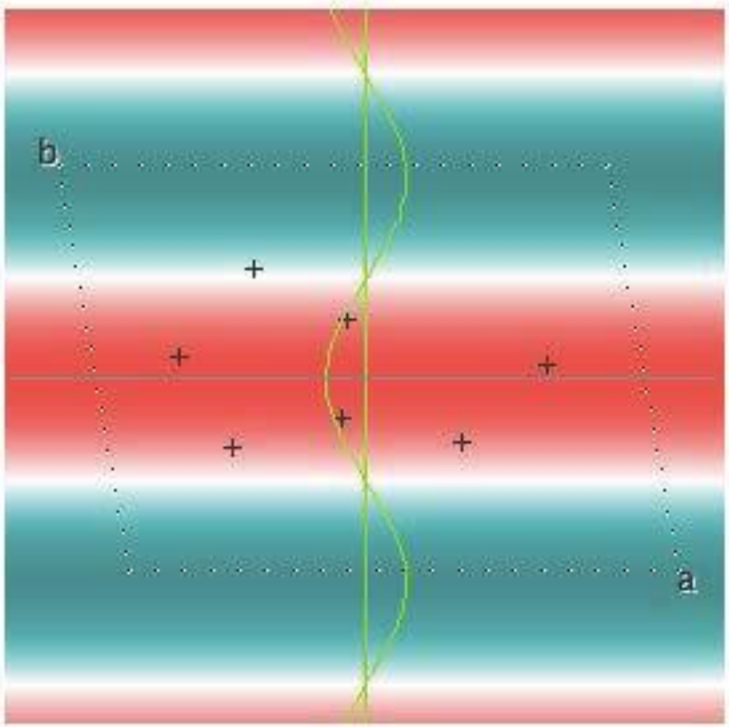


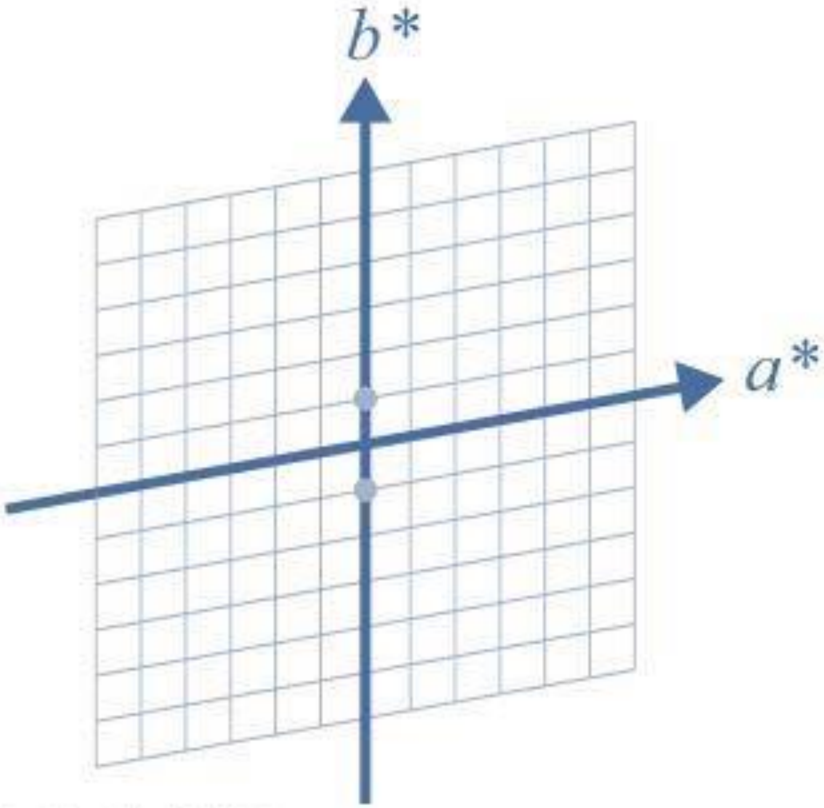
Spazio reciproco

Reconstruction of electron density in X-ray crystallography

$$\rho(x,y) = \frac{1}{A}\left\{\mathbf{F}_{01}e^{i\varphi_{01}}\right\}$$

h=0,k=1
$\mathbf{F}_{01}$

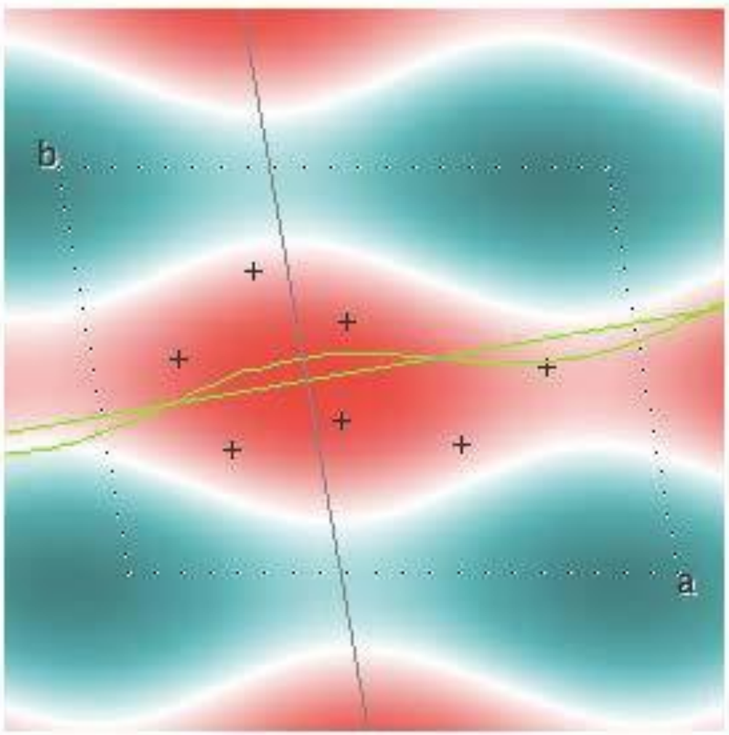


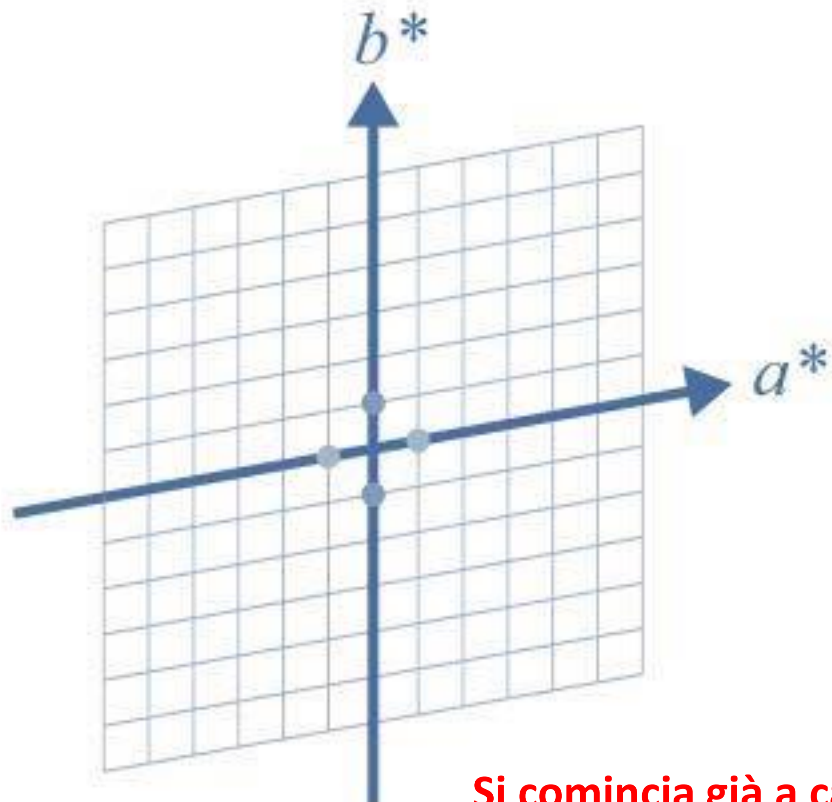


Reconstruction of electron density in X-ray crystallography

$$\rho(x,y) = \frac{1}{A}\left\{\mathbf{F}_{01}e^{i\varphi_{01}} + \mathbf{F}_{10}e^{i\varphi_{10}}\right\}$$

Quando calcolo la trasformata di fourier dei fattori di struttura di due riflessi F1,0 e F0,1, possiamo apprezzare l'interferenza tra i due. Densità positiva (rossa, quando il il rosso incontra il rosso ; densità nulla (bianca, quando il rosso incontra il blu); densità negativa (blu quando il blu incontra il blu).





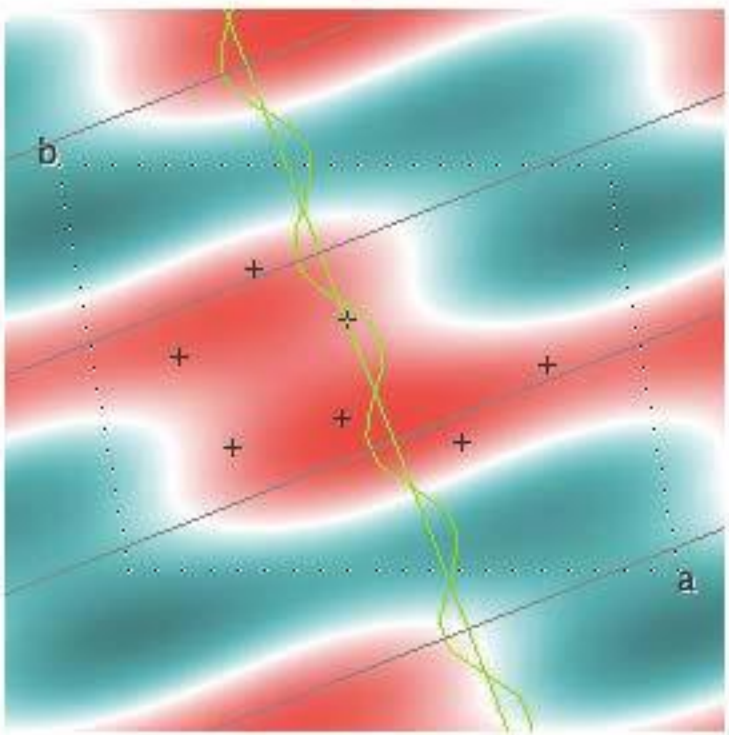
Si comincia già a capire Dove si trova la molecola

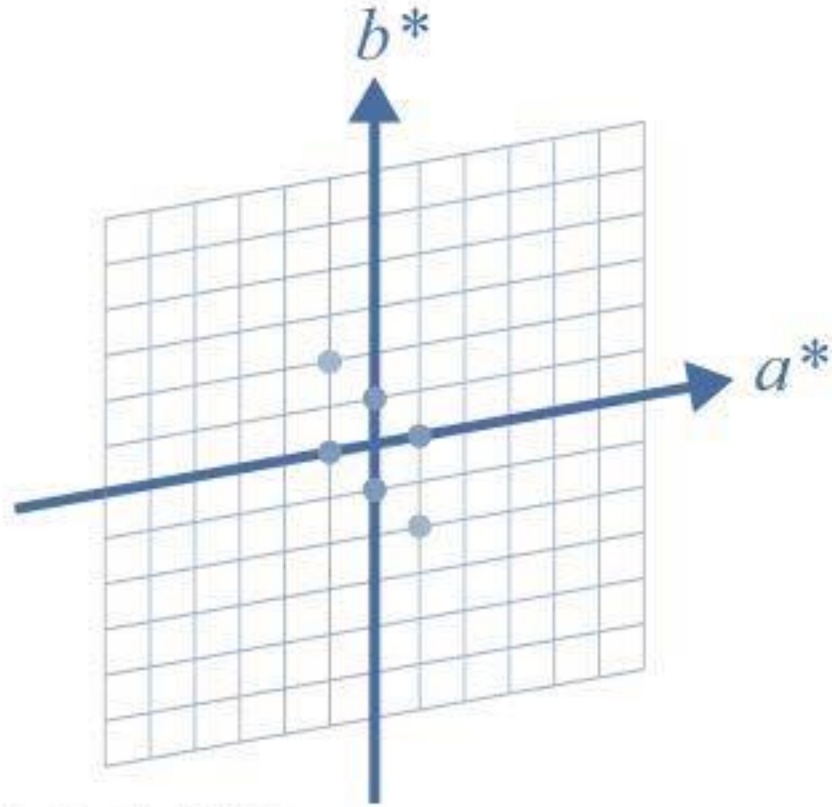
Reconstruction of electron density in X-ray crystallography

$$\rho(x,y) = \frac{1}{A}\left\{\mathbf{F}_{01}e^{i\varphi_{01}} + \mathbf{F}_{10}e^{i\varphi_{10}} + \mathbf{F}_{\bar{1}2}e^{i\varphi_{\bar{1}2}}\right\}$$

h=-1,k=2

$\mathbf{F}_{-12}$

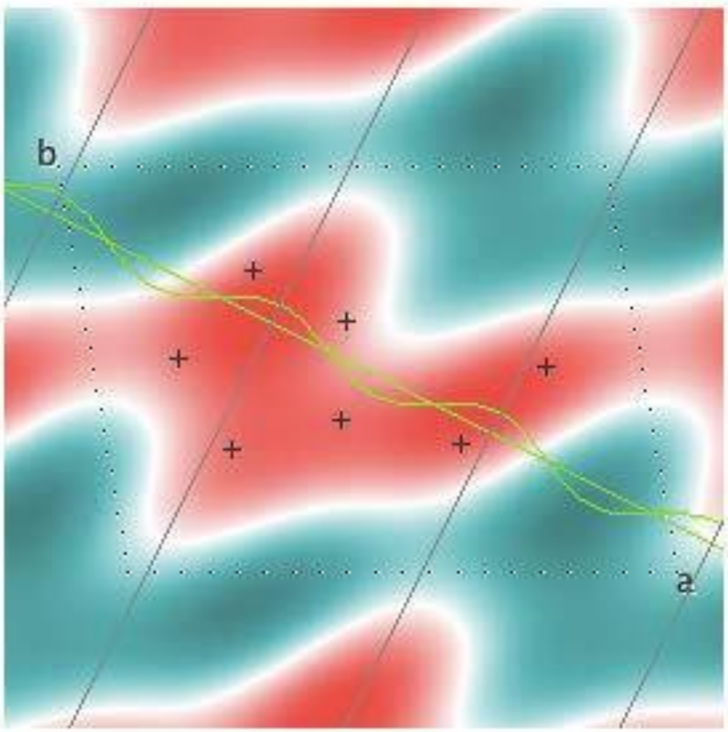


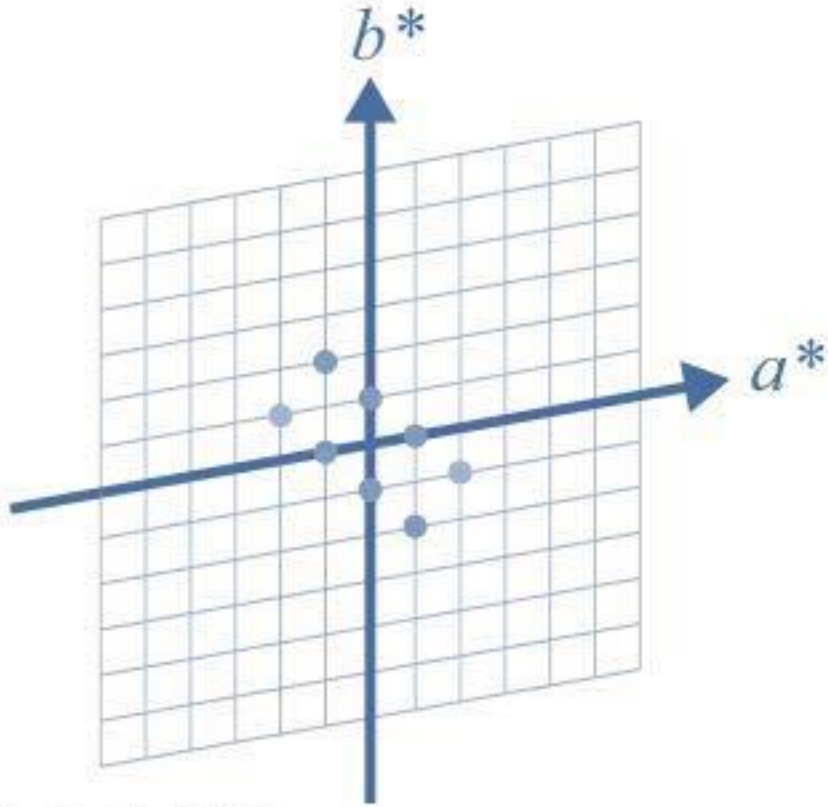


Reconstruction of electron density in X-ray crystallography

$$\rho(x,y) = \frac{1}{A}\left\{\mathbf{F}_{01}e^{i\varphi_{01}} + \mathbf{F}_{10}e^{i\varphi_{10}} + \mathbf{F}_{\bar{1}2}e^{i\varphi_{\bar{1}2}} + \mathbf{F}_{\bar{2}1}e^{i\varphi_{\bar{2}1}}\right\}$$

h=-2,k=1
$\mathbf{F}_{-21}$



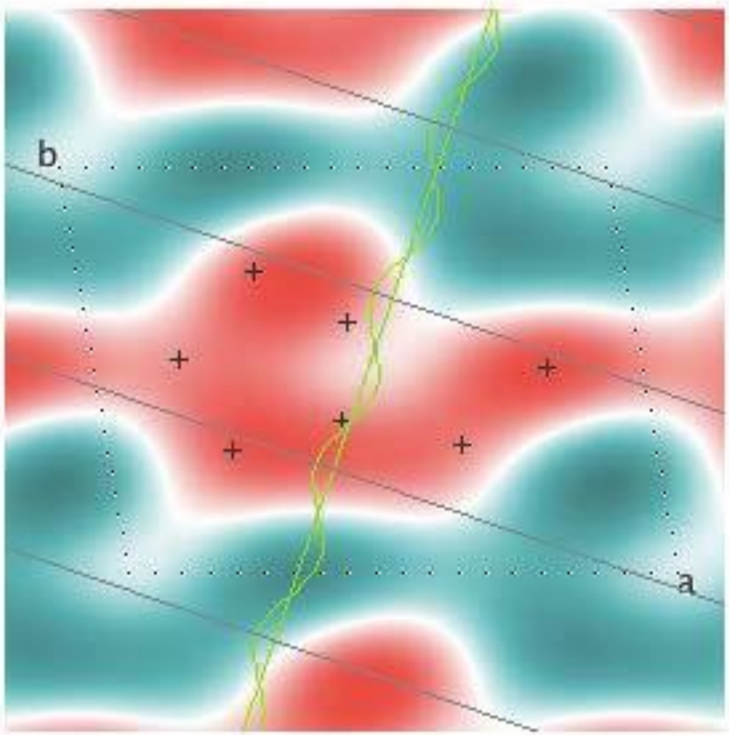


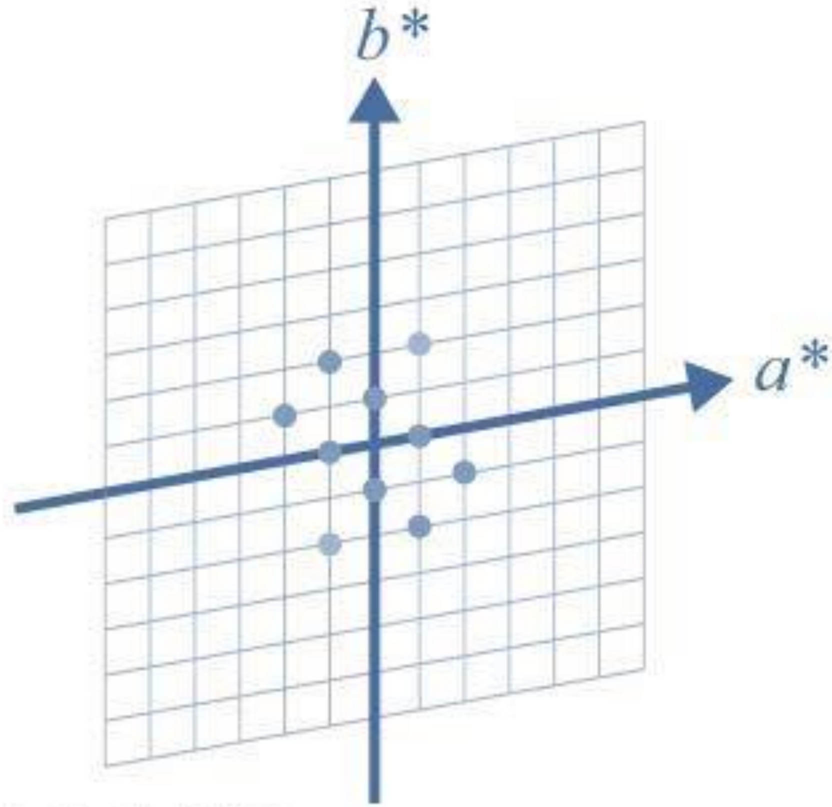
Reconstruction of electron density in X-ray crystallography

$$\rho(x,y) = \frac{1}{A}\left\{\mathbf{F}_{01}e^{i\varphi_{01}} + \mathbf{F}_{10}e^{i\varphi_{10}} + \mathbf{F}_{\bar{1}2}e^{i\varphi_{\bar{1}2}} + \mathbf{F}_{\bar{2}1}e^{i\varphi_{\bar{2}1}} + \mathbf{F}_{12}e^{i\varphi_{12}}\right\}$$

h=1,k=2

$\mathbf{F}_{12}$



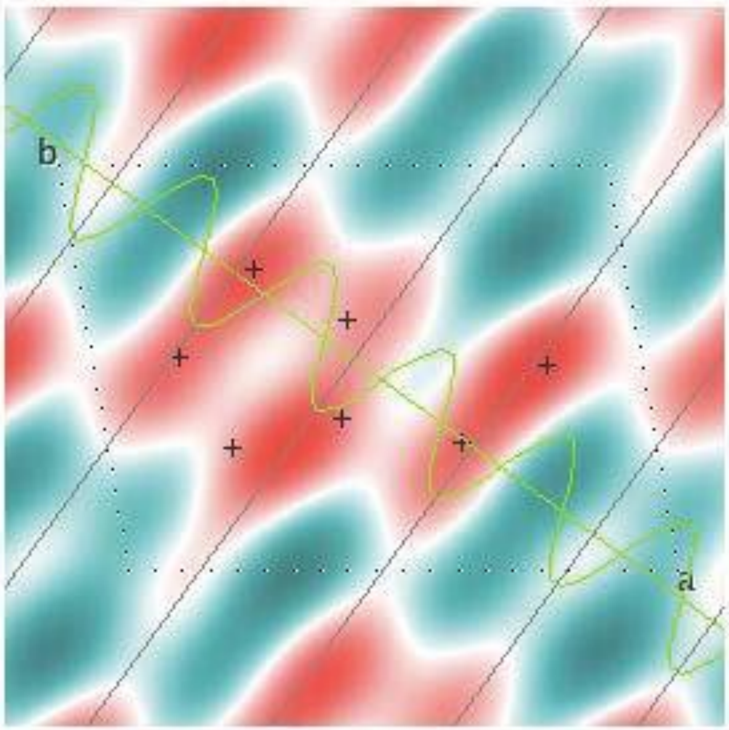


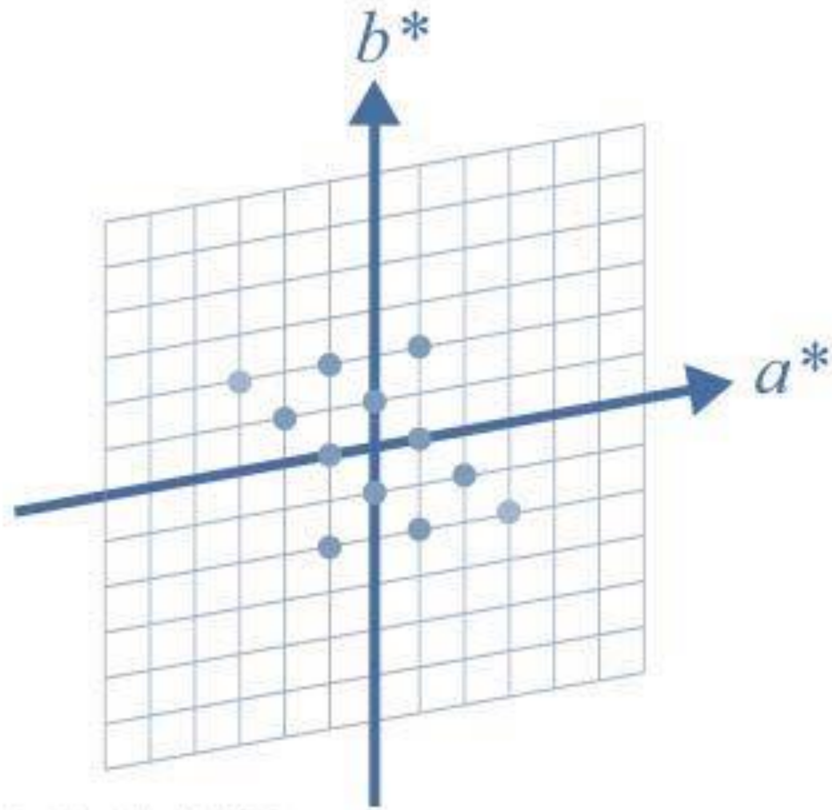
Reconstruction of electron density

$$\rho(x,y) = \frac{1}{A}\left\{\mathbf{F}_{01}e^{i\varphi_{01}} + \mathbf{F}_{10}e^{i\varphi_{10}} + \mathbf{F}_{\bar{1}2}e^{i\varphi_{\bar{1}2}} + \mathbf{F}_{\bar{2}1}e^{i\varphi_{\bar{2}1}} + \mathbf{F}_{12}e^{i\varphi_{12}} + \mathbf{F}_{3\bar{2}}e^{i\varphi_{3\bar{2}}}\right\}$$

h=3,k=-2

$\mathbf{F}_{3\text{-}2}$



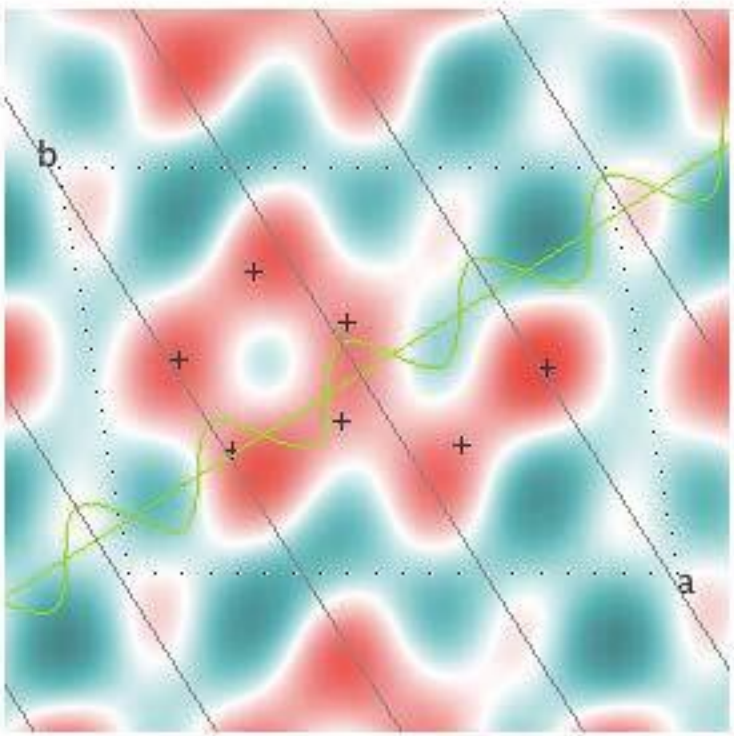


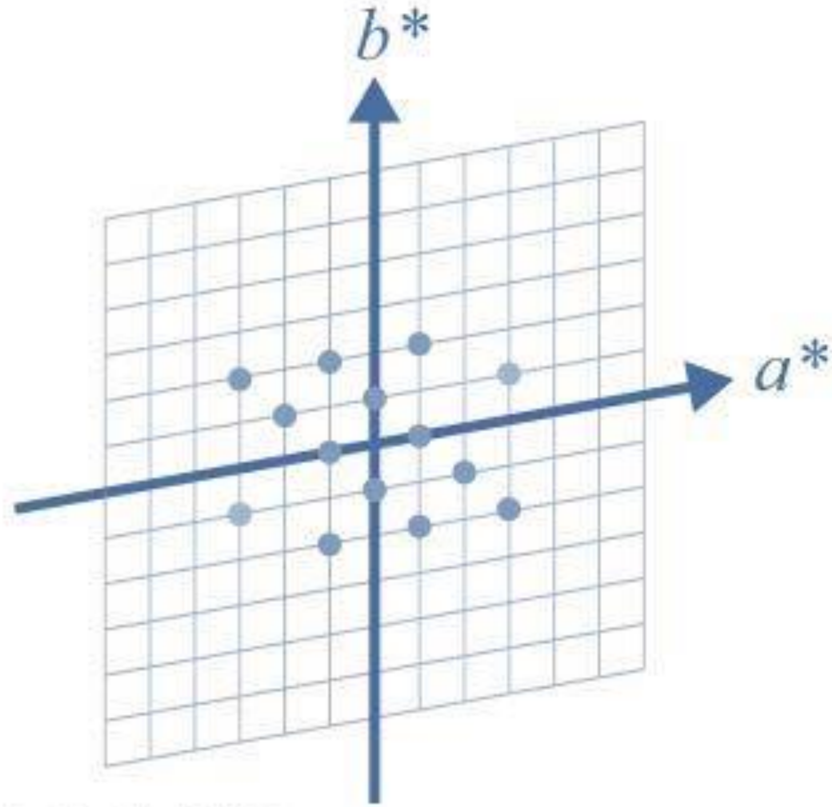
Reconstruction of electron density in X-ray crystallography

$$\rho(x,y) = \frac{1}{A}\left\{\mathbf{F}_{01}e^{i\varphi_{01}} + \mathbf{F}_{10}e^{i\varphi_{10}} + \mathbf{F}_{\bar{1}2}e^{i\varphi_{\bar{1}2}} + \mathbf{F}_{\bar{2}1}e^{i\varphi_{\bar{2}1}} + \mathbf{F}_{12}e^{i\varphi_{12}} + \mathbf{F}_{3\bar{2}}e^{i\varphi_{3\bar{2}}} + \mathbf{F}_{31}e^{i\varphi_{31}}\right\}$$

h=3,k=1

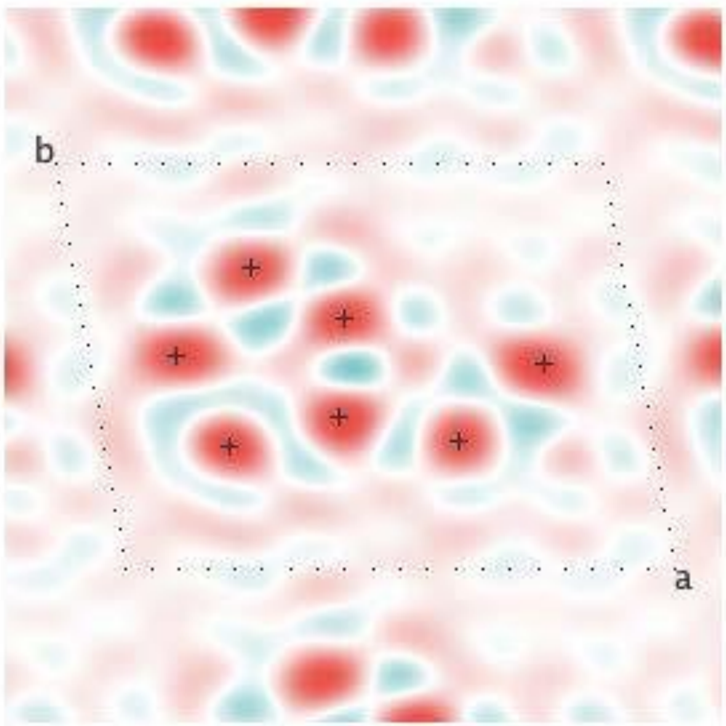
$\mathbf{F}_{31}$

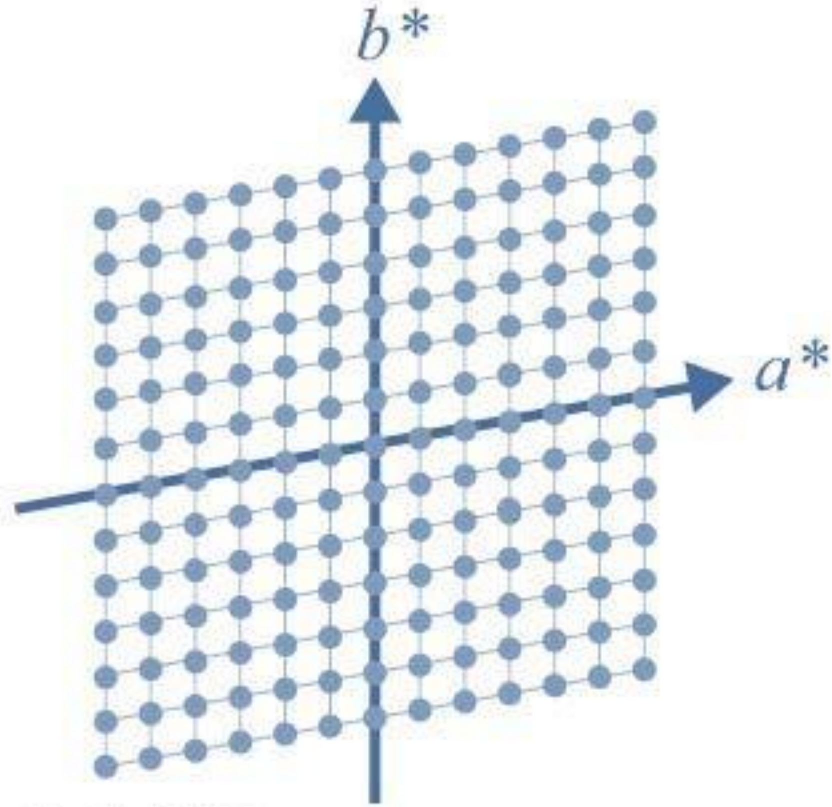


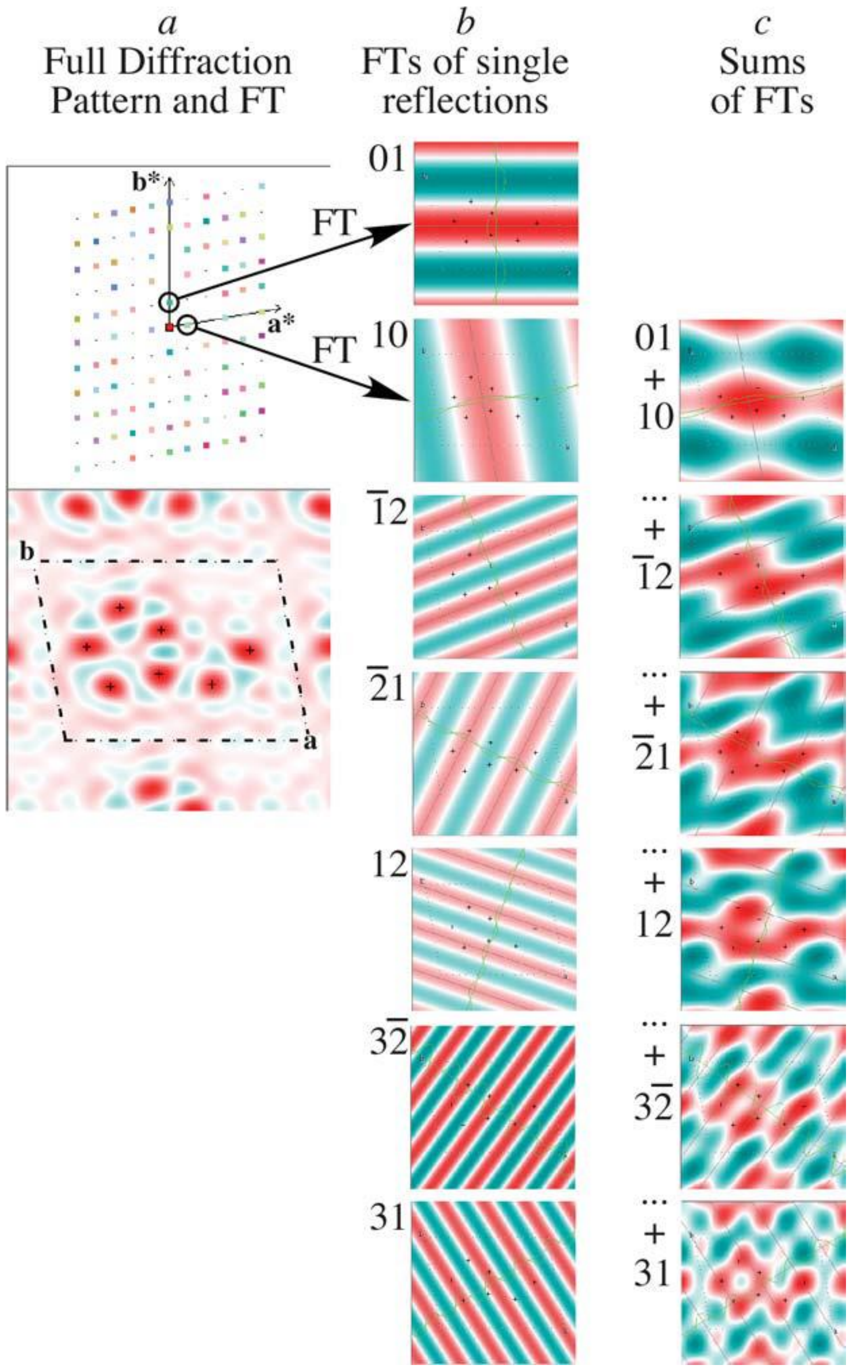


Reconstruction of electron density in X-ray crystallography

$$\rho(x,y) = \frac{1}{A}\sum_{h=-\infty}^{\infty}\sum_{k=-\infty}^{\infty} \mathbf{F}_{hk} \exp[-2\pi i(hx+ky)$$







a
Full Diffraction Pattern and FT
b
FTs of single reflections
c
Sums of FTs
b*
a*
FT
FT
b
a
01
10
$\bar{1}2$
$\bar{2}1$
12
$3\bar{2}$
31
01 + 10
... + $\bar{1}2$
... + $\bar{2}1$
... + 12
... + $3\bar{2}$
... + 31