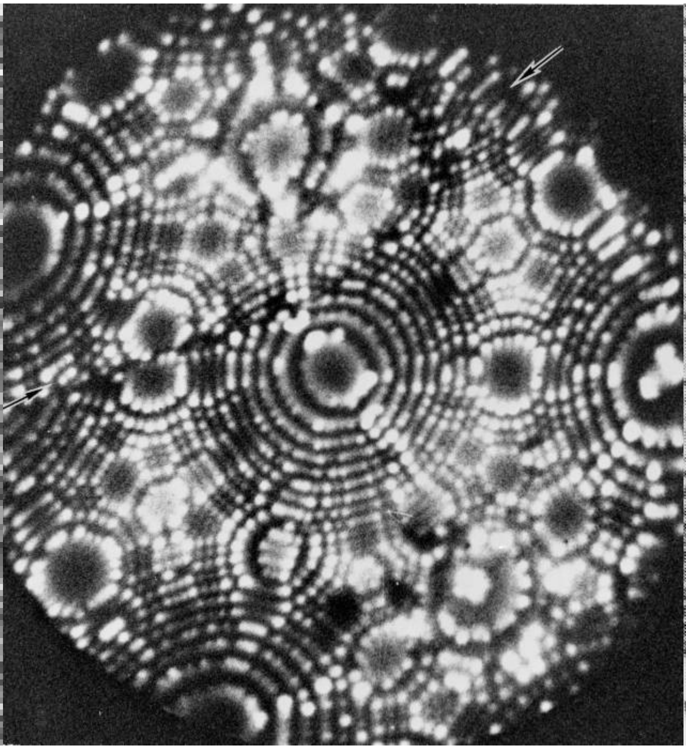
Fourier series

Reciprocal space

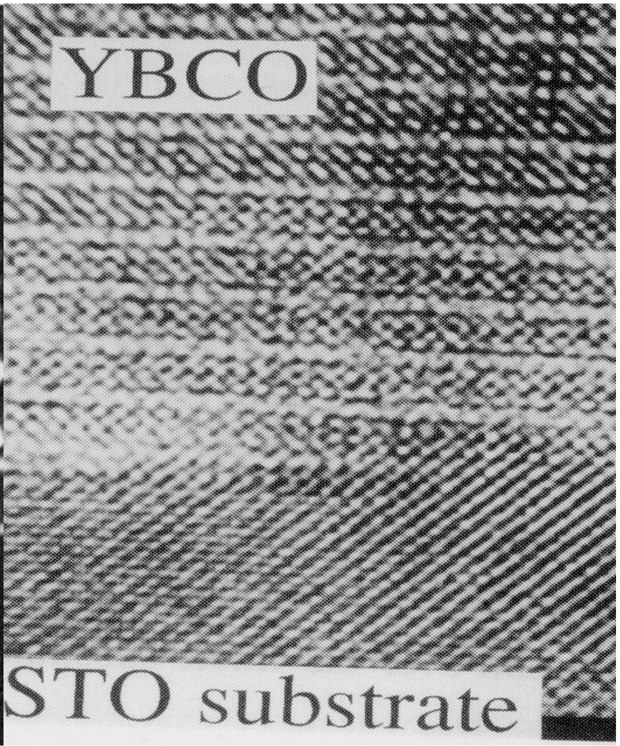
Peter Hadley

Crystal structure determination

Scanning tunneling microscope



Field ion microscope



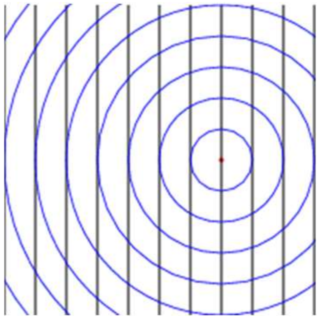
Transmission electron microscope

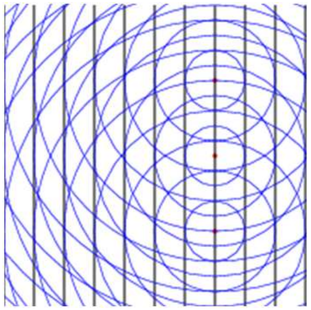
Usually x-ray diffraction is used to determine the crystal structure

Crystal diffraction (Beugung)

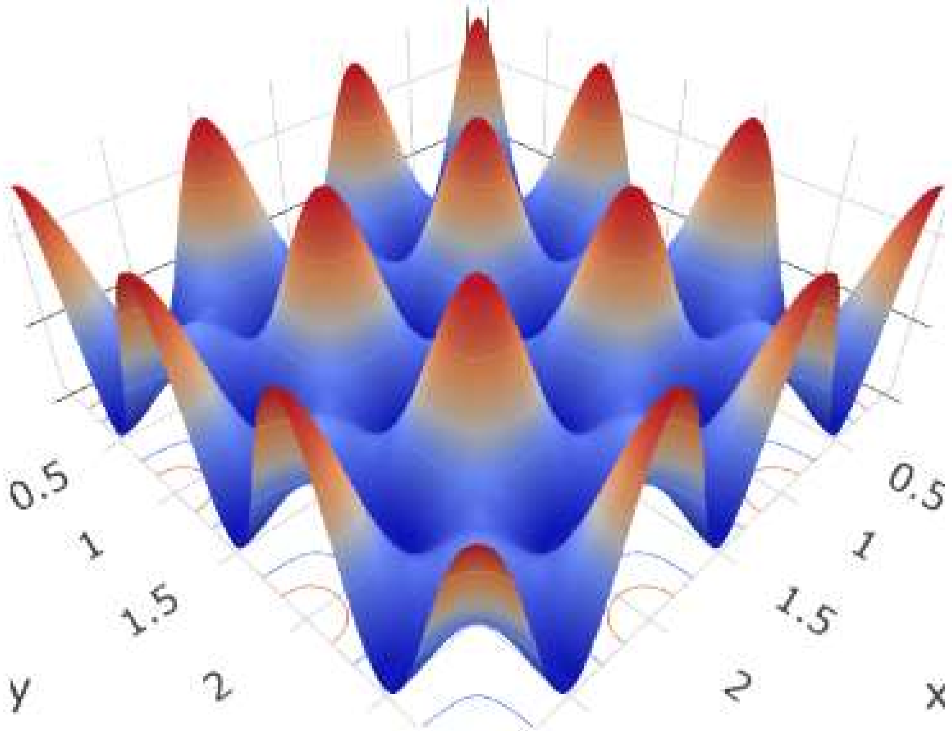
Everything moves like a wave but exchanges energy and momentum as a particle

light	photons
sound	phonons
electron waves	electrons
neutron waves	neutrons
positron waves	positrons
plasma waves	plasmons



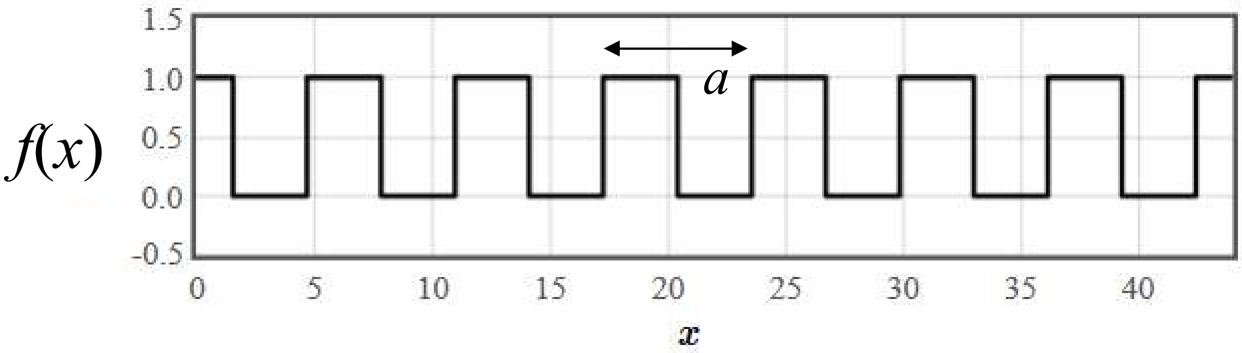


Periodic functions



Use a Fourier series to describe periodic functions

Expanding a 1-d function in a Fourier series



Any periodic function can be represented as a Fourier series.

$$f(x) = f_0 + \sum_{p=1}^{\infty} c_p \cos(2\pi px/a) + s_p \sin(2\pi px/a)$$

multiply by $\cos(2\pi p'x/a)$ and integrate over a period.

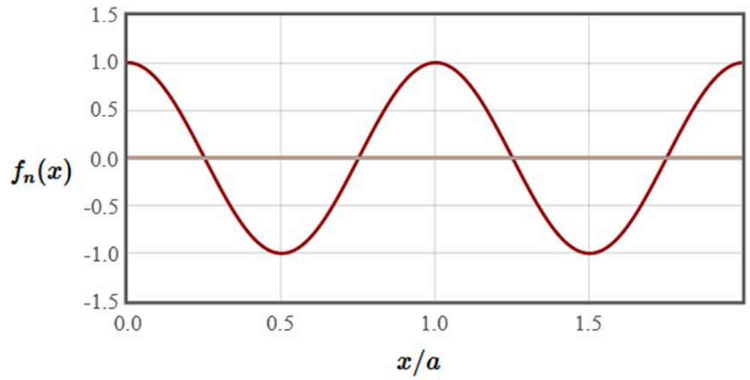
$$\int_0^a f(x)\cos\left(2\pi p'x/a\right)dx = c_p \int_0^a \cos\left(2\pi p'x/a\right)\cos\left(2\pi p'x/a\right)dx = \frac{ac_{p'}}{2}$$

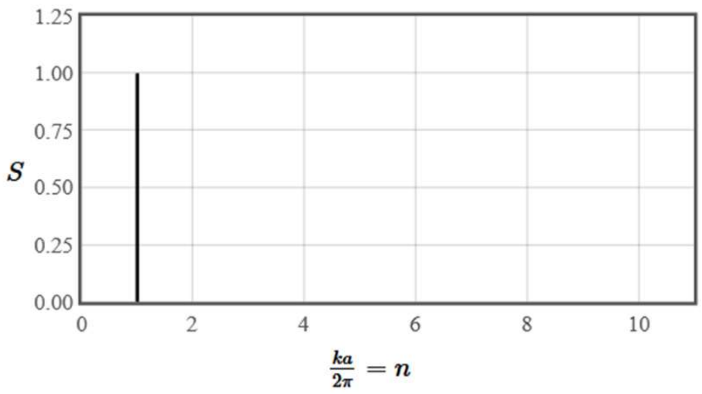
$$c_p = \frac{2}{a}\int_0^a f(x)\cos\left(2\pi px/a\right)dx$$

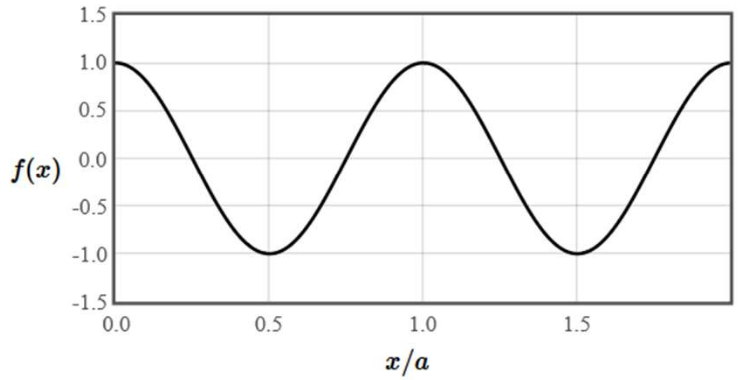
Fourier synthesis

A periodic function with period a can be written as a Fourier series of the form,

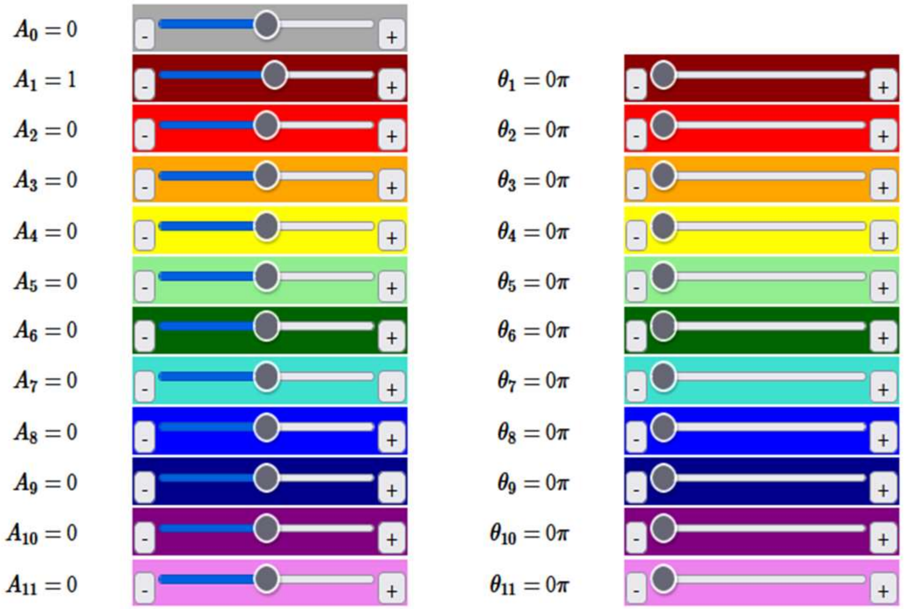
$$f(x) = A_0 + \sum_n A_n \left(\cos(\theta_n)\cos(2\pi nx/a) + \sin(\theta_n)\sin(2\pi nx/a)\right).$$







Number of periods displayed: 2



$A_0 = 0$

$A_1 = 1$ $\theta_1 = 0\pi$

$A_2 = 0$ $\theta_2 = 0\pi$

$A_3 = 0$ $\theta_3 = 0\pi$

$A_4 = 0$ $\theta_4 = 0\pi$

$A_5 = 0$ $\theta_5 = 0\pi$

$A_6 = 0$ $\theta_6 = 0\pi$

$A_7 = 0$ $\theta_7 = 0\pi$

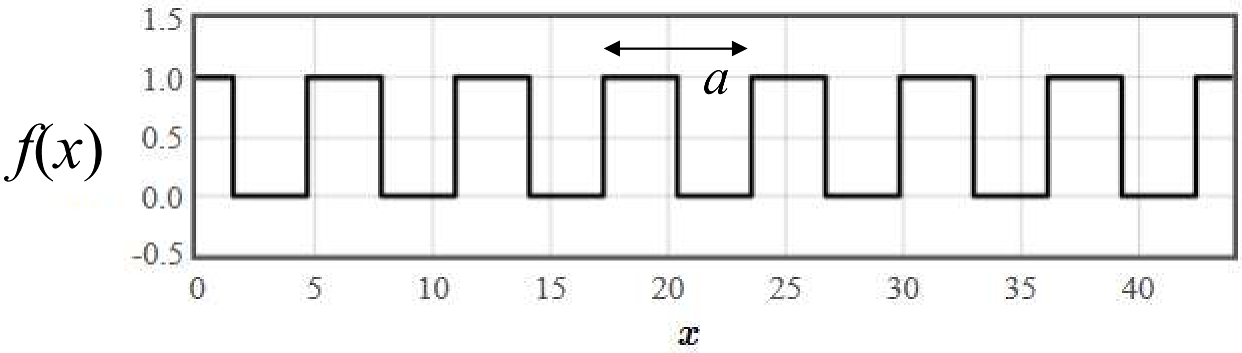
$A_8 = 0$ $\theta_8 = 0\pi$

$A_9 = 0$ $\theta_9 = 0\pi$

$A_{10} = 0$ $\theta_{10} = 0\pi$

$A_{11} = 0$ $\theta_{11} = 0\pi$

Expanding a 1-d function in a Fourier series



Any periodic function can be represented as a Fourier series.

$$f(x) = f_0 + \sum_{p=1}^{\infty} c_p \cos(2\pi px/a) + s_p \sin(2\pi px/a)$$

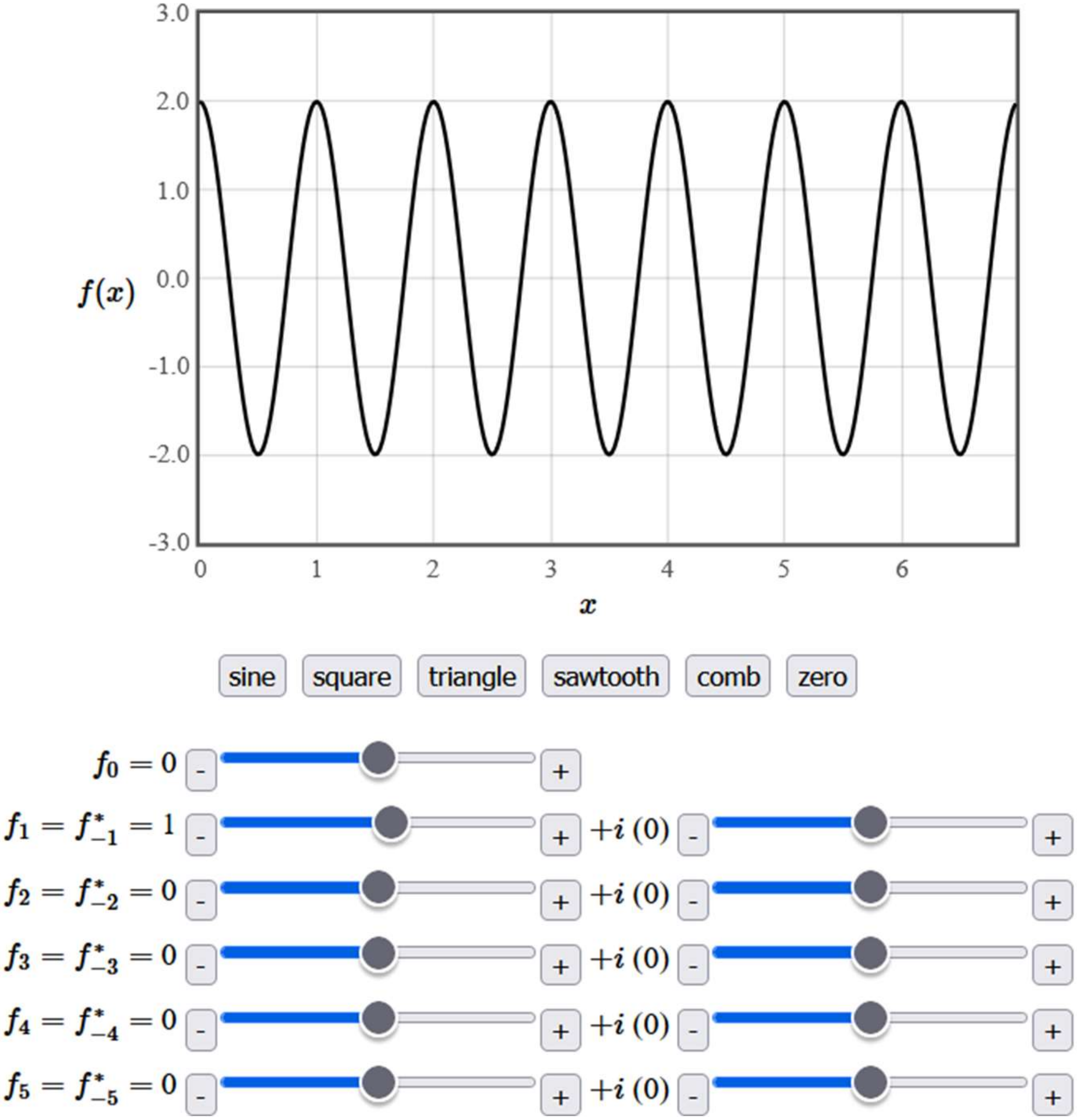
$$\cos x = \frac{e^{ix} + e^{-ix}}{2} \qquad \sin x = \frac{e^{ix} - e^{-ix}}{2i}$$

$$f(x) = \sum_{G=-\infty}^{\infty} f_G e^{iGx} \qquad f_G = \frac{c_p}{2} - i\frac{s_p}{2} \qquad G = \frac{2\pi p}{a}$$

For real functions: $f_G^* = f_{-G}$

reciprocal lattice vector

Fourier series in 1-D



$f_0 = 0$

$f_1 = f^*_{-1} = 1 \; +i\,(0)$

$f_2 = f^*_{-2} = 0 \; +i\,(0)$

$f_3 = f^*_{-3} = 0 \; +i\,(0)$

$f_4 = f^*_{-4} = 0 \; +i\,(0)$

$f_5 = f^*_{-5} = 0 \; +i\,(0)$

Determine the Fourier coefficients in 1-D

$$f(x)=\sum_G f_G e^{iGx}$$

Multiply by $e^{-iG'x}$ and integrate over a period a

$$\int_{\text{unit cell}} f(x)\, e^{-iG'x} dx = \int_{unit\ cell} \sum_G f_G e^{i(G-G')x} dx \quad = f_{G'} a$$

$$f_G = \frac{1}{a}\int_{-\infty}^{\infty} f_{cell}(x) e^{-iGx} dx$$

The Fourier coefficient is proportional to the Fourier transform of the pattern that gets repeated on the Bravais lattice, evaluated at that *G*-vector.

Fourier series in 1-D, 2-D, or 3-D

$$f(\vec{r}) = \sum_{\vec{G}} f_{\vec{G}} e^{i\vec{G}\cdot\vec{r}}$$

Reciprocal lattice vectors *G*
(depend on the Bravais lattice)

Structure factors
(complex numbers)

$$\vec{T}_{hkl} = h\vec{a}_1 + k\vec{a}_2 + l\vec{a}_3$$

$$\vec{G} = \nu_1\vec{b}_1 + \nu_2\vec{b}_2 + \nu_3\vec{b}_3$$

$$\vec{a}_i \cdot \vec{b}_j = 2\pi\delta_{ij} \qquad \delta_{ij} = \begin{cases} 1 & \text{for } i = j \\ 0, & \text{for } i \neq j \end{cases}$$

Reciprocal lattice (Reziprokes Gitter)

Any periodic function can be written as a Fourier series

$$f(\vec{r}) = \sum_{\vec{G}} f_{\vec{G}} e^{i\vec{G}\cdot\vec{r}}$$

Reciprocal lattice vector *G*

Structure factor

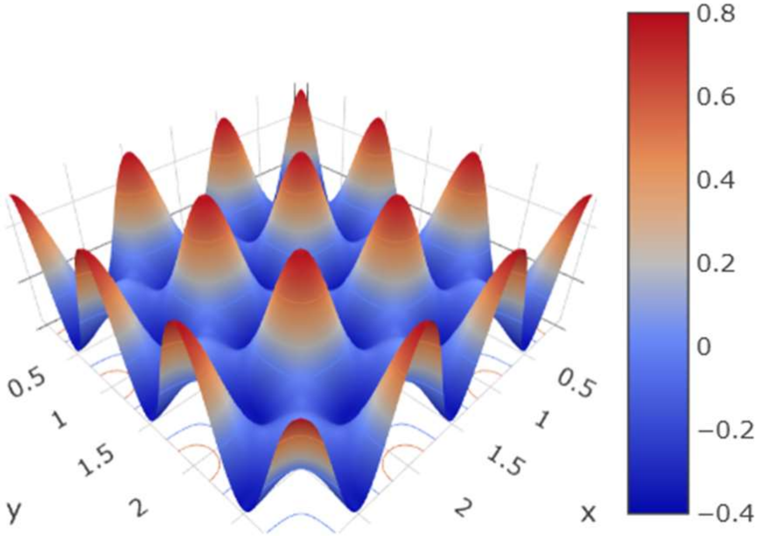
$$\vec{G} = \nu_1 \vec{b}_1 + \nu_2 \vec{b}_2 + \nu_3 \vec{b}_3$$

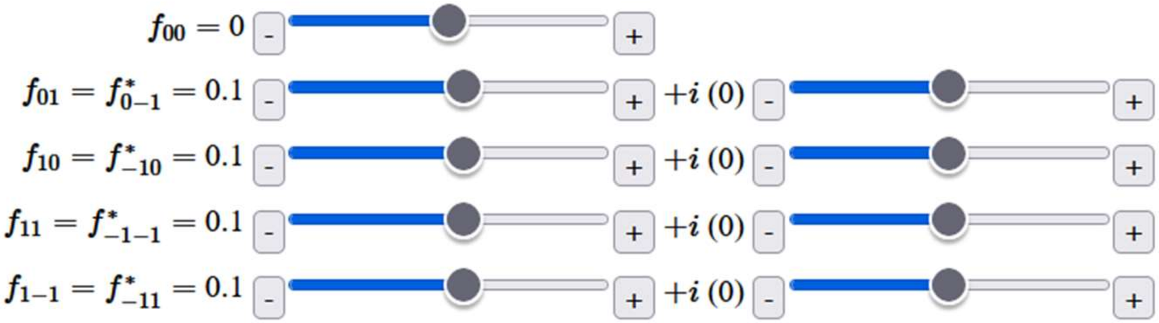
v_i integers

$$\vec{a}_i \cdot \vec{b}_j = 2\pi\delta_{ij}$$

$$\vec{b}_1 = 2\pi \frac{\vec{a}_2 \times \vec{a}_3}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)}, \qquad \vec{b}_2 = 2\pi \frac{\vec{a}_3 \times \vec{a}_1}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)}, \qquad \vec{b}_3 = 2\pi \frac{\vec{a}_1 \times \vec{a}_2}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)}$$

Two dimensional periodic functions





$f_{00} = 0$

$f_{01} = f^*_{0-1} = 0.1$ $+i\,(0)$

$f_{10} = f^*_{-10} = 0.1$ $+i\,(0)$

$f_{11} = f^*_{-1-1} = 0.1$ $+i\,(0)$

$f_{1-1} = f^*_{-11} = 0.1$ $+i\,(0)$

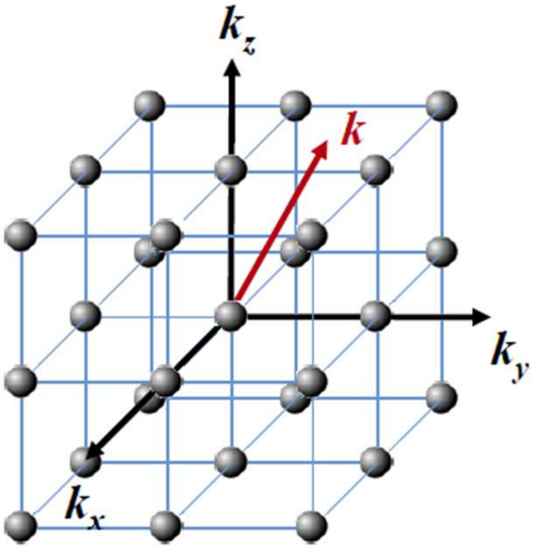
Reciprocal space (Reziproker Raum)
k-space (*k*-Raum)

k-space is the space of all wave-vectors.

A *k*-vector points in the direction a wave is propagating.

wavelength: $\lambda = \frac{2\pi}{|\vec{k}|}$

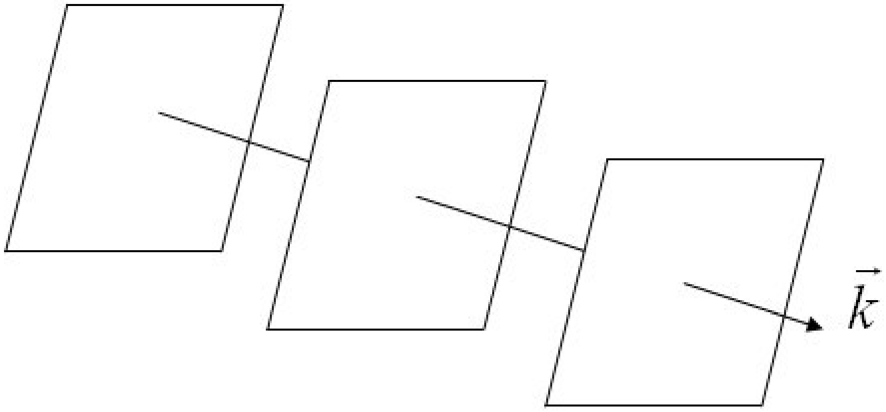
momentum: $\vec{p} = \hbar\vec{k}$



Plane waves (Ebene Wellen)

$$e^{i\vec{k}\cdot\vec{r}} = \cos\left(\vec{k}\cdot\vec{r}\right) + i\sin\left(\vec{k}\cdot\vec{r}\right)$$

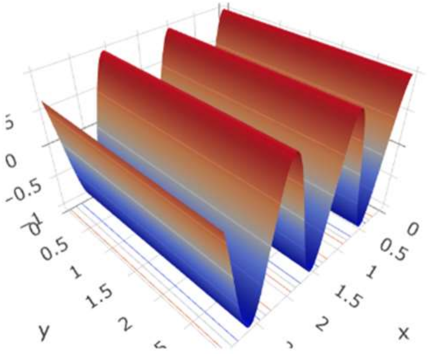
$$\lambda = \frac{2\pi}{\left|\vec{k}\right|}$$



$$\exp\left(i\vec{k}\cdot(\vec{r}+\vec{r}_{\perp})\right) = \exp\left(i\vec{k}\cdot\vec{r}\right)$$

Most functions can be expressed in terms of plane waves

$$f(\vec{r}) = \int F\left(\vec{k}\right) e^{i\vec{k}\cdot\vec{r}} d\vec{k}$$



A *k*-vector points in the direction a wave is propagating.

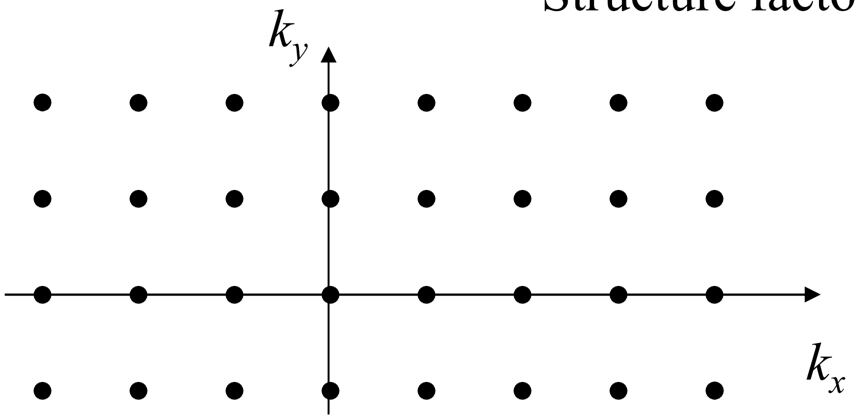
Reciprocal lattice (Reziprokes Gitter)

Any periodic function can be written as a Fourier series

$$f(\vec{r}) = \sum_{\vec{G}} f_{\vec{G}} e^{i\vec{G}\cdot\vec{r}}$$

Reciprocal lattice vector *G*

Structure factor



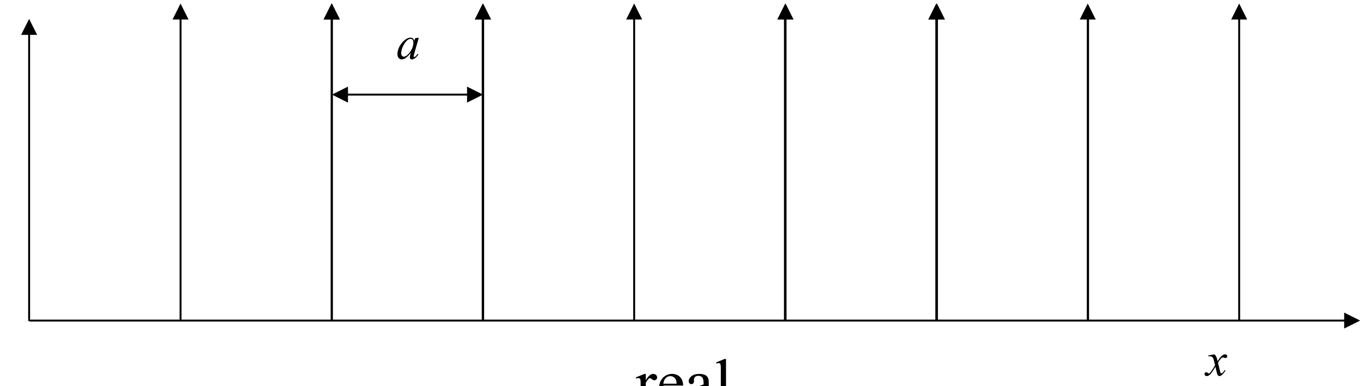
$$\vec{G} = \upsilon_1\vec{b}_1 + \upsilon_2\vec{b}_2 + \upsilon_3\vec{b}_3$$

v_i integers

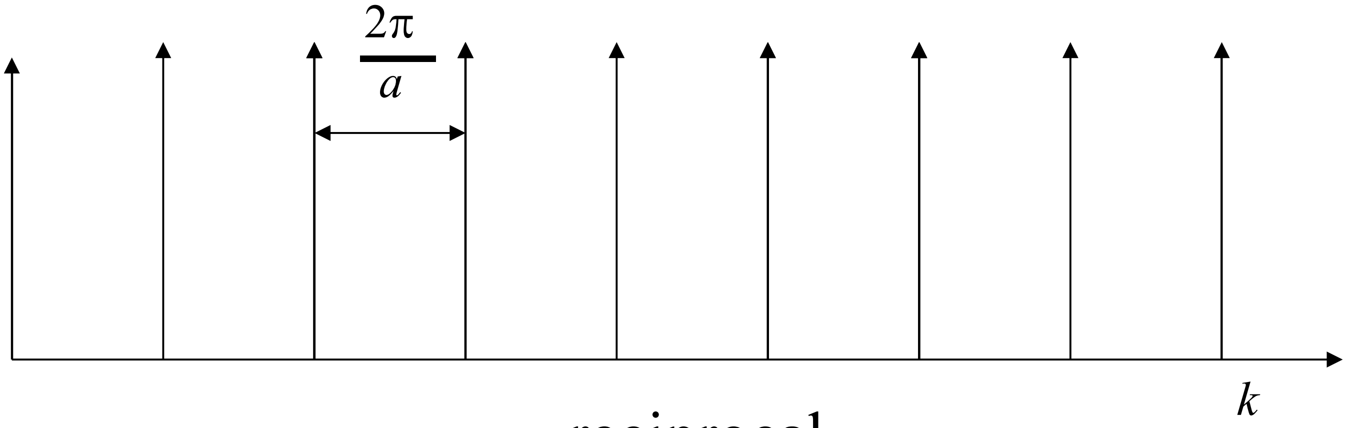
$$\vec{a}_i \cdot \vec{b}_j = 2\pi\delta_{ij}$$

$$\vec{b}_1 = 2\pi \frac{\vec{a}_2 \times \vec{a}_3}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)}, \qquad \vec{b}_2 = 2\pi \frac{\vec{a}_3 \times \vec{a}_1}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)}, \qquad \vec{b}_3 = 2\pi \frac{\vec{a}_1 \times \vec{a}_2}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)}$$

Bravais lattice and reciprocal lattice in 1-D



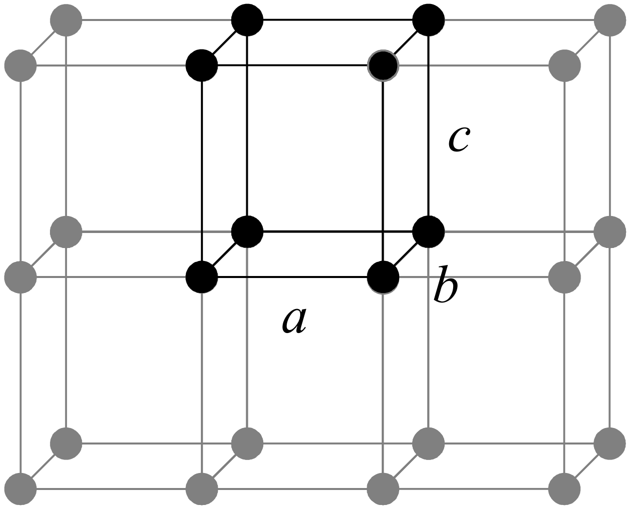
real

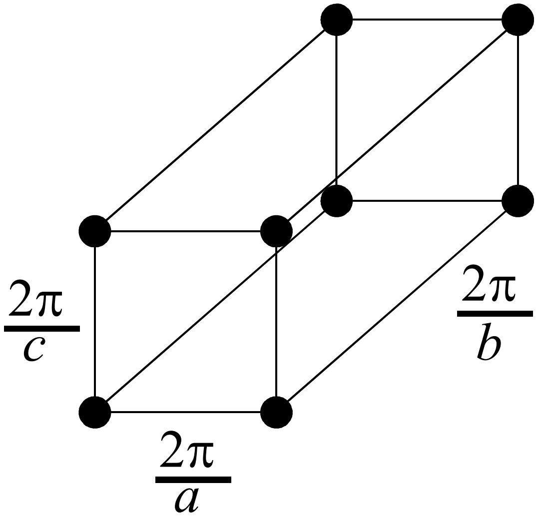


reciprocal

$$\cos\left(\frac{2\pi p x}{a}\right) \Rightarrow \cos(Gx) \qquad G = p\frac{2\pi}{a}$$

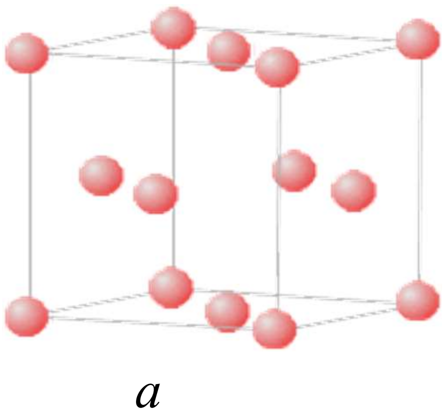
Reciprocal lattice of an orthorhombic lattice is an orthorhombic lattice

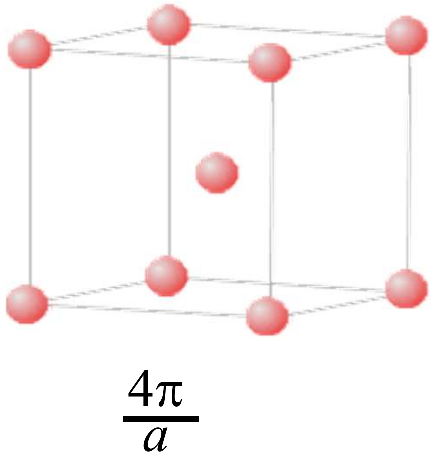




reciprocal lattice

The reciprocal lattice of an fcc lattice is a bcc lattice





$$\vec{a}_1 = \frac{a}{2}\hat{x} + \frac{a}{2}\hat{y}$$

$$\vec{a}_2 = \frac{a}{2}\hat{x} + \frac{a}{2}\hat{z}$$

$$\vec{a}_3 = \frac{a}{2}\hat{y} + \frac{a}{2}\hat{z}$$

$$\vec{b}_3 = 2\pi \frac{\vec{a}_1 \times \vec{a}_2}{\vec{a}_1 \cdot \left(\vec{a}_2 \times \vec{a}_3\right)}$$

$$\vec{b}_3 = \frac{2\pi}{a}\left(\hat{x} - \hat{y} - \hat{z}\right)$$

Reciprocal lattice (Reziprokes Gitter)

$$\text{sc:}\qquad \vec{a}_1 = a\hat{x}, \quad \vec{a}_2 = a\hat{y}, \quad \vec{a}_3 = a\hat{z},$$

$$\vec{b}_1 = \frac{2\pi}{a}\hat{k}_x, \quad \vec{b}_2 = \frac{2\pi}{a}\hat{k}_y, \quad \vec{b}_3 = \frac{2\pi}{a}\hat{k}_z.$$

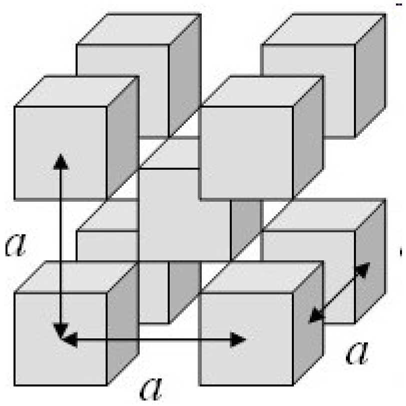
$$\text{fcc:}\qquad \vec{a}_1 = \frac{a}{2}(\hat{x}+\hat{z}), \quad \vec{a}_2 = \frac{a}{2}(\hat{x}+\hat{y}), \quad \vec{a}_3 = \frac{a}{2}(\hat{y}+\hat{z}),$$

$$\vec{b}_1 = \frac{2\pi}{a}(\hat{k}_x - \hat{k}_y + \hat{k}_z), \quad \vec{b}_2 = \frac{2\pi}{a}(\hat{k}_x + \hat{k}_y - \hat{k}_z), \quad \vec{b}_3 = \frac{2\pi}{a}(-\hat{k}_x + \hat{k}_y + \hat{k}_z).$$

$$\text{bcc:}\qquad \vec{a}_1 = \frac{a}{2}(\hat{x}+\hat{y}-\hat{z}), \quad \vec{a}_2 = \frac{a}{2}(-\hat{x}+\hat{y}+\hat{z}), \quad \vec{a}_3 = \frac{a}{2}(\hat{x}-\hat{y}+\hat{z}),$$

$$\vec{b}_1 = \frac{2\pi}{a}(\hat{k}_x + \hat{k}_y), \quad \vec{b}_2 = \frac{2\pi}{a}(\hat{k}_y + \hat{k}_z), \quad \vec{b}_3 = \frac{2\pi}{a}(\hat{k}_x + \hat{k}_z).$$

Cubes on a bcc lattice



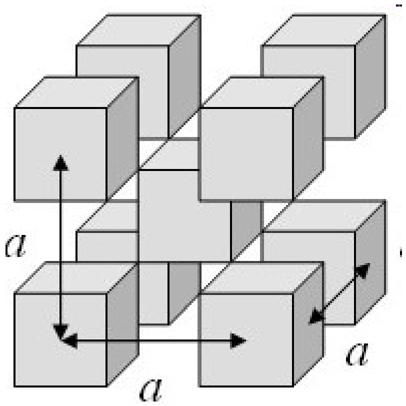
$$f(\vec{r}) = \sum_{\vec{G}} f_{\vec{G}} e^{i\vec{G}\cdot\vec{r}}$$

Multiply by $e^{-i\vec{G}'\cdot\vec{r}}$ and integrate over a primitive unit cell.

$$\int_{\text{unit cell}} f(\vec{r}) e^{-i\vec{G}\cdot\vec{r}} d^3r = f_{\vec{G}} V$$

http://lamp.tu-graz.ac.at/~hadley/ss1/crystaldiffraction/fourier.php

Cubes on a bcc lattice



$$\int_{\text{unit cell}} f(\vec{r})e^{-i\vec{G}\cdot\vec{r}}d^3r = f_{\vec{G}}V$$

V is the volume of the primitive unit cell.

$$f_{\vec{G}} = \frac{1}{V}\int f_{cell}(\vec{r})\exp\left(-i\vec{G}\cdot\vec{r}\right)d^3r$$

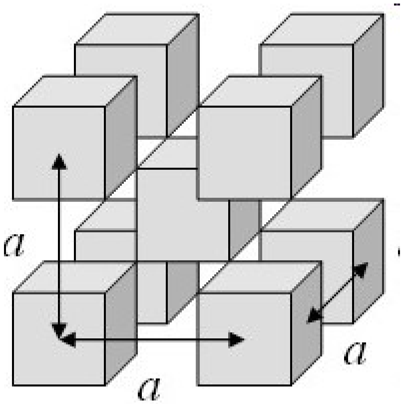
f_G is the Fourier transform of f_{cell} evaluated at G.
f_{cell} is zero outside the primitive unit cell.

$$f_{\vec{G}} = \frac{1}{V}\int f_{cell}(\vec{r})\exp\left(-i\vec{G}\cdot\vec{r}\right)d^3r = \frac{2C}{a^3}\int_{\frac{-a}{4}}^{\frac{a}{4}}\int_{\frac{-a}{4}}^{\frac{a}{4}}\int_{\frac{-a}{4}}^{\frac{a}{4}}\exp\left(-iG_xx\right)\exp\left(-iG_yy\right)\exp\left(-iG_zz\right)dxdydz$$

Volume of conventional u.c. a^3. Two Bravais points per conventional u.c.

Cubes on a bcc lattice

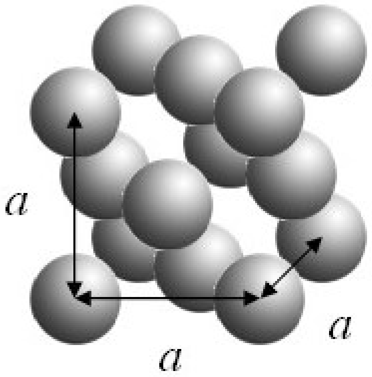
$$\int_{-\frac{a}{4}}^{\frac{a}{4}} \exp\left(-iG_x x\right)dx = \left.\frac{\exp\left(-iG_x x\right)}{-iG_x}\right|_{\frac{-a}{4}}^{\frac{a}{4}} = \left.\frac{\cos\left(-G_x x\right)+i\sin\left(-G_x x\right)}{-iG_x}\right|_{\frac{-a}{4}}^{\frac{a}{4}} = \frac{2\sin\left(\frac{G_x a}{4}\right)}{G_x}$$



$$f_{\vec{G}} = \frac{16C\sin\left(\frac{G_x a}{4}\right)\sin\left(\frac{G_y a}{4}\right)\sin\left(\frac{G_z a}{4}\right)}{a^3 G_x G_y G_z}$$

The Fourier series for any rectangular cuboid with dimensions $L_x \times L_y \times L_z$ repeated on any three-dimensional Bravais lattice is:

$$f(\vec{r}) = \sum_{\vec{G}} \frac{8C\sin\left(\frac{G_x L_x}{2}\right)\sin\left(\frac{G_y L_y}{2}\right)\sin\left(\frac{G_z L_z}{2}\right)}{VG_x G_y G_z}\exp\left(i\vec{G}\cdot\vec{r}\right)$$



Spheres on an fcc lattice

$$f(\vec{r}) = \sum_{\vec{G}} f_{\vec{G}} e^{i\vec{G}\cdot\vec{r}}$$

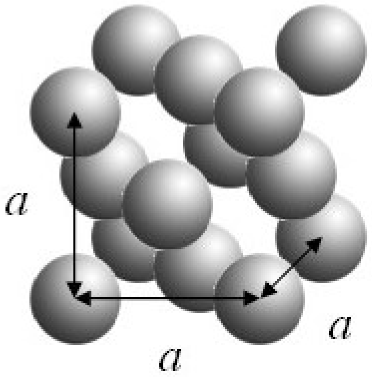
Multiply by $e^{-i\vec{G}'\cdot\vec{r}}$ and integrate over a primitive unit cell.

$$f_{\vec{G}} = \frac{1}{V}\int f_{cell}(\vec{r})\exp\left(-i\vec{G}\cdot\vec{r}\right)d^3r = \frac{C}{V}\int_{\text{sphere}} \exp\left(-i\vec{G}\cdot\vec{r}\right)d^3r.$$

The Fourier series for non-overlapping spheres on any three-dimensional Bravais lattice is:

$$f(\vec{r}) = \frac{4\pi C}{V}\sum_{\vec{G}} \frac{\sin\left(|G|R\right)-|G|R\cos\left(|G|R\right)}{|G|^3}\exp\left(i\vec{G}\cdot\vec{r}\right).$$

Spheres on an fcc lattice



$$f(\vec{r}) = \sum_{\vec{G}} f_{\vec{G}} e^{i\vec{G}\cdot\vec{r}}$$

Multiply by $e^{-i\vec{G}'\cdot\vec{r}}$ and integrate over a primitive unit cell.

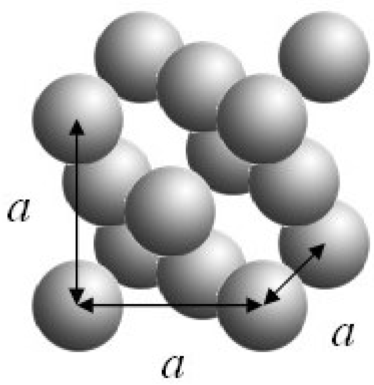
$$f_{\vec{G}} = \frac{1}{V}\int f_{cell}(\vec{r})\exp\left(-i\vec{G}\cdot\vec{r}\right)d^3r = \frac{C}{V}\int_{\text{sphere}} \exp\left(-i\vec{G}\cdot\vec{r}\right)d^3r.$$

$$f_{\vec{G}} = \frac{C}{V}\int_0^R\int_0^\pi\int_{-\pi}^{\pi} \exp(-i\vec{G}\cdot\vec{r})r^2 \sin\theta dr d\theta d\varphi$$

$$= \frac{C}{V}\int_0^R\int_0^\pi\int_{-\pi}^{\pi}\left(\cos\left(|G|r\cos\theta\right) - i\sin\left(|G|r\cos\theta\right)\right)r^2\sin\theta dr d\theta d\varphi$$

Integrate over φ

$$f_{\vec{G}} = \frac{2\pi C}{V}\int_0^R\int_0^\pi\left(\cos\left(|G|r\cos\theta\right) - i\sin\left(|G|r\cos\theta\right)\right)r^2\sin\theta dr d\theta$$



Spheres on an fcc lattice

$$f_{\vec{G}}=\frac{2\pi C}{V}\int_0^R\int_0^\pi\left(\cos\left(|G|r\cos\theta\right)-i\sin\left(|G|r\cos\theta\right)\right)r^2\sin\theta drd\theta$$

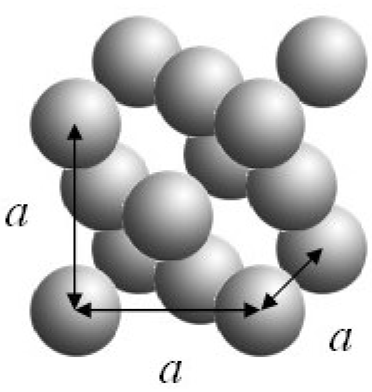
Both terms are perfect differentials

$$\frac{d}{d\theta}\cos\left(|G|r\cos\theta\right)=|G|r\sin\left(|G|r\cos\theta\right)\sin\theta \qquad \text{and}$$

$$\frac{d}{d\theta}\sin\left(|G|r\cos\theta\right)=-|G|r\cos\left(|G|r\cos\theta\right)\sin\theta,$$

Integrate over θ: $$f_{\vec{G}}=\frac{2\pi C}{V}\int_0^R\left(-\sin\left(|G|r\cos\theta\right)-i\cos\left(|G|\cancelto{0}{r}\cos\theta\right)\right)\Big|_0^\pi dr$$

$$f_{\vec{G}}=\frac{4\pi C}{V}\int_0^R\frac{\sin\left(|G|r\right)}{|G|}rdr$$



Spheres on any lattice

$$f_{\vec{G}} = \frac{4\pi C}{V}\int_0^R \frac{\sin\left(\left|G\right|r\right)}{\left|G\right|r} r^2 dr$$

Integrate over r

$$f_G = \frac{4\pi C}{V\left|G\right|^3}\left(\sin\left(\left|G\right|R\right) - \left|G\right|R\cos\left(\left|G\right|R\right)\right).$$

The Fourier series for non-overlapping spheres on any three-dimensional Bravais lattice is:

$$f\left(\vec{r}\right) = \frac{4\pi C}{V}\sum_{\vec{G}} \frac{\sin\left(\left|G\right|R\right) - \left|G\right|R\cos\left(\left|G\right|R\right)}{\left|G\right|^3}\exp\left(i\vec{G}\cdot\vec{r}\right).$$

Molecular orbital potential

$$U(\vec{r}) = \frac{-Ze^2}{4\pi\varepsilon_0} \sum_{r_j} \frac{1}{\left|\vec{r} - \vec{r}_j\right|}$$

position of atom *j*

The Fourier series for any molecular orbital potential is:

$$U(\vec{r}) = \frac{-Ze^2}{V\varepsilon_0} \sum_{\vec{G}} \frac{\exp\left(i\vec{G} \cdot \vec{r}\right)}{\left|G\right|^2}$$

Volume of the primitive unit cell

Muffin tin potential

The potential is $U(\vec{r}) = -\frac{Ze^2}{4\pi\epsilon_0}\sum_j \frac{1}{|\vec{r}-\vec{r}_j|}$ around the Bravais lattice points

The potential is constant between the spheres.

$$U(\vec{r}) = \frac{Ze^2}{V\epsilon_0}\sum_{\vec{G}}\left(\frac{\cos(|G|R)-1}{|G|^2} + \frac{\sin(|G|R)-|G|R\cos(|G|R)}{R|G|^3}\right)\exp\left(i\vec{G}\cdot\vec{r}\right).$$