Fourier series
Reciprocal space

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)

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

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

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

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

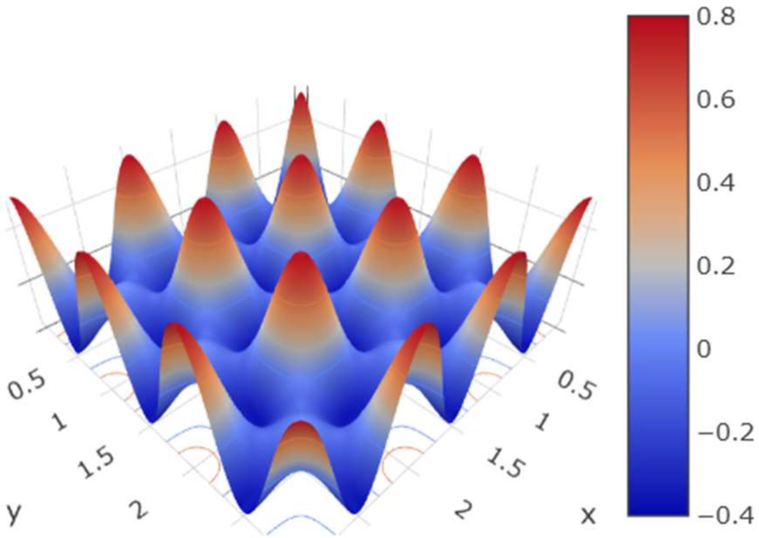
$$\vec{G} = \nu_1 \vec{b}_1 + \nu_2 \vec{b}_2 + \nu_3 \vec{b}_3$$

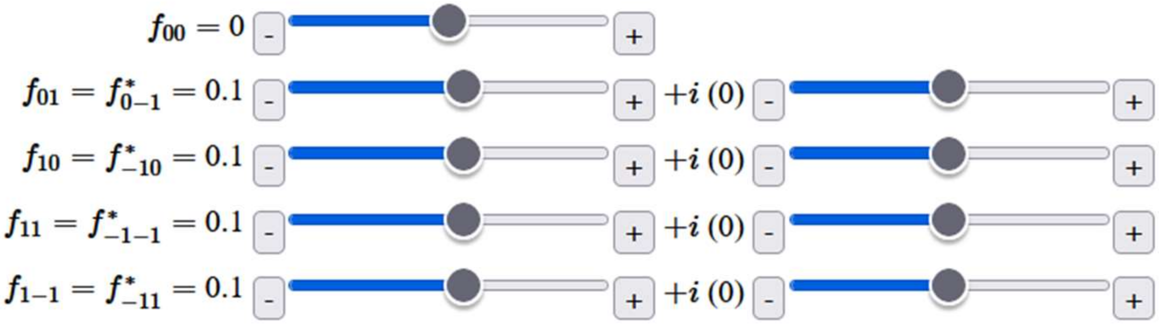
v_i integers

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

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

Two dimensional periodic functions





$f_{00} = 0$

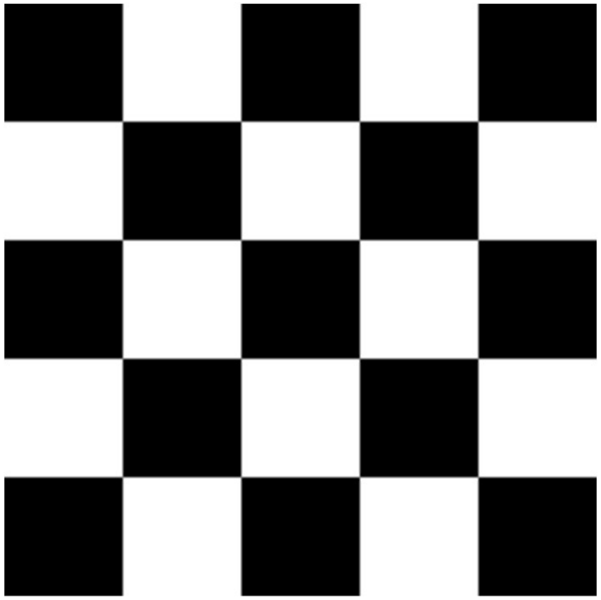
$f_{01} = f^*_{0-1} = 0.1$ $+i\,(0)$

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

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

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

Determine the Fourier coefficients



$$f(\vec{r}) = \sum_{\vec{G}} f_{\vec{G}} \exp\left(i\vec{G} \cdot \vec{r}\right)$$

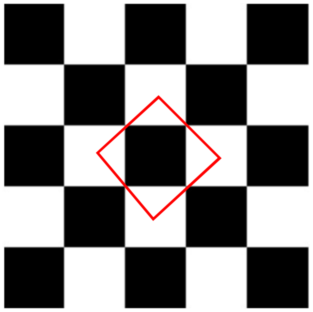
Determine the Fourier coefficients

$$f(\vec{r}) = \sum_{\vec{G}} f_{\vec{G}} \exp\left(i\vec{G}\cdot\vec{r}\right)$$

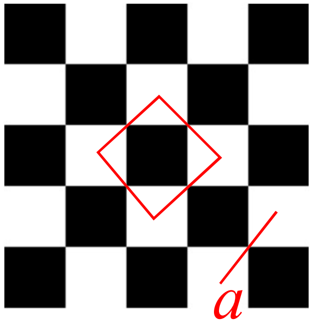
Multiply by $\exp(-i\vec{G}'\cdot\vec{r})$ and integrate over a unit cell

$$\int\limits_{\text{unit cell}} f(\vec{r})\exp(-i\vec{G}'\cdot\vec{r})d\vec{r} = \sum_{\vec{G}} \int\limits_{\text{unit cell}} f_{\vec{G}}\exp(-i\vec{G}'\cdot\vec{r})\exp(i\vec{G}\cdot\vec{r})d\vec{r}$$

$$f_{\vec{G}} = \frac{1}{V_{\text{uc}}} \int\limits_{\text{unit cell}} f(\vec{r})\exp(-i\vec{G}\cdot\vec{r})d\vec{r}$$



Determine the Fourier coefficients



$$f_{\vec{G}} = \frac{C}{a^2} \int_{-\sqrt{2}a/4}^{\sqrt{2}a/4} \int_{-\sqrt{2}a/4}^{\sqrt{2}a/4} \exp(-i\vec{G}\cdot\vec{r})dxdy$$

$$f_{\vec{G}} = \frac{C}{a^2} \int_{-\sqrt{2}a/4}^{\sqrt{2}a/4} \int_{-\sqrt{2}a/4}^{\sqrt{2}a/4} \exp(-iG_x x)\exp(-iG_y y)dxdy$$

$$f_{\vec{G}} = \frac{C}{a^2} \frac{\left(\exp(-iG_x\sqrt{2}a/4) - \exp(iG_x\sqrt{2}a/4)\right)\left(\exp(-iG_y\sqrt{2}a/4) - \exp(iG_y\sqrt{2}a/4)\right)}{-G_xG_y}$$

$$f_{\vec{G}} = \frac{4C}{a^2} \frac{\sin(G_x\sqrt{2}a/4)\sin(G_y\sqrt{2}a/4)}{G_xG_y}$$

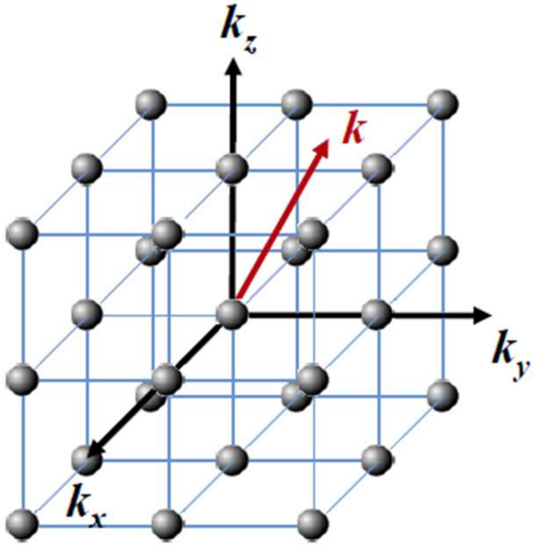
Reciprocal space (Reziproker Raum)
k-space (*k*-Raum)

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

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

wavelength: $\lambda = \dfrac{2\pi}{\left|\vec{k}\right|}$

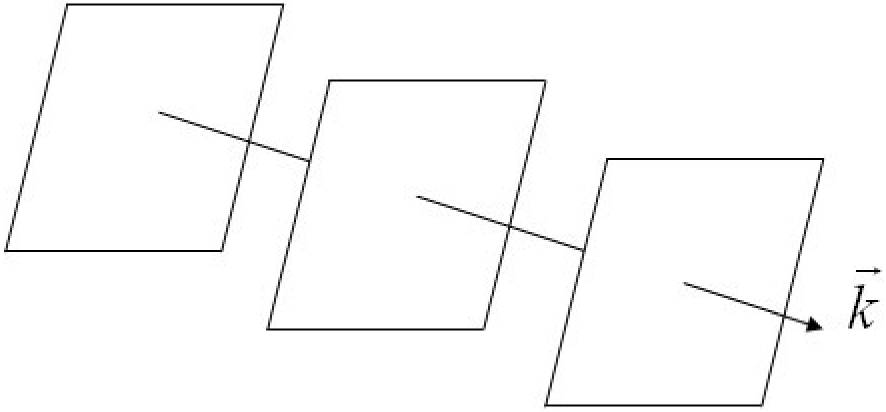
momentum: $\vec{p} = \hbar\vec{k}$



Plane waves (Ebene Wellen)

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

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

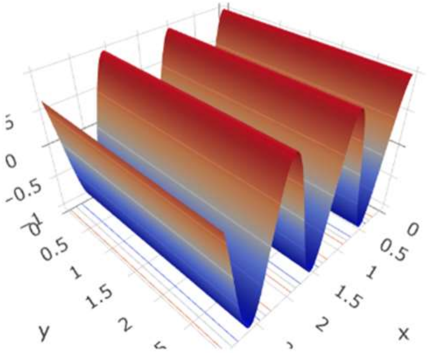


$$\exp\left(i\vec{k}\cdot(\vec{r}+\vec{r}_\perp)\right) = \exp\left(i\vec{k}\cdot\vec{r}\right)$$

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.



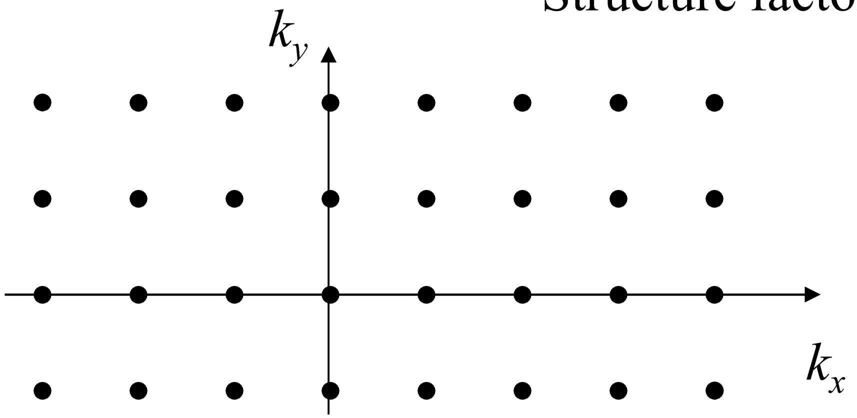
Reciprocal lattice (Reziprokes Gitter)

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



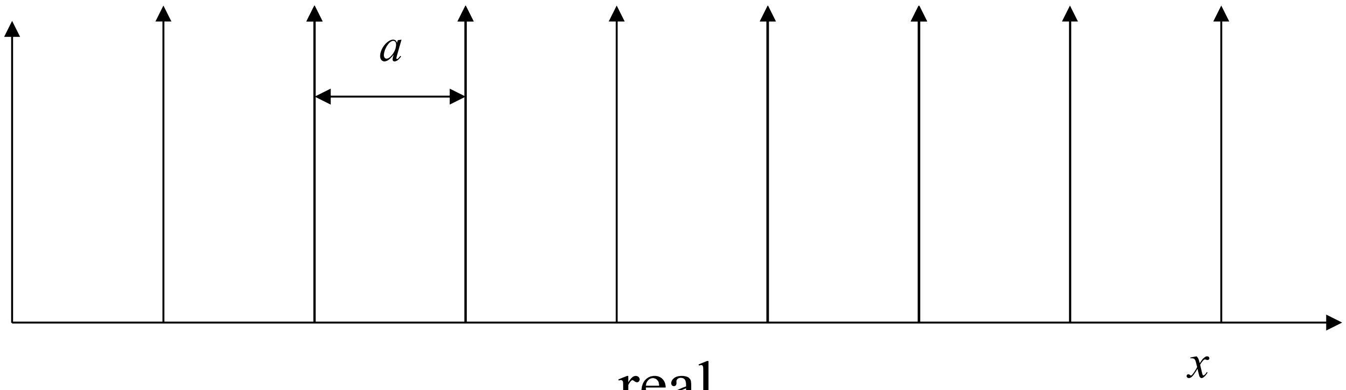
$$\vec{G} = \upsilon_1\vec{b}_1 + \upsilon_2\vec{b}_2 + \upsilon_3\vec{b}_3$$

v_i integers

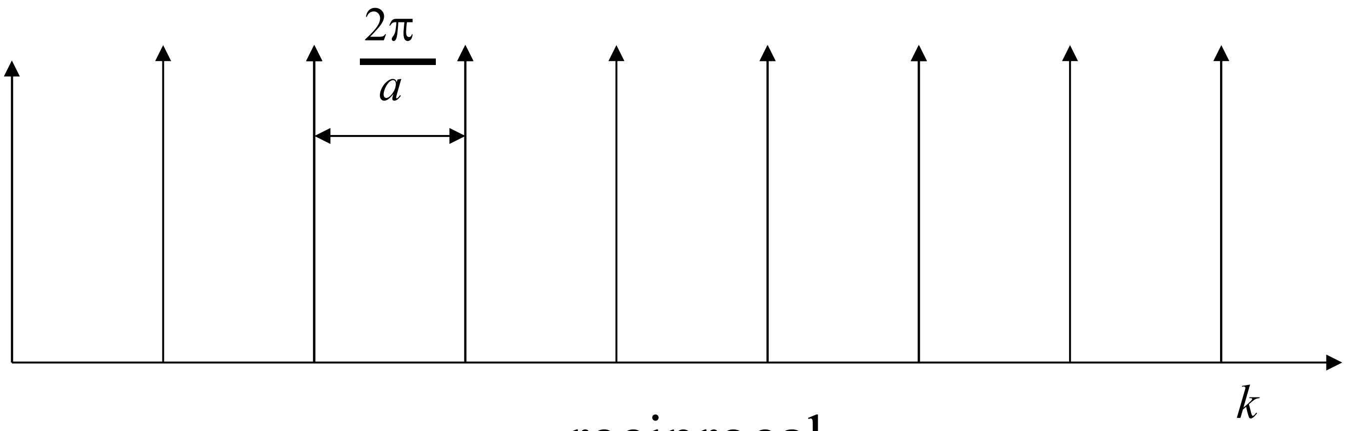
$$\vec{a}_i \cdot \vec{b}_j = 2\pi\delta_{ij}$$

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

Bravais lattice and reciprocal lattice in 1-D



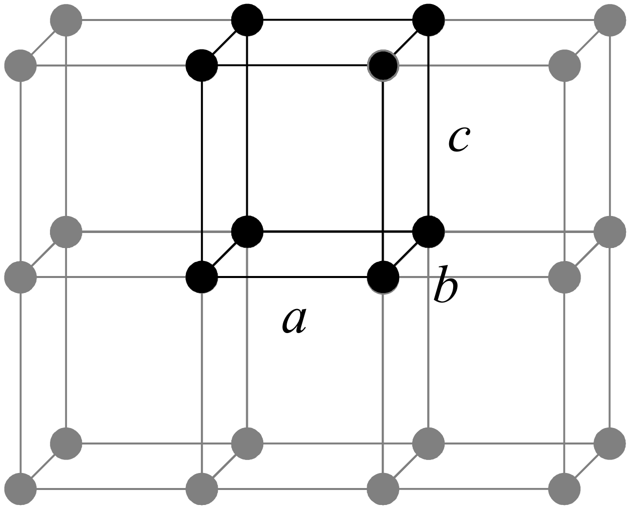
real

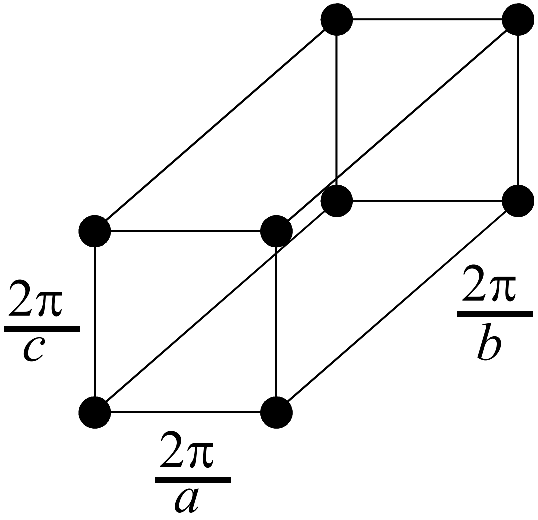


reciprocal

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

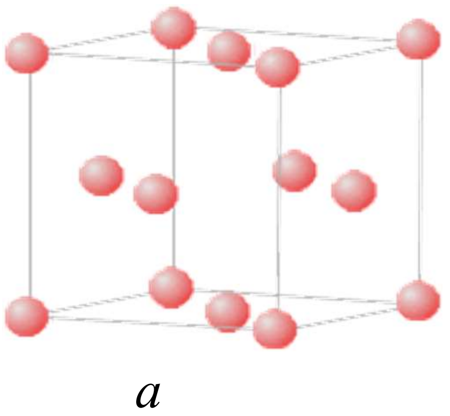
Reciprocal lattice of an orthorhombic lattice is an orthorhombic lattice

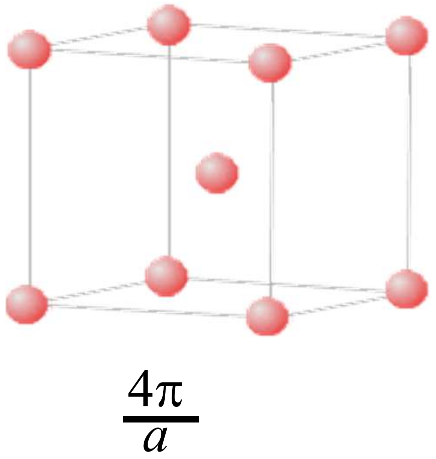




reciprocal lattice

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)

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

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

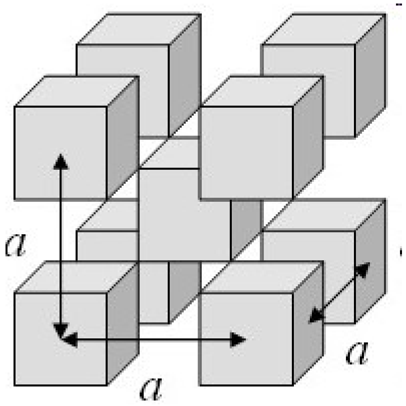
$$\text{fcc:} \qquad \vec{a}_1 = \frac{a}{2}(\hat{x}+\hat{z}), \quad \vec{a}_2 = \frac{a}{2}(\hat{x}+\hat{y}), \quad \vec{a}_3 = \frac{a}{2}(\hat{y}+\hat{z}),$$

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

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

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

Cubes on a bcc lattice



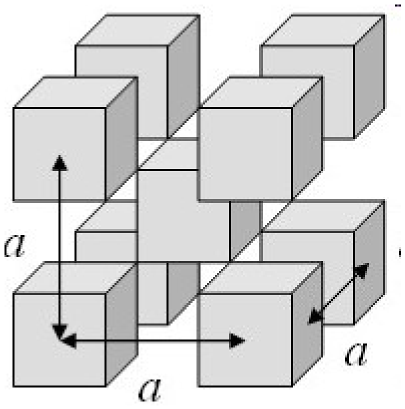
$$f(\vec{r}) = \sum_{\vec{G}} f_{\vec{G}} e^{i\vec{G}\cdot\vec{r}}$$

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.

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

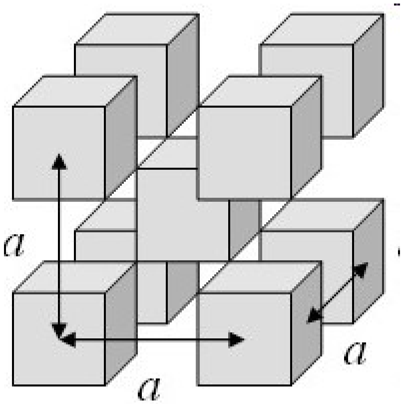
f_G is the Fourier transform of f_{cell} evaluated at G.
f_{cell} is zero outside the primitive unit cell.

$$f_{\vec{G}} = \frac{1}{V}\int f_{cell}(\vec{r})\exp\left(-i\vec{G}\cdot\vec{r}\right)d^3r = \frac{2C}{a^3}\int\limits_{\frac{-a}{4}}^{\frac{a}{4}}\int\limits_{\frac{-a}{4}}^{\frac{a}{4}}\int\limits_{\frac{-a}{4}}^{\frac{a}{4}}\exp\left(-iG_x x\right)\exp\left(-iG_y y\right)\exp\left(-iG_z z\right)dxdydz$$

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

Cubes on a bcc lattice

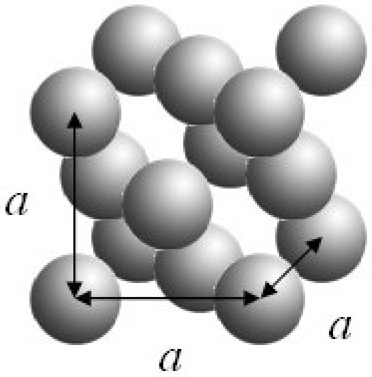
$$\int_{-\frac{a}{4}}^{\frac{a}{4}} \exp(-iG_x x)dx = \left.\frac{\exp(-iG_x x)}{-iG_x}\right|_{-\frac{a}{4}}^{\frac{a}{4}} = \left.\frac{\cos(-G_x x)+i\sin(-G_x x)}{-iG_x}\right|_{-\frac{a}{4}}^{\frac{a}{4}} = \frac{2\sin\left(\frac{G_x a}{4}\right)}{G_x}$$



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

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

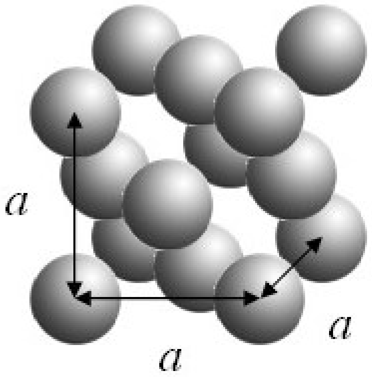
$$f(\vec{r}) = \sum_{\vec{G}} f_{\vec{G}} e^{i\vec{G}\cdot\vec{r}}$$

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.

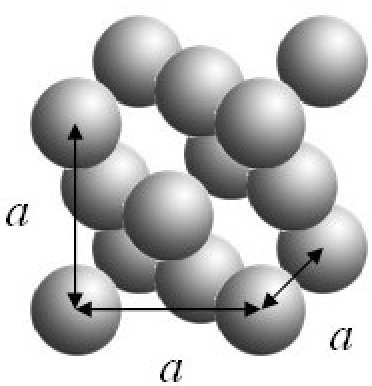
$$f_{\vec{G}} = \frac{1}{V}\int f_{cell}(\vec{r})\exp\left(-i\vec{G}\cdot\vec{r}\right)d^3r = \frac{C}{V}\int_{\text{sphere}} \exp\left(-i\vec{G}\cdot\vec{r}\right)d^3r.$$

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

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

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

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

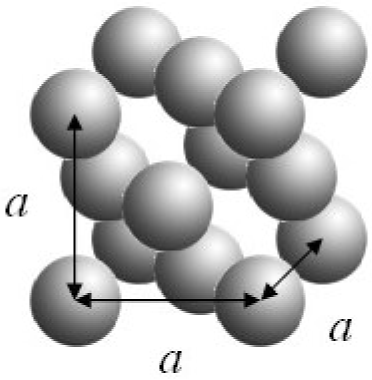
Both terms are perfect differentials

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

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

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

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



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:

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

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

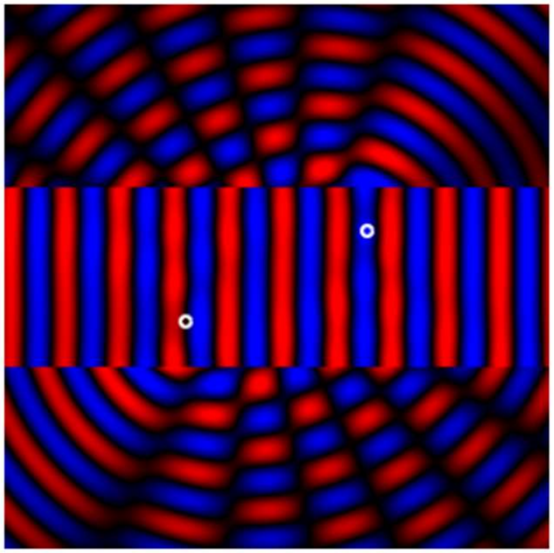
Muffin tin potential

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.

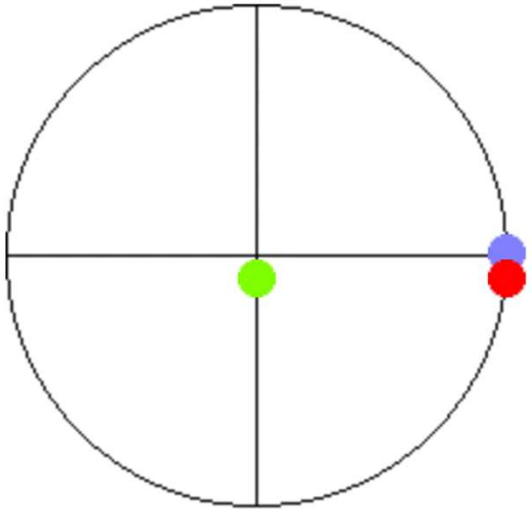
$$U(\vec{r}) = \frac{Ze^2}{V\epsilon_0}\sum_{\vec{G}}\left(\frac{\cos(|G|R)-1}{|G|^2} + \frac{\sin(|G|R) - |G|R\cos(|G|R)}{R|G|^3}\right)\exp\left(i\vec{G}\cdot\vec{r}\right).$$

Intensity of the scattered waves

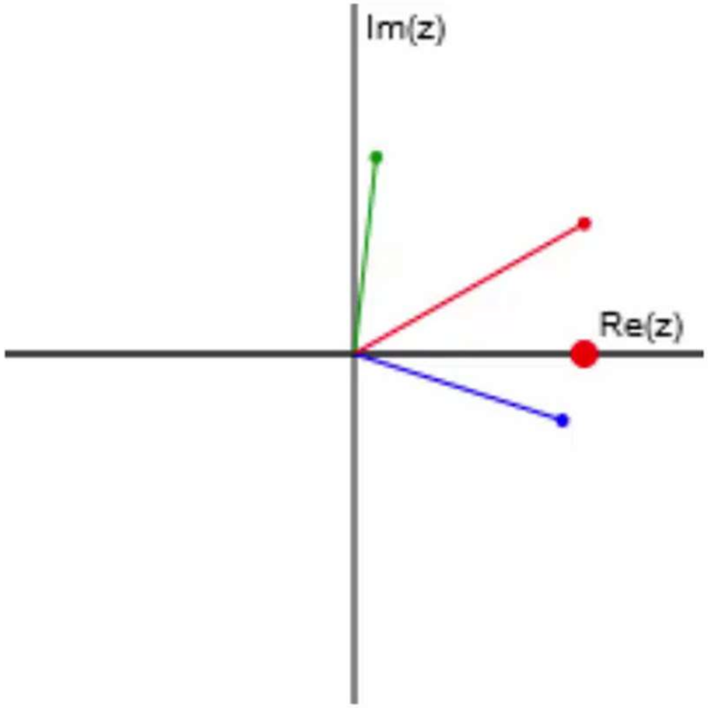


$$F_1 \frac{\cos(k|\vec{r}-\vec{r}_1| - \omega t + kx_1)}{\sqrt{|\vec{r}-\vec{r}_1|}} + F_2 \frac{\cos(k|\vec{r}-\vec{r}_2| - \omega t + kx_2)}{\sqrt{|\vec{r}-\vec{r}_2|}}.$$

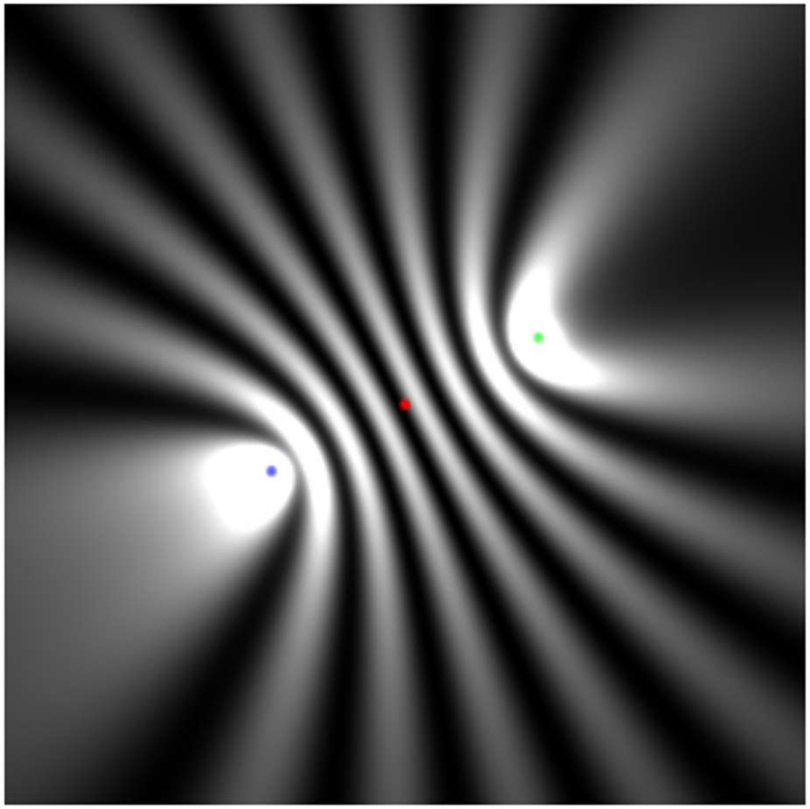
Using complex numbers to describe oscillations



$$e^{i\omega t} = \cos(\omega t) + i\sin(\omega t)$$

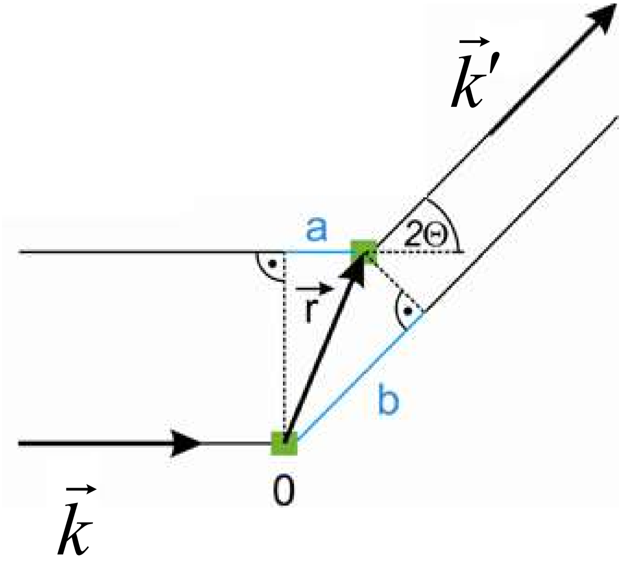


Intensity of the scattered waves



$$\left(\frac{F_1}{\sqrt{|\vec{r}-\vec{r}_1|}}e^{i(k|\vec{r}-\vec{r}_1|+kx_1)}+\frac{F_2}{\sqrt{|\vec{r}-\vec{r}_2|}}e^{i(k|\vec{r}-\vec{r}_2|+kx_2)}\right)e^{-i\omega t}$$

Interference



$$a = \frac{\vec{r}\cdot\vec{k}}{|k|} \qquad b = \frac{\vec{r}\cdot\vec{k}'}{|k|}$$

elastic scattering

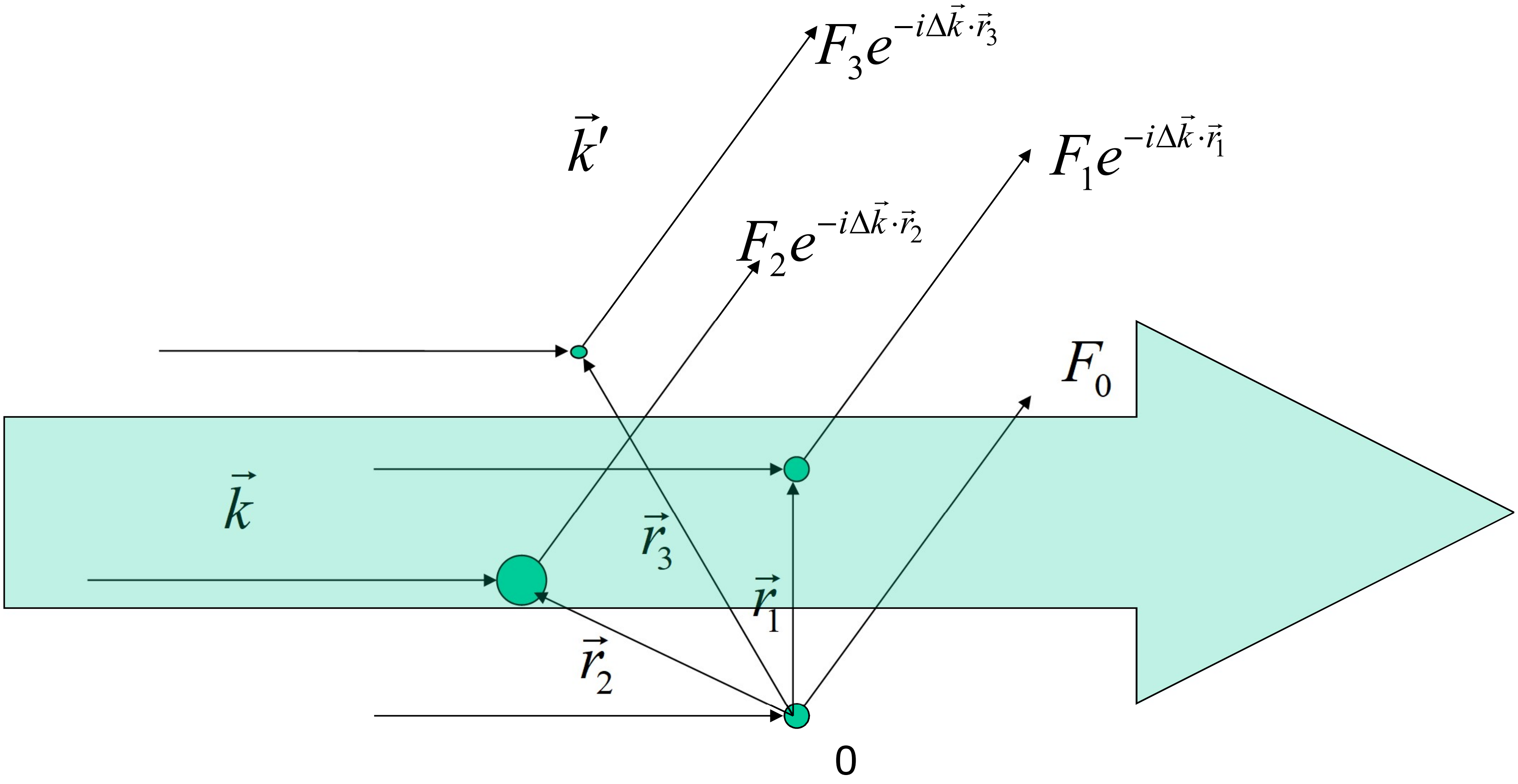
$$|k| = |k'|$$

path difference: $$a - b = \frac{-\vec{r}\cdot\left(\vec{k}' - \vec{k}\right)}{|k|}$$

phase shift: $$\varphi = 2\pi\frac{a-b}{\lambda} = 2\pi\frac{-\vec{r}\cdot\left(\vec{k}' - \vec{k}\right)}{|k|\,\lambda} = -\vec{r}\cdot\left(\vec{k}' - \vec{k}\right) = -\Delta\vec{k}\cdot\vec{r}$$

Amplitude: $$F = F_0 + F_0 e^{-i\Delta\vec{k}\cdot\vec{r}}$$

Interference

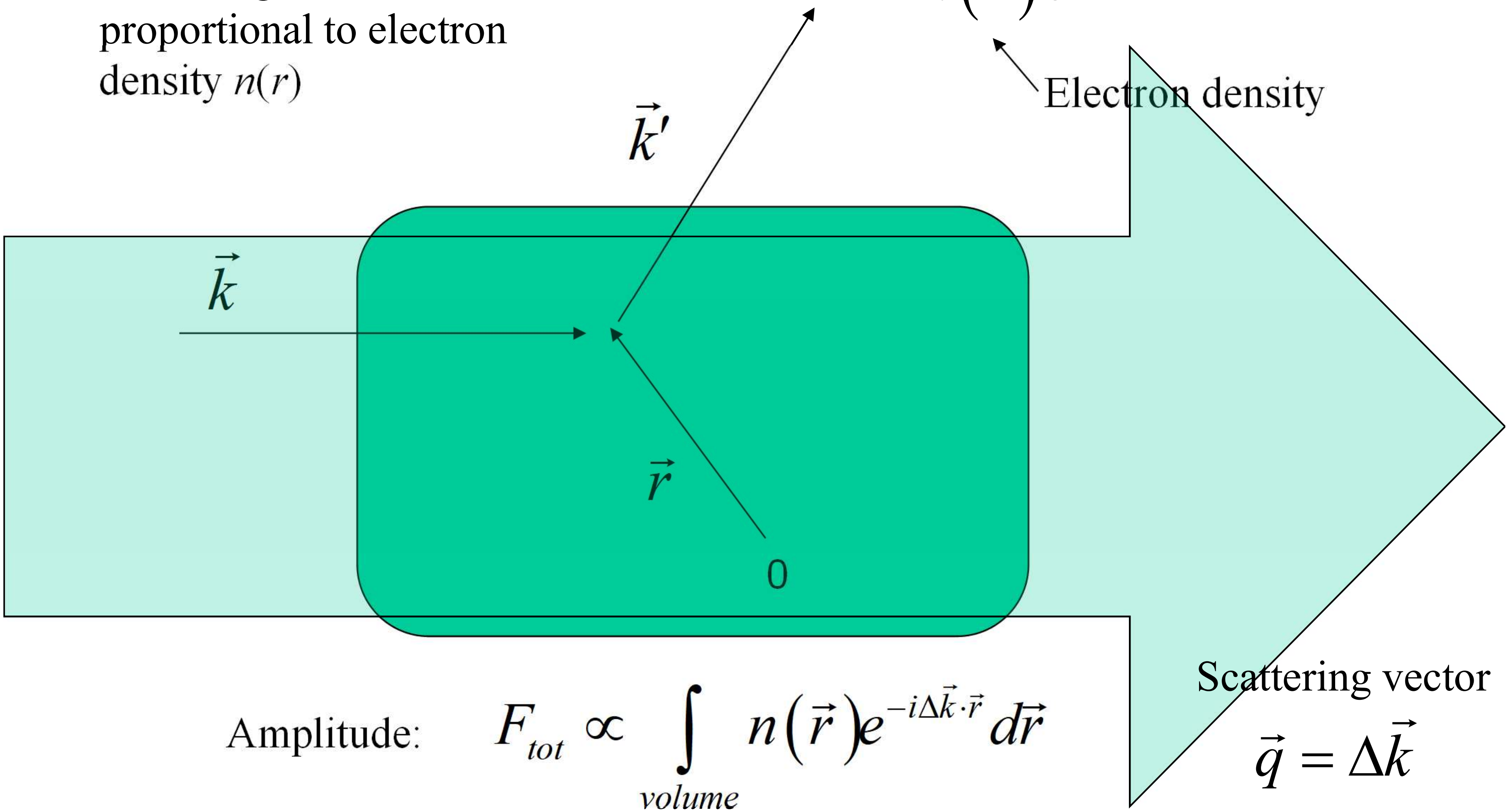


Amplitude: $F_{tot} = \sum_i F_i e^{-i\Delta\vec{k}\cdot\vec{r}_i}$

Interference

Scattering is proportional to electron density $n(r)$

$$\propto n\left(\vec{r}\right)e^{-i\Delta\vec{k}\cdot\vec{r}}$$



Electron density

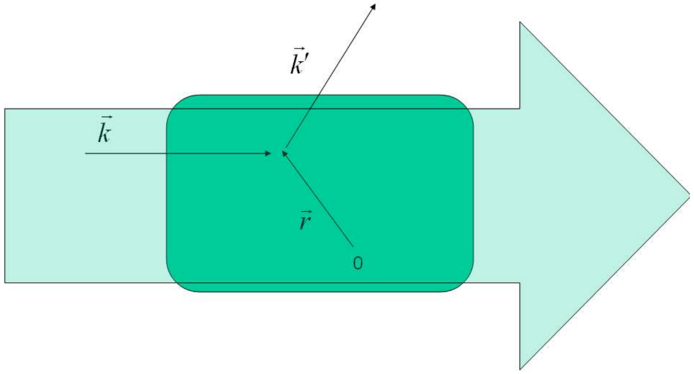
Amplitude: $$F_{tot} \propto \int_{volume} n\left(\vec{r}\right)e^{-i\Delta\vec{k}\cdot\vec{r}}\,d\vec{r}$$

Scattering vector

$$\vec{q} = \Delta\vec{k}$$

The scattering amplitude is proportional to the Fourier transform of the electron density.

Scattering amplitude



$$F \propto \int n(\vec{r}) \exp(-i\Delta\vec{k}\cdot\vec{r})dV$$

expand $n(r)$ in a Fourier series

$$n(\vec{r}) = \sum_{\vec{G}} n_{\vec{G}} \exp(i\vec{G}\cdot\vec{r})$$

$$F \propto \sum_{G} \int n_G \exp(i(\vec{G}-\Delta\vec{k})\cdot\vec{r})dV$$

if $\vec{G} = \Delta\vec{k}$, all components add coherently

diffraction condition: $\boxed{\vec{G} = \Delta\vec{k}}$

The intensity of the peak at G is $|n_G|^2$