Reciprocal Space

Please see:
Massa, Werner. *Crystal Structure Determination. 2nd ed.* Translated into English by R. O. Gould.
New York, NY: Springer, 2004. ISBN: 3540206442.

The reflection h, k, l is generated by diffraction of the X-ray beam at the Bragg plane set h, k, l, which intersects the three edges of the unit cell at $1/h$, $1/k$ and $1/l$. Sets of planes in real space (with spacing d) correspond to points in reciprocal space (distance d^* from the origin). The vector d^* is perpendicular to the Bragg planes and has the length $|d^*| = 2\sin\theta/\lambda$.
A reflection is visible when the corresponding set of Bragg planes is in reflex position, that is when Bragg's law is fulfilled. In an alternative description:
a reflection is visible when the corresponding scattering vector $s = d^*$ intersects with the Ewald sphere.

Reciprocal Space

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The reflections form a lattice in reciprocal space. Reciprocal unit cell: a^*, b^*, c^*
The dimensions and angles of the reciprocal cell are inversely proportional to the real space cell: if the unit cell doubles, the space between the X-ray reflections will be reduced by factor two.

Reciprocal Space

For orthorhombic tetragonal and cubic unit cells:
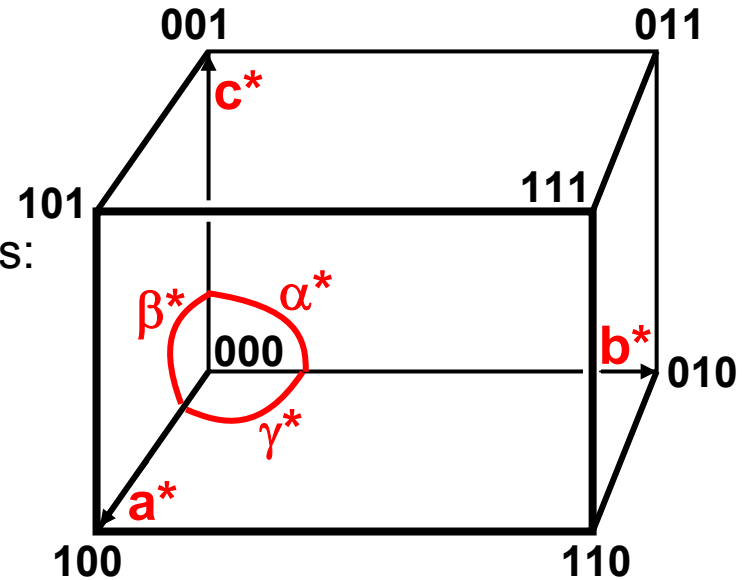
$a* = 1/a$

$b* = 1/b$

$c* = 1/c$

$\alpha* = \beta* = \gamma* = \alpha = \beta = \gamma = 90°$

Triclinic more complicated:

Courtesy of George M. Sheldrick. Used with permission.

$$1/V = V* = a*b*c* \left[1 - \cos^2\alpha* - \cos^2\beta* - \cos^2\gamma* + 2\cos\alpha*\cos\beta*\cos\gamma* \right]^{\frac{1}{2}}$$
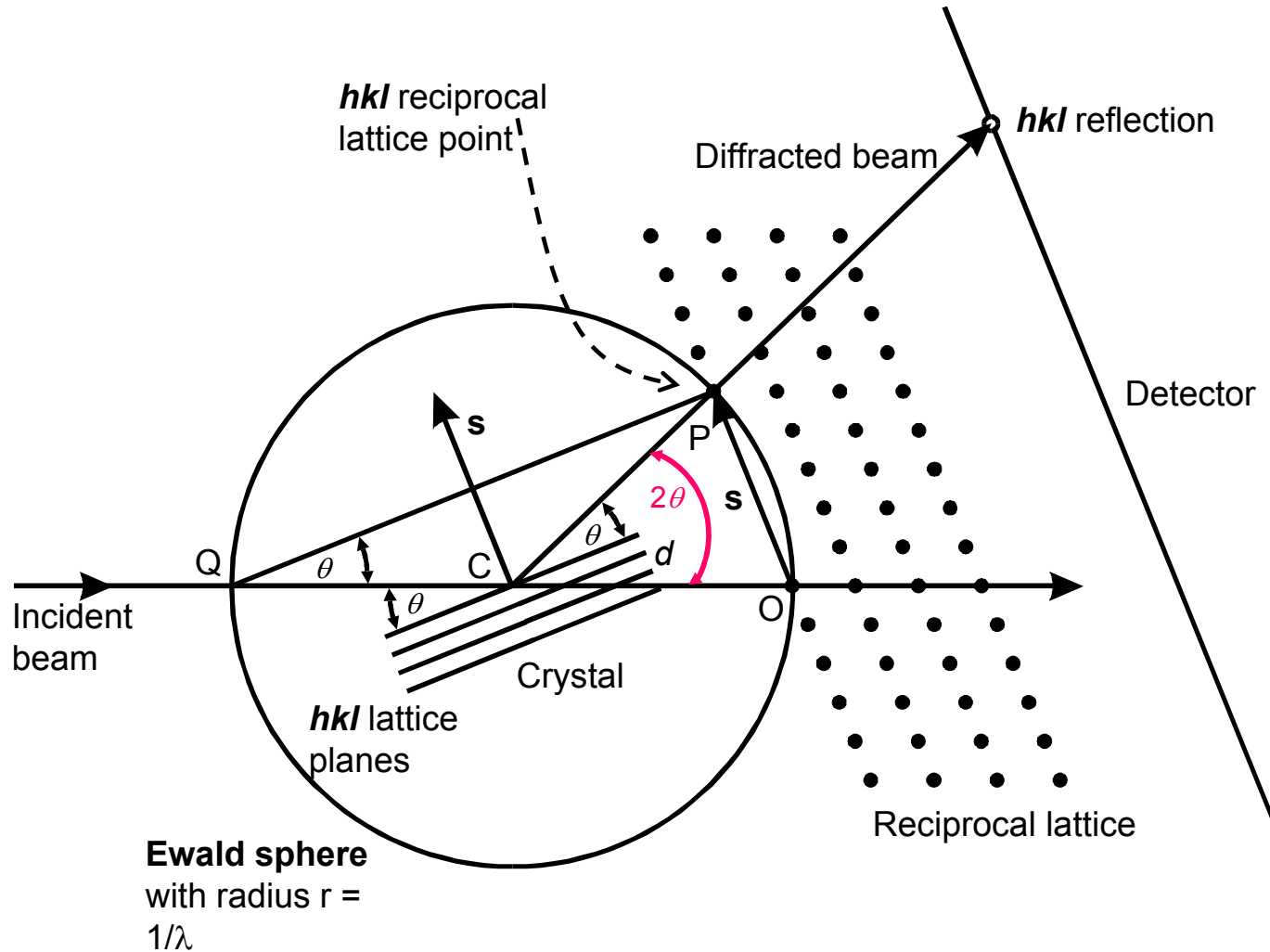
$$a = b*c*\sin\alpha* / V* \quad \text{and} \quad \cos\alpha = (\cos\beta*\cos\gamma* - \cos\alpha*) / (\sin\beta*\sin\gamma*)$$

Same thing for b, c, $\cos\beta$, $\cos\gamma$ and for $a*$, $\cos\alpha*$ *etc.*

The Reciprocal Lattice: Ewald Construction

Intensities of the Reflections

With the help of Braggs law and the Ewald construction, we can calculate the place of a reflection on the detector, provided we know the unit cell dimensions. Indeed, the position of a spot is determined alone by the metric symmetry of the unit cell. The intensity of a spot, however, depends on the contents of the unit cell (and, of course, on exposure time, crystal size, *etc.*).

The intensity of a reflection depends, among other things, on the population of the corresponding set of Bragg planes with atoms. If there are many atoms on a plane, the corresponding reflection is strong, if the plane is empty, the reflection is weak or absent.

Other factors are the thermal motion of the atoms and the atomic radius.

Atomic Form Factors

X-rays are scattered by the electrons of an atom, hence the point atom approximation does not hold too well. Ergo: Bragg planes are not mathematical planes but have a fuzzy thickness, which means there is a path difference occurring *within* each individual Bragg plane.

Displacement of the place of diffraction from the ideal position of δ leads to a path difference of $\delta \cdot 2\pi/d$. This has a weakening effect on the intensity of the corresponding reflection. This effect is a function of the distance d between the Bragg planes: it becomes stronger with smaller distances (*i.e.* at higher resolution).
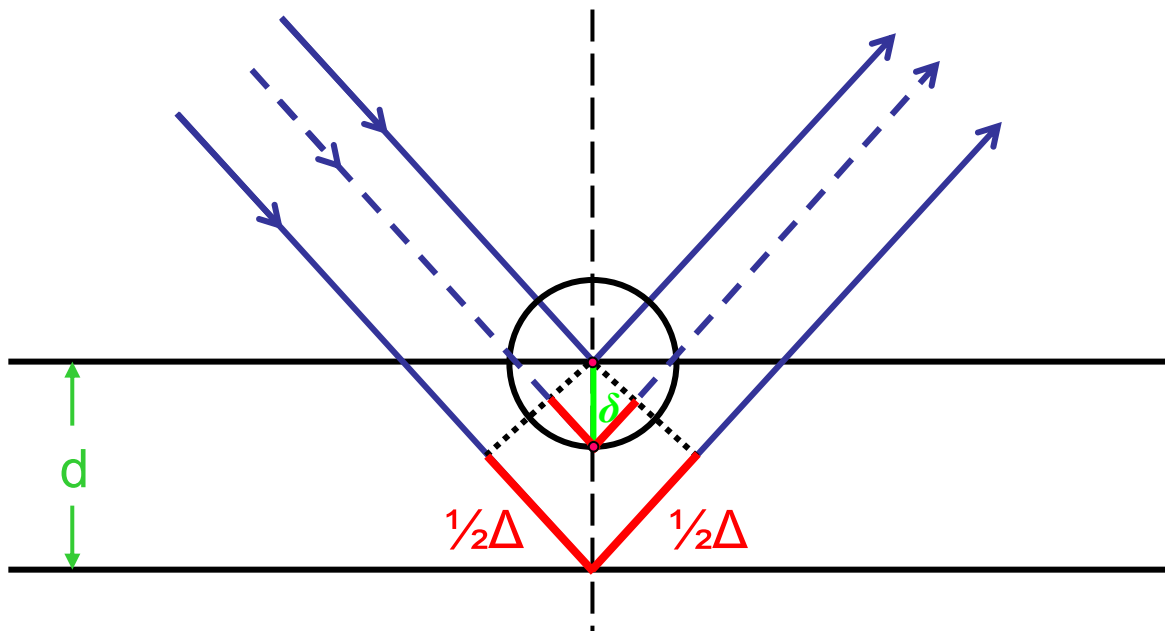
Atomic Form Factors

In a first approximation the atomic scattering factor is dependent on the atom number (number of electrons). With increasing resolution (that is decreasing Bragg plane distance, equivalent to higher scattering angles 2Θ) the scattering factor becomes smaller.

Removed due to copyright restrictions.

Please see:
Massa, Werner. *Crystal Structure Determination. 2nd ed.* Translated into English by R. O. Gould.
New York, NY: Springer, 2004, pp. 34. ISBN: 3540206442.

Fig. 5.2

Atomic Displacement Factors

Atoms not only have a radius, they also move. With the displacement of an atom from its ideal position on the Bragg plane, an additional path difference is added.

The same principle as with the atomic form factors applies (stronger weakening at high scattering angles), but this effect is stronger when the thermal motion is higher.

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Fig. 5.3

$$f' = f \cdot \exp\left[\frac{-2\pi^2 u^2}{d^2}\right]$$

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$$f' = f \cdot \exp\left[\frac{-2\pi^2 u^2}{d^2}\right]$$

f': atomic scattering factor; f: atomic form factor;
u: mean vibration amplitude; d: Bragg plane spacing

$U = u^2$ is the **atomic displacement factor** or **temperature factor**.

Atomic Displacement Factors

$$f' = f \cdot \exp\left[\frac{-2\pi^2 u^2}{d^2}\right]$$

We know: $d = 1/d* = 1/(2\sin\theta/\lambda)$ and: $U = u^2$. Thus:

$$f' = f \cdot \exp\left[-2\pi^2 U d*^2\right]$$

$$f' = f \cdot \exp\left[-8\pi^2 U \frac{\sin^2\theta}{\lambda^2}\right]$$

Substitue: $B = 8\pi^2 U$:

$$f' = f \cdot \exp\left[-B \frac{\sin^2\theta}{\lambda^2}\right]$$

f': atomic scattering factor; f: atomic form factor; u: mean vibration amplitude;
U: temperature factor; d: Bragg plane spacing, $d*$ scattering vector; B: Debye-Weller Factor.

Structure Factors

So far we were talking about single atoms at $0,0,0$ in the unit cell.

Lets assume two identical atoms: atom 1 is at $0,0,0$ and atom 2 is at x_2, y_2, z_2.

Contribution of the blue atoms to the 1 1 0 reflection is same as that of the red atoms, however with a phase shift.
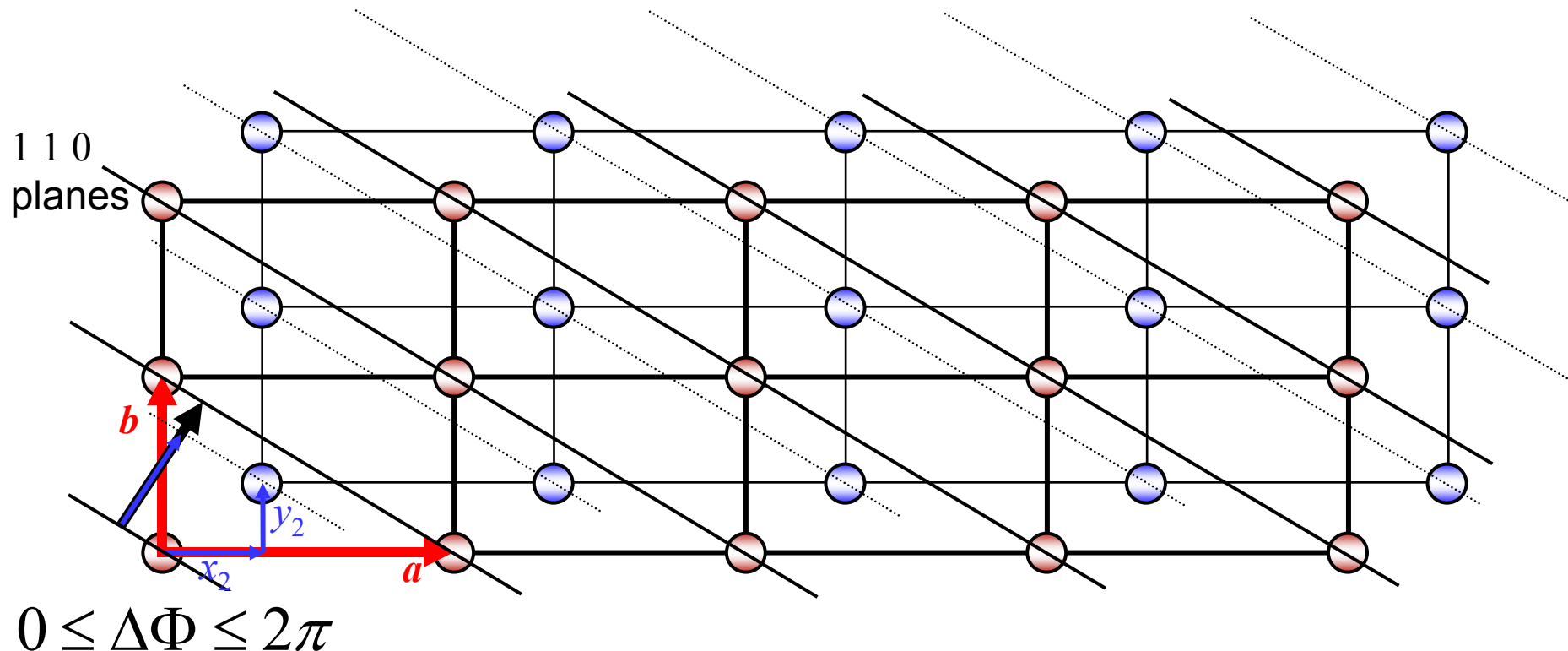
1 1 0 planes

b

y_2

x_2

a

$$0 \leq \Delta\Phi \leq 2\pi$$

Structure Factors

$$\Phi_i = \Delta\Phi_{i(a)} + \Delta\Phi_{i(b)} + \Delta\Phi_{i(c)} = 2\pi\left(hx_i + ky_i + lz_i\right)$$

This makes the structure factor a complex number:

$$F_i = f_i \cdot \exp\left[i\Phi_i\right] = f_i\left(\cos\Phi_i + i\sin\Phi_i\right)$$

Not the same i !

Structure Factors

$$\Phi_i = \Delta\Phi_{i(a)} + \Delta\Phi_{i(b)} + \Delta\Phi_{i(c)} = 2\pi\left(hx_i + ky_i + lz_i\right)$$

This makes the structure factor a complex number:

$$F_i = f_i \cdot \exp\left[i\Phi_i\right] = f_i\left(\cos\Phi_i + i\sin\Phi_i\right)$$

Every atom i in the unit cell contributes to every structure factor $F(hkl)$ (that is reflection) according to its position in the cell and its chemical nature (different values for f_i !):

$$F(hkl) = \sum_i f_i\left[\cos 2\pi\left(hx_i + ky_i + lz_i\right) + i\sin 2\pi\left(hx_i + ky_i + lz_i\right)\right]$$

Structure Factors

$$F(hkl) = \sum_i f_i \left[\cos 2\pi \left(hx_i + ky_i + lz_i \right) + i \sin 2\pi \left(hx_i + ky_i + lz_i \right) \right]$$

Argand plane
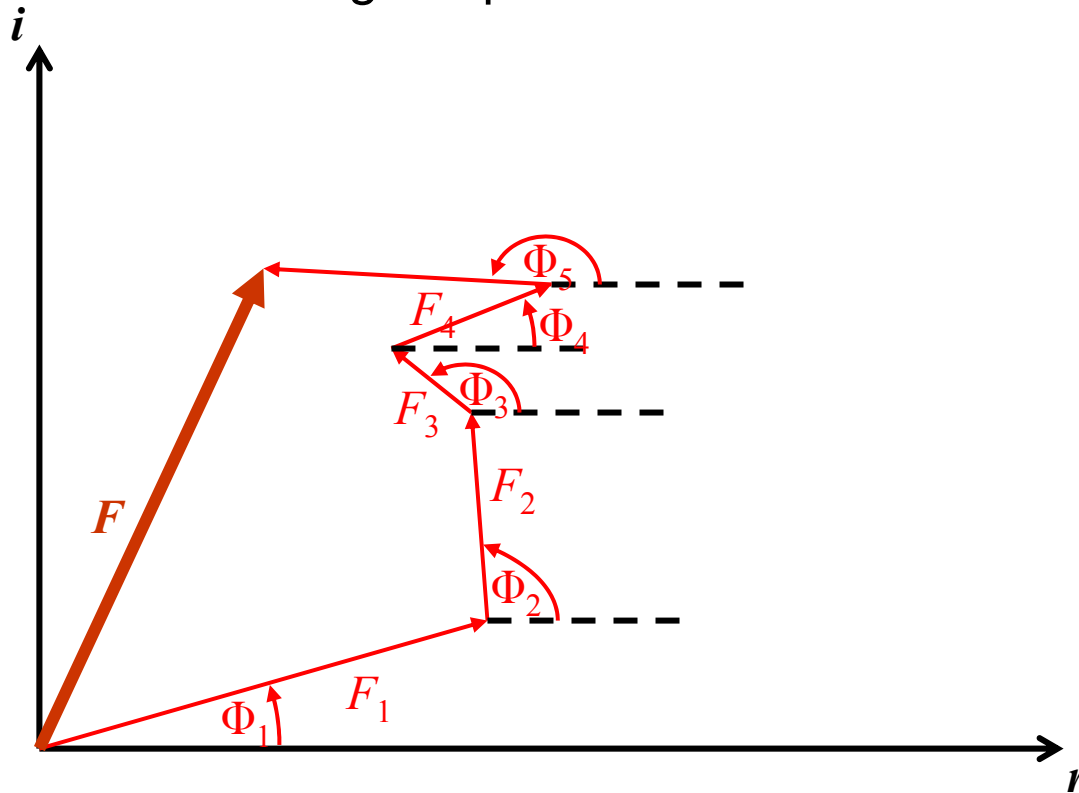
Structure Factors

$$F(hkl) = \sum_i f_i \left[\cos 2\pi \left(hx_i + ky_i + lz_i \right) + i \sin 2\pi \left(hx_i + ky_i + lz_i \right) \right]$$

↓ **FT** ↑

$$\rho_{x,y,z} = \frac{1}{V} \sum_{hkl} F_{hkl} \cdot \exp\left[-i 2\pi \left(hx + ky + lz \right) \right]$$

The electron density at every given place in the unit cell (real space) can be calculated from the equation above.

Note that x_i, y_i, z_i in the structure factor equation refer to atomic coordinates, while x, y, z in the electron density equation refer to arbitrary places anywhere in the unit cell. Of course, the electron density at the place of an atom is supposed to be much higher than the electron density at a place where there is "nothing".

Electron Density

$$\rho_{x,y,z} = \frac{1}{V} \sum_{hkl} F_{hkl} \cdot \exp[-i2\pi(hx + ky + lz)]$$

1.7 Å
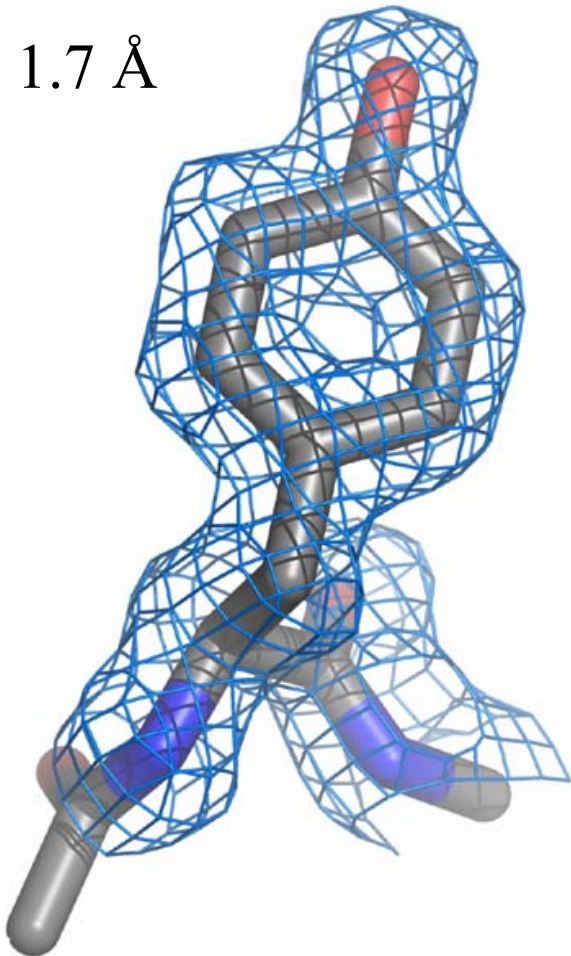
It is sufficient to calculate the electron density at a number of grid points within the unit cell and extrapolate between the points.

0.9 Å

N(3) C(3) N(2) N(4) C(4)

C(1) C(2) C(5)

N(1) O(1) S

Courtesy of George M. Sheldrick. Used with permission.
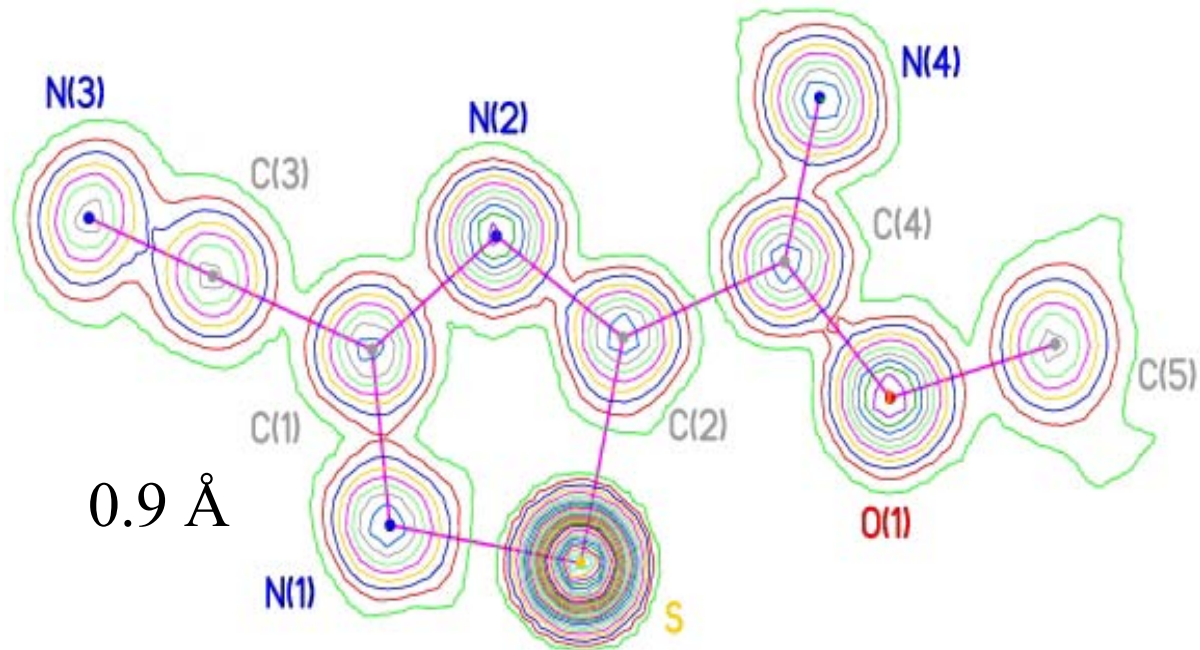
Resolution

The maximum resolution d can be calculated from the Bragg equation:

$$d = \lambda / 2 \sin(\theta_{max})$$

This d corresponds approximately to the distance between two atoms (or more generally points in space), which can still be resolved from one another in an electron density map calculated from data at that particular resolution.

For centrosymmetric structures one would expect ca. $80/d^3$ independent reflections per non-hydrogen atom. For non-centrosymmetric structures only half that number (assuming Friedel's law is true). That means, for a protein structure at 1.5 Å resolution we have ca. 12 reflections per atom. At 2.5 Å only ca. 2.6 reflections per atom. There are many protein structures at 3 Å (1.5 spots per atom) and worse…

~ d
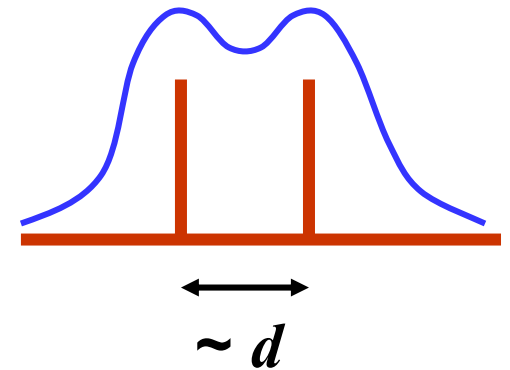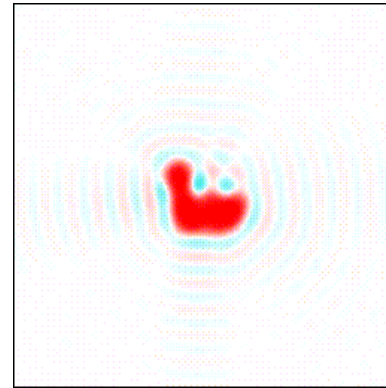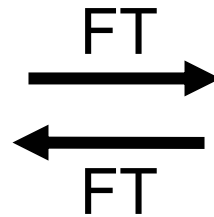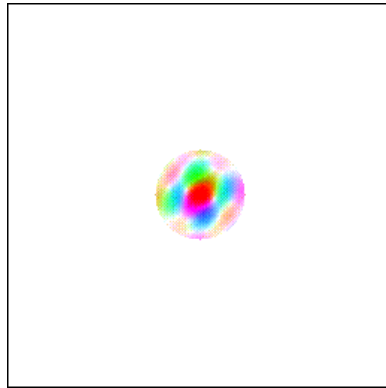
Courtesy of George M. Sheldrick.
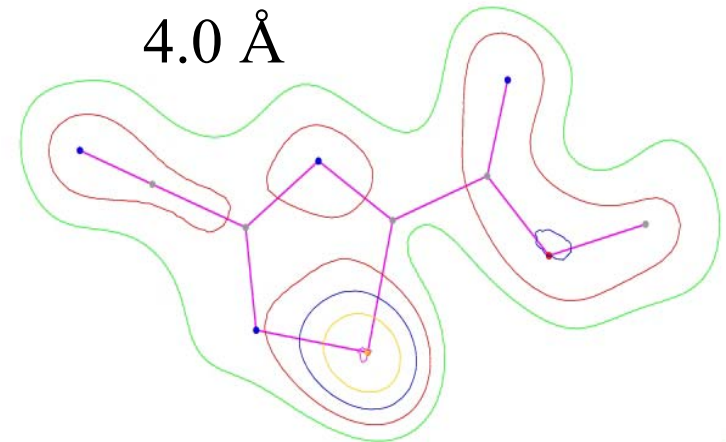Used with permission.

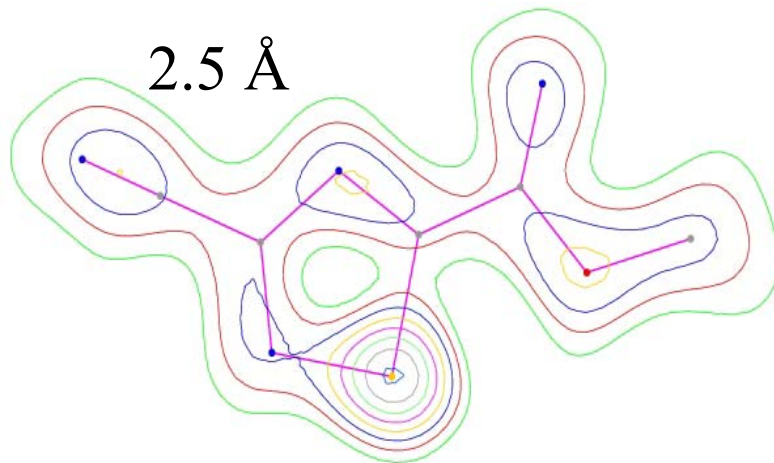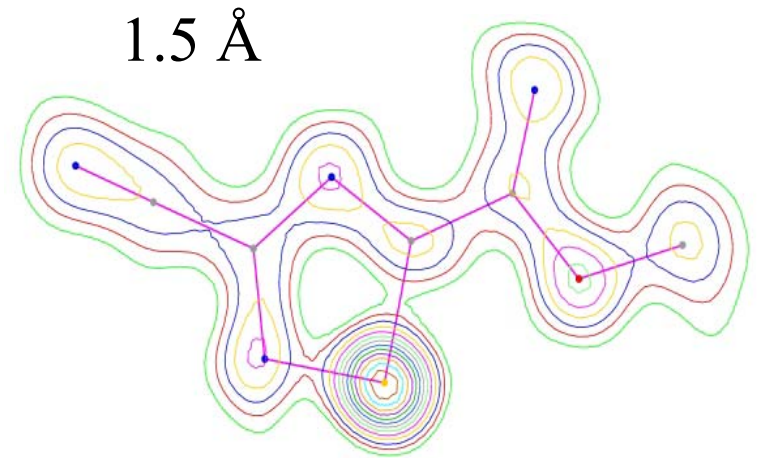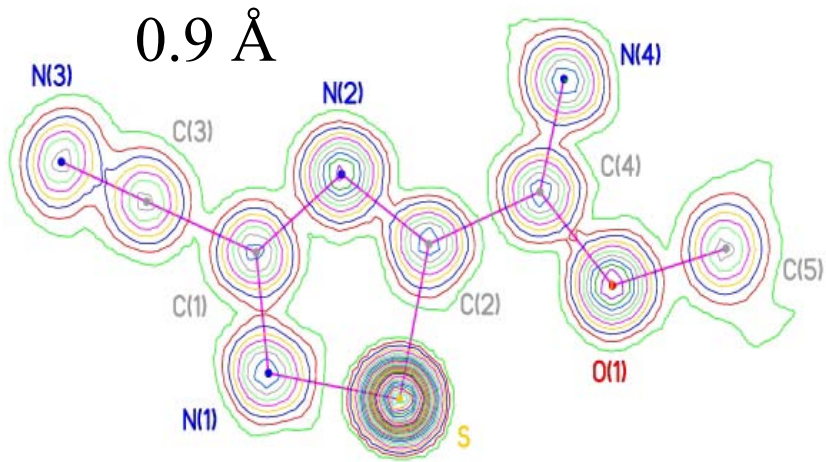# Resolution

FT of a duck

FT →

← FT
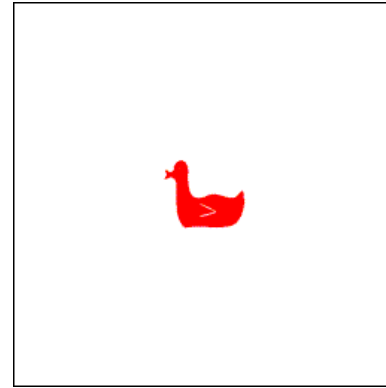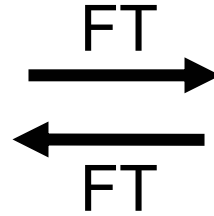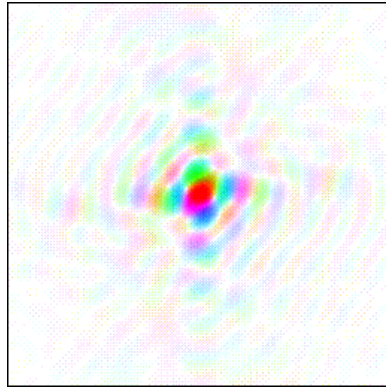
A duck

FT of a duck with high resolution data removed

FT →

← FT

A low resolution duck

Resolution

Electron density contour plots of the same molecule at different resolutions.

Calculating Electron Density

$$\rho_{x,y,z} = \frac{1}{V} \sum_{hkl} F_{hkl} \cdot \exp\left[-i2\pi\left(hx + ky + lz\right)\right]$$

To make this equation work we need the volume of the unit cell (easy), a dataset with the intensities for h, k and l (also easy) and the phase of every structure factor (not quite so easy).

We can measure the intensities and determine the unit cell from the locations of the reflections, but it is very difficult to actually measure the relative phase of the reflections. This is known as the "crystallographic phase problem".

5.069 Crystal Structure Analysis
Spring 2008