Before Beginning

- Must copy over the p4p file
- Enter `../xl.p4p .`
- Enter `../xl.hkl  .`
- Do `ls` to see the files are there
- Since the .p4p file has been created it does not matter whether the source was the Nonius ccd, the Rigaku image plate or some other source. However, when creating the .p4p file the source is required.

The p4p File

- This is the input to XPREP (note program names are always entered in all lower case letters).
- It contains information about the crystal and data collection
- It is generated by locally written programs.
- XPREP will help you analyze the data, determine the space group, etc. and produce the .ins file which is the input to most programs
- To print the file on the screen `cat xl.p4p`

Running XPREP

Start solve gui by solve (nonius) or rsolve (rigaku)

- Select the xprep button.
- Basically use defaults in the program studying the output.
- If when you go to save there is no default file name use “xll”
- If XPREP is run from the command line files will NOT be set up correctly.
- When answering questions the value in [] is what is entered if return is entered

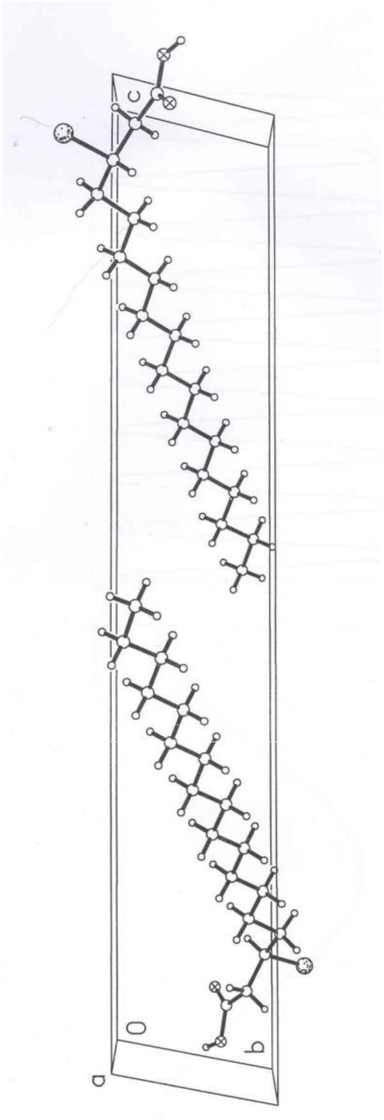
XPREP IO

- The input to XPREP is the .hkl file and the .p4p file
- At Purdue each structure is stored in its own directory and the files all begin with xl
- So xl.p4p and xl.hkl
- The output is xl.ins plus several output programs
- The GUI will copy this original file to xl.org which is used by the solution programs.
- If you do ls you should now see xl.ins and xl.org

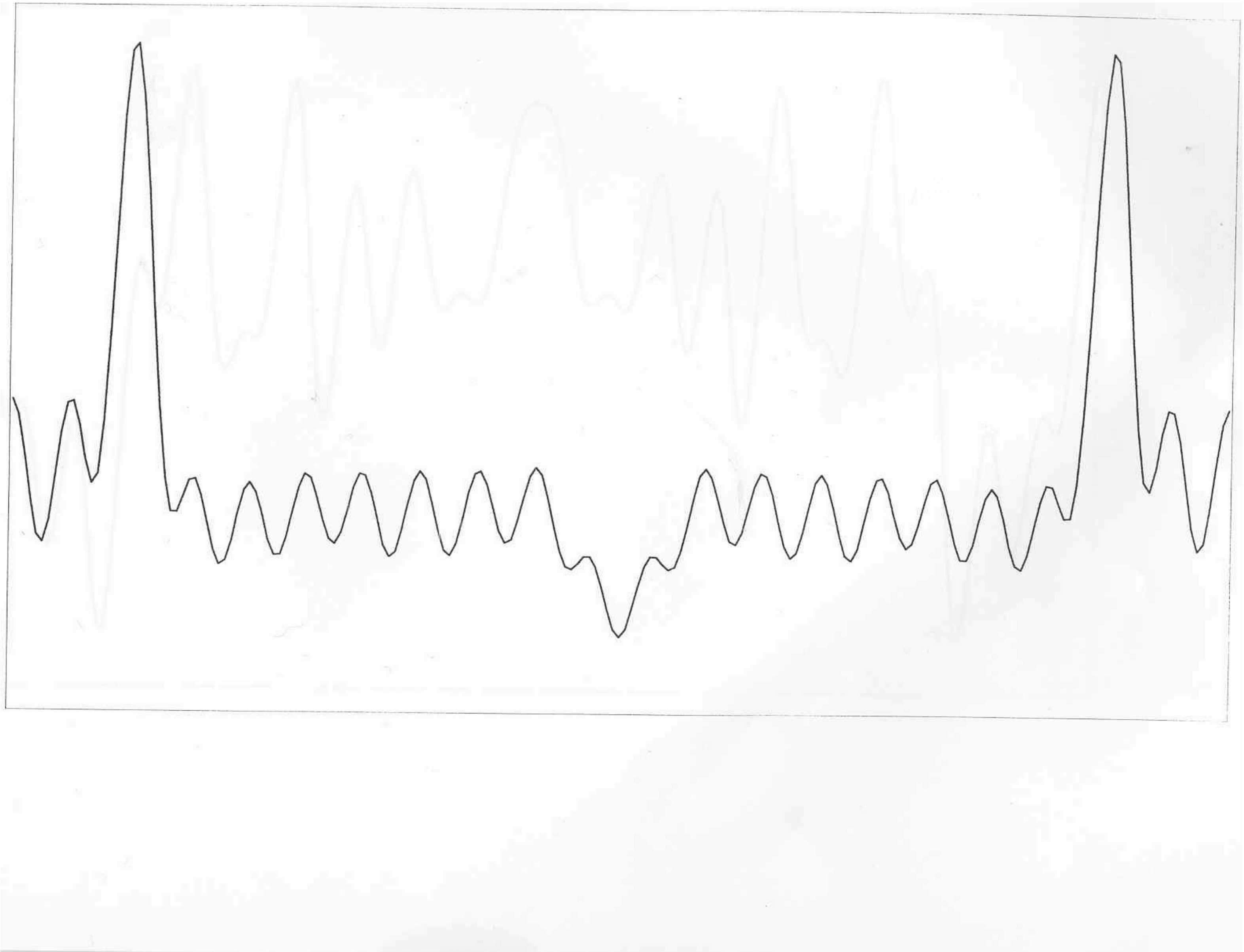
Electron Density in Crystals

- Since the crystal is made up of repeating unit cells, the electron density in the cell must be periodic!
- This is called the Charge Density Wave.
- In 1-dimension, the length of the charge density wave is the cell length.

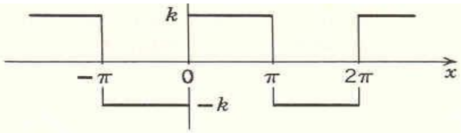
One-Dimensional Crystal



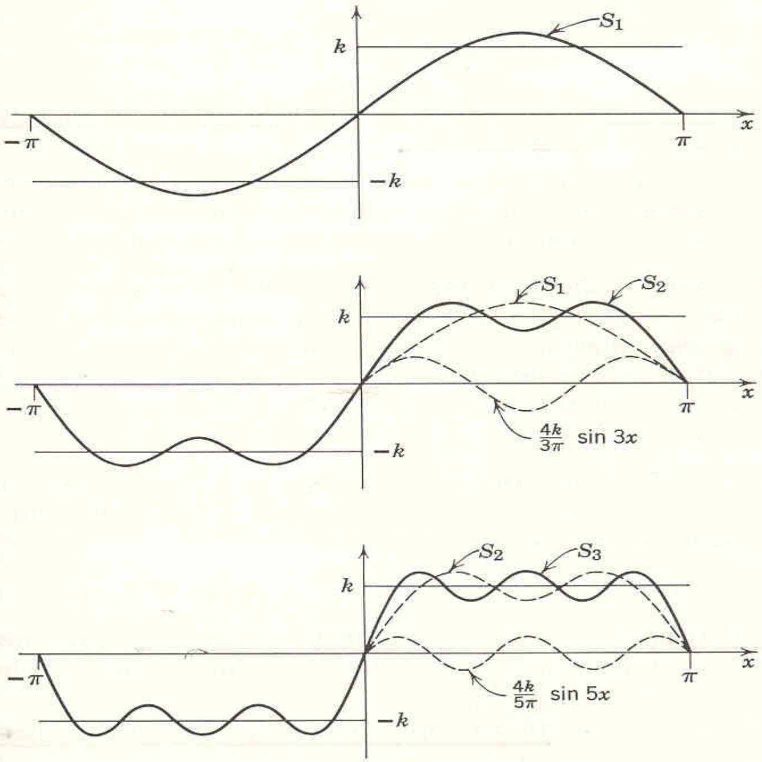
Charge Density Wave



Fourier Series



(*a*) The given function $f(x)$.



(*b*) The first three partial sums of the corresponding Fourier series.

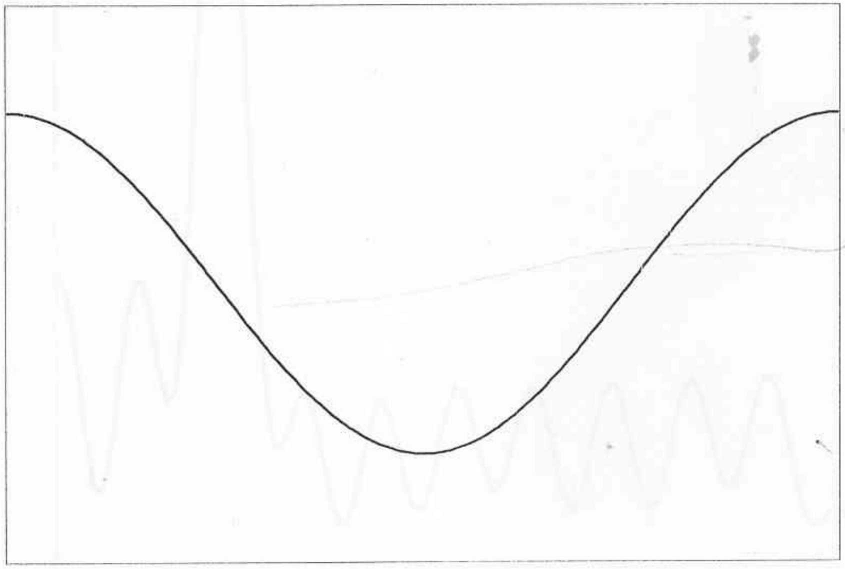
Fig. 217. Example 1.

Fourier Series on the web

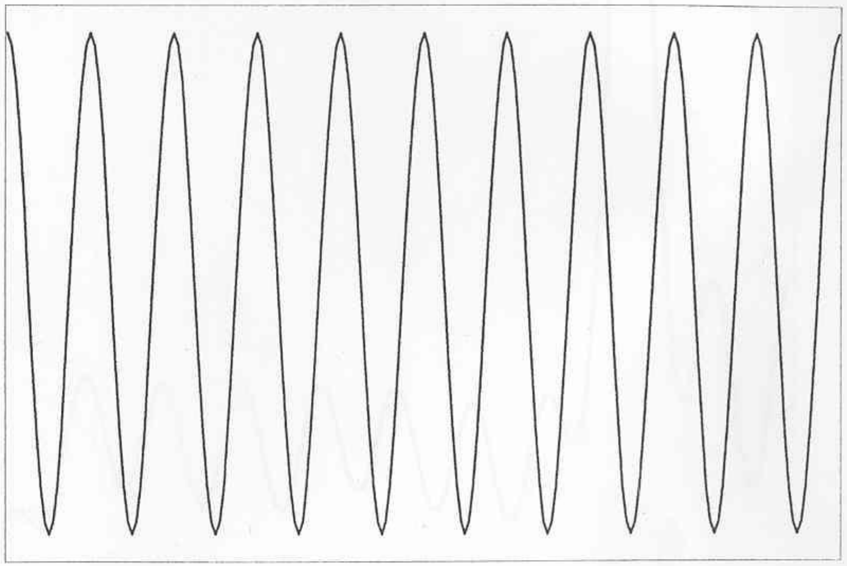
http://www.youtube.com/watch?v=y6crWlxKB_E

http://www.falstad.com/fourier/

Wave Components



One wavelength/cell   h=1



ten wavelengths/cell   h=10

Diffraction in 1-D

$$\rho(x) = \frac{1}{a}\left\{F(0) + 2\sum_{h} F(h)\cos(2\pi hx)\right\}$$

ρ is the electron density at any point x

F(h) is called the structure factor and is indexed by the value h

F is related to the square root of the intensity of the diffracted beam.

F_o is the observed structure factor F_c calculated

Note the amplitude of the diffraction is the Fourier coefficient!

A Comparison

- The Charge Density Wave (CDW) can be decomposed into Fourier components which when summed give the CDW.
- The CDW can also be calculated from a Fourier sum of the diffracted waves.
- The structure factors F represent the Fourier components of the CDW
- The amplitude F is the Fourier coeffcient!

Fourier Domains

- In the crystal the electron density makes up real space.
- Real space has the symmetry of the space group
- The Fourier Transform generates reciprocal space
- Reciprocal Space is the diffraction space
- Reciprocal space has the same symmetry as real space.

The phase problem

- **In order to calculate an electron density map, we need both the intensities (|*F* | is proportional to the square root of *I*) and the phases ϕ of the X-ray reflections *hkl*.**

- **The information content of the phases is significantly greater than that of the intensities.**

- **It is unfortunately not normally possible to determine the phases experimentally.**

This is known as the *crystallographic phase problem* and would appear to be impossible to solve!

In spite of this, small molecule structure are solved routinely these days, usually without serious problems, with the help of the *Patterson function* and the *heavy atom method*, or (more commonly) by so-called *direct methods* based on probability relations involving phases.

The structure factor *F* and the electron density ρ

$I_{hk\ell}$ ***is proportional to*** $|F_{hk\ell}|^2$

$$F_{hk\ell} = {}_V\!\int \rho_{xyz} \exp[+2\pi i(hx+ky+\ell z)]\, dV$$

$$\rho_{xyz} = (1/V) \sum_{hk\ell} F_{hk\ell} \exp[-2\pi i(hx+ky+\ell z)]$$

$F_{hk\ell}$ and ρ_{xyz} are related to each other by means of these *Fourier transformations*. The electron density ρ is real and positive, but the structure factor F is a complex number: to calculate the electron density from the structure factors, we also need the *phase* (ϕ) of *F*.

Under normal conditions we can only measure the diffracted intensities *I* and not the phase ϕ of a reflection *h*,*k*,ℓ, so it appears that we are faced with an insoluble problem, the *crystallographic phase problem.*

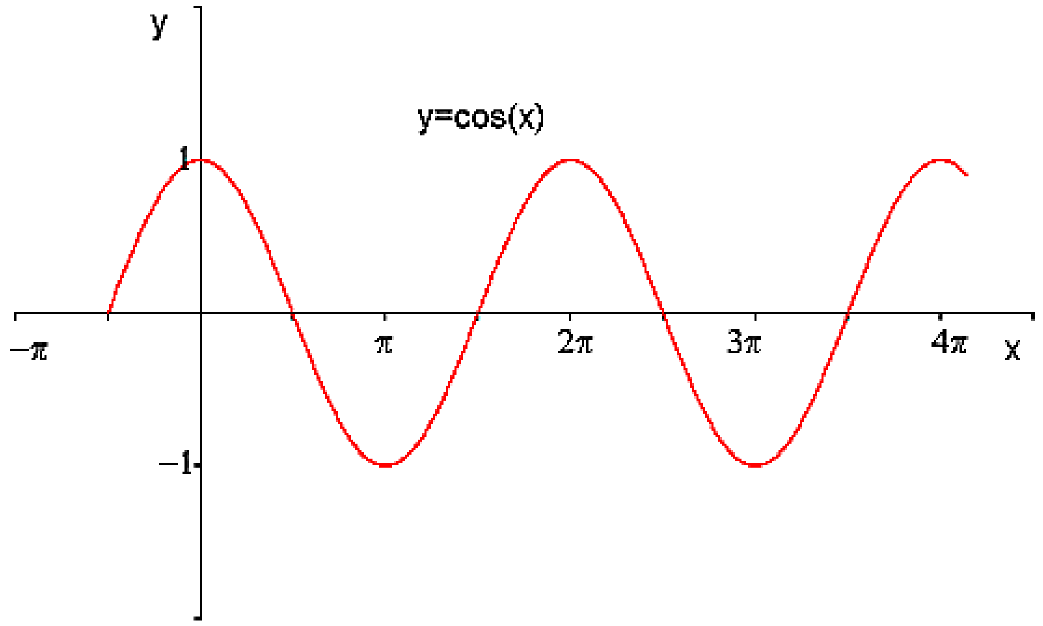
Centric Crystals

- In order for the origin to be an inversion center can only use cosine waves
- If the wave is phase shifted then it will not be symmetric about the origin.
- The one exception is a shift of 180° which simply inverts the wave. This means the Fourier coefficient is either + or - F.
- For 5000 reflections the number of ± combinations is $2^{(5000-1)}$ or 1.412467032e+1505
- This is a problem!!

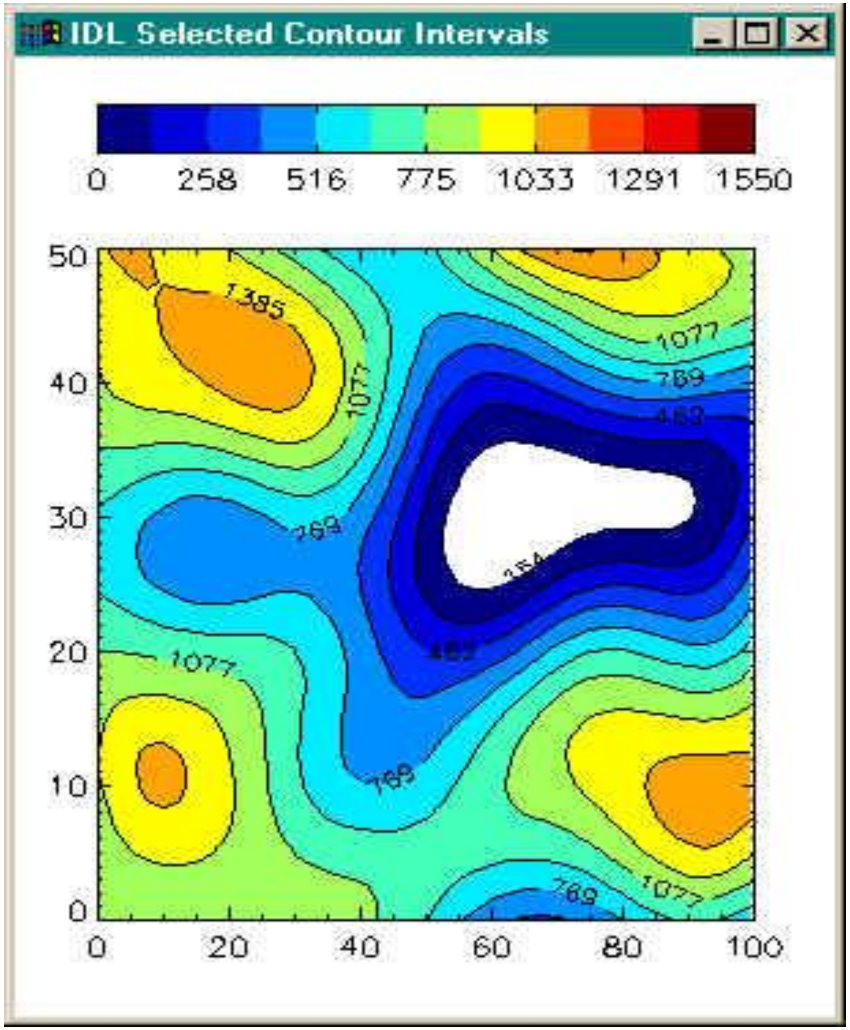
Why are there no signs?

- We measured the intensity of the Fourier component I which is proportional to F^2
- What we need is F
- The problem is that whether F is positive or negative when squared it gives the same value of F^2
- There is no way to get the sign of F from our data.

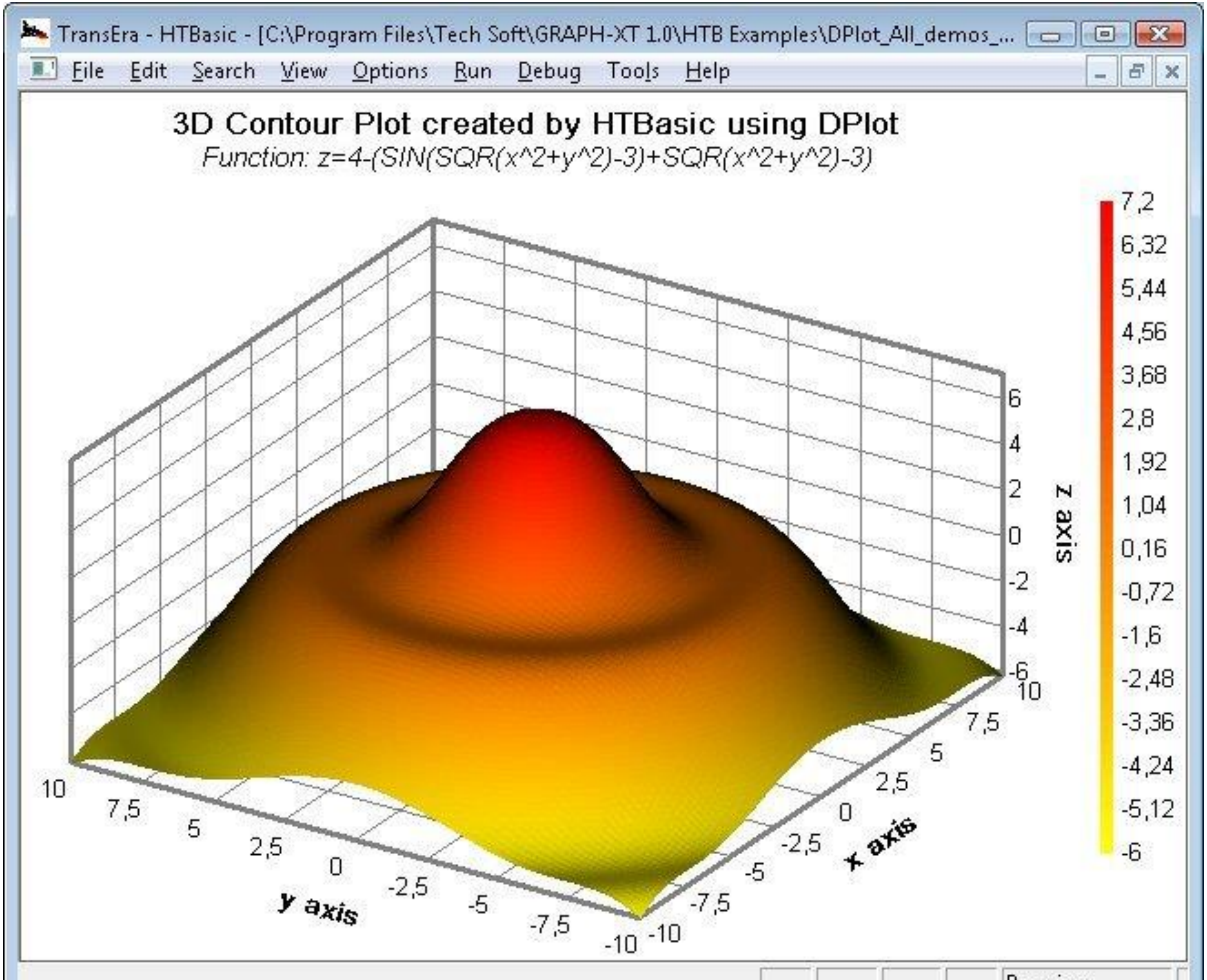
Symmetry



2-d Contour Plot



3-d Contour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File
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3D Contour Plot created by HTBasic using DPlot
Function: z=4-(SIN(SQR(x^2+y^2)-3)+SQR(x^2+y^2)-3)
6
4
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z axis
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3,68
2,8
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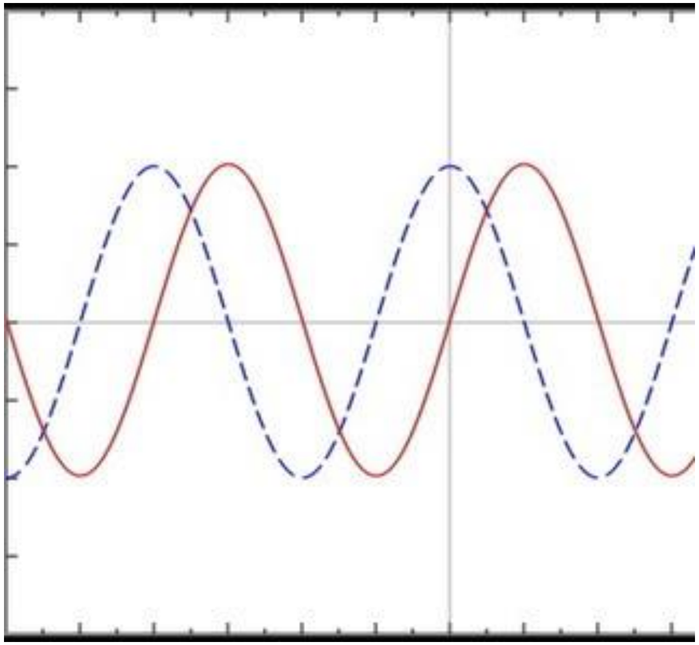
-3,36
-4,24
-5,12
-6

Phase Shift



What are phases (1)?

The electron density is obtained by Fourier transformation of the structure factors F_{hkl}. F_{hkl} are complex numbers with amplitudes and phases.

$$\rho_{xyz} = (1/V) \sum_{hkl} F_{hkl} \exp[-2\pi i(hx+ky+lz)]$$

The reciprocal transformation to calculate F_{hkl} from ρ_{xyz}:

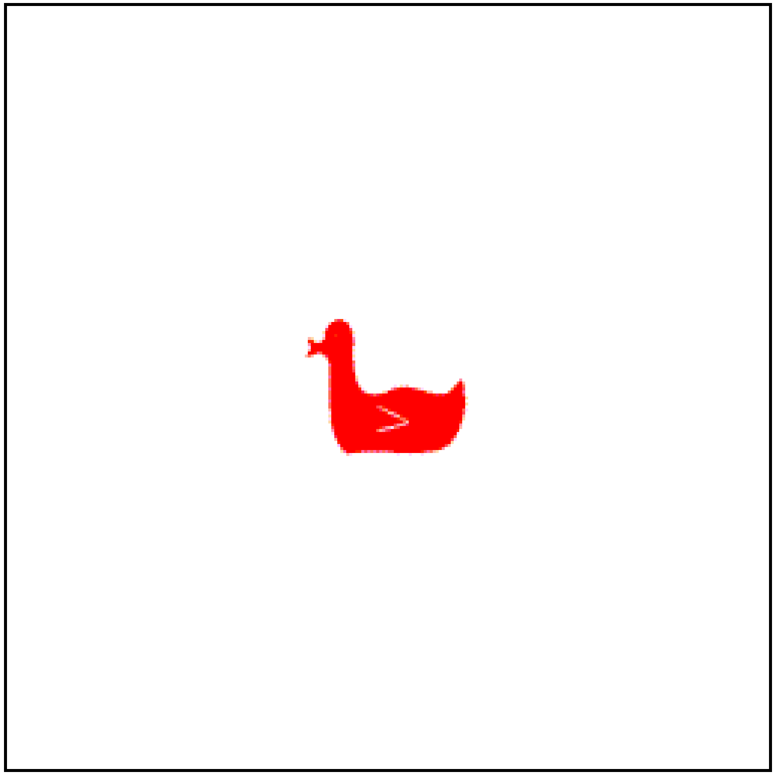
$$F_{hkl} = \int_V \rho_{xyz} \exp[+2\pi i(hx+ky+lz)]\, dV$$

can also be represented as a sum over the *n* atoms in one unit-cell:

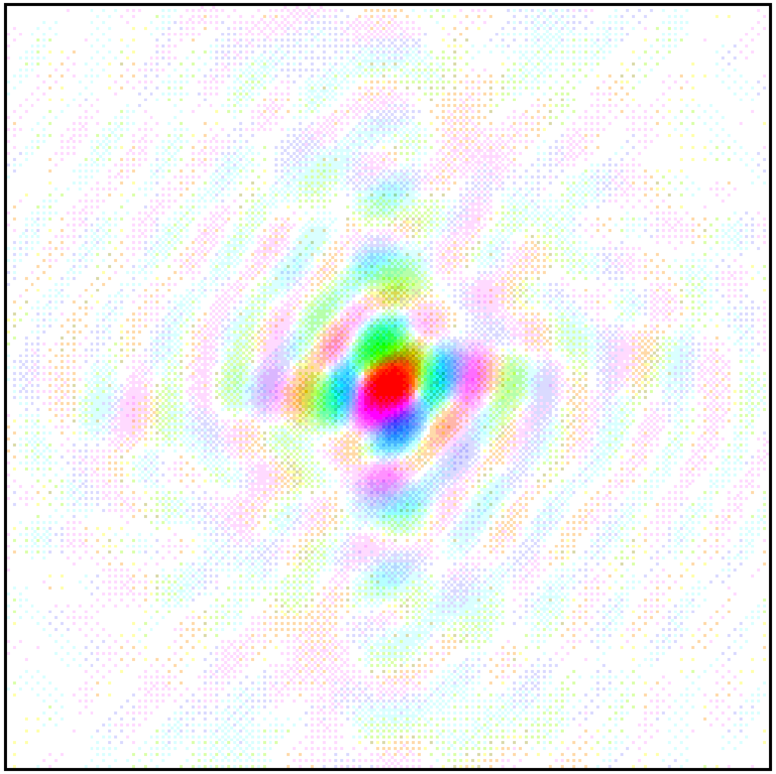
$$F_{hkl} = \sum_{j=1}^{n} f_j \exp[+2\pi i(hx_j+ky_j+lz_j)] \quad \text{or}$$

$$F_{hkl} = \sum_{j=1}^{n} f_j \{ \cos[2\pi(hx_j+ky_j+lz_j)]+i\cdot\sin[2\pi(hx_j+ky_j+lz_j)] \}$$

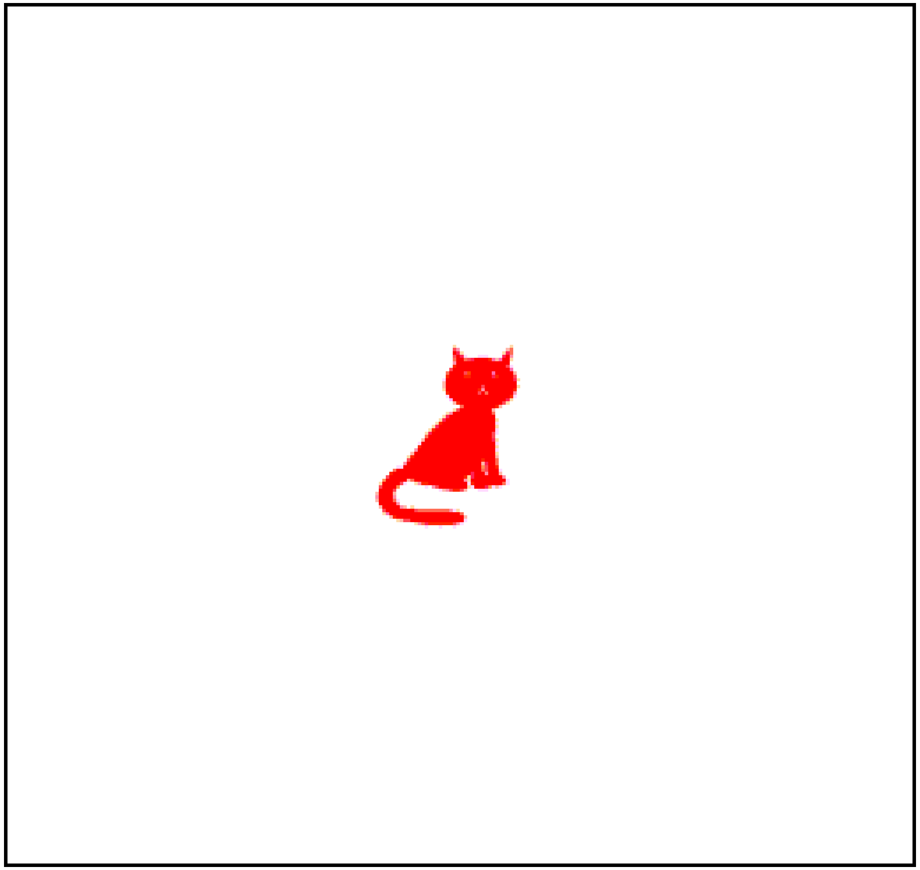
where f_j is the scattering factor of atom *j* (including thermal motion). If the structure is centrosymmetric, the sine terms for x,y,z and $-x,-y,-z$ cancel, with the result that the phase of F_{hkl} must be 0º or 180º. In the special case of one atom on the origin, all phases must be 0º.

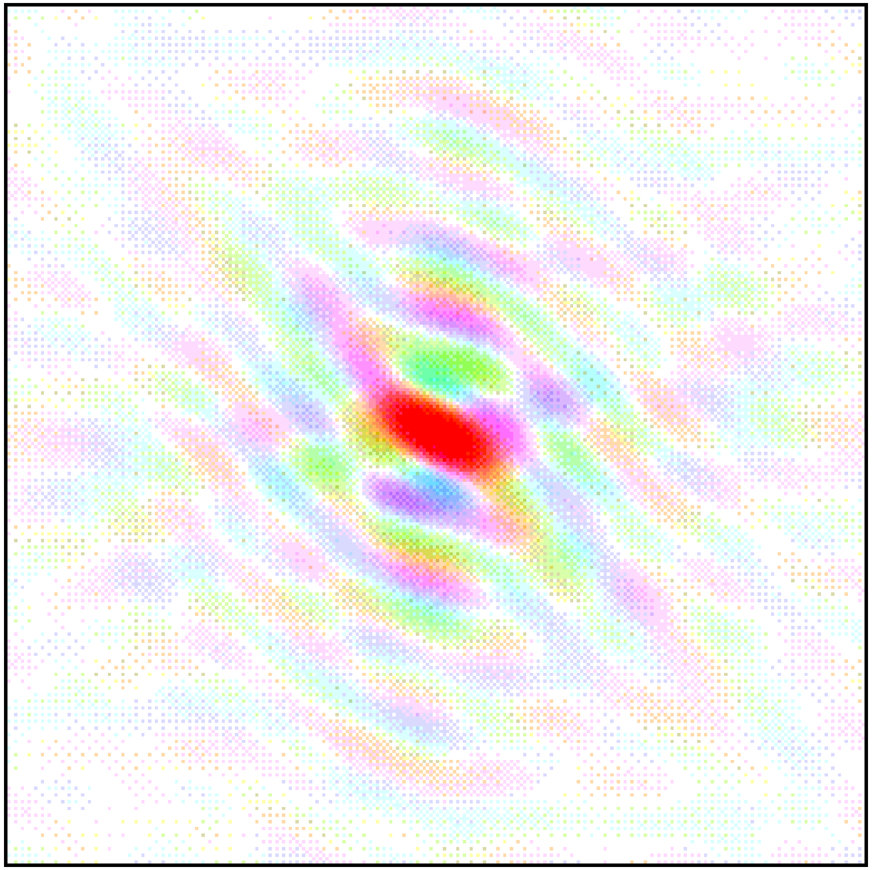


Duck

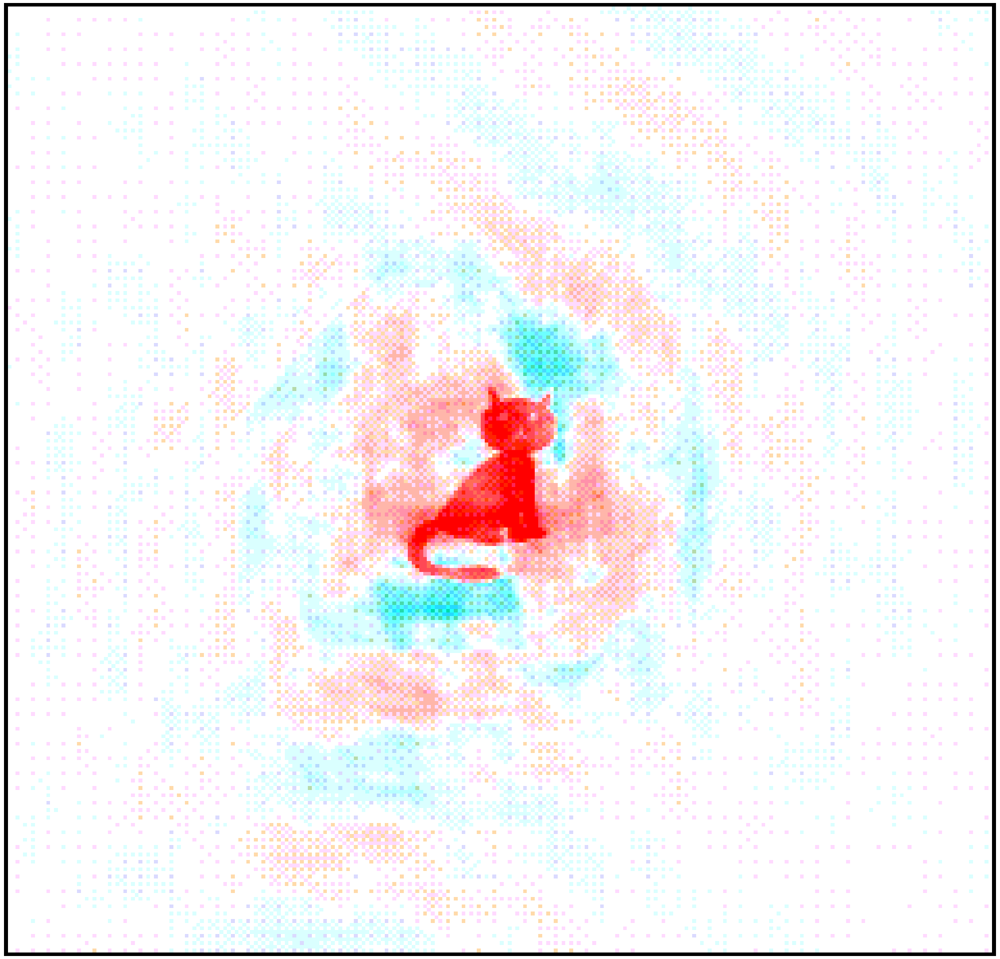


Its Fourier

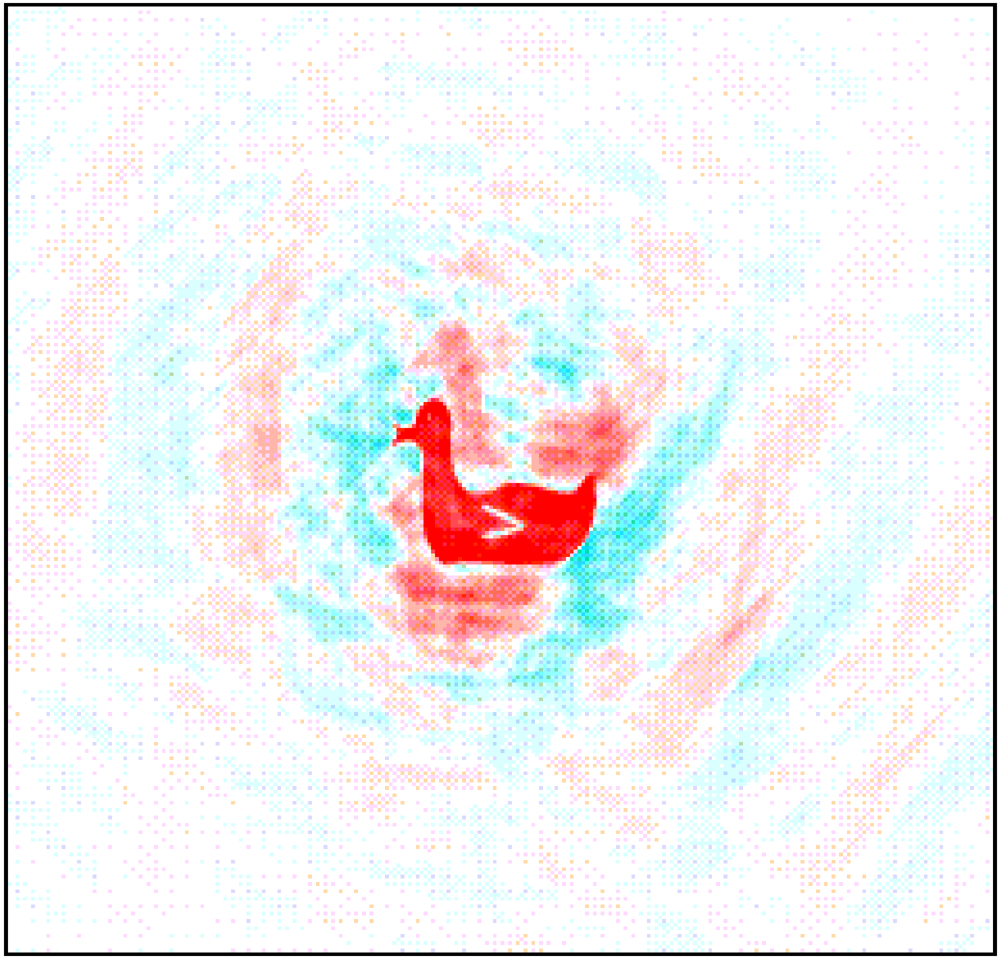




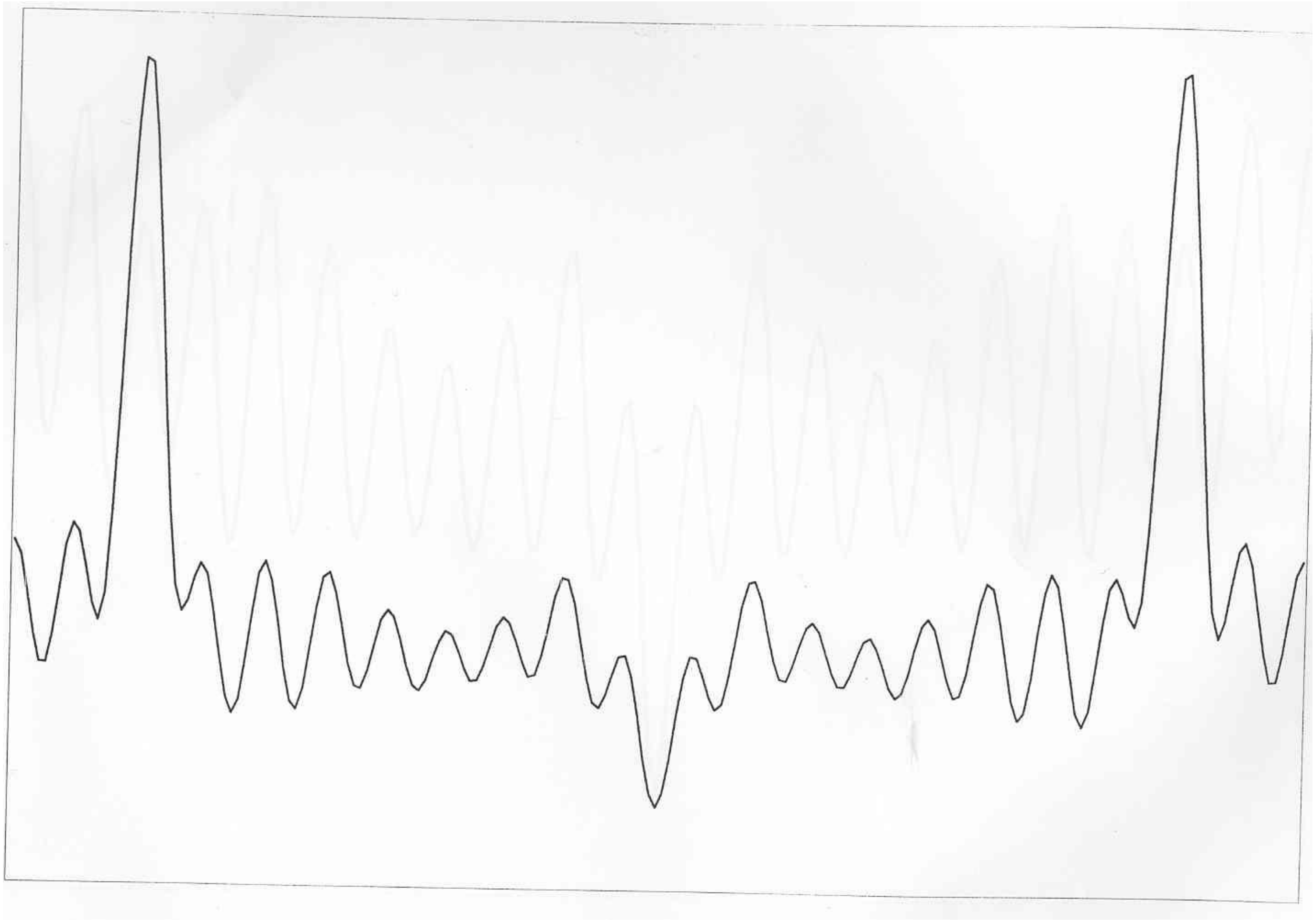
Duck Intensity Cat Phases



Cat Intensity Duck Phases



Correct Phasing



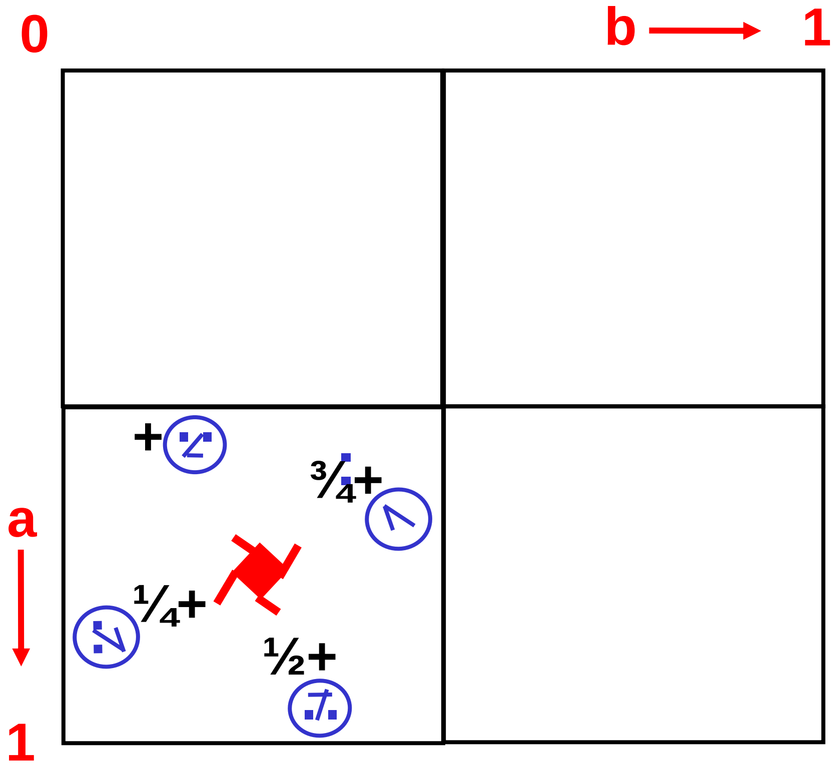
Incorrect Phasing

How to know correct phasing

- The electron density is always greater or equal to zero
- The electron density is highly localized at the atom positions.
- Since the distance between maxima represents bond distances, the peaks should be distinct.

Exercises

- Find the 11 enantiomorphic pairs of space groups (hint: all are of course chiral and possess 3_N, 4_N or 6_N axes).
- The incomplete picture should show the space group $I4_1$. Why is there no space group $I4_3$?



3. Assign the space group of a tetragonal crystal with the systematic absences: $hk\ell$, $h+k+\ell = 2\cancel{n}$; $hk0$, $h = 2\cancel{n}$ or $k = 2\cancel{n}$; $hh\ell$, $2h+\ell = 4\cancel{n}$