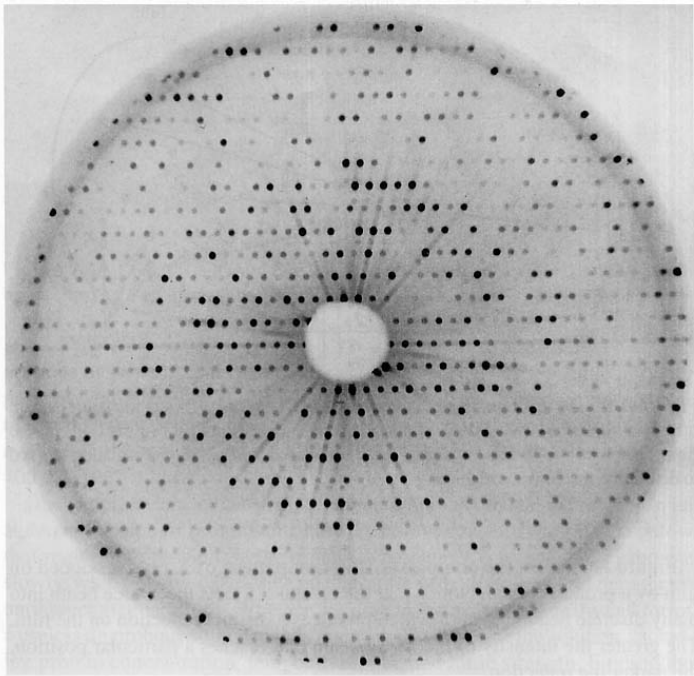


# X-ray Crystallography



**Figure 2.6** Diffraction pattern from a crystal of the MoFe (molybdenum–iron) protein of the enzyme nitrogenase from *Clostridium pasteurianum*. Notice that the re-

- Rhodes, Chapters 2, 5
  - Chapters 3 and 4 include some general considerations
- MacPherson (on reserve in library), Chapters 1, 3, and 4

# What does anything look like?

- We see objects by the light which is scattered from their surfaces
- We have optical devices (lenses) which "reconstruct" an image of the object...
- ...by gathering together all light rays scattered from a give point at the focal plane to form an image
- ...by gathering together all light rays scattered at a particular angle together to form a diffraction pattern

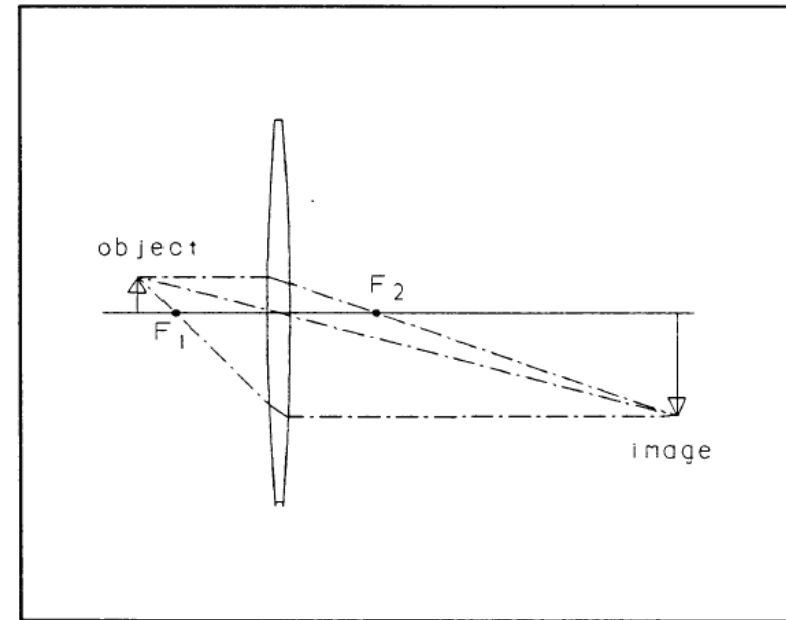
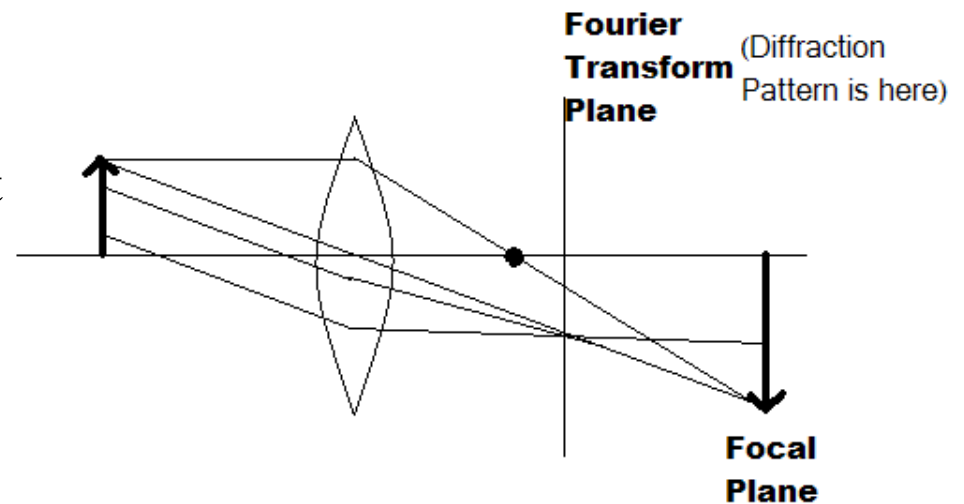


Figure 18. Imaging by a convex lens.

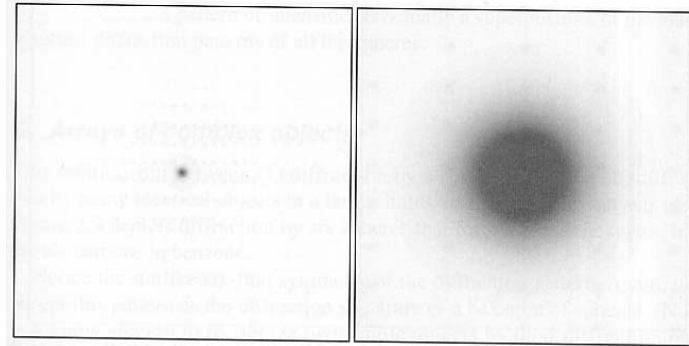


# Looking at molecules

- Looking requires light with wavelengths shorter than object of interest
  - Visible light ( $\lambda$  ca 1 mm) not short enough
  - Light with wavelength good for atoms (ca 1 Å) is an X-ray
- X-rays only interact weakly with matter
  - Use them to see through things
  - No lens (so complex math required instead)
  - Poor illumination of single molecules (so we look at crystals)
- Short wavelength = high energy
  - Destroys molecules as they are observed (complicated technology)

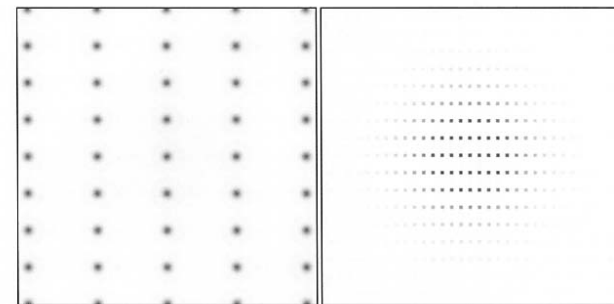
# Diffraction from simple objects

- Sphere
  - Scatters light over a sphere
  - Scattered light over different size than sphere
  - Bigger the object sphere, the smaller the scattered sphere
  - Scattered light image has diffuse edges



**Figure 2.7** Sphere (cross-section, on left) and its diffraction pattern (right). Images for Figures 2.7–2.10 were generously provided by Dr. Kevin Cowtan.

- Lattice of spheres
  - Scattering from lattice yields a lattice of scattered light!?
  - Reciprocal lattice
  - "Convolution" of lattice scatter and sphere scatter



**Figure 2.8** Lattice of spheres (left) and its diffraction pattern (right). If you look at the pattern and blur your eyes, you will see the diffraction pattern of a sphere. The pattern is that of the average sphere in the real lattice, but it is sampled at the reciprocal lattice points.

# Diffraction from more complex objects

- Lattice
- Molecule
  - Information on constituent atoms
  - Info on arrangement in space
- Lattice of molecules
  - Convolution of both atomic and molecular patterns

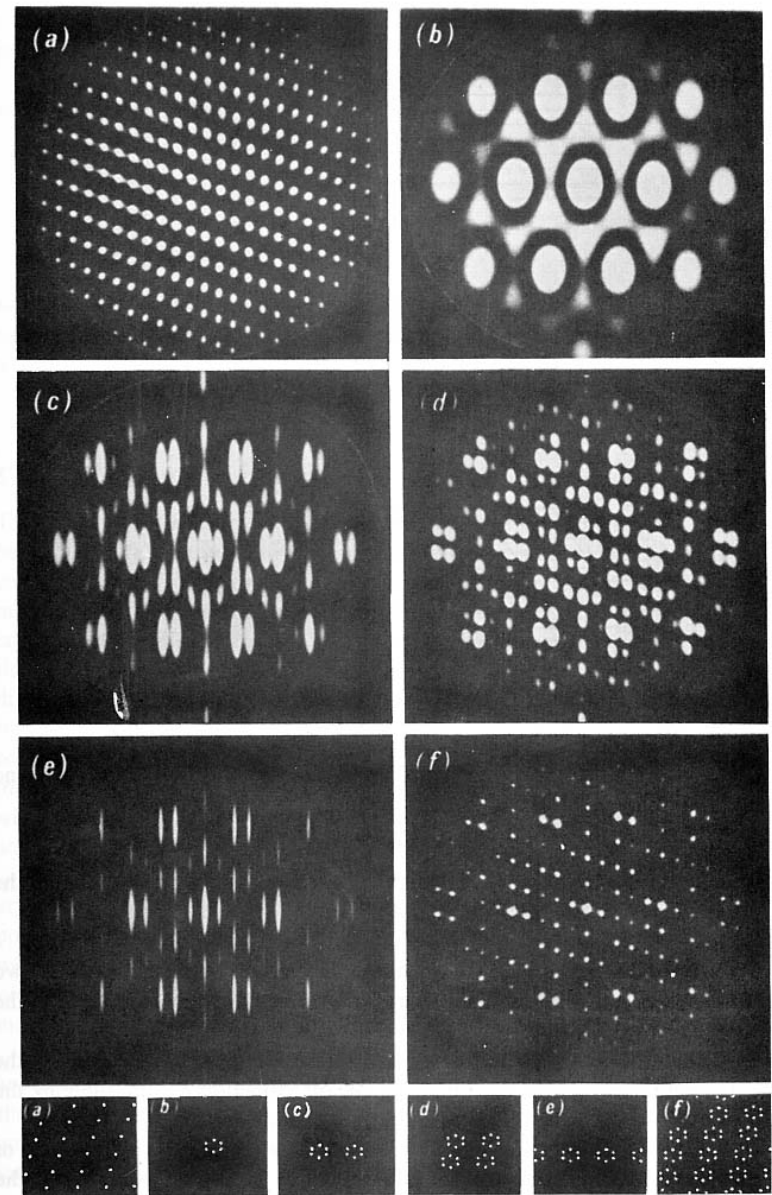


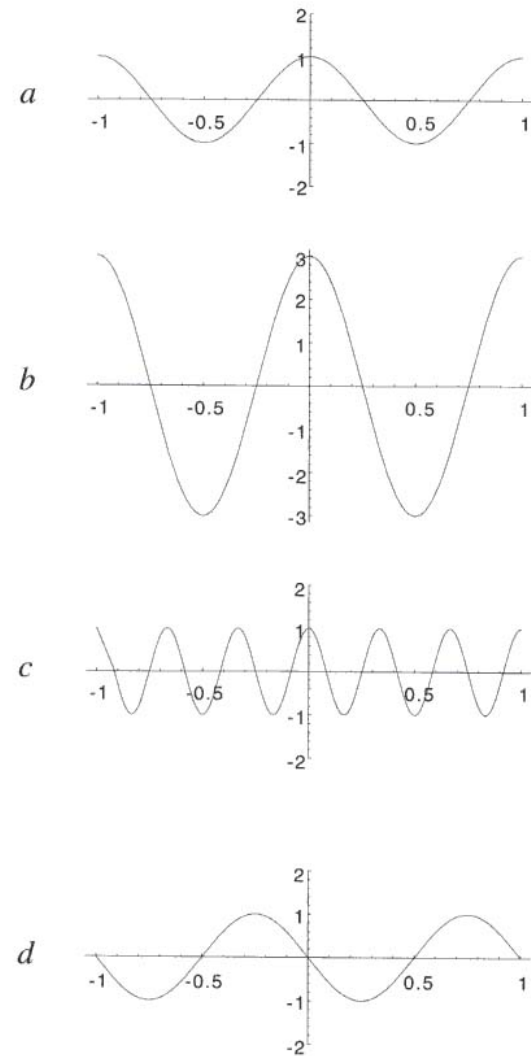
FIG. 5.5 Optical diffraction patterns illustrating scattering by (a) a lattice, (b) a single molecule, (c) two molecules, (d) four molecules, (e) a row of six molecules and (f) a small crystal. (From Taylor and Lipson, 1964.)

# Questions

- What determines where you find scattered light?
- What is the relationship between the shape of the object and the "shape" of the diffraction pattern?

# Wave Basics

- $f(x) = F \cos [2\pi (hx + \alpha)]$ 
  - $F$  = amplitude
  - $h = 1/\lambda$  (inverse wavelength)
  - $\alpha$  = phase
- Compact version of same
  - Euler formula
    - $\exp(ix) = \cos x + i \sin x$
    - So  $F \cos [2\pi (hx + \alpha)]$  is the  $\text{Re}\{A \exp(i(2\pi(hx + \alpha)))\}$
  - Where  $\text{Re}\{\dots\}$  often dropped



**Figure 2.13** Graphs of four simple wave equations  $f(x) = F \cos 2\pi(hx + \alpha)$ . (a)  $F = 1$ ,  $h = 1$ ,  $\alpha = 0$ :  $f(x) = \cos 2\pi(x)$ . (b)  $F = 3$ ,  $h = 1$ ,  $\alpha = 0$ :  $f(x) = 3 \cos 2\pi(x)$ . Increasing  $F$  increases the amplitude of the wave. (c)  $F = 1$ ,  $h = 3$ ,  $\alpha = 0$ :  $f(x) = \cos 2\pi(3x)$ . Increasing  $h$  increases the frequency (or decreases the wavelength  $\lambda$ ) of the wave. (d)  $F = 1$ ,  $h = 1$ ,  $\alpha = 1/4$ :  $f(x) = \cos 2\pi(x + 1/4)$ . Changing  $\alpha$  changes the phase (position) of the wave.

# Diffraction from a 1D lattice

- Fraunhofer diffraction
  - Parallel beam of light
  - Wavelength =  $\lambda$  (NB: for x-rays, a constant)
  - Spacing of objects =  $a$
  - If  $\sin \psi = \lambda/a$
  - ...diffracted waves from neighboring objects are in phase and reinforce
  - Ditto for  $\sin \psi_h = h\lambda/a$ , where  $h$  is an integer

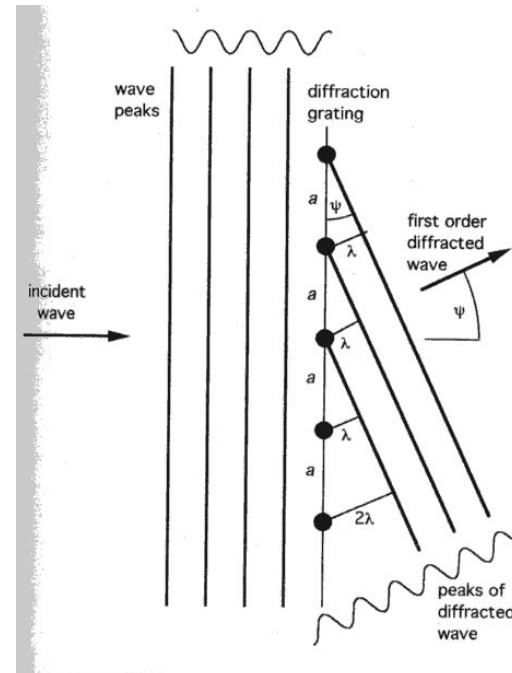


Fig. 4.2 First-order diffraction by a series of equally spaced scattering points.

Box 4.1 A simple diffraction grating

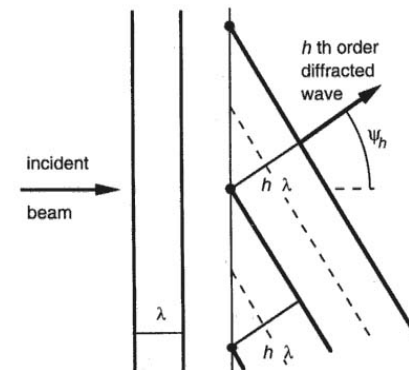
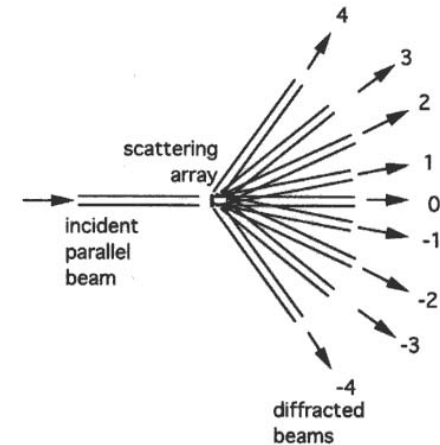


Fig. 4.3 Second-order diffraction by a series of equally spaced scattering points. In this example the path lengths differ by two wavelengths and the order  $h$  is 2.



# Consequences and words

- Where  $\sin \psi \neq h\lambda/a$ 
  - Somewhere down the line from any one particle is another particle scattering exactly out of phase, cancelling each out
  - Only diffracted rays at  $h =$  integers (discontinuous function)
  - $=$  *orders of diffraction*
  - Number of observable diffracted rays limited to maximum  $h = a/\lambda$  (limit to resolution - longer  $\lambda$  means fewer orders can be observed, limiting number of possible observations)



**Fig. 4.1** Fraunhofer diffraction of a parallel beam by a regular array of scatterers.

## Complicated diffractors

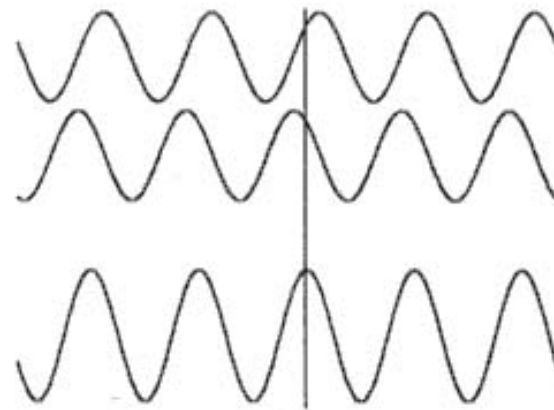
- Some things are simple
  - Use "x" to describe location of any part of !, where "x" is a fraction of the unit length a
  - Each point along the ! Operates as a single point, diffracting rays at  $\psi$  where  $\sin \psi = h\lambda/a$
- Some aren't
  - For density along x of  $\rho(x)$ , scattering is proportional to  $\rho(x)dx$ , but with a phase shifted from 0 to  $2\pi h$  as x goes from 0 to 1, or  $2\pi hx$  at point x



**Fig. 4.4** Regular repeating array of scattering density. The density at any point is the same as the density at a distance  $a$  from it.

# "Structure factors"

- Scattering at hth order obtained by adding contribution from all of !  
In the form of integral  $\int_0^1 \rho(x) \exp[2\pi i h x] dx$
- Which is a complex number  $F_h$  with amplitude  $|F_h|$  and a phase  $\alpha_h$  with  $F_h = |F_h| \exp[i\alpha_h]$
- "Structure Factor" for hth order of diffraction

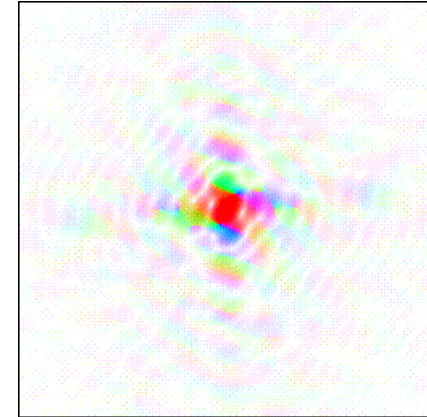
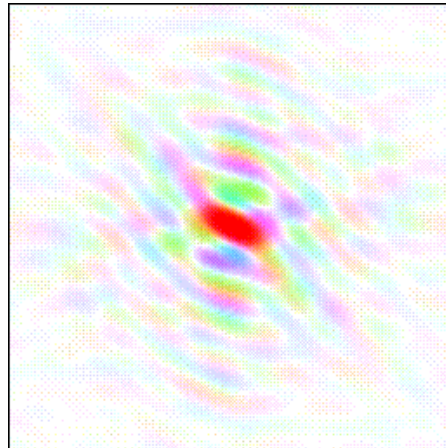
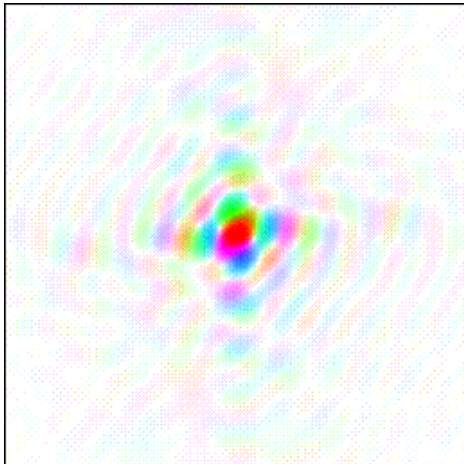


**Fig. 4.5** The sum of two waves of the same wavelength, which have different phases. The wave representing the sum has the same wavelength as the original waves, but the amplitude and phase are different.

# Issues

- Generalizing to 3 dimensions (and objects not in lattices)
- Nature of information required
  - (Roughly)  $|F_h|$  (amplitude of structure factor) from  $\rho$ , and phase from  $x$
  - See <http://www.yorvic.york.ac.uk/~cowtan/fourier/fourier.html> (from CMCC web site)

# Phases and intensities



Duck intensities,  
but cat phases

"In X-ray diffraction experiments, we collect only the diffraction magnitudes, and not the phases. Unfortunately the phases contain the bulk of the structural information. That is why crystallography is difficult." - Kevin Cowhan

