

# Handout 7: Fourier Transforms

Chem 6850/8850

X-ray Crystallography

Department of Chemistry & Biochemistry

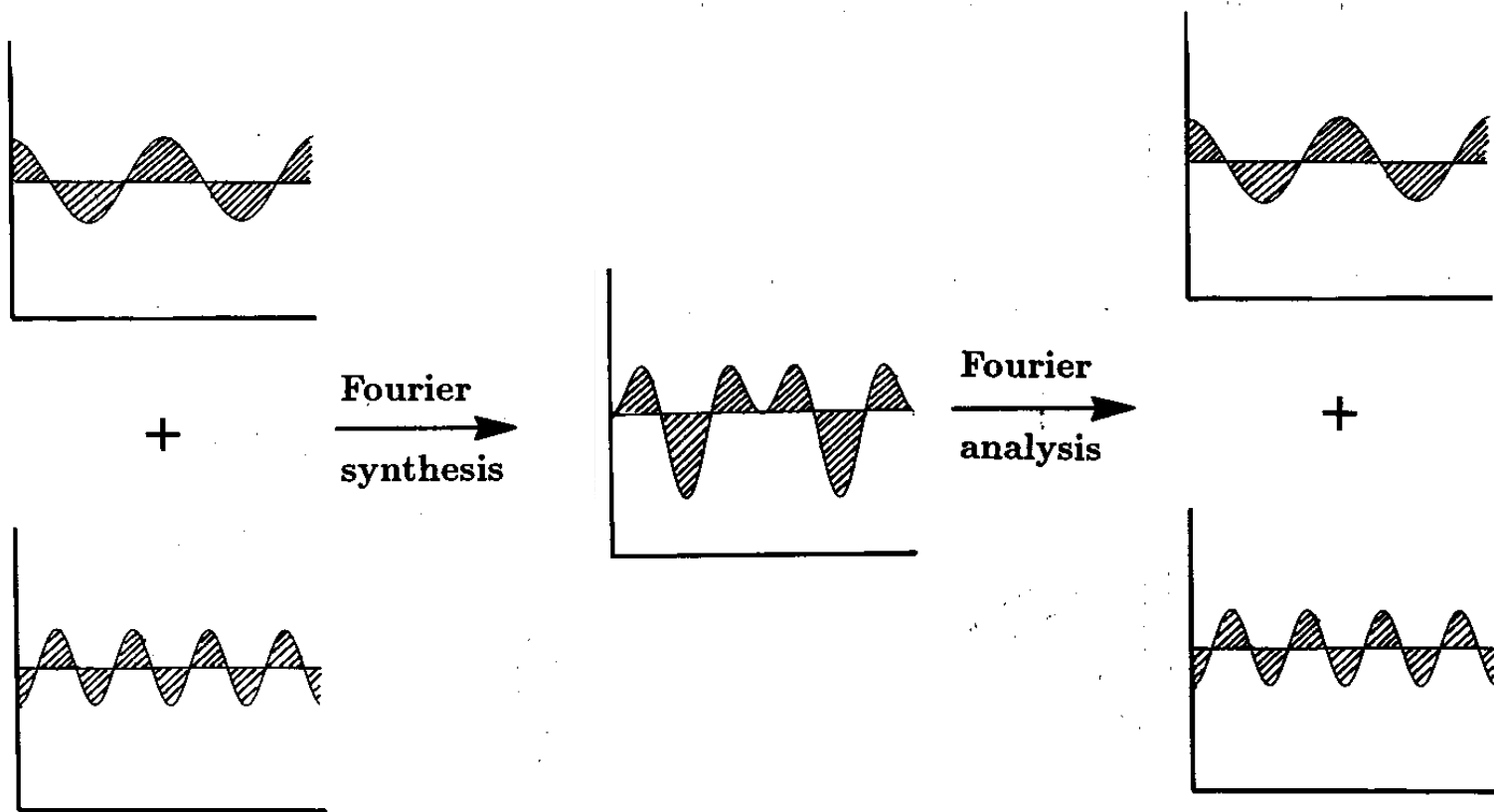
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# The electron density

- The electron density in a crystal can be described as a **periodic function**
  - same contents in each unit cell
  - represented by a sum of cosine and sine functions
  - wavelength is related to lattice periodicity
- The construction of a periodic function by the summation of sine and cosine waves is called a *Fourier synthesis*
- The decomposition of a periodic function into sine and cosine waves is called a *Fourier analysis*

# Fourier synthesis and analysis



"Crystal Structure Analysis for Chemists and Biologists", Glusker, Lewis and Rossi, VCH, 1994.

# Fourier series

- The complete set of components that are necessary to describe a periodic function is called a *Fourier series*
- The intensity of a Bragg reflection is related to the amplitude of an electron density wave in the crystal in *hkl* direction
  - all Bragg peaks: Fourier series describing the electron density of a crystal
  - scattering of X-rays by atoms can be regarded as a Fourier analysis, producing the  $\mathbf{F}_{hkl}$  structure factor waves
- The electron density can be determined from the diffraction pattern by a Fourier synthesis:

$$\rho(xyz) = \frac{1}{V} \sum_h \sum_k \sum_l |F(hkl)| \exp(-2\pi i(hx + ky + lz) - \varphi_{hkl})$$



# Electron density waves

- In order to obtain the electron density, we need to sum all contributing electron density waves (Fourier synthesis)
- Note that the electron density waves do *not* have the same frequencies (wavelengths)!
  - periodicity depends on  $hkl$
  - wavelength is  $d_{hkl}$

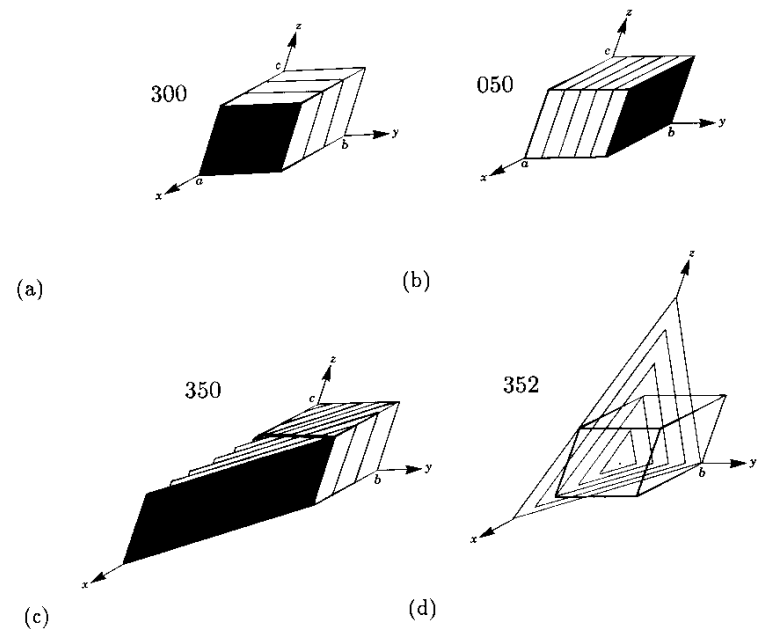


FIGURE 6.10. Periodicities of waves and their representation. Shown, for the same unit cell in each case, are various waves  $F(hkl)$  with different periodicities. (a) 300, (b) 050, (c) 350, and (d) 352. Note that, for  $F(352)$ , the wave repeats 3 times in the  $a$  direction, 5 times in the  $b$  direction, and 2 times in the  $c$  direction.

“Crystal Structure Analysis for Chemists and Biologists”, Glusker, Lewis and Rossi, VCH, 1994.



# Summing electron density waves

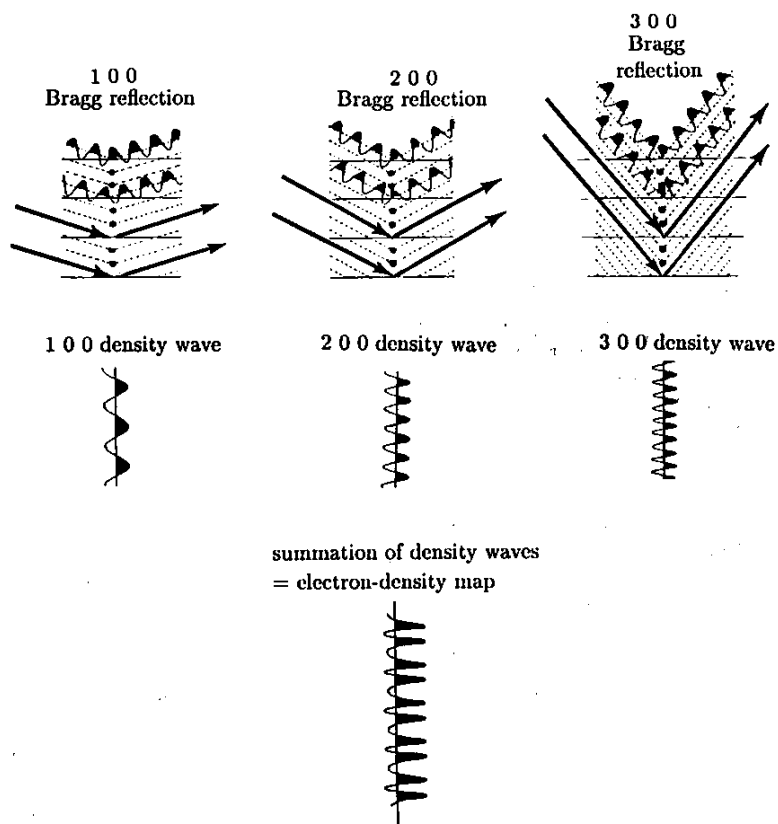
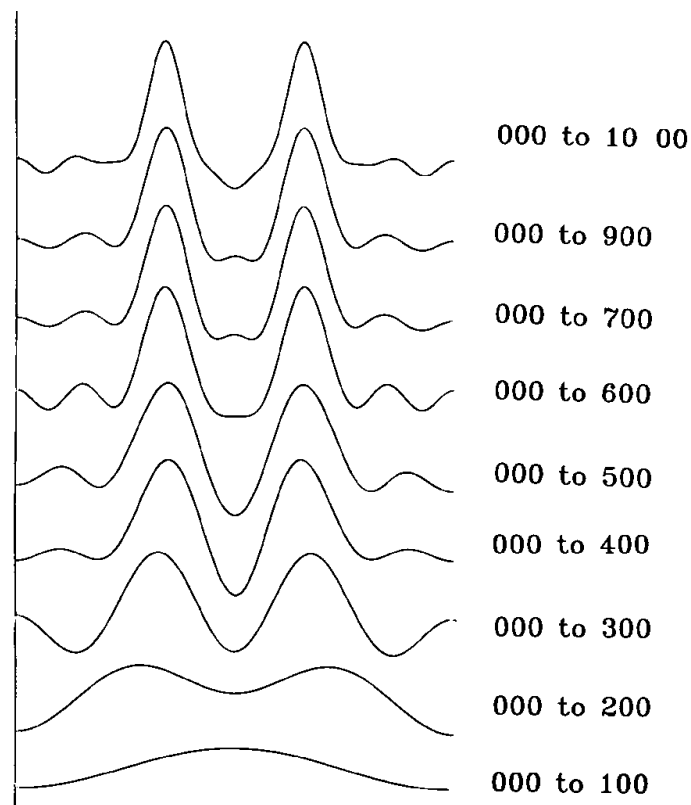
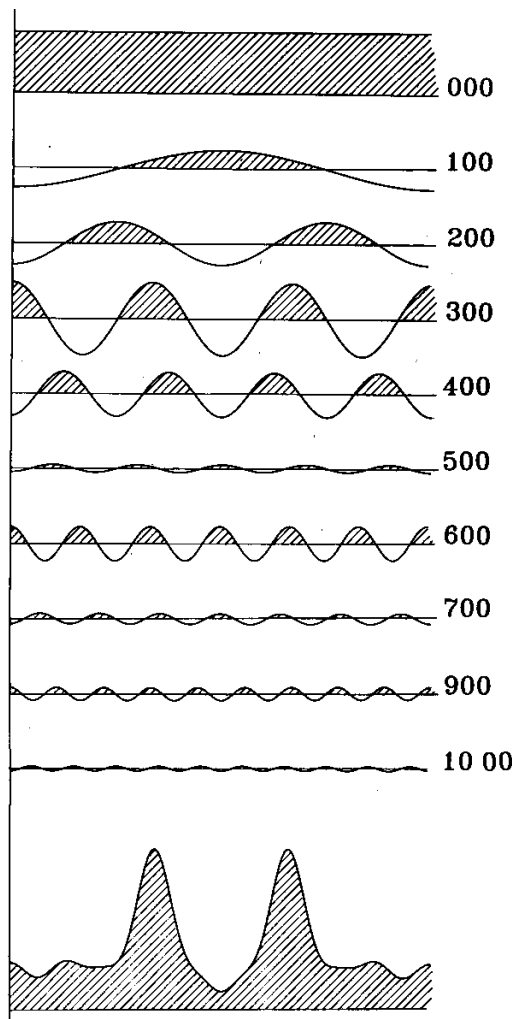


FIGURE 6.11. The meaning of electron-density waves from the Bragg reflections 100, 200, and 300, and their summation to give an electron-density map with peaks at atomic positions (PD means path difference). These electron-density waves have amplitudes and relative phases that depend on the atomic arrangement in the  $a$  direction. When the corresponding electron-density map is calculated, it should contain peaks in the positions corresponding to actual atomic positions.

“Crystal Structure Analysis for Chemists and Biologists”, Glusker, Lewis and Rossi, VCH, 1994.



# A 1D example of a Fourier synthesis



(b) Effects of successive addition of terms in (a). Note how the inclusion of more terms leads the formation of distinct electron density peaks.

"Crystal Structure Analysis for Chemists and Biologists", Glusker, Lewis and Rossi, VCH, 1994.

FIGURE 6.9. Contributions to terms in a Fourier synthesis. (a) Individual terms from 000 to 10 00 ( $h = 10$ ,  $k = 0$ ,  $l = 0$ ) are represented with positive areas shaded. These ten electron-density waves combine to give the electron density shown at the bottom of the diagram. This electron density is dependent on the phases ( $+ = 0^\circ$ ,  $- = 180^\circ$ ) which are: 000 +; 100 -; 200 -; 300 +; 400 -; 500 -; 600 +; 700 -; 800 unobs'd; 900 +; 10 00 - (see Reference 6).

# Fourier transforms

- Generic definition:

$$f(x) = \int_{-\infty}^{\infty} e^{i2\pi xy} g(y) dy \quad \text{FT}$$

$$g(y) = \int_{-\infty}^{\infty} e^{-i2\pi xy} f(x) dx \quad \text{FT}^{-1}$$

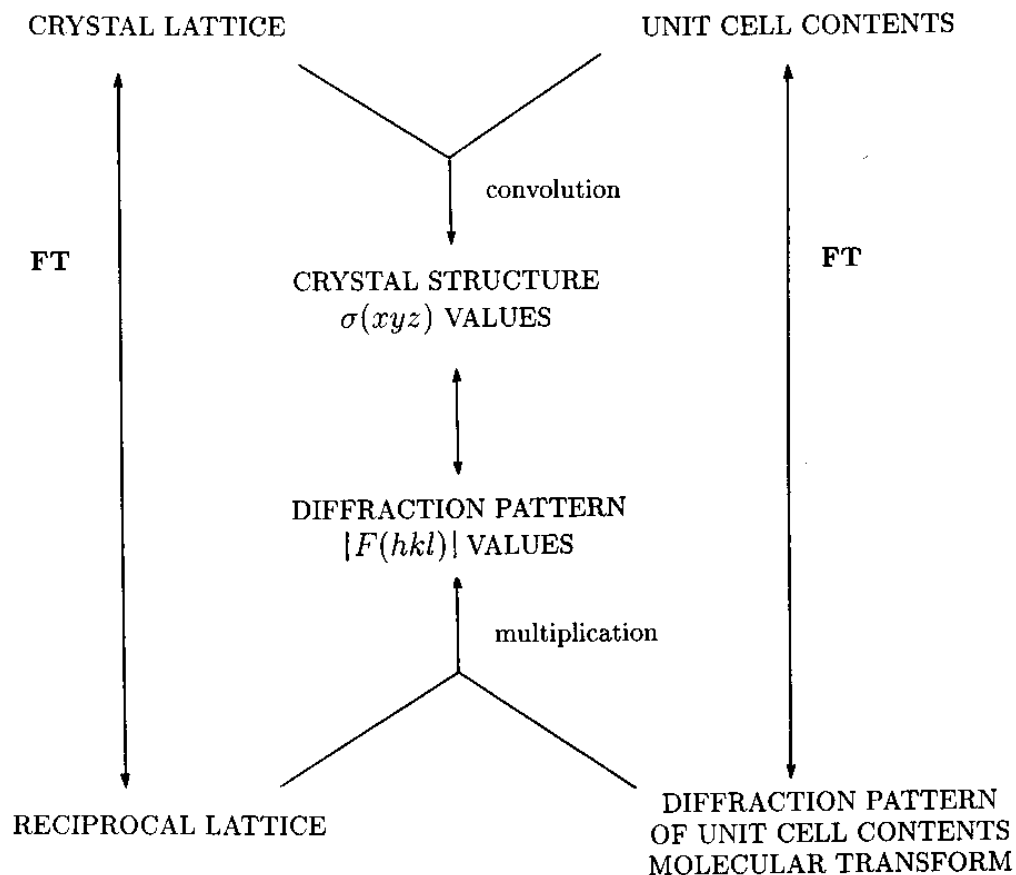
- Convolution\* of two Fourier transforms:

$$h(x) = f(x) \otimes g(x) = \int_{-\infty}^{\infty} f(x) \cdot g(x - x') dx$$

\* A convolution is an integral which expresses the amount of overlap of one function  $g$  as it is shifted over another function  $f$ . It therefore "blends" one function with another.



# Fourier transforms of crystals



“Crystal Structure Analysis for Chemists and Biologists”, Glusker, Lewis and Rossi, VCH, 1994.

FIGURE 6.17. Scheme of the relationship between a crystal structure and its diffraction pattern in terms of Fourier transforms (FT), convolutions, and multiplications.

# The relationship between $F$ and $\rho$

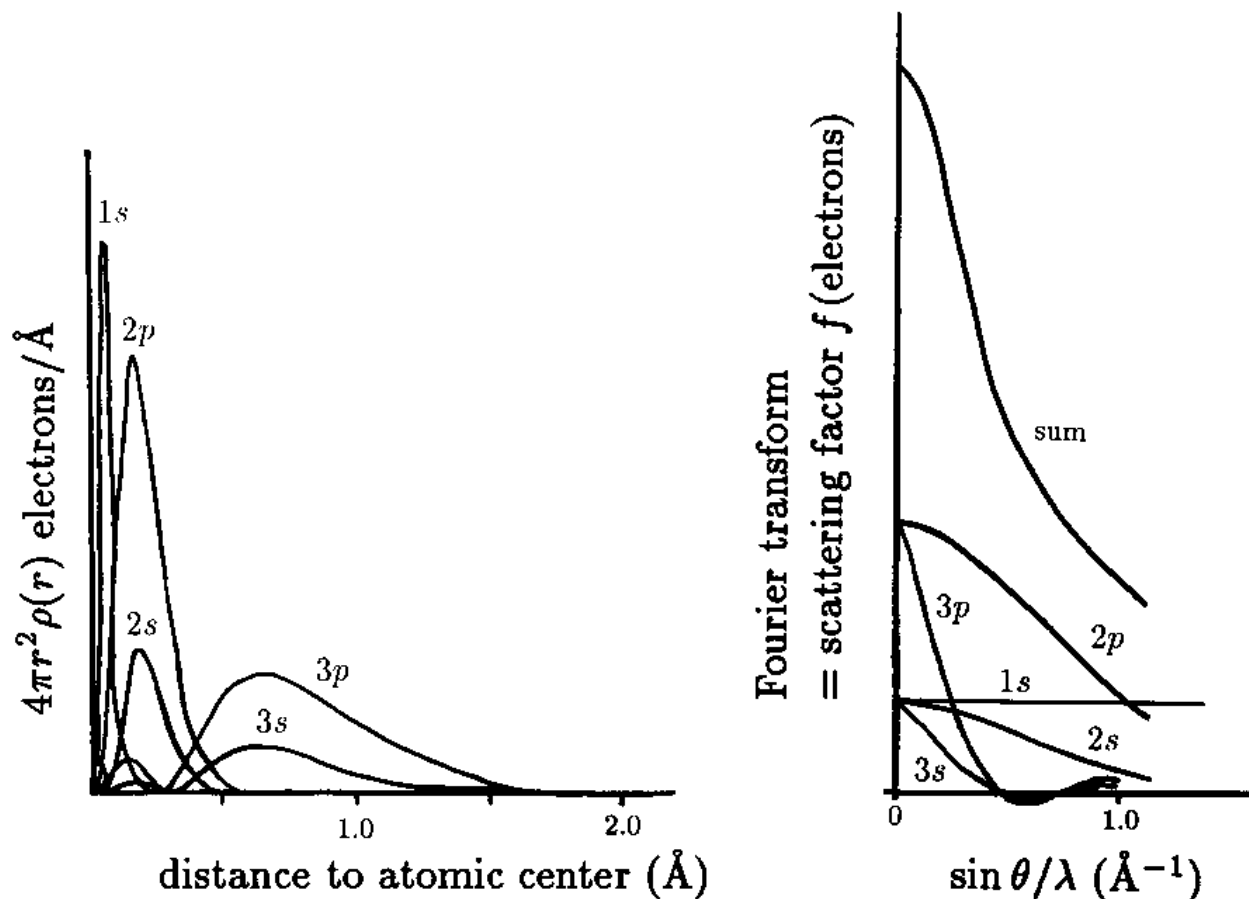
- We have shown that the structure factors can be described by a Fourier synthesis from waves scattered by a crystal
  - A diffraction pattern is the Fourier transform of an “object” (e.g., the crystal for crystallographic experiments)
- We have also shown that the electron density can be obtained by a Fourier synthesis of electron density waves (structure factors)
  - The inverse Fourier transform of the diffraction pattern gives the original object again

$$F(hkl) = \int_V e^{i2\pi(hx+ky+lz)} \rho(xyz) dV$$

$$\rho(xyz) = \int_v e^{-i2\pi(hx+ky+lz)} F(hkl) dv = \frac{1}{V} \sum_{hkl} e^{-i2\pi(hx+ky+lz)} F(hkl)$$



# The FT relationship between $f$ and $\rho_{atomic}$



“Crystal Structure Analysis for Chemists and Biologists”, Glusker, Lewis and Rossi, VCH, 1994.

# Diffraction from holes – a FT perspective

- Diffraction from a single hole gives a ring pattern
- What happens when we have a second, identical hole at a distance  $\mathbf{a}$  from it?

For one hole, we can write:

$$A_0(\mathbf{S}) = \int_{V_r}^{\infty} e^{i2\pi\mathbf{S}\cdot\mathbf{r}} \rho(\mathbf{r}) dV_r$$

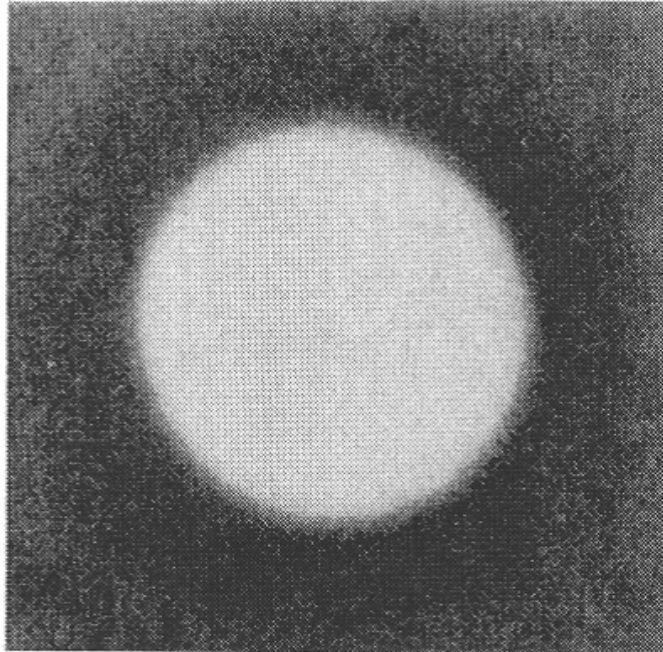
For two holes as described above:

$$\begin{aligned} A(\mathbf{S}) &= \int_{V_r}^{\infty} e^{i2\pi\mathbf{S}\cdot\mathbf{r}} \rho(\mathbf{r}) dV_r + \int_{V_r}^{\infty} e^{i2\pi\mathbf{S}\cdot(\mathbf{r}+\mathbf{a})} \rho(\mathbf{r}) dV_r \\ &= A_0(\mathbf{S}) \cdot \{1 + e^{i2\pi\mathbf{S}\cdot\mathbf{a}}\} \end{aligned}$$

The second hole superimposes a *fringe function* that will double the amplitude of  $A_0$  when  $\mathbf{a}\cdot\mathbf{S}$  is integral, and will lead to extinction halfway in between

# Fringe patterns

(a)



(b)

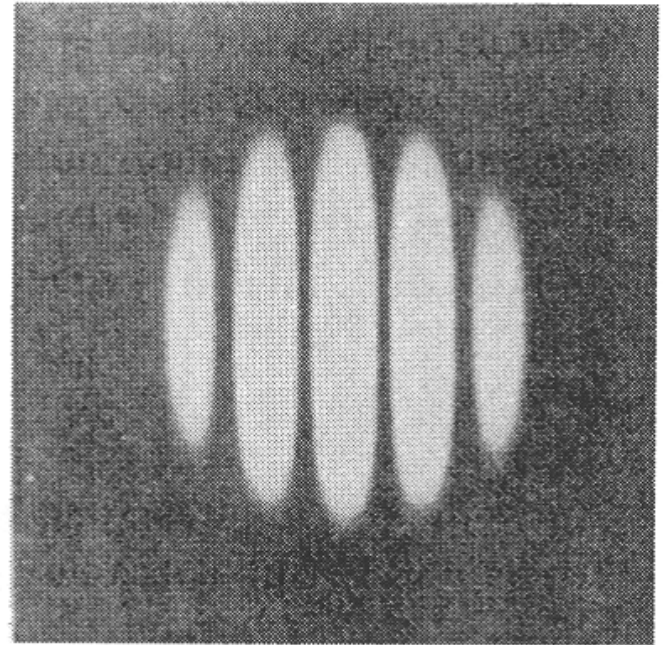


FIGURE 5.5. Diffraction patterns from one and two circular holes: (a) hole of 1 mm diameter, (b) two holes each of 1 mm diameter, set 3 mm apart in the horizontal direction. [Reproduced from *Diffraction*, by C. Taylor, with the permission of the Institute of Physics.]

“Structure Determination by X-ray Crystallography”, Ladd and Palmer, Plenum, 1994.



# What's a hole got to do with a crystal?

- The hole scatters the light rays
- An electron scatters X-rays
- Imagine a crystal as a “hole pattern” of electrons!

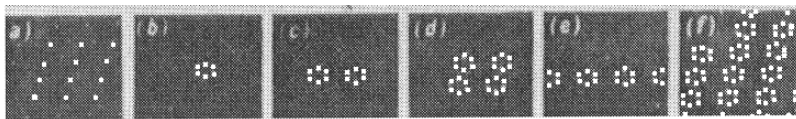
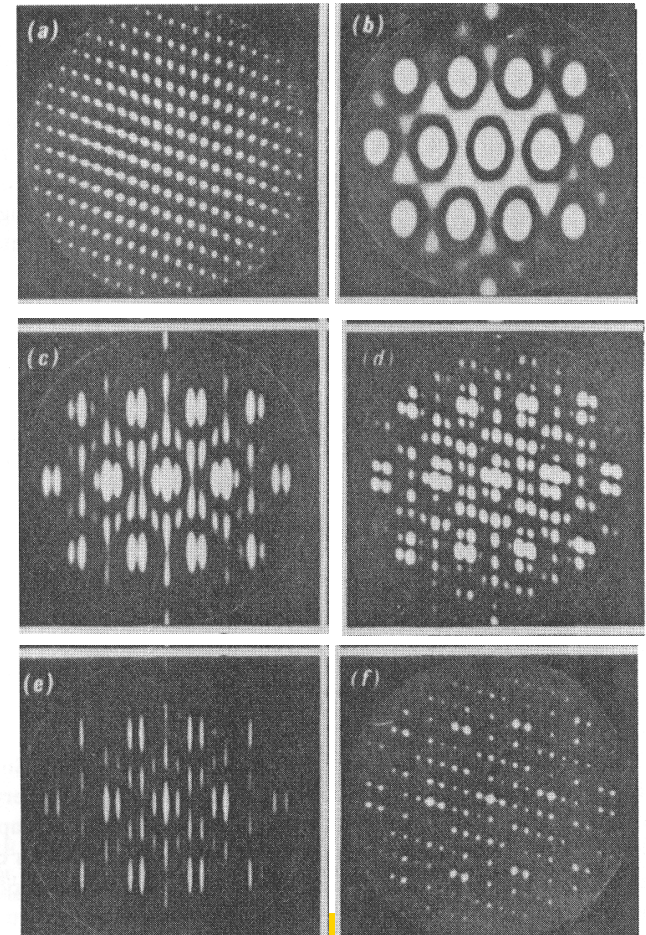


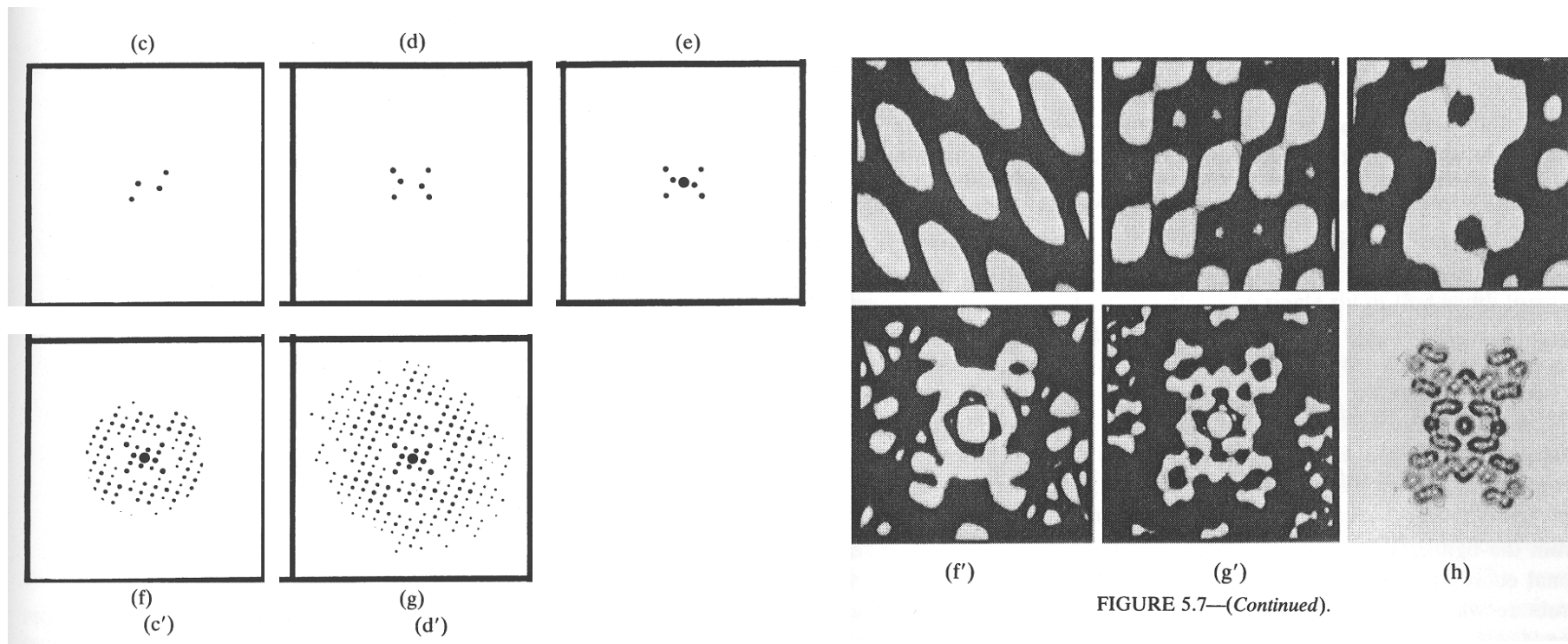
FIGURE 5.6. Optical diffraction patterns illustrating scattering by (a) a two-dimensional monatomic lattice (portion only), (b) a single molecule (benzene ring), (c) two molecules, (d) four molecules, (e) a “row” of six molecules (portion only), (f) a net of molecules (portion only). [Reproduced from *Optical Transforms*, by C. A. Taylor and H. Lipson, with the permission of Routledge.]



“Structure Determination by X-ray  
Crystallography”, Ladd and Palmer, Plenum, 1994.

# The opposite approach...

- ...transforming your diffraction pattern into an electron density



The resolution of your electron density map will strongly depend on how many reflections you use in creating it!

“Structure Determination by X-ray  
Crystallography”, Ladd and Palmer, Plenum, 1994.