Electron density projections

There is a section with this title on page 335 of Dennis Sherwood's original book which is worth summarising as it covers an early method of structure solution for small, often planar, organic molecules. This relates to the projection of the three-dimensional electron density distribution $\rho(x, y, z)$ onto a plane, such as the xy plane giving us $\rho(x, y)$. Before electronic computers were available this was about the only practical way of calculating an electron density map.

The two-dimensional function $\rho(x, y)$ may be derived from the three-dimensional one $\rho(x, y, z)$ by integration over the coordinate above the xy plane. Relative to the absolute axial coordinate Z, which has units of Ångstroms (Å), $\rho(x, y)$ becomes:

$\rho(x, y) = \int_0^c \rho(x, y, z)\, dZ$ where $Z = z\,c$. Hence:

$$\rho(x, y) = c \int_0^1 \rho(x, y, z)\, dz$$

We can substitute the standard electron density equation:

$$\rho(x, y, z) = \frac{1}{V} \sum_h \sum_k \sum_l F_{hkl}\, e^{-2\pi i(hx+ky+lz)}$$

giving:

$$\rho(x, y) = \frac{c}{V} \int_0^1 \sum_h \sum_k \sum_l F_{hkl}\, e^{-2\pi i(hx+ky+lz)}\, dz$$

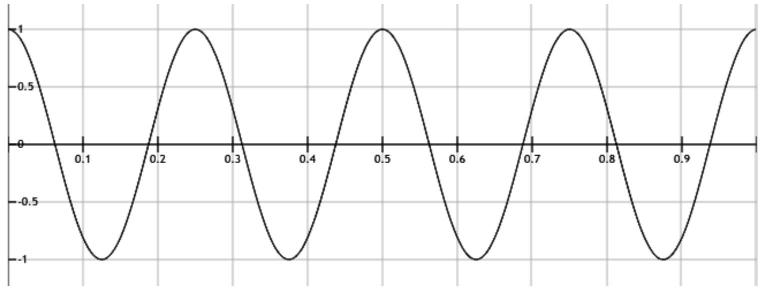
or:

$$\rho(x, y) = \frac{c}{V} \sum_h \sum_k \sum_l F_{hkl}\, e^{-2\pi i(hx+ky)} \int_0^1 e^{-2\pi i l z}\, dz$$

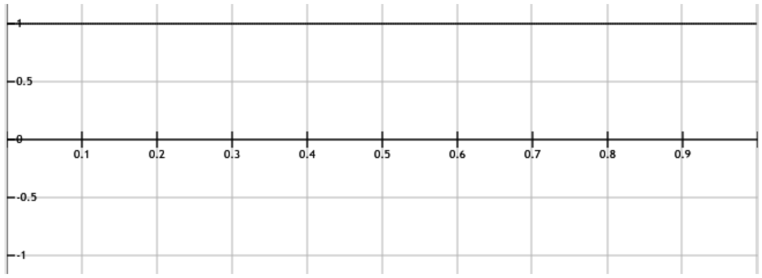
The term:

$$\int_0^1 e^{-2\pi i l z}\, dz$$

is a delta function $\delta(l)$ of the variable l which has the property of being zero for all values of l except 0. The point is that if l is non-zero the summation of sin and cos terms in the function being integrated will cancel out exactly over the range of 0 to 1 on the z axis. This is shown below for the cos terms when $l = 4$ *i.e.* there are exactly 4 peaks and troughs within the range of $0 \leq z \leq 1$. The areas of the peaks and troughs cancel out exactly. The same would apply to the imaginary sin terms.



In contrast, when $l = 0$, the integral is 1 in the range of $0 \leq z \leq 1$ due to all of the cos terms being unity and the sin terms being zero.



We can show this effect by doing the integration.

$$\int_0^1 e^{-2\pi ilz}\ dz = \int_0^1 \cos(2\pi lz)\text{-}i\sin(2\pi lz)\ dz$$

$$= \frac{1}{2\pi l}\left[\ \sin(2\pi lz)+i\cos(2\pi lz)\ \right]_{z=0}^{z=1}$$

$$= \frac{1}{2\pi l}[\ \sin(2\pi l)+i\cos(2\pi l)\ -\ i\ ]$$

If $l = 0$ then the imaginary terms cancel and we are left with

$$\lim_{l \to 0} \frac{\sin(2\pi l)}{2\pi l} = 1$$

Hence:

$$\rho(x,\ y) = \frac{c}{V} \sum_h \sum_k F_{hkl}\ e^{-2\pi i(hx+ky)}$$

Only one plane of reflections, in this case with $l = 0$ *i.e.* the (hk0) zone or layer, needs to be used in the calculation. Centrosymmetric crystals and the centric zones of all crystals have structure factors with phases restricted 0 or 180 degrees. The two possible values for the phase correspond to a difference in the sign of the structure factor amplitude when it is used in the Fourier summation. Estimating the phases of reflections in a centric zone e.g. from isomorphous differences with a heavy atom derivative, can be sufficient to give an interpretable map with a small planar structure. The example given in the original edition of the book is that of phthalocyanine which was solved using a nickel derivative and calculating an (h, 0, l) electron density projection (Robertson, J. M. (1936). *J. Chem. Soc.*, **1936**, 1195-1209). The coordinate of the molecule which is normal to the plane of projection is unknown, but in principle it can be determined from a projection calculated with a different zone.