

Peak Fitting in Analysis

The Gaussian fitting function in N dimensions is

$$G(x) = h \prod_{i=1}^N e^{-(x_i - c_i)^2 / a_i^2}$$

where h is the height (intensity) and c_i is the center and a_i is the “width”.

The linewidth, l_i , is the full width at half max. We solve $e^{-x^2/a^2} = 1/2$ to find that $x = a\sqrt{\ln 2}$. Thus the linewidth $l = 2a\sqrt{\ln 2}$ and so $a = l/(2\sqrt{\ln 2})$.

In terms of the linewidth we have

$$G(x) = h \prod_{i=1}^N e^{-4 \ln 2 (x_i - c_i)^2 / l_i^2}$$

The Lorentzian fitting function in N dimensions is

$$L(x) = h \prod_{i=1}^N \frac{a_i^2}{a_i^2 + (x_i - c_i)^2}$$

To find the linewidth we solve $\frac{a^2}{a^2 + x^2} = 1/2$ to find that $x = a$. Thus the linewidth $l = 2a$ and so $a = l/2$.

In terms of the linewidth we have

$$L(x) = h \prod_{i=1}^N \frac{l_i^2}{l_i^2 + 4(x_i - c_i)^2}$$

Note that there are $1+2N$ parameters for the fitting, (h, c_i, l_i) . For nonlinear fitting we need derivatives of the functions with respect to the parameters. We have

$$\begin{aligned} \frac{\partial G}{\partial h} &= \frac{G}{h} \\ \frac{\partial G}{\partial c_i} &= \frac{8 \ln 2 (x_i - c_i) G}{l_i^2} \\ \frac{\partial G}{\partial l_i} &= \frac{8 \ln 2 (x_i - c_i)^2 G}{l_i^3} \end{aligned}$$

and

$$\begin{aligned}\frac{\partial L}{\partial h} &= \frac{L}{h} \\ \frac{\partial L}{\partial c_i} &= \frac{8(x_i - c_i)L}{l_i^2 + 4(x_i - c_i)^2} \\ \frac{\partial L}{\partial l_i} &= \frac{2L}{l_i} - \frac{2l_i L}{l_i^2 + 4(x_i - c_i)^2} = \frac{8(x_i - c_i)^2 L}{l_i(l_i^2 + 4(x_i - c_i)^2)}\end{aligned}$$

The volume of the Gaussian function is

$$\int G(x) = h \prod_{i=1}^N \sqrt{\pi} a_i = h \prod_{i=1}^N \frac{\sqrt{\pi} l_i}{2\sqrt{\ln 2}} = h \left(\frac{1}{2} \sqrt{\frac{\pi}{\ln 2}} \right)^N \prod_{i=1}^N l_i$$

The volume of the Lorentzian function is

$$\int L(x) = h \prod_{i=1}^N \pi a_i = h \prod_{i=1}^N \frac{\pi l_i}{2} = h \left(\frac{\pi}{2} \right)^N \prod_{i=1}^N l_i$$

For a peak that is fitted with a Gaussian, there is a Lorentzian line shaped peak with the same volume. Let $l'_i = s l_i$ be the equivalent Lorentzian linewidth. Then

$$h \left(\frac{1}{2} \sqrt{\frac{\pi}{\ln 2}} \right)^N \prod_{i=1}^N l_i = h \left(\frac{\pi}{2} \right)^N \prod_{i=1}^N l'_i$$

and so

$$\frac{1}{2} \sqrt{\frac{\pi}{\ln 2}} = s \frac{\pi}{2}$$

and thus

$$s = \frac{1}{\sqrt{\pi \ln 2}} \approx 0.678$$

Assuming we have a peak with an actual maximum, then the initial values can be determined somewhat sensibly. So h can be set to the value of the peak at the maximum position, and c_i can be set to the maximum (or using a parabolic interpolation to a non-grid point), and l_i can be set by seeing where the peak decreases to half its value or starts to turn up again (again, interpolation can be used).

So for isolated peaks, this fitting should work fairly well.

With overlapped peaks you have to do sums of the functions, which starts to give huge numbers of parameters for fitting, which is not ideal. It's quite possible that the fitting in this case is very sensitive.