Introduction to EELS curve fitting

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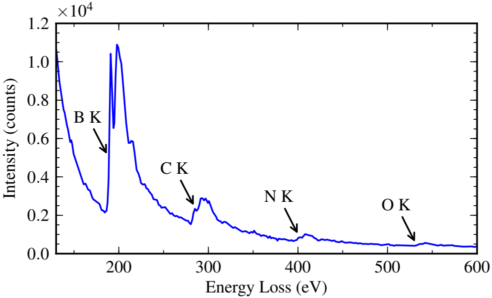
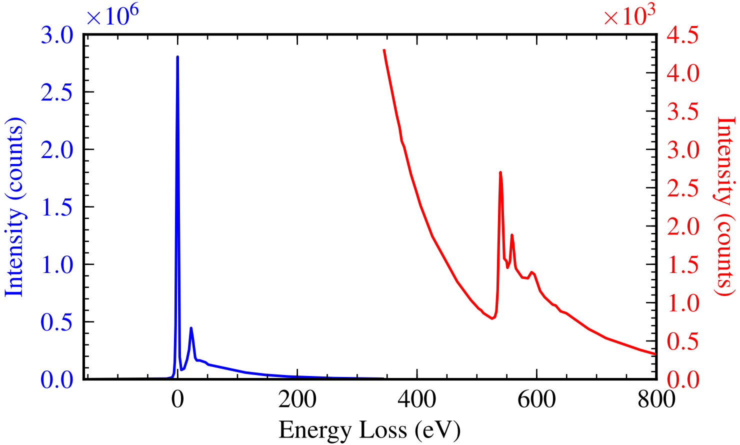
Université de Lille

HyperSpy Workshop 2021
ePSIC Diamond Light Source (Cloud)
20th of April 2021

EELS spectrum from BN NPs



The “windows” method



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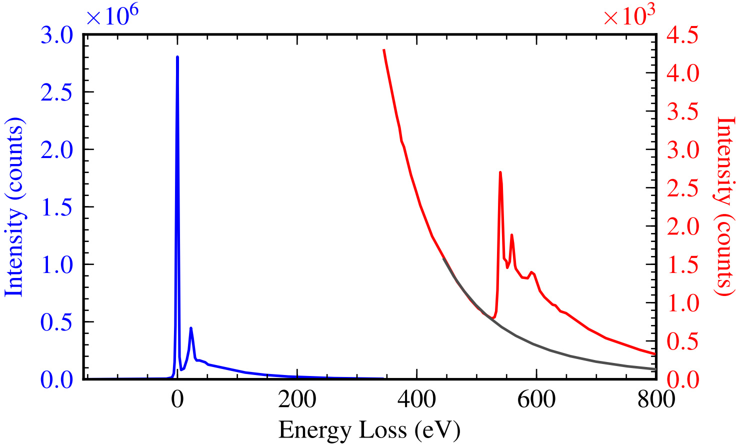
$$N_O \approx \text{———}$$



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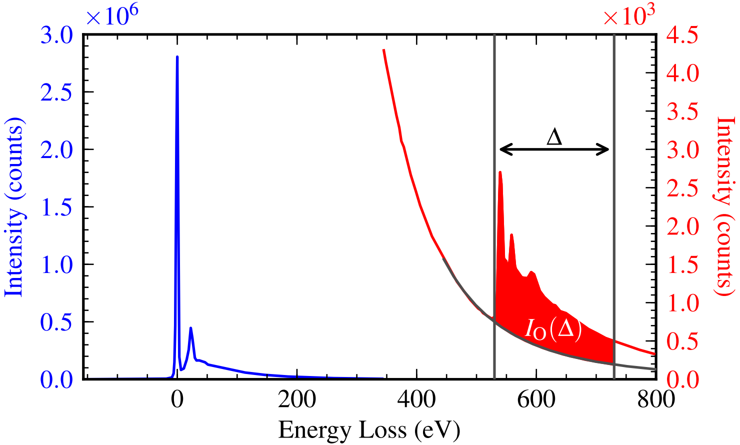
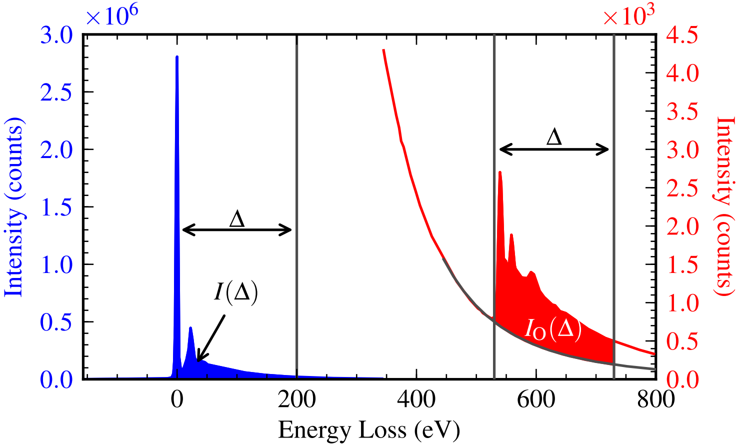
$$N_{\mathrm{O}} \approx \frac{I_{\mathrm{O}}(\Delta,\beta)}{}$$



The "windows" method

$$N_O \approx \frac{I_O(\Delta,\beta)}{I(\Delta,\beta)}\sigma_O^{-1}(\Delta,\beta)$$



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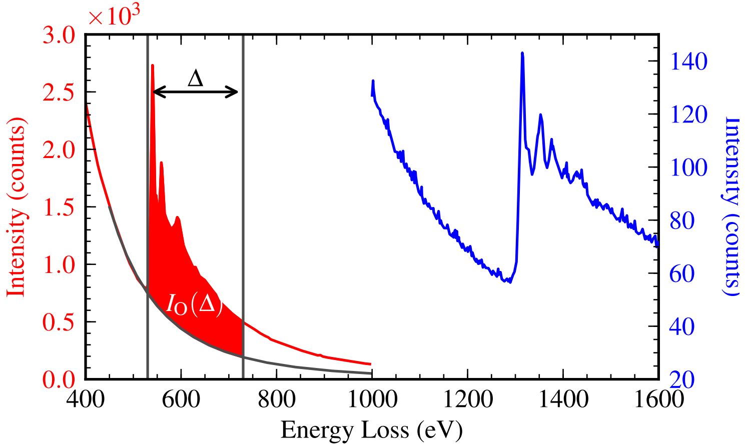
$$N_{\mathrm{O}} \approx \frac{I_{\mathrm{O}}(\Delta,\beta)}{I(\Delta,\beta)}\sigma_{\mathrm{O}}^{-1}(\Delta,\beta) \qquad N_{\mathrm{Mg}} \approx \frac{I_{\mathrm{Mg}}(\Delta,\beta)}{I(\Delta,\beta)}\sigma_{\mathrm{Mg}}^{-1}(\Delta,\beta)$$



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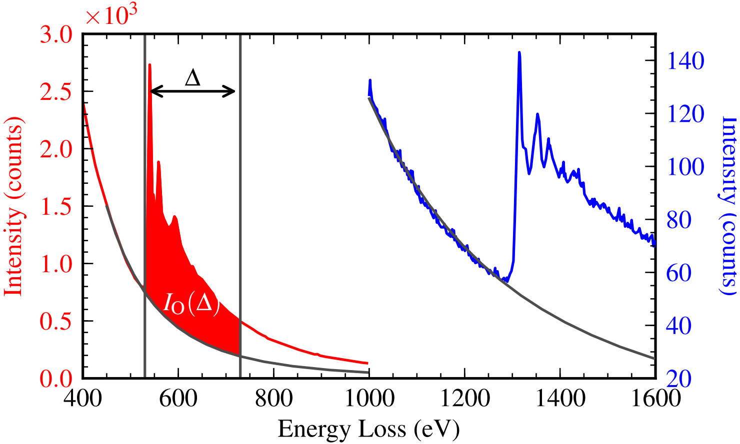

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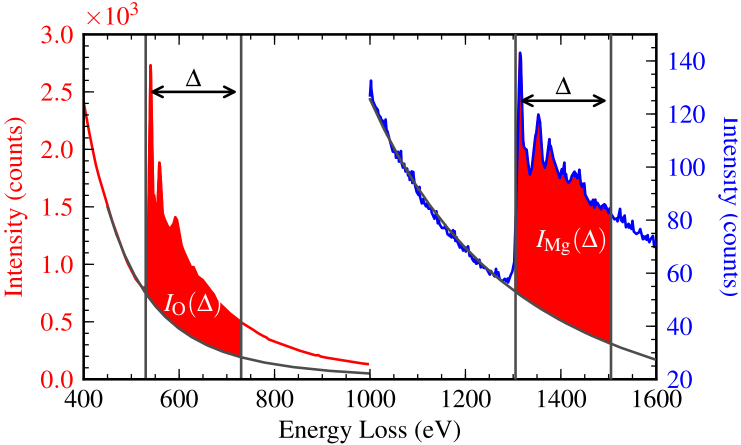

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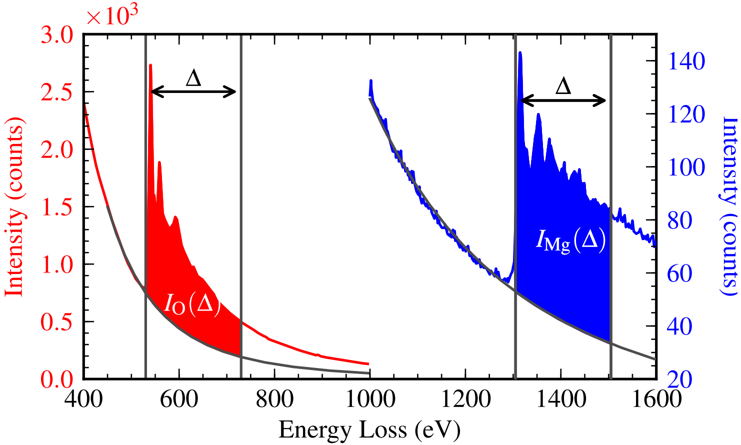
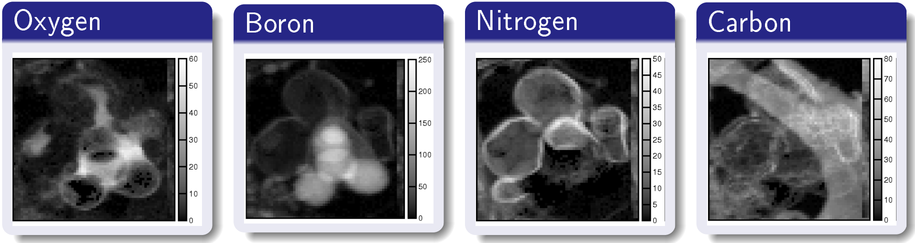
$$\frac{N_{\mathrm{O}}}{N_{\mathrm{Mg}}} \approx \frac{I_{\mathrm{O}}(\Delta,\beta)}{I_{\mathrm{Mg}}(\Delta,\beta)} \frac{\sigma_{\mathrm{Mg}}(\Delta,\beta)}{\sigma_{\mathrm{O}}(\Delta,\beta)}$$



EELS elemental of BN nanoparticle



Arenal et al., Ultramicroscopy 2008

Some limitations of the “windows” method

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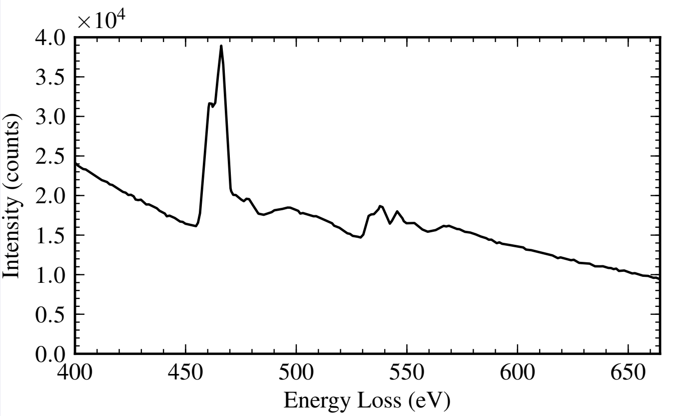
- It always returns a result (what feels good) but, how do we know that it is correct?
- Only analyses a fraction of the available signal (non-optimal SNR)
- Useful information gets lost (fine structures changes, energy onset shifts...)

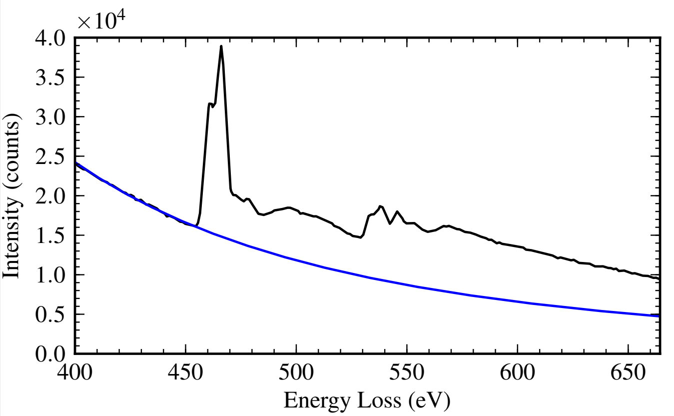
The curve fitting method: an example

$SrTiO_3$ Spectrum



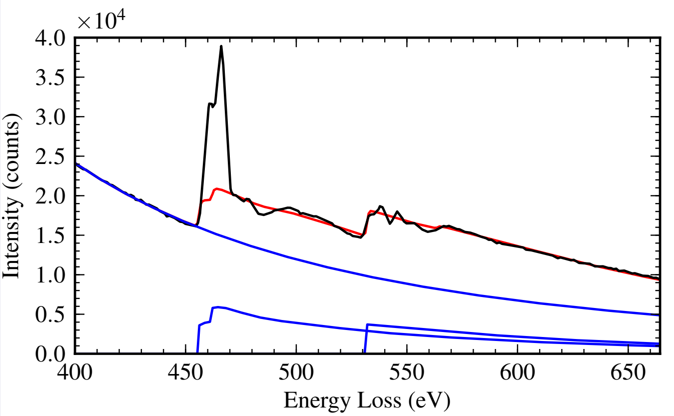
The curve fitting method: an example

$M(E) = AE^{-r}$



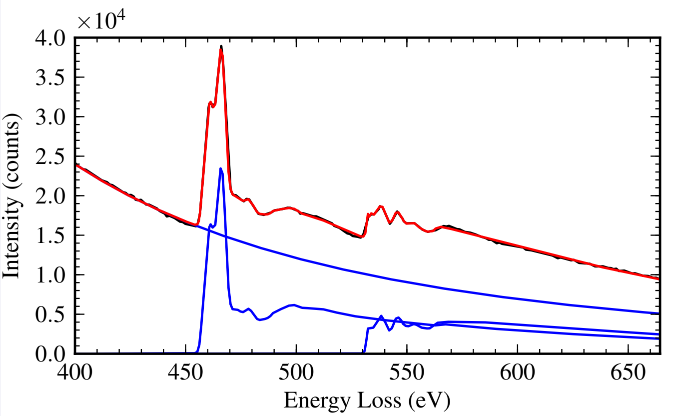
The curve fitting method: an example

$$M(E) = AE^{-r} + I_{\mathrm{Ti}}\sigma_{\mathrm{Ti}}(E) + I_{\mathrm{O}}\sigma_{\mathrm{O}}(E)) * L(E)$$



The curve fitting method: an example

$$M(E) = AE^{-r} + (N_{\mathrm{Ti}} f_{\mathrm{Ti}}(E)\sigma_{\mathrm{Ti}}(E) + N_{\mathrm{O}} f_{\mathrm{O}}(E)\sigma_{\mathrm{O}}(E)) * L(E)$$



Assumptions

- There is a *known* function, f, that relates the *independent variable* X and the *dependent variable* Y.
  $Y \approx f(X, \beta) + \epsilon(f(X, \beta))$

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  $Y \approx f(X, \beta) + \epsilon(f(X, \beta))$
- The number of unknown parameters, β is *equal or less* thant the number of different observations of the independent variable
- The probability distribution of the statistical error (ϵ) is known

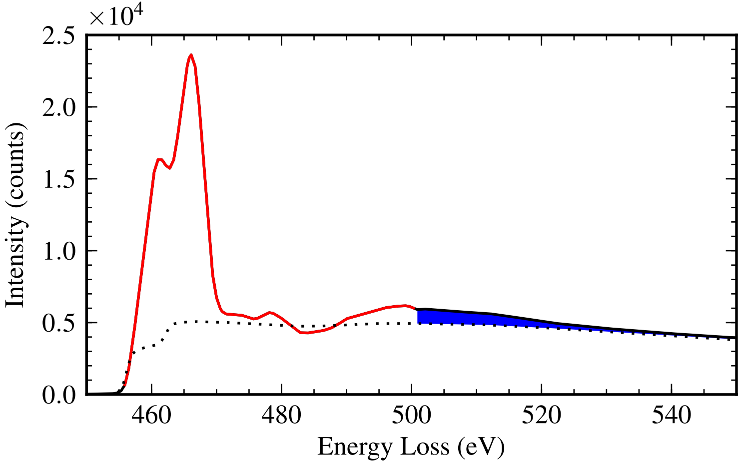
Components of the model

Parametric model of the high energy loss spectrum for elemental and bonding quantification:

$$M(E;\mathrm{parameters}) = AE^{-r} + \left(\sum_i N_i f_i\left(E\right) \int_0^{q(\beta)} \sigma_i\left(E,q\right) dq\right) * L(E)$$

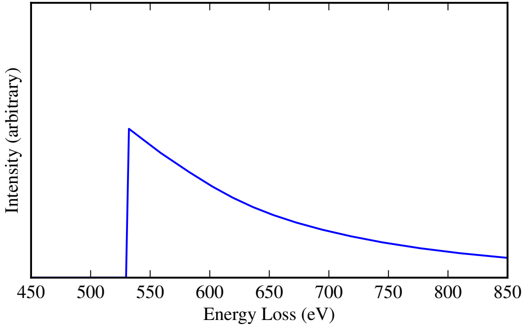
- AE^{-r}: background model
- σ_i^{FS}: cross section of each ionization edge, i
- N_i: $\mathrm{atoms}/\mathrm{nm}^2$
- $f_i(E)$: function that mimics the fine structure of each ionization edge, e.g. gaussian, fingerprints, splines...
- $L(E)$: experimental low loss spectrum.

Why adding the fine structure to the model?



Ionization edge fine structure

Oxygen K ionization edge from MgO



Ionization edge fine structure

- In solids, the first $\sim 40\,\mathrm{eV}$ are strongly modified by the final density of states $\Rightarrow$ carries bonding information

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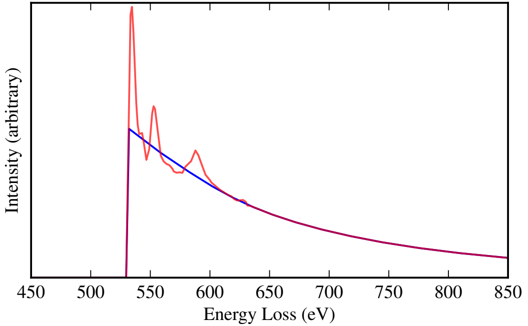
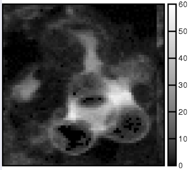
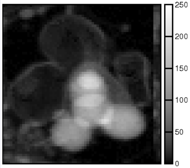


EELS elemental and bonding maps of BN nanoparticle

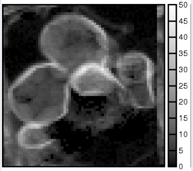
Oxygen



Boron



Nitrogen



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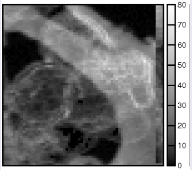

Arenal et al., Ultramicroscopy 2008

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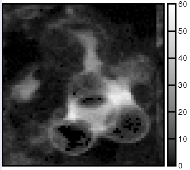

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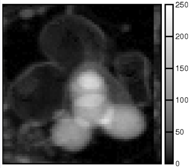

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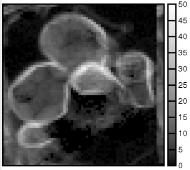

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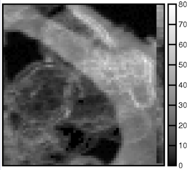
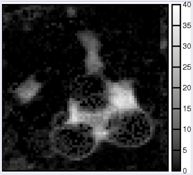
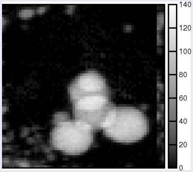


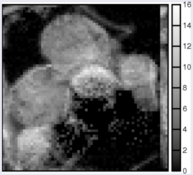
Boron oxide



Boron pure



BN $\perp$



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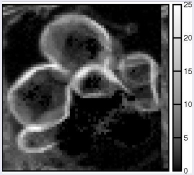

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  - Maximum likelihood estimation (ML)

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- In EELS the noise is a mixture of *Poisson and Gaussian noise.*
- WNNLS can approximate well Poissonian noise when the number of counts is high enough (almost always in EELS)
- Non-linear parameter estimation is an iterative process that *is very sensitive to the starting parameters*

Key articles

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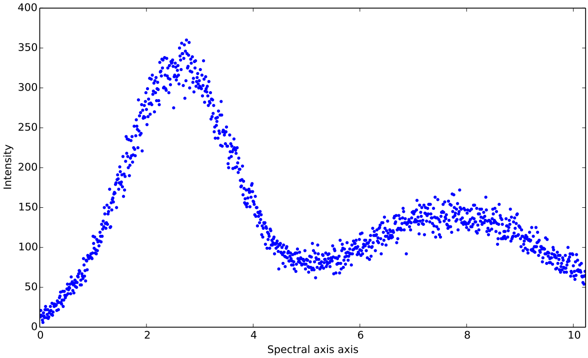
- Verbeeck, J. and Aert, S. V. (2004). Model based quantification of EELS spectra. Ultramicroscopy, 101(2-4):207–224.

Software

- EELSModel http://www.eelsmodel.ua.ac.be/ (open source)
- HyperSpy http://hyperspy.org (open source)
- Digital Micrograph

Non-linear optimisation routine



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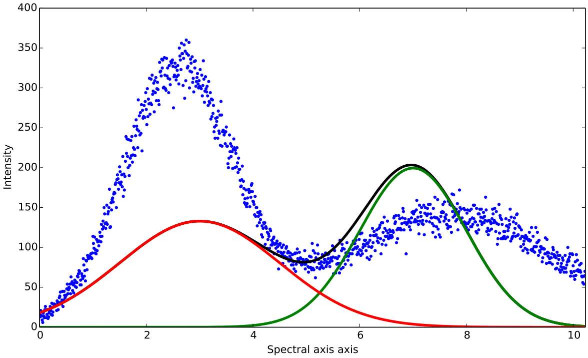

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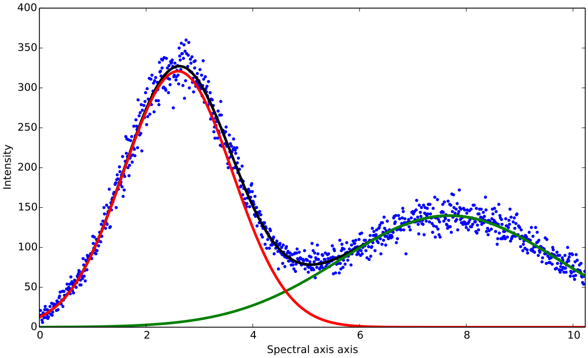

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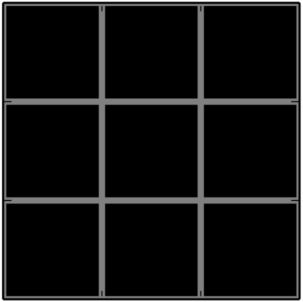

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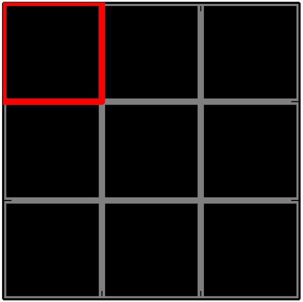

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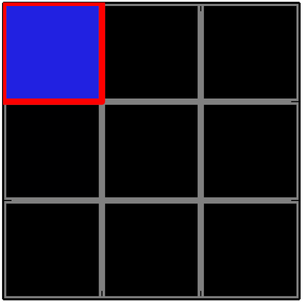

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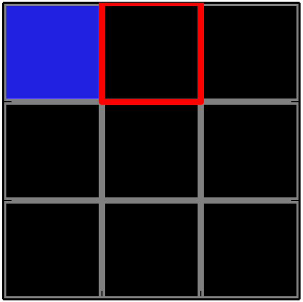

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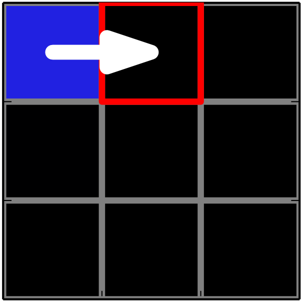

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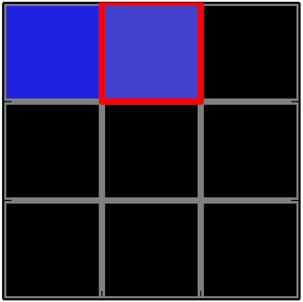

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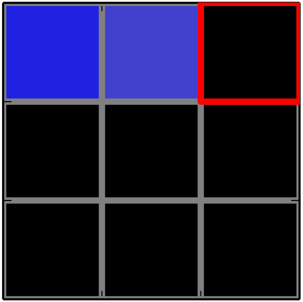

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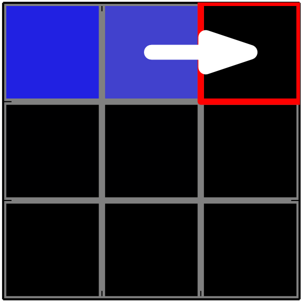

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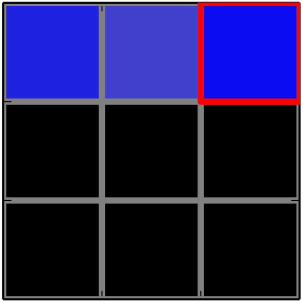

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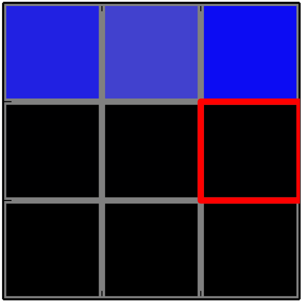

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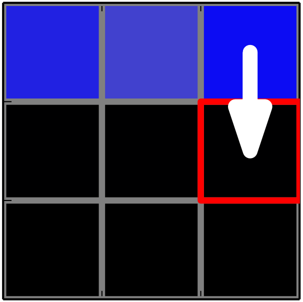

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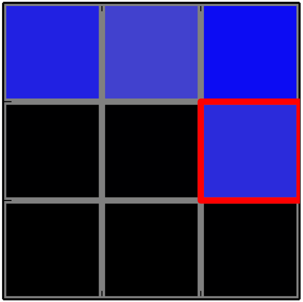

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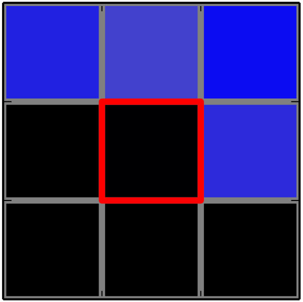

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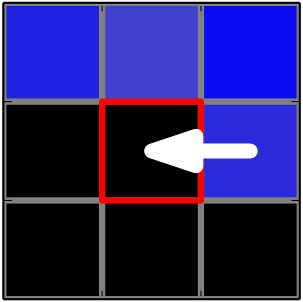

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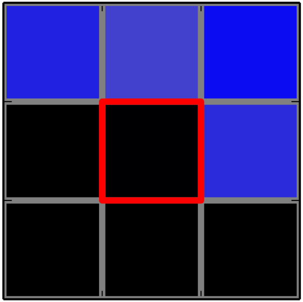

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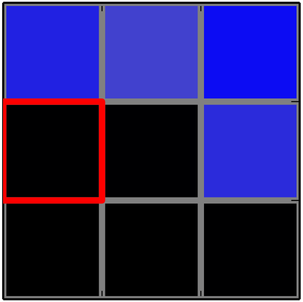
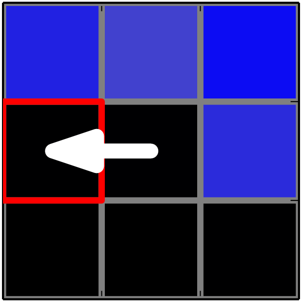


Fitting routine n-dimensions

- Set stating parameters.
- Fit.
- Move to next element.
- Copy parameter values from previous fit.



Fitting routine n-dimensions

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- Fit.
- Move to next element.
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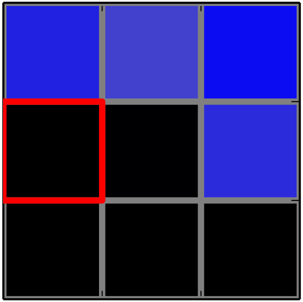

Fitting routine n-dimensions

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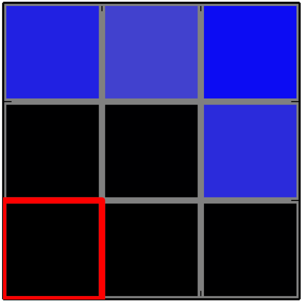

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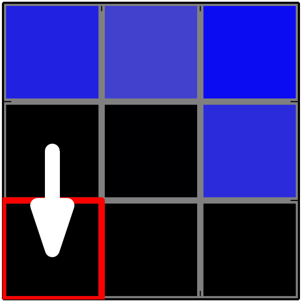

Fitting routine n-dimensions

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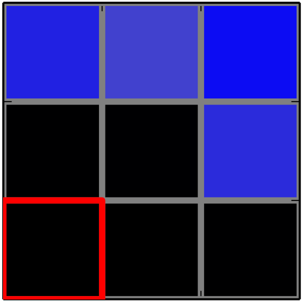

Fitting routine n-dimensions

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