

# Extending Linear Methods

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# Overview

- 1 Preliminaries
- 2 Transformation of inputs
- 3 Piece-wise polynomials
- 4 Gaussian basis functions
- 5 Wavelet and Fourier basis functions

# Preliminaries

- It is highly unlikely that the true function  $f(X)$  is linear in  $X$ .
- In some cases, linearity is a reasonable assumption, e.g., a first order Taylor series expansion:

$$f(x) = f(a) + f'(a)(x - a) + f''(a)\frac{(x - a)^2}{2!} + f'''(a)\frac{(x - a)^3}{3!} + \dots$$

- Examples where this is used in materials science - linear elasticity (Hooke's law), etc.
- More frequently, we perform a transformation of inputs to create a linear basis expansion.

# General concept

- Express:

$$f(X) = \sum_{m=1}^M \beta_m h_m(X)$$

where  $h_m$  is the  $m^{th}$  transformation of  $X$ .

- This is known as a linear basis expansion in  $X$ .
- The key lies in choice of the basis functions  $h_m$ .

# Examples of basis expansions

- $h_m(X) = X_j^2, h_m(X) = X_i X_j$ 
  - Polynomial expansion to higher-order Taylor series terms.
  - No. of terms increases exponentially with degree of polynomial. For  $p$  variables, we have  $O(p^2)$  square and cross-product terms in a quadratic model. For a degree  $d$  polynomial, we have  $O(p^d)$ .
- $h_m(X) = \log(X_j), \text{sqrt}(X_j), \exp(iX_j)$ : non-linear transformations in  $X$ .
- $h_m(X) = I(L_m \leq X_k < U_m)$ : Piece-wise division of regions of  $X$ .  
E.g., cubic splines.
- $h_m(X) = \text{RBF}(\|X - X_m\|)$ : radial basis function, e.g., Gaussian.
- Typically, basis functions are used simply to allow a more flexible representation of the data. The basis functions can span a very large (sometimes infinite) set, from which a selection has to be made:
  - Restriction - Truncate the choice of basis functions using some criteria.
  - Selection - Choose basis functions that contribute significantly to the fit.
  - Regularization - Use the whole and/or very large subset and apply regularization techniques (e.g., ridge or LASSO) to restrict coefficients.

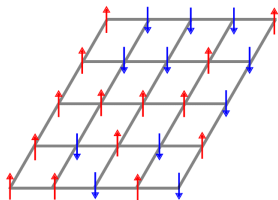
# Linearization from physical laws

- Arrhenius law:

$$r = A \exp\left(-\frac{E_a}{RT}\right) \longrightarrow \log(r) = \log(A) - \frac{E_a}{RT}$$

- Ising model:

$$H(\sigma) = - \sum_{\langle i,j \rangle} J_{ij} \sigma_i \sigma_j - \mu \sum_j h_j \sigma_j$$

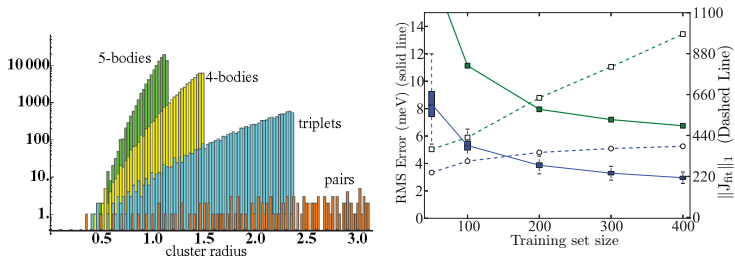


# Compressive sensing for cluster expansions

- Cluster expansion of energy on lattice points:

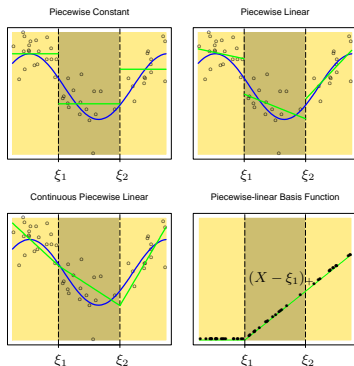
$$H(\sigma) = E_0 + \sum_f J_f \prod_f(\sigma)$$

- $\sigma$  is the vector representing occupation of lattice sites,  $\prod_f$  are the cluster basis functions,  $J_f$  are effective cluster interactions (ECIs).
- Compressive sensing: essentially a LASSO to solve for ECIs.<sup>[1]</sup>



# Piecewise polynomials

$$h_1(X) = I(X < \xi_1), h_2(X) = I(\xi_1 \leq X < \xi_2), h_3(X) = I(X \geq \xi_2)$$



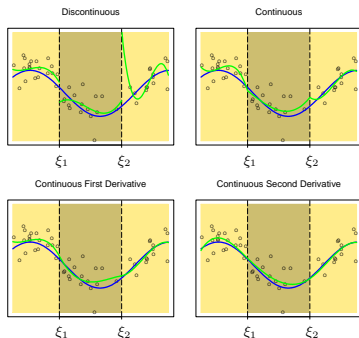
Parameters:

- No. of knots
- Order of polynomial
- Continuity at knots (value, first derivative, second derivative, etc.). For a polynomial of order  $N$ , we usually want all derivatives  $< N$  to be continuous.



# Cubic splines

Piecewise Cubic Polynomials



- Probably the most commonly used.
- Continuous 1st and 2nd derivatives.
- Natural cubic spline: polynomial is linear beyond boundaries.
- Smoothing spline: Use regularization to control complexity:

$$RSS(f, \lambda) = \sum_{i=1}^N \{y_i - f(x_i)\}^2 + \lambda \int \{f''(t)\}^2 dt$$

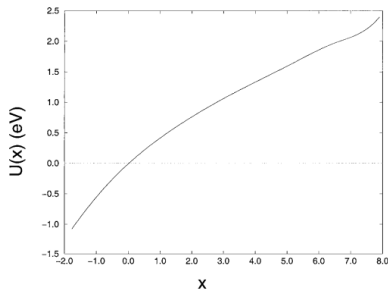
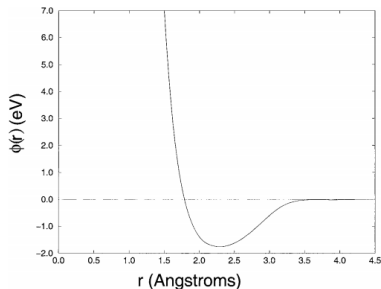
# Examples of cubic spline fitting

- Spline-based Modified Embedded Atom Method (MEAM)

$$E = \sum_{i < j} \phi(r_{ij}) + \sum_i U(n_i),$$

$$n_i = \sum_j \rho(r_{ij}) + \sum_{i < k, j, k \neq i} f(r_{ij})f(r_{ik})g[\cos(\theta_{jik})]$$

where  $\phi$ ,  $U$ ,  $\rho$ ,  $f$  and  $g$  can be approximated by cubic splines.



## Demo: Cubic spline fitting in scipy

```
import numpy as np
## Import CubicSpline from scipy
from scipy.interpolate import CubicSpline

## x, y data for generating the spline fitting
x = np.arange(10)
y = np.sin(x)

## Fit the spline
cs = CubicSpline(x, y)

## Generate new x values
xs = np.arange(-0.5, 9.6, 0.1)

## Perform the interpolation on the new points
ys = cs(xs)
```

# Gaussian basis functions

$$h_m(x) = \exp(-k(x - x_m)^2)$$

- Gaussian functions centered at  $x_m$ .
- Other similar types of functions include Lorentzian ( $h_m(x) = \frac{1}{1+kx^2}$ ), Gaussian-Lorentzian, Voigtian, Pearson type IV, and beta profiles.

# Example: Rietveld refinement

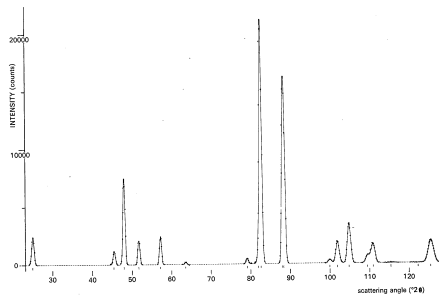


Figure: Neutron powder diffraction diagram of  $\text{CaUO}_4$

- Least squares fitting of theoretical line profile to match a measured diffraction pattern (e.g., X-ray, neutron).[2]

## Example: Rietveld refinement, contd.

- Peak shape function:

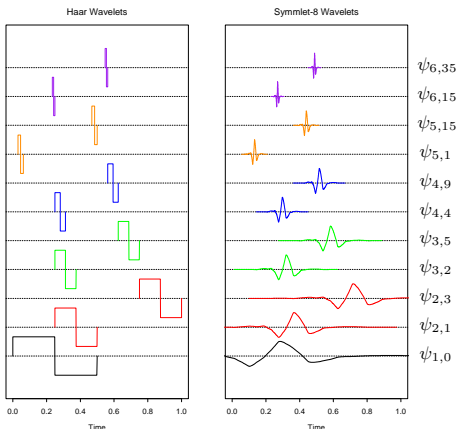
$$PSF(\theta) = \Omega(\theta) \otimes \Lambda(\theta) \otimes \Psi(\theta) + b(\theta)$$

- $\Omega$ : Instrument broadening,  $\Lambda$ : Wavelength dispersion,  $\Psi$ : Specimen function.
- For single phase, minimize:

$$\Phi = \sum_{i=1}^N w_i \left( Y_i^{obs} - \left( b_i + K \sum_{j=1}^m I_j y_j(x_j) \right) \right)^2$$

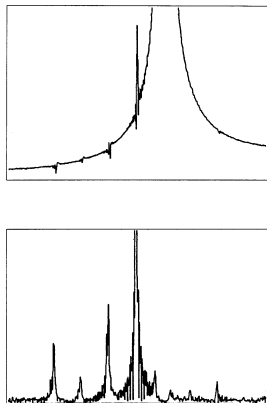
- where  $y_j(x_j)$  is typically a pseudo-Voigt (mix of Gaussian and Lorentzian function) function.
- Note that the background ( $b_i$ ) holds no useful structural information and should be minimized in experiments.

# Wavelet smoothing



- Complete orthonormal basis
- Shrink and select toward **sparse** representation.
- Able to represent both time and frequency localization efficiently (Fourier basis can only do frequency localization).

## Example: NMR Spectroscopy



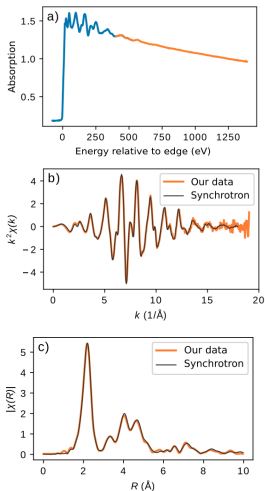
**Figure:** Subtraction of a large spectral line: (top) the original spectrum of polyethylene, (bottom) reconstructed spectrum after removal of  $\text{CH}_2$  peak.[3]

### Applications:

- Suppression of large unwanted spectral line (left).
- Rephasing spectrum perturbed by time-dependent magnetic field.
- Noise filtering
- Detecting phases in a mixture



# Example: Fourier transform for analysis of extended X-ray absorption fine structure (EXAFS)



- (a) The extended edge (orange part) contains information of atom chemical environment.
- (b) Subtract the background, convert energy to  $k$ -space unit, and multiply the normalized intensity by  $k^2$
- (c) Fourier transform  $k$ -space information to real space and obtain the first shell bond length.

# Bibliography



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# The End