10.34, Numerical Mehods Applied to Chemical Engineering
Professor William H. Green
Lecture #24: Uncertainties in model predictions.

Cookbook: How to Compare Models to Data

1) Model definition: Understand your model
2) Assess what you already knew before adjusting any parameters
3) Adjust parameters to find a choice $\underline{\theta}$ that makes data and model consistent
4) Refine parameters using the data (actually refine error bars on $\underline{\theta}$)

Model Definition

1) Write some equations → $\underline{Y}_{model}(\underline{x}_i, \underline{\theta}, \underline{q})$

numerical error in solving → Implicit ← Sensitivity Analysis $d/d\theta$

Explicit Algebra ← $\partial \underline{Y}_{max}/\partial\theta_n$ (→ $\underline{\theta}$)

parameters not to be adjusted (→ $\underline{q}$)

2) Where do the numbers in model come from? Error bars?
3) Approximations, Assumptions → Equations
4) Look for built in dependencies between θ's

(may not be able to separately determine each one)

→ Reformulate model to depend on $\underline{\tilde{\theta}}$

Assess what you already know.

May already have $p(\underline{\theta})$ from previous results

σ_i ← explicit uncertainties

$\pm\delta x$ $\pm\partial q_m$ → initial guess of $\underline{\theta}$ for nonlinear least squares $\chi^2(\underline{\theta}_{guess})$

Adjusting Parameters

$\min_{\underline{\theta}} \chi^2(\underline{\theta})$

such that $\theta_{n,min} < \theta_n < \theta_{n,max}$

Linear Model:

$Y_{model,i} = Y_{model}(\underline{x}_i) = \Sigma_n \theta_n \underline{F}_n(\underline{x}_i)$

$$\chi^2(\underline{\theta}) = \sum_{i=1}^{N_{data}} \left(\frac{Y_{i\,data} - Y_{i\,model}}{\sigma_i^2} \right) \qquad A_{in} \equiv \frac{F_n(\underline{x}_i)}{\sigma_i} \quad b_i \equiv \frac{Y_i^{data}}{\sigma_i}$$

$\chi^2 = ||\underline{\underline{A}}\cdot\underline{\theta} - \underline{b}||^2$

$$\frac{\partial \chi^2}{\partial \theta} = 0 \rightarrow \underbrace{(\underline{\underline{A}}^T\underline{\underline{A}})}\underline{\theta} = \underline{\underline{A}}^T\underline{b}$$

usually ill-conditioned

SVD $\underline{\underline{A}} = \underline{\underline{U}}\,\underline{\underline{\Lambda}}\,\underline{\underline{V}}^T$

$$\underline{\theta}_{best} = \sum_{i=1}^{N_{data}} \left(\frac{\underline{u}_i \cdot \underline{b}}{\lambda_i} \right) \underline{v}_i \pm \frac{v_1}{\lambda_1} \pm \frac{v_2}{\lambda_2} \pm \ldots$$

$\sigma^2(\theta_j) = \Sigma(v_{ji}/\lambda_i)^2$

covariance$(\theta_j,\theta_k) = \Sigma(v_{ji}v_{ki}/\lambda_i^2)$

When minimizing, consider Hessian:

$$\frac{\partial^2(\chi^2)}{d\theta_m d\theta_n} = \sum_{i=1}^{N_{data}} \frac{1}{\sigma_i^2} \frac{\partial Y_{model,i}}{\partial \theta_m} \frac{\partial Y_{model,i}}{\partial \theta_n} + \sum_{i=1}^{N_{data}} \left(\frac{Y_{i\,data} - Y_{i\,model}}{\sigma_i^2} \right) \frac{\partial^2 Y_{model,i}}{\partial \theta_m \partial \theta_n}$$

Usually just noise (2^{nd} derivative)

$\chi^2 = \chi^2(\theta_{best}) + ½(\underline{\theta} - \underline{\theta}_{best})\, H^T(\underline{\theta} - \underline{\theta}_{best})$

$½[\lambda_1(\tilde{v}_1)^2 + \lambda_2(\tilde{v}_2)^2]$

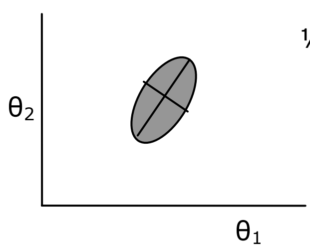

Figure 1. Two parameter fitting.