10.34, Numerical Methods Applied to Chemical Engineering
Professor William H. Green
Lecture #8: Constructing And Using The Eigenvector Basis.

Homework

1) For those who haven't programmed before – expect it to take time
2) If you get stuck and are beyond the point of learning, stop and move on. The homework is a learning activity.

Matrix Definitions

$\underline{\underline{A}} \cdot \underline{w}_i = \lambda_i \cdot \underline{w}_i$

eigenvalue of $\underline{\underline{A}}$ — an eigenvector of $\underline{\underline{A}}$

$\underline{\underline{A}} \cdot \underline{\underline{W}} = \underline{\underline{W}} \cdot \underline{\underline{\Lambda}}$

$$\underline{\underline{W}} = \begin{array}{c} \begin{pmatrix} \vdots & \vdots & \vdots \\ \vdots & \vdots & \vdots \\ \vdots & \vdots & \vdots \end{pmatrix} \\ w_1 \; w_2 \; w_3 \end{array} \qquad \underline{\underline{\Lambda}} = \begin{pmatrix} \lambda_1 & 0 & 0 \\ 0 & \lambda_2 & 0 \\ 0 & 0 & \lambda_3 \end{pmatrix}$$

symmetric: come from second derivatives of scalars

i.e. Hessians $\underline{\underline{H}}_{ij} = \dfrac{\partial^2 V}{\partial x_i \partial x_j}$ are always symmetrical

all real symmetric matrices are 'normal'

transpose of a complex-conjugate $(\underline{\underline{A}}^T)^* = \underline{\underline{A}}^H$ (Hermitian conjugate)

if $\underline{\underline{A}} = \underline{\underline{A}}^T$ 'symmetric'

if $\underline{\underline{A}} = \underline{\underline{A}}^H$ 'Hermitian'

if $\underline{\underline{A}} \cdot \underline{\underline{A}}^H = \underline{\underline{A}}^H \cdot \underline{\underline{A}}$ 'normal'

if $\underline{\underline{A}}^T = \underline{\underline{A}}^{-1}$ 'orthogonal'

if $\underline{\underline{A}}^H = \underline{\underline{A}}^{-1}$ 'unitary'

Square matrices (NxN)

$\underline{\underline{A}} = \underline{\underline{U}}\underline{\underline{R}}\underline{\underline{U}}^H$ $\underline{\underline{U}}$: unitary

upper triangular ($\underline{\underline{R}}$)

Schur decomposition: schur($\underline{\underline{A}}$)

$\underline{\underline{A}}$ could be dense matrix

$\underline{\underline{U}}$ has hermitian conjugate as inverse

If a real matrix is symmetric, it is also Hermitian.

For normal matrices $\underline{\underline{A}} = \underline{\underline{W}} \cdot \underline{\underline{\Lambda}} \cdot \underline{\underline{W}}^H$

diagonal — eigenvectors & unitary

$\underline{\underline{A}} \cdot \underline{\underline{W}} = \underline{\underline{W}} \cdot \underline{\underline{\Lambda}} (\cancel{\underline{\underline{W}}^H \cdot \underline{\underline{W}}})$ Back to eigenvalue problem

Hermitian matrices come up in quantum mechanics. All steady states in quantum mechanics are hermitian eigenvalue problems. Unitary matrices also come up in quantum mechanics and are basis transformations.

Hessian matrix: $H_{ij} = \frac{\partial^2 V}{\partial x_i \partial x_j}$. Always symmetric, because of the equality of mixed partials.

Because they are symmetric, they are also 'normal'.

Similarity Transform

$\underline{\underline{A}}\cdot\underline{w}_i = \lambda_i \underline{w}_i \quad \underline{\underline{B}}(\underline{\underline{S}}^{-1}\underline{w}_i) = \underline{\underline{S}}^{-1}\underline{\underline{A}}\overbrace{(\underline{\underline{S}}\cdot\underline{\underline{S}}^{-1})}^{\text{identity matrix}}\underline{w} = \underline{\underline{S}}^{-1}\underline{\underline{A}}\cdot\underline{w} = \underline{\underline{S}}^{-1}\lambda_i\underline{w}_i = \lambda_i(\underline{\underline{S}}^{-1}\underline{w}_i)$

$\underline{\underline{B}} = \underline{\underline{S}}^{-1}\underline{\underline{A}}\,\underline{\underline{S}}$ '$\underline{\underline{B}}$ is similar to $\underline{\underline{A}}$" $\underline{\underline{A}}$ & $\underline{\underline{B}}$ have the same eigenvalues

This is used in practice to calculate eigenvalues.

Find a diagonal matrix similar to $\underline{\underline{A}}$ to find eigenvalues of $\underline{\underline{A}}$.

$\underline{\underline{S}}_2^{-1}\ldots\underline{\underline{S}}_1^{-1}\underline{\underline{A}}\,\underline{\underline{S}}_1\ldots\underline{\underline{S}}_2 \rightarrow \rightarrow \underline{\underline{\Lambda}}$
continue to add $\underline{\underline{S}}$ and $\underline{\underline{S}}^{-1}$
on each side and eventually
you will get at the eingenvalues

How to find $\underline{\underline{S}}$?
if you're GOOD – find perfect $\underline{\underline{S}}$ such that $\underline{\underline{S}}\cdot\underline{\underline{A}}\cdot\underline{\underline{S}} = \underline{\underline{\Lambda}}$
very difficult to find this $\underline{\underline{S}}$ unless someone tells you the eigenvector

In quantum mechanics people use matrices of $10^9 \times 10^9$

"You have to be very crafty to find the $\underline{\underline{S}}$ of such a matrix."

$\underline{\underline{A}} = \underline{\underline{Q}}\cdot\underline{\underline{R}}$

orthogonal ($\underline{\underline{Q}}^{-1} = \underline{\underline{Q}}^T$)   upper triangular

$\underline{\underline{B}} = \underline{\underline{Q}}^{-1}\underline{\underline{A}}\cdot\underline{\underline{Q}}$ ($\underline{\underline{B}}$ is similar to $\underline{\underline{A}}$)

$= (\underline{\underline{Q}}^{-1}\underline{\underline{Q}})\underline{\underline{R}}\cdot\underline{\underline{Q}} = \underline{\underline{R}}\cdot\underline{\underline{Q}} = \underline{\underline{B}}$ (QR Algorithm is found in textbook and is very complex)

$\underline{\underline{A}}(c\cdot\underline{w}_i) = \lambda_i(c\cdot\underline{w}_i)$ does not matter how you scale, still get the same eigenvalue

eig($\underline{\underline{A}}$) gives eigenvalues/vectors   (see help eig)

*Uses EISPACK, which is available from netlib

Why is this useful?

singular matrix $\rightarrow \lambda_i = 0$

cond($\underline{\underline{A}}$) = $|\lambda|_{max}/|\lambda|_{min}$ trace: tr($\underline{\underline{A}}$) – sum of λ_i ($\Sigma(\lambda_i) = \Sigma a_{ii}$)

Example Problem

Initial Conditions

${}^{dy}/_{dt} = \underline{\underline{A}}\cdot\underline{y}$ $\underline{y}(t=0) = \underline{y}_0$

if $\underline{\underline{A}}$ is normal

${}^{dy}/_{dt} = \underline{\underline{W\Lambda W}}^H\underline{y}$ multiply both sides by $\underline{\underline{W}}^H$ $\underline{\underline{W}}^H\, {}^{dy}/_{dt} = \underline{\underline{W}}^H\underline{\underline{W\Lambda W}}^h\underline{y}$

${}^{d}/_{dt}(\underline{\underline{W}}^H\underline{y}) = \underline{\underline{\Lambda}}(\underline{\underline{W}}^H\underline{y})$ $\underline{q}(t) = \underline{\underline{W}}^H\underline{y}(t)$ ${}^{d\underline{q}}/_{dt} = \underline{\underline{\Lambda}}\underline{q}$ ${}^{d}/_{dt}(q_1) = \lambda_1 q_1$ $q_1 = q_{1,0}e^{\lambda_1 t}$

${}^{d}/_{dt}(q_2) = \lambda_2 q_2$ $\underline{q}_0 = \underline{\underline{W}}^H\underline{y}_0$ look at initial conditions

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Schur Decomposition

$\underline{y}(t) = \underline{\underline{W}}\cdot\underline{q}(t)$

$$\underline{y}(t) = \underline{\underline{W}} \begin{pmatrix} q_{o1} e^{\lambda_1 t} \\ q_{o2} e^{\lambda_2 t} \\ \vdots \end{pmatrix}$$

Using 'eig' function you can get $\underline{\underline{W}}$

Sometimes things are asymmetrical so 'eig' function will give you a matrix. However, you can always do Schur decomposition: $\underline{\underline{A}} = \underline{\underline{URU}}^H$

If you do Schur you get: $\frac{d}{dt}(\underline{\underline{W}}^H \underline{y}) = \lambda(\underline{\underline{W}}^H \underline{y})$

If $\underline{\underline{A}}$ were not normal, use Schur: $\underline{\underline{A}} = \underline{\underline{URU}}^H$

$\frac{dy}{dt} = \underline{\underline{U}} \cdot \underline{\underline{R}} \underbrace{(\underline{\underline{U}}^H \underline{y})}_{\underline{q}}$ $\qquad$ $\frac{d}{dt}\underset{(\underline{q})}{(\underline{\underline{U}}^H \underline{y})} = \underline{\underline{R}}\underline{q}$ $\qquad$ $\frac{d\underline{q}}{dt} = \underline{\underline{R}}\underline{q}$

$q_{last}(t) = q_{o,last} e^{\lambda t}$

$$\frac{dq_{N-1}}{dt} = R_{N-1,N-1} q_{N-1} + R_{N-1,N} q_N(t)$$

$$\frac{dq_{N-1}}{dt} = R_{N-1,N-1} q_{N-1} + R_{N-1,N} q_{N_0} e^{\lambda t_1}$$

$$R = \begin{pmatrix} 0 & \cdots & \cdots & \cdots \\ 0 & 0 & \cdots & \cdots \\ & & & \\ 0 & 0 & 0 & \lambda \end{pmatrix}$$

can get this if you weren't sleeping in ODE class
(this makes solution more difficult than EIG solution)

Quantum chemistry

Something more complicated

$\hat{H}\Psi(\underline{x}) = E\Psi(\underline{x})$ $\qquad$ $Q \sim \sum e^{-E_i / k_b T}$

interaction between fundamental particles $\qquad$ eigenvalues of equation $\qquad$ (thermo)

$\Psi(\underline{x}) = \Sigma c_i \varphi i(\underline{x})$

find these values that will solve $H\psi = E\psi$

Crafty Solution

$$\hat{H} \sum c_i \phi_i(x) = E \sum c_i \phi_i(x)$$

integrate and multiply by φ_n^*

$$\int \phi_n^* \hat{H} \left(\sum c_i \phi_i(x) \right) = \int E \left(\phi_n^* \sum c_i \phi_i(x) \right)$$

$$\sum c_i \underbrace{\int \phi_n^* \hat{H} \phi_i}_{H_{ni}} = E \sum c_i \underbrace{\int \phi_n^* \phi_i}_{\delta_{ni}}$$

Property of orthonormal basis functions: $\int \phi_j^* \phi_i \, dx = \delta_{ij}$

$$\sum c_i \int \phi_n^* \hat{H} \phi_i = E \sum c_i \int \phi_n^* \phi_i$$

$$\sum H_{ni} c_i = E c_n$$

$$\underline{\underline{H}}\underline{c} = E\underline{c} \qquad \{\text{Eigenvalue Problem}\}$$

Find the eigenvalues E. These are needed for calculations of G (free energy), thermodynamic constants, rate constants, and spectroscopic values.