10.34 Numerical Methods Applied to Chemical Engineering

Quiz 1

- This quiz consists of three problems worth 20, 40 and 40 points respectively. The problem statements are found on pages 2, 3 and 5 in this exam packet.

- You have 2 hours to complete the quiz.

- You are free to use a calculator or any notes you brought with you.

- It is important, however, that only the scientific – arithmetic and trigonometric – function of the calculator is used throughout the quiz. You are on your honor not to employ any built-in numerical linear algebra routines. This includes but is not limited to the calculation of determinants, eigenvalues, eigenvectors and solutions of linear equations.

- The ends of problems 2 and 3 provide an opportunity to do a little more work and earn 2 *bonus* points each. Be sure to complete the rest of the quiz before attempting these.

Problem 1 (20 points)–

1. (4 points) Create a real 2×2 matrix with a determinant and trace equal to 0 that is not the zero matrix (or explain why this is impossible)

   There are many possible answers but all reduce to the same matrix:

   $$\begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}$$

   (4 points) for a matrix that satisfies these constraints.

2. (4 points) Create a real 3×3 matrix with a determinant and trace equal to 6 (or explain why this is impossible)

   There are many possible answers. A diagonal matrix with trace and determinant equal to 6 would be:

   $$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 2 & 0 \\ 0 & 0 & 3 \end{pmatrix}$$

   (4 points) for a matrix that satisfies these constraints.

3. (6 points) Create a real 4×4 matrix with rank 2. Propose a vector $\mathbf{b} \in \mathbb{R}^4$ such that the system of equations $\mathbf{A}\mathbf{x} = \mathbf{b}$ has a family solutions. What is that family of solutions? Propose a vector $\mathbf{b} \in \mathbb{R}^4$ such that the system of equations $\mathbf{A}\mathbf{x} = \mathbf{b}$ has no solutions. Explain why this is the case.

   There are many possible answers. A diagonal matrix with rank 2 would be:

   $$\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}$$

   A value of $\mathbf{b} = (1, 0, 0, 0)$ would give a family of solutions $\mathbf{x} = (1, 0, a, b)$ where a and b are arbitrary. A value of $\mathbf{b} = (0, 0, 1, 0)$ would give no solution since this vector is not in the range space of the matrix.
   (2 points) for a rank 2 matrix.
   (1 point each) for a vector that admits a solution and the correct family.
   (1 point each) for a vector that does not admit a solution and the reason why.

4. (6 points) Notice that vectors from the null space of your matrix are orthogonal to the rows of that matrix. This is a general property of matrices which you will prove now. In particular, for a matrix $\mathbf{A} \in \mathbb{R}^{N \times M}$, prove that vectors from the null space, $\mathcal{N}(\mathbf{A})$, are orthogonal to vectors from the row space, $\mathcal{R}(\mathbf{A}^T)$.

   Let $\mathbf{y}$ be a vector in the null space of $\mathbf{A}$ so that $\mathbf{A}\mathbf{y} = 0$. Let $\mathbf{z}$ be a vector from the row space of $\mathbf{A}$ so that $\mathbf{z} = \mathbf{A}^T\mathbf{x}$. Then, $\mathbf{y}^T\mathbf{z} = \mathbf{y}^T\mathbf{A}^T\mathbf{x} = \mathbf{x}^T(\mathbf{A}\mathbf{y}) = 0$. Thus vectors from the

null space are orthogonal to vectors from the row space.
(2 points each) for correct definitions of null space and row space applied somewhere in the problem.
(2 points) for proving that the spaces are orthogonal.
(-3 points) for proving this using rows of matrix A but not generalizing to any vector in the row space

Problem 2 (40 points) –

Problem statement:

Biological signaling and regulation networks often involve *cycles* in which a protein backbone is transformed through a collection of modified states with different numbers of phosphate groups attached. A basic cycle might be described by the reaction network:

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C \xrightarrow{k_3} A,$$
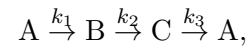
where A, B and C have the same protein backbone with different numbers of phosphate groups. Of course, some kind of energy input is required to maintain a cycle, which is not represented above.

Questions to be answered:

1. (2 points) Write down the stoichiometry matrix $\mathbf{S}$ for this reaction network.

$$\mathbf{S} = \begin{pmatrix} -1 & 0 & 1 \\ 1 & -1 & 0 \\ 0 & 1 & -1 \end{pmatrix}$$

   (2 points) for the correct matrix.

2. (5 points) Characterize the null space of $\mathbf{S}$ in terms of a dimension and a basis. What does this tell you about the fluxes (reaction rates) in the network at steady state? What physical interpretation can you provide for this?

   The null space has dimension 1 and a basis: $(1, 1, 1)$. This indicates that the fluxes are equal at steady state.
   (3 points) for the correct dimension
   (2 points) for a correct basis

3. (5 points) Characterize the left null space of $\mathbf{S}$ in terms of a dimension and a basis. What does this tell you about the time evolution of the protein concentrations? What physical interpretation can you provide for this?

   The left null space has dimension 1 and a basis: $(1, 1, 1)$. This indicates that the sum of the protein concentrations is constant in time.
   (3 points) for the correct dimension
   (2 points) for a correct basis

4. (5 points) Write down a model for the dynamics of the protein concentrations in a compartment of a mammalian cell using matrix-vector notation. State any assumptions in your model.

$$\frac{d\mathbf{c}}{dt} = \mathbf{S} \begin{pmatrix} k_1 & 0 & 0 \\ 0 & k_2 & 0 \\ 0 & 0 & k_3 \end{pmatrix} \mathbf{c}$$

   This assumes that the cell is well mixed and acts like a batch reactor with constant volume, the cell is isothermal (so that k_i can be treated constant), the reactions are elementary and first-order, and that protein neither enters nor leaves the cell.
   (3 points) for a model of a batch reaction.
   (2 points) for model assumptions and some discussion of the limits of applicability.

5. (8 points) Let $k_1 = 1$, $k_2 = 2$ and $k_3 = 1$. Does your model admit a steady-state solution? If so, describe it physically? Is that solution stable?

The model does admit a steady state solution since

$$\det\left[\mathbf{S}\begin{pmatrix} k_1 & 0 & 0 \\ 0 & k_2 & 0 \\ 0 & 0 & k_3 \end{pmatrix}\right] = \det \underbrace{\begin{pmatrix} -1 & 0 & 1 \\ 1 & -2 & 0 \\ 0 & 2 & -1 \end{pmatrix}}_{\mathbf{SK}} = 0.$$

This solution is characterized by the null space of the above matrix, which is easily observed to be of dimension 1 with a basis of $(2, 1, 2)$. This follows from $r_1 = r_2 = r_3$ at steady state, which implies $k_1 C_A = k_2 C_B = k_3 C_B$ such that $C_A = 2C_B = C_B$ at steady state (this fits with the null space of the $\mathbf{SK}$ matrix). That is, the steady state solution has A and C with equal concentrations with values twice that of the concentration of B. The stability of the solution can be determined by examining the eigenvalues of the above matrix. These are described by the secular polynomial:

$$\det\left[\mathbf{S}\begin{pmatrix} k_1 & 0 & 0 \\ 0 & k_2 & 0 \\ 0 & 0 & k_3 \end{pmatrix} - \lambda\mathbf{I}\right] = (-k_1 - \lambda)(-k_2 - \lambda)(-k_3 - \lambda) + k_1 k_2 k_3$$

$$= -\lambda(\lambda^2 + (k_1 + k_2 + k_3)\lambda + k_1 k_2 + k_1 k_3 + k_2 k_3).$$

Therefore, $\lambda = 0$ or

$$\lambda = \frac{-(k_1 + k_2 + k_3) \pm \sqrt{(k_1 + k_2 + k_3)^2 - 4(k_1 k_2 + k_1 k_3 + k_2 k_3)}}{2}$$

$$= \frac{-4 \pm \sqrt{4^2 - 4(2 + 1 + 2)}}{2}$$

$$= \frac{-4 \pm \sqrt{-4}}{2}$$

$$= -2 \pm i$$

We see that we do not have any eigenvalue with positive real part, so the system is stable. One eigenvalue is zero, so the system is neutrally stable. The other two eigenvalues are complex, which induces oscillations in the solution. However, these oscillations decay (because the real part of these complex eigenvalues are negative) and thus the system will approach a (non-zero) steady state.

(4 points) for recognizing the steady state solution and describing it.

(2 points) for calculating the eigenvalues of $\mathbf{SK}$

(2 points) for identifying that the eigenvalues have non-positive real parts and thus the steady-state solution is stable.

Now let us consider a cycle of length N

$$\text{A} \xrightarrow{k_1} \text{B} \xrightarrow{k_2} \text{C} \xrightarrow{k_3} \text{D} \xrightarrow{k_4} \cdots \xrightarrow{k_N} \text{A},$$
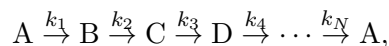
6. (5 points) Sketch the sparsity pattern of the stoichiometry matrix $\mathbf{S}$ for this N component cyclic system.

The sparsity pattern has a diagonal element, an element below the diagonal, and a single element in the first row and last column.

$$\begin{pmatrix} -1 & 0 & \dots & 0 & 1 \\ 1 & -1 & \ddots & 0 & 0 \\ 0 & 1 & -1 & \ddots & 0 \\ \vdots & \ddots & \ddots & \ddots & \vdots \\ 0 & 0 & \dots & 1 & -1 \end{pmatrix}$$

(3 points) for a sparsity pattern that includes the diagonal and lower diagonal
(2 points) for the additional element in row 1, column N.

7. (5 points) Write a MATLAB®function that takes advantage of this sparsity pattern to compute the product of $\mathbf{S}$ with a vector. Your function should take as an input the fluxes associated with each reaction in the cycle and return the rate of change for the concentration of each species in the cycle. Be sure that your function does not compute the stoichiometry matrix explicitly.

```
function y = sparse_mult( x )

    y(1) = -x(1) + x(end)

    for i = 2:length(x)

        y(i) = x(i-1) - x(i);

    end;
```

(1 points) for a working function
(4 points) for the sparse implementation

8. (5 points) Develop an expression for the characteristic polynomial of the N component stoichiometry matrix, $\mathbf{S}$. The roots represent the eigenvalues of $\mathbf{S}$.

$$\det(\mathbf{S} - \lambda\mathbf{I}) = (-1 - \lambda)M_{11} + (-1)^{N-1}M_{1N} = 0$$

Because the minors are determinants of diagonal/upper triangular matrices, these are simple to calculate: $M_{11} = (-1 - \lambda)^{N-1}$, $M_{1N} = 1$. Therefore the secular polynomial satisfies $(-1 - \lambda)^N + (-1)^{N-1} = 0$.
(3 points) for utilizing the determinant defined in terms of minors.
(2 points) for arriving at the correct equation.

Problem 3 (40 points) −

Problem statement:

An autocatalytic reaction converts A to B as

$$A + 2B \rightarrow 3B.$$

The reaction is elementary so the net rates of consumption/formation of A and B are

$$r_A = -r_B = -k[A][B]^2.$$

where k is the rate constant.

If the reaction takes place in an isothermal, continuously stirred tank, the concentrations of species A and B exiting the reactor at time t, denoted C_A and C_B, satisfy the equation:

$$\frac{d}{dt}\begin{pmatrix} C_A \\ C_B \end{pmatrix} = \begin{pmatrix} \theta^{-1}(C_{A,f} - C_A) - kC_A C_B^2 \\ \theta^{-1}(C_{B,f} - C_B) + kC_A C_B^2 \end{pmatrix}. \tag{1}$$

Here, θ is the residence time in the reactor and $C_{A,f}$ and $C_{B,f}$ are the concentrations of species A and B fed to the reactor. We seek the concentrations of A and B in the effluent when the reactor reaches steady-state: $dC_A/dt = dC_B/dt = 0$.

Problem 3 (cont.) –

Questions to be answered:

1. (4 points) Show that at steady-state, equation 1 can be written as a system of nonlinear equations:

$$0 = \mathbf{f}(\hat{C}_A, \hat{C}_B) = \begin{pmatrix} \alpha \left(1 - \hat{C}_A \right) - \hat{C}_A \hat{C}_B^2 \\ \alpha \left(\beta - \hat{C}_B \right) + \hat{C}_A \hat{C}_B^2 \end{pmatrix}, \tag{2}$$

where $\hat{C}_A = C_A/C_{A,f}$, $\hat{C}_B = C_B/C_{A,f}$, $\alpha = (k\theta C_{A,f}^2)^{-1}$, and $\beta = C_{B,f}/C_{A,f}$. This dimensionless form of the species balance at steady-state will prove useful in the remainder of the problem.

This is a trivial exercise in setting the derivative equal to zero and factoring the resulting equation.
(1 point) for stating $\frac{d(C_A, C_B)}{dt} = 0$ at steady state
(3 points) for arriving at the correct equation

2. (10 points) Calculate the Jacobian, $\mathbf{J}_f(\hat{C}_A, \hat{C}_B)$, of the vector-valued function, $\mathbf{f}(\hat{C}_A, \hat{C}_B)$, from equation 2. Under what conditions (α, β, $\hat{C}_A$, $\hat{C}_B$) will the Jacobian be singular? Assume these quantities take on physical values – that is, they are real and non-negative. In each of those circumstances, find a vector that belongs to the null space of the Jacobian.

The Jacobian is

$$\mathbf{J} = \begin{pmatrix} -\alpha - \hat{C}_B^2 & -2\hat{C}_A\hat{C}_B \\ \hat{C}_B^2 & -\alpha + 2\hat{C}_A\hat{C}_B \end{pmatrix}.$$

The Jacobian is singular when

$$0 = \det \mathbf{J} = (\alpha + \hat{C}_B^2)(\alpha - 2\hat{C}_A\hat{C}_B) + 2\hat{C}_A\hat{C}_B^3 = \alpha^2 + \alpha\hat{C}_B(\hat{C}_B - 2\hat{C}_A).$$

So either $\alpha = 0$ or

$$\hat{C}_A = \frac{1}{2} \left(\frac{\alpha}{\hat{C}_B} + \hat{C}_B \right).$$

When $\alpha = 0$, the Jacobian is

$$\mathbf{J} = \begin{pmatrix} -\hat{C}_B^2 & -2\hat{C}_A\hat{C}_B \\ \hat{C}_B^2 & 2\hat{C}_A\hat{C}_B \end{pmatrix}.$$

Vectors in the null space of this matrix are proportional to $(1, -\hat{C}_B/(2\hat{C}_A))$.
When $\hat{C}_A = (\alpha/\hat{C}_B + \hat{C}_B)/2$, with $\hat{C}_B \neq 0$, the Jacobian is

$$\mathbf{J} = \begin{pmatrix} -\alpha - \hat{C}_B^2 & -\alpha - \hat{C}_B^2 \\ \hat{C}_B^2 & \hat{C}_B^2 \end{pmatrix}.$$

Vectors in the null space of this matrix are proportional to $(1, -1)$.
(5 points) for the correct Jacobian.
(1 point) for correct expression for det$\mathbf{J}$=0
(1 point each) for the two conditions that make the determinant zero.
(1 point each) for two correct null space vectors.

3. (8 points) When $\beta = 0$, no B is fed to the reactor and no A is converted. Therefore, the steady-state concentrations are $\hat{C}_A = 1$, $\hat{C}_B = 0$. Sketch an algorithm that would use this information to accelerate a search for the steady state solution at another value of the parameters (α, β), say $(1, 1)$.

Describe how to use continuation to track from an initial set of parameters $(\alpha, \beta) = (1, 0)$ to $(1, 1)$. Sketch out the loops that would be employed and specify the solution method for the nonlinear equation.
(4 points) for recognizing that continuation is the appropriate procedure.
(4 points) for a working sketch of the algorithm that includes the correct initial state (1 point), the search space (1 point) and details for the solution method of $\mathbf{f} = 0$ using the previous solution as the initial condition (2 points).

4. (10 points) In a CSTR, an autocatalytic reaction can exhibit multiple steady-states. The steady-state mass balance requires that: $C_{A,f} + C_{B,f} = C_A + C_B$. This can be used to recast equation 2 as a single, cubic equation for the steady-state concentration of A or B, which may admit as few as one and as many as three solutions depending on the values of the parameters α and β. There may be a connected set of points (α, β) at which this bifurcation occurs. Describe in detail a computational approach to finding the elements of this parameter set – that is, an algorithm to search for values of α, β at which the CSTR begins to possess multiple steady states.

The key here is to recognize that $\det \mathbf{J} = 0$ at a bifurcation point. Since we are searching a two dimensional parameter space, there are a number of different ways to effect a search. In one, you might fix the value of α and change β until you find a sign change in $\det \mathbf{J}$. Then you could solve the augmented equations to find the exact value of β at which the bifurcation occurs. This could be repeated for many values of α. A continuation procedure using the exact value of β and the steady state solution at a found bifurcation point could be used to expedite the search. Since not all values of α will necessarily have a bifurcation, we could search for where the Jacobian of the augmented equations become singular. This will be the first point in the space (α, β) at which multiple steady states begin to exist. For this method, we find the solution $(\hat{C}_A, \hat{C}_B, \alpha, \beta)$ to

$$\begin{pmatrix} \mathbf{f} \\ \det \mathbf{J} \\ \det \begin{pmatrix} \mathbf{J} & d\mathbf{f}/d\beta \\ \nabla \det \mathbf{J} & d\det \mathbf{J}/d\beta \end{pmatrix} \end{pmatrix} = 0,$$

where ∇ is the gradient with respect to $(\hat{C}_A, \hat{C}_B)$. This is the first value of α, β at which the bifurcation occurs. One can show that this critical point is $\hat{C}_A = 3/4, \hat{C}_B = 3/8, \alpha =$

$27/64, \beta = 1/8$. The null space of the Jacobian of these augmented-augmented equations will suggest the directions to perturb a search for the bifurcation throughout the parameter space.
(4 points) For describing the correct condition for a bifurcation.
(4 points) For detailing an algorithm that searches the parameter space for this point is some fashion.
(2 points) For describing a solution of the augmented equations $\mathbf{f} = 0$, $\det \mathbf{J} = 0$ to find the exact value of either α or β at which the bifurcation occurs given a corresponding value of β or α, respectively.

5. (8 points) When $(\alpha, \beta) = (1, 1)$, Newton's method converges to the solution: $\hat{C}_A^* = 0.2451$, $\hat{C}_B^* = 1.7549$. You will evaluate the stability of this steady state solution to the ODE:

$$\frac{d}{d\hat{t}} \begin{pmatrix} \hat{C}_A \\ \hat{C}_B \end{pmatrix} = \mathbf{f}(\hat{C}_A, \hat{C}_B). \tag{3}$$

Use a Taylor expansion about the steady state solution to show that:

$$\frac{d}{d\hat{t}} \begin{pmatrix} \hat{C}_A - \hat{C}_A^* \\ \hat{C}_B - \hat{C}_B^* \end{pmatrix} = \mathbf{J}_f(\hat{C}_A^*, \hat{C}_B^*) \begin{pmatrix} \hat{C}_A - \hat{C}_A^* \\ \hat{C}_B - \hat{C}_B^* \end{pmatrix}, \tag{4}$$

when $\|(\hat{C}_A - \hat{C}_A^*, \hat{C}_B - \hat{C}_B^*)\|_p \Rightarrow 0$. Use this linear equation to evaluate the stability of the steady state solution. Under what conditions can this result be expected to hold?

It is important to recognize that $\mathbf{f}(\hat{C}_A^*, \hat{C}_B^*) = 0$ since it is the steady state solution. Additionally, $d/dt(C_A^*, C_B^*) = 0$ since the steady state solution is independent of time.

$$\frac{d}{d\hat{t}} \begin{pmatrix} \hat{C}_A - \hat{C}_A^* \\ \hat{C}_B - \hat{C}_B^* \end{pmatrix} = \frac{d}{d\hat{t}} \begin{pmatrix} \hat{C}_A \\ \hat{C}_B \end{pmatrix} - \underbrace{\frac{d}{d\hat{t}} \begin{pmatrix} \hat{C}_A^* \\ \hat{C}_B^* \end{pmatrix}}_{0} = \mathbf{f}(\hat{C}_A, \hat{C}_B)$$

Then we apply a Taylor series expansion about $(\hat{C}_A^*, \hat{C}_B^*)$ to the right hand side of the above equation:

$$\mathbf{f}(\hat{C}_A, \hat{C}_B) \approx \underbrace{\mathbf{f}(\hat{C}_A^*, \hat{C}_B^*)}_{0} + \mathbf{J}_f(\hat{C}_A^*, \hat{C}_B^*) \begin{pmatrix} \hat{C}_A - \hat{C}_A^* \\ \hat{C}_B - \hat{C}_B^* \end{pmatrix} + O(\hat{\mathbf{C}}^2),$$

where $\hat{\mathbf{C}} = (\hat{C}_A, \hat{C}_B)$. In the limit of small $\|(\hat{C}_A - \hat{C}_A^*, \hat{C}_B - \hat{C}_B^*)\|_p$, we neglect the 2nd and higher order terms. Combining the results from the above two equations, we arrive at the final expression,

$$\frac{d}{d\hat{t}} \begin{pmatrix} \hat{C}_A - \hat{C}_A^* \\ \hat{C}_B - \hat{C}_B^* \end{pmatrix} = \mathbf{f}(\hat{C}_A, \hat{C}_B) = \mathbf{J}_f(\hat{C}_A^*, \hat{C}_B^*) \begin{pmatrix} \hat{C}_A - \hat{C}_A^* \\ \hat{C}_B - \hat{C}_B^* \end{pmatrix}$$

The eigenvalues of the Jacobian dictate the stability since this is a linear differential equation:

$$\det(\mathbf{J} - \lambda \mathbf{I}) = (-\alpha - \hat{C}_B^{*2} - \lambda)(-\alpha + 2\hat{C}_A^* \hat{C}_B^* - \lambda) - (-2\hat{C}_A^* \hat{C}_B^*)(\hat{C}_B^{*2})$$

$$= \lambda^2 + (\alpha + \hat{C}_B^{*2} + \alpha - 2\hat{C}_A^* \hat{C}_B^*)\lambda + 2\hat{C}_A \hat{C}_B^{*3} + (\alpha + \hat{C}_B^{*2})(\alpha - 2\hat{C}_A^* \hat{C}_B^*) = 0$$

$$\Rightarrow \lambda = -\alpha, -\alpha + 2\hat{C}_A \hat{C}_B^* - \hat{C}_B^{*2} = -1, -3.219$$

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The eigenvalues are negative, so that the perturbation to the steady state solution: $(C_A - C_A^*, C_B - C_B^*)$ decays to zero exponentially in time. This means the steady state is stable, but only to small perturbations since a Taylor expansion in the limit of small $\|(\hat{C}_A - \hat{C}_A^*, \hat{C}_B - \hat{C}_B^*)\|_p$ was used to evaluate the stability.

(1 point) for $\mathbf{f}(\hat{C}_A^*, \hat{C}_B^*) = 0$.

(3 points) for the Taylor expansion

(1 point) for stating that stability of the steady state solution is determined by the eigvenvalues of the Jacobian matrix

(3 points) for calculating the eigenvalues and determining the stability of the system

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Fall 2015