Chem237: Lecture 1

Shane Flynn, Alan Robledo

4/5/18

Course Overview

The course will not directly follow the textbook. However, it will provide a rough guideline for important topics. The lecture and homework are the most important aspects of the course. The homework will be split into both analytical and numerical problems, any programming language is fine for the numerical problems. However, mathematica and other highly developed languages are discouraged. For the numerical problems, if you are asked to make an algorithm, you CANNOT use pre-built algorithms available to the languages.

Chapter 1: Differential Equations

A Differential Equation simply refers to an equation containing a function and its derivatives. An **Ordinary Differential Equation** (ODE) refers to any differential equation with functions that depend on only one independent variable. In contrast a **Partial Differential Equation** (PDE) contains functions that depend on more than one independent variable. We can further categorize differential equations (both ODE and PDE) into linear or nonlinear. As you can imagine, linear equations are simpler to solve compared to nonlinear ones and ODEs are easier to solve than PDEs.

Linear Equations

Linear Equations are a general topic; there are linear differential equations, linear algebraic equations, and etc. A linear equation has the form

$$\hat{A}f(x, y, \ldots) = B(x, y, \ldots) \tag{1}$$

Where the RHS (B) is known, and the function f is an unknown function. To be a linear equation, the operator $\hat{A}$ must be a linear operator. For example, take the equation above and let $\hat{A}$ be the differential operator wrt a single dimension, and you get a linear ordinary differential equation.

If the RHS (B) is equal to 0, the linear equation is called **Homogeneous** and if the RHS is anything other than 0, the linear equation is called **Inhomogeneous**. Another way to explain this is by saying that if every term in the differential equation contains the function f or any of its derivatives, it is called Homogenous. If there is at least one term that does not contain the function and/or its derivative, it is called Inhomogeneous.

Homogeneous Linear Equations

Consider equation **??** below

$$\hat{A}f = 0 \tag{2}$$

If we assume f_1 and f_2 are solutions to equation **??**, then by the principle of superposition, we immediately know another solution to be a linear combination of f_1 and f_2

$$f_3 = c_1 f_1 + c_2 f_2. \tag{3}$$

This result is true for any set of linear homogeneous equations. The linear combination of two unique solutions to a linear homogeneous equation gives another unique solution.

Inhomogeneous Linear Equations

If we now consider the Inhomogeneous linear equation, equation **??**

$$\hat{A}f = B \tag{4}$$

we can construct the solution to this equation as

$$f = f_0 + \sum_i c_i f_i \tag{5}$$

Where the specific solution f_0 is known as a **Particular Solution** and the f_i solutions refer to the solutions of the associated homogeneous equation. Finding the particular solution can be done by choosing from a number of methods from the Method of Undetermined Coefficients to the Method of Variation of Parameters.

ODE: Linear, Homogeneous, Constant Coefficients

We will start with the simplest ODEs, the linear, homogeneous, constant coefficient expressions. Various books use different notation for presenting ODEs. For example, it is very common in physics to consider functions that only depend on time ==> x = x(t). We may switch between using t and x as independent variables in class. If you are given a differential equation and cannot determine the independent variable by inspection, you can make the variable whatever you want.

We can also define notation for a derivative as

$$x^(n) \equiv \frac{d^n}{dt^n}x \equiv D^n x \tag{6}$$

Hopefully it is clear that D is the linear differential operator. If you apply a linear operator n times it is still linear, therefore D^n is also a linear operator. The general form of these differential equations is

$$\sum_{n=0}^{N} a_n x^{(n)} = f(t) \tag{7}$$

If we consider the homogeneous, linear, constant coefficients case, then equation **??** simplifies to

$$\sum_{n=0}^{N} a_n x^{(n)} = 0 \tag{8}$$

To solve these equations, we assume a solution of the form: x(t) = $e^{\lambda t}$ and substitute this into equation **??**.

$$\begin{aligned}
\sum_{n=0}^{N} a_n x^{(n)} &= 0 \\
\sum_{n=0}^{N} a_n \left(e^{\lambda t}\right)^{(n)} &= 0 \\
\sum_{n=0}^{N} a_n \lambda^n e^{\lambda t} &= 0 \\
e^{\lambda t}\sum_{n=0}^{N} a_n \lambda^n &= 0 \\
\sum_{n=0}^{N} a_n \lambda^n &= 0
\end{aligned} \tag{9}$$

The last line is known as the **Characteristic Polynomial** and it helps us find the general solution to the linear constant coefficient ODE. The above polynomial is of degree N, and a theorem in ODEs says that there exists exactly N roots (in general complex) that can potentially be degenerate.

The reason for using this approach comes solely from mathematical intuition. Our differential equation requires a function x(t) such that the function and its derivatives cancel out to satisfy the RHS. The only function we know of that satisfies this condition is x(t) = $e^{\lambda t}$. In order to account for different multiples of the function, we include the λ in our assumed solution, since its derivative is equal to λ $e^{\lambda t}$. One would think that trigonometric functions and several derivatives of itself can satisfy this condition as well. While this may sometimes be true, it is not true generally. Even if you consider a combination of sine and cosine, such a function would not always work. Consider the example ODE below,

$$\frac{dy}{dt} + y = 0. \tag{10}$$

Suppose that we assume the solution to be x(t) = sin(λt) + cos(λt). Plugging this and its derivative into the original equation yields

$$\lambda \cos(\lambda t) - \lambda \sin(\lambda t) + \sin(\lambda t) + \cos(\lambda t) = 0. \tag{11}$$

However, there are no values of λ that could satisfy this equation. Therefore, we are only left with generally assuming that the solution to linear, constant coefficient ODEs is an exponential function to avoid situations similar to the above example.

We begin exploring situations of non-degenerate and degenerate roots of the characteristic polynomial by starting with the non-degenerate case (i.e. $\lambda_i \neq \lambda_j$). Since each root of the polynomial gives us the λ_n in the general solution, we can write the general solution to the ODE as

$$x(t) = \sum_{n=1}^{N} c_n e^{\lambda_n t} \tag{12}$$

Finding the general solution for the degenerate case is not as straightforward because if we have two roots that are the same (e.g. $\lambda_1 = \lambda_2$), we would not be able to form 2 unique solutions from these roots. We would only be able to form one unique solution. However, there are multiple ways to show that for each repeated root, each solution will be different by a multiple of the exponential. For example, if we had a 3rd order linear ODE with repeated roots, $\lambda_1 = \lambda_2 = \lambda_3$, the general solution would be

$$x(t) = c_1 e^{\lambda_1 t} + c_2 t e^{\lambda_1 t} + c_3 t^2 e^{\lambda_1 t}. \tag{13}$$

There are 2 ways to show that this can be done for repeated roots of the characteristic polynomial. For the first way, consider the following second order ODE with constant coefficients

$$a\frac{d^2y}{dt^2} + b\frac{dy}{dt} + cy = 0 \tag{14}$$

If the above ODE has two repeated roots, λ_1 and λ_2, we can say that one unique solution to the ODE is

$$y_1(t) = c_1 e^{\lambda_1 t} \tag{15}$$

Let's first assume we do not have a degeneracy so we would have $\lambda_1 \neq \lambda_2$. We can consider evaluating the following limit to obtain the resulting second unique solution

$$\lim_{\lambda_1 \to \lambda_2} \frac{e^{\lambda_2 t} - e^{\lambda_1 t}}{\lambda_2 - \lambda_1} = te^{\lambda_1 t}. \tag{16}$$

For the second way, we again consider equation **??**. Since one unique solution is $c_1 e^{\lambda_1 t}$, we can replace the constant c_1 with a function v(t) and try to determine the function v(t) such that $v(t)e^{\lambda_1 t}$ is also a solution of equation **??**. After plugging in your new guess for the second solution into the original ODE, you will obtain a new differential equation for v(t). You can see for yourself that your v(t) will be equal to t or some multiple of t.

In general an Nth order equation, assuming degenerate roots

$$\sum_{n=0}^{N} a_n x^{(n)} = 0 \xrightarrow{\text{degenerate}} \sum_{n=0}^{N} a_n \lambda^n = 0. \tag{17}$$

In the degenerate case, this maps to

$$\sum_{n=0}^{N} a_n \lambda^n = 0 \Leftrightarrow (\lambda - \lambda_1)^{k_1} (\lambda - \lambda_2)^{k_2} \cdots = 0 \tag{18}$$

With a general solution of

$$x(t) = \left(A_0 + A_1 t + A_2 t^2 + \cdots + A_{k_1} t^{k_1}\right) e^{\lambda_1 t} + \left(B_0 + B_1 t + B_2 t^2 + \cdots + B_{k_2} t^{k_2}\right) e^{\lambda_2 t} \tag{19}$$

Where there are N free paramaters such that $k_1 + k_2 + \cdots = N$.

Damped Harmonic Oscillator

Let's consider an example, the **Damped Harmonic Oscillator**; a very common physics example with analytic solutions.

$$\frac{d^2}{dt^2}x + 2\gamma\frac{d}{dt}x + \omega_o^2 x = 0 \tag{20}$$

The γ is interpreted as the damping constant, and the ω_o term is interpreted as the frequency of oscillations if no damping was present, aka the natural frequency. While we do not live in an imaginary world, we would prefer to generalize $x(t)$ by making it a complex function. If we ever need to compute real observables of the oscillator, this can be done by just taking the real part of the general solution. Now, if we assume ==> x = $e^{\lambda t}$ we can find the characteristic equation.

$$\lambda^2 + 2\gamma\lambda + \omega^2 = 0 \tag{21}$$

Since the ODE is second order, we can predict that the characteristic equation will be quadratic with two roots λ_+ and λ_-

$$\lambda_\pm = -\gamma \pm \sqrt{\gamma^2 - \omega_o^2}. \tag{22}$$

In order to observe the behavior of the oscillator (i.e. solve the differential equation), we need to consider 3 different cases:

1. $\omega > \gamma$, the underdamped solution.
2. $\omega < \gamma$, the overdamped solution.
3. $\omega = \gamma$, the degenerate solution ($\lambda_1 = \lambda_2$).

Underdamping ($\omega_o > \gamma$)

In the case of underdamping, the damping constant is small compared to ω_o. In this case, the square root in equation **??** is imaginary and we can say

$$\sqrt{\gamma^2 - \omega_o^2} = i\Omega = i\sqrt{\omega_o^2 - \gamma^2} \tag{23}$$

Therefore,

$$\lambda_\pm = -\gamma \pm i\Omega. \tag{24}$$

And we can write the general solution as

$$\begin{aligned} x(t) &= c_1 e^{(-\gamma+i\Omega)t} + c_2 e^{(-\gamma-i\Omega)t} \\ &= e^{-\gamma t}(c_1 e^{i\Omega t} + c_2 e^{-i\Omega t}) \end{aligned} \tag{25}$$

Here c_1 and c_2 can be complex. The term within parenthesis is an oscillating component, and the outside terms shows an exponential decay.

Now that we have found the general solution, we would like to plot the position as a function of time. Since it is difficult to visualize in its current form, let's rewrite it in terms of sine and cosine using euler's identity

$$\begin{aligned} x(t) &= e^{-\gamma t}\left[c_1(\cos(\Omega t) + i\sin(\Omega t)) + c_2(\cos(\Omega t) - i\sin(\Omega t))\right] \\ x(t) &= e^{-\gamma t}\left[(c_1 + c_2)\cos(\Omega t) + i(c_1 - c_2)\sin(\Omega t)\right] \end{aligned} \tag{26}$$

and introduce new coefficients B_1 and B_2

$$\begin{aligned} B_1 &= c_1 + c_2 \\ B_2 &= i(c_1 - c_2). \end{aligned} \tag{27}$$

This turns the general solution into

$$x(t) = e^{-\gamma t}\left[B_1 cos(\Omega t) + B_2 sin(\Omega t)\right] \tag{28}$$

Since we know that $x(t)$ is real, along with $\cos(\Omega t)$ and $\sin(\Omega t)$, c_1 and c_2 must be chosen carefully to ensure that B_1 and B_2 are real. To continue reducing the solution to a more manageable form, we need to introduce one last variable

$$A = \sqrt{B_1^2 + B_2^2} \tag{29}$$

where B_1 and B_2 can be thought of as the adjacent and opposite sides of a right triangle, respectively, with A as the hypotenuse and δ as the lower angle. With that, we can use some geometry to rewrite the general solution as

$$\begin{aligned} x(t) &= Ae^{-\gamma t}\Big[\frac{B_1}{A}cos(\Omega t) + \frac{B_2}{A}sin(\Omega t)\Big] \\ &= Ae^{-\gamma t}[cos(\delta)cos(\Omega t) + sin(\delta)sin(\Omega t)] \\ &= Ae^{-\gamma t}cos(\Omega t - \delta) \end{aligned} \tag{30}$$

where we used the trig identity $cos(A)cos(B) + sin(A)sin(B) = cos(A - B)$.

We now have a very nice and compact equation to describe the motion of the oscillator. By looking at the solution in this form, we can see that the oscillatory motion comes from the cosine term and the oscillator tending towards equilibrium comes from the negative exponential term.

Overdamping ($\omega_o < \gamma$)

The overdamping case can be physically interpreted as having a very large friction contribution. In the case of overdamping, the square root in equation **??** is real and not complex, so we can just write the general solution as

$$\begin{aligned} x(t) &= c_1e^{-\gamma+\sqrt{\gamma^2-\omega_o^2}} + c_2e^{-\gamma-\sqrt{\gamma^2-\omega_o^2}} \\ &= c_1e^{-(\gamma-\sqrt{\gamma^2-\omega_o^2})} + c_2e^{-(\gamma+\sqrt{\gamma^2-\omega_o^2})} \end{aligned} \tag{31}$$

The reason for rewriting the general solution is to see more clearly what is happening to the oscillator's position by noticing the two negative exponential terms. In the case of overdamping, the resistive force, proportional to the damping constant, dominates the spring force. So once the oscillator is kicked at time t = 0, it will move to its maximum displacement and then quickly decay to zero displacement without anymore oscillations.

Critical Damping ($\omega_o = \gamma$)

In the case of critical damping, the damping constant is equal to the natural frequency, $\lambda_+ = \lambda_-$. To find the general solution, we can use either of the two methods discussed earlier when we have repeated roots of the auxiliary equation. So the general solution can be written as

$$x(t) = (c_1 + c_2t)e^{\lambda_+ t} = (c_1 + c_2t)e^{\lambda_- t} \tag{32}$$

With arbitrary constants c_1 and c_2. This means that the characteristic equation has two equal roots and the general solution can be written as

$$\begin{aligned} x(t) &= c_1e^{\lambda_1 t} + c_2te^{\lambda_2 t} \\ &= c_1e^{-\gamma t} + c_2te^{-\gamma t} \end{aligned} \tag{33}$$

Here we see that our ODE is second order, and we get 2 free (potentially complex) parameters, meaning the dimensionality of the solution space is 2.

Inhomogeneous Linear ODE (constant Coefficients)

The general form for an inhomogeneous equation with constant coefficients is given by

$$\sum_{n=0}^{N} a_n x^{(n)} = f(t). \tag{34}$$

A well known example of the n=2 case is the **Driven Harmonic Oscillator**. The general solution for this problem is of the form

$$x(t) = x_0(t) + \sum_{n=1}^{N} c_n x_n(t) \tag{35}$$

Where $x_0(t)$ is a **Particular Solution** to the inhomogeneous equaiton, and $x_n(t) = e^{\lambda_n t}$. Unfortunately there is no general method to solve for the particular solution. But it is very convenient to use the **Method of Undetermined Coefficients**. The following cases show you how to approach obtaining the particular solution.

Case 1

If we have f(t) = $Be^{\Omega t}$, we can assume the particular solution to be of the form $x_0(t) = Ae^{\Omega t}$. Substituting this guess into the into the inhomogeneous equation to find

$$A\sum_{n=0}^{N} a_n\omega^n B \Rightarrow A = \frac{B}{\sum_{n=0}^{N} a_n\omega_n} \tag{36}$$

At no point did we assume $\Omega \in \Re$, so this derivation is in general complex.

Case 2

Our next special case is of the form $f(t) = B_1e^{\Omega_1 t} + B_2e^{\Omega_2 t} + \cdots$ We will guess a solution of the form $x_0(t) = A_1e^{\Omega_1 t} + A_2e^{\Omega_2 t} + \cdots$ Substituting this into the inhomigeneous equation we find (truncating to 2 terms for simplicity)

$$e^{\omega_1 t}A_1\sum_{n=0}^{N} a_n\Omega_1^n + e^{\omega_2 t}A_2\sum_{n=0}^{N} a_n\Omega_2^n = B_1e^{\Omega_1 t} + B_2e^{\Omega_2 t} \tag{37}$$

This can be re-written as a set of equations if you perfer

$$\begin{aligned} A_1\sum_{n=0}^{N} a_n\Omega_1^n &= B_1 \\ A_2\sum_{n=0}^{N} a_n\Omega_1^n &= B_2 \end{aligned} \tag{38}$$

Notice our solution is a linear combination of expotential terms, so we can probably guess that a sin or cos function can also fit this form of equation. For example if f(t) = sin(Ω t) or f(t) = cos(Ωt) then we can re-write f(t) in terms of expotentials and find

$$\begin{aligned} \cos(\Omega t) &= \frac{e^{i\Omega t} + e^{-i\Omega t}}{2} \\ \sin(\Omega t) &= \frac{e^{i\Omega t} - e^{-i\Omega t}}{2i} \end{aligned} \tag{39}$$

Case 3

Our next case assumes f(t) = $B_0 + B_1t + B_2t^2$ We guess that $x_0(t) = A_0 + A_1t + A_2t^2$, and substituting into the inhomogeneous equation we find

$$a_0\left(A_0 + A_1t + A_2t^2\right) + a_1\left(A_1 + 2A_2t\right) + 2a_2A_2 = 0 \tag{40}$$

This is a second order polynomial, we have 3 coefficients and 3 equations, and we can solve for A_1, A_2, and A_3.

$$\begin{aligned} a_0A_0 + a_1A_1 + 2a_2A_2 &= B_0 \\ a_0A_1 + 2a_1A_2 &= B_1 \\ a_0A_2 &= B_2 \end{aligned} \tag{41}$$

Case 4

Our final case to consider is of the form f(t) = $e^{\Omega t}\left(B_0 + B_1t + B_2t^2\right)$. We make our guess as $x_0(t) = \left(A_0 + A_1t + A_2t^2\right)e^{\Omega t}$ and substitute into the inhomogeneous equation (In the homework we will show that we get a set of linear equations for the roots). This is the last special case that Vladimir is aware of!

What we have seen from these various cases is that a RHS containing a linear combination of expotentials and polynomials will produce a system of equations.

Linear ODE with Variable Coefficients

Constant coefficient linear ODEs can be solved with linear algebra as we saw. Unfortunately problems with variable coefficients are a bit more tricky.

An example of a first order variable coefficient ordinary differential equation is the 1-D Schrodinger Equation!

$$-\frac{\hbar^2}{2m}\Psi''(x) + [E - V(x)]\Psi(x) = 0 \tag{42}$$

Here V(x) is changing (is is a function of x) so the coefficients are changing.

In general we don't have a general approach to solve these problem.

The SE is a good example, guessing a Harmonic Oscillator for the potential ($\mathrm{V(x)} = \mathrm{kx}^2$) we can get analytic solutions.

Some other examples of linear ODEs with variable coefficients are the Morse Potential, and a piecewise constant potential.

Another example of a second order variable coefficient OD eis teh Vertically Forced Pendulumn. The equation for this system is non-trivial and can be approximated as

$$u'' + (\alpha + \beta\cos(t))u = 0 \tag{43}$$

This problem is very interesting, if you allow the focal point where the pendulumn connects to the base to move you can generate a stable solution to the problem.

All of these examples are just to motivate the problems, we do not need to know these specific cases.