

CHEM1034 - Week 19 Lecture – Ordinary Differential Equations, Part I

Sections 11.1-11.6 of Steiner, "The Chemistry Maths Book", 2nd edition.

A *differential equation* is an equation that involves derivatives of a function. Such equations are ubiquitous in all areas of science and engineering – the most powerful and general theories of reality (general relativity theory, quantum field theory, hydrodynamics, etc.) are formulated in terms of differential equations. In the context of chemistry their primary application area is chemical kinetics.

Definitions and terminology

Differential equations are classified into *ordinary differential equations* (ODEs) that involve derivatives with respect to one variable only, for example:

$$x^2 \frac{d^2 f(x)}{dx^2} + \alpha x \frac{df(x)}{dx} + \beta f(x) = S(x) \quad \text{[Euler equation, hydrodynamics]} \quad (1)$$

and *partial differential equations* (PDEs) that involve derivatives with respect to multiple variables, e.g.

$$\frac{\partial^2 f(x, y, z)}{\partial x^2} + \frac{\partial^2 f(x, y, z)}{\partial y^2} + \frac{\partial^2 f(x, y, z)}{\partial z^2} = 0 \quad \text{[Laplace equation, electromagnetism]} \quad (2)$$

The task of solving a differential equation consists in finding such a function as would satisfy the equation. In some cases the solutions are simple (e.g. for $f'(x) = \cos x$), but in most practical situations the solutions cannot be expressed in any simple-looking form.

Example problem 1: demonstrate that $f(t) = \sin(\omega t)$ satisfies the *wave equation* $f''(t) = -\omega^2 f(t)$.

A differential equation is called *linear* if the function and its derivatives occur linearly, e.g.

$$f'(t) + f(t) \sin(\omega t) + 2 = 0 \quad (3)$$

The *order* of the differential equation is defined as the order of the highest derivative found in it. Equation (1) is therefore linear and second order. A first order differential equation is called *separable* if it may be written in the following form:

$$g(y)dy = f(x)dx \quad (4)$$

Solutions to such equations tend to be particularly simple and may be obtained in a single integration operation. In particular, such equations occur in chemical kinetics.

In order to simplify description and analysis of differential equations, it is convenient to introduce the notion of an operator. An *operator* is a generic prescription about what should be done to a function. There are differential operators, integral operators, operators that invert the function, etc. The action of an operator on a function is accomplished by placing an operator before that function, e.g.

$$\hat{D} = a \frac{d}{dx} + b, \quad \hat{D}f(x) = \left(a \frac{d}{dx} + b \right) f(x) = af'(x) + bf(x) \quad (5)$$

Operator language is used extensively in quantum mechanics and theory of relativity, as well as in every mathematically advanced sub-field of modern science and engineering.

Example problem 2: apply the Laplace operator $\hat{L} = \partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2$ to $x^2 y^2 z^2$.

With this notation in place, a large class of ordinary differential equations, called linear ODEs, may be written in a very simple general form: $\hat{D}f(x) = 0$, where \hat{D} is some differential operator.

Initial and boundary conditions

The differential equation itself does not usually define the function uniquely. For example, the equation describing radioactive decay:

$$\frac{dA(t)}{dt} = -kA(t) \quad (6)$$

is satisfied by the following class of functions (prove it as an exercise):

$$A(t) = C \exp(-kt) \quad (7)$$

where C is an arbitrary constant. To pin down the value of this constant, additional information must be provided. In the case of radioactive decay it is usually the amount of substance at time zero:

$$A(0) = A_0 \quad \Rightarrow \quad A(t) = A_0 \exp(-kt) \quad (8)$$

Additional information of this kind is called the *initial condition*. It specifies the state of the system at the beginning of the dynamical process described by the equation.

Differential equations describing various spatial distributions, for example, the oscillation equation:

$$\frac{\partial^2 y}{\partial t^2} = \frac{T}{\mu} \frac{\partial^2 y}{\partial x^2} \quad (9)$$

additionally require the values of the function at different points in space – in the case of a vibrating string described by Equation (9), the information amounts to saying that the string is clamped at both ends. That is, any solution $y(x, t)$ of Equation (9) must additionally satisfy

$$y(0, t) = 0, \quad y(L, t) = 0 \quad (10)$$

where L is the length of the string. Additional information of this kind is called the *boundary condition*. Without such information many differential equations would have infinitely many solutions.

It is worth noting that it is the presence of the boundary conditions for the solution of the Schrodinger equation for the wavefunction of the hydrogen-like atom $\psi(r, \theta, \varphi)$:

$$\psi(\infty, \theta, \varphi) = 0, \quad \psi(r, \theta + 2\pi, \varphi) = \psi(r, \theta, \varphi), \quad \psi(r, \theta, \varphi + 2\pi) = \psi(r, \theta, \varphi) \quad (11)$$

that leads to the emergence of the three quantum numbers $\{l, m, n\}$ and therefore determines the structure of the Periodic Table. Many physical laws that are often presented as "fundamental" (conservation of energy, conservation of momentum, conservation of angular momentum) can, in the actual fact, be *derived* from similar considerations.

Example problem 3: demonstrate that the function describing the $2p_z$ orbital of the hydrogen atom

$$\psi(r, \theta, \varphi) = \frac{r \cos \theta}{4\sqrt{2\pi}a_0^{5/2}} e^{-\frac{r}{2a_0}} \quad (12)$$

satisfies the boundary conditions specified in Equation (11).

The higher the order of the differential equation, the greater the amount of additional information that must be provided in the initial and the boundary conditions. The reason for this is that some information

is *lost* in the differentiation procedure – the second derivative of $\sin x + ax + b$ would carry no information on either a or b because both disappear in the differentiation process.

Solving simple ordinary differential equations

The procedure that undoes the changes brought about by differentiation and recovers the function from its derivative is called *integration*, and the result of the operation is called the *indefinite integral* of the function. The word *indefinite* reflects the fact that the resulting function contains an arbitrary constant:

$$f(x) = F'(x) \quad \Rightarrow \quad F(x) = \int f(x) dx + C \quad (13)$$

While the calculation of derivatives is largely a mechanical process (there exists a finite algorithm that can differentiate any finite expression in finite time), the calculation of indefinite integrals *is an art*. You will get plenty of practice with integration in CHEM1030, a few examples are given below.

$$\int x^n dx = \frac{x^{n+1}}{n+1} + C, \quad n \neq -1; \quad \int \frac{1}{x} dx = \ln|x| + C; \quad (14)$$

$$\int \frac{1}{x^2 - a^2} dx = \frac{1}{2a} \ln \left| \frac{x-a}{x+a} \right| + C$$

Solving a differential equation essentially amounts to bringing it into a form that allows integration, taking the indefinite integral and using the initial and / or boundary conditions to eliminate the arbitrary coefficients. The recipe, for first-order ODEs, is roughly as follows:

1. Using appropriate mathematical transformations, bring the equation to the following form:

$$g(y) dy = f(x) dx \quad (15)$$

2. Integrate both sides and note that a sum or difference of two unknown constants is a *single* unknown constant. The solution that contains this constant is called the *general solution*.
3. Use the initial condition to determine the constant. The solution with all unknown constants eliminated is called the *particular solution*.

Example problem 4: find general solutions for the following ODEs

$$(a) \quad xy' - y = y^2 \qquad (b) \quad \tan(x) \sin^2(y) dx + \cos^2(x) \cot(y) dy = 0$$

Example problem 5: find particular solutions for the following ODEs and initial conditions

$$(a) \quad (1 + e^x) yy' = e^x, \quad y(0) = 1 \qquad (b) \quad (xy^2 + x) dx + (x^2 y - y) dy = 0, \quad y(0) = 1$$

For practical purposes, one of the most safe and convenient ways of getting a differential equation solved is to use *Mathematica*. Its output would not necessarily be simple, however:

$$\text{In[2]:= DSolve}[x y' [x] - y[x] == y[x]^2, y[x], x]$$

$$\text{Out[2]=} \left\{ \left\{ y[x] \rightarrow -\frac{e^{c[1] x}}{-1 + e^{c[1] x}} \right\} \right\}$$

$$\text{In[3]:= DSolve}[\{(1 + \text{Exp}[x]) y[x] y' [x] == \text{Exp}[x], y[0] == 1\}, y[x], x]$$

DSolve::bvnul : For some branches of the general solution, the given boundary conditions lead to an empty solution. >>

$$\text{Out[3]=} \left\{ \left\{ y[x] \rightarrow \sqrt{1 - 2 \text{Log}[2] + 2 \text{Log}[1 + e^x]} \right\} \right\}$$

In the example above it is convenient to notice that exponential of an arbitrary constant is another arbitrary constant.

Week 20 workshop exercises

Steiner, 2nd edition: section 11.8, problems 1-6, 10-15, 19-21, 30-32.

Extra difficulty exercises for the brave

Steiner, 2nd edition: section 11.8, problems 16-18, 22-25, 41,42.