CHEM1030 - Week 30 Lecture - partial differential equations

Chapter 14 of Steiner, "The Chemistry Maths Book", 2nd edition.

Product representations

A very fundamental theorem (it is used across physical sciences) states that any sufficiently well-behaved[1] function of two variables $h(x,y)$ may be represented in the following way:

$$h(x,y)=\sum_{n,k}\alpha_{nk}f_n(x)g_k(y) \tag{1}$$

where $\{f_n(x)\}$ is a complete basis set on the space of all well behaved functions of x, $\{g_k(y)\}$ is a complete basis set on the space of all well behaved functions of y and α_{nk} are expansion coefficients. Similar relations also hold for functions of three or more variables. Such representations are useful for solving partial differential equations – if the basis sets are chosen to be eigenfunctions of the differential operators that the equation contains, the transformations become quite easy: the action of the operator on its eigenfunctions is simple and the only unknowns are the expansion coefficients that are determined from the initial condition. We do not have sufficient time in this course to go deeper into these matters, but two practically important examples will be given below.

Variable separation 1: Schrödinger equation

For the now familiar case of a particle in a box, the time-dependent Schrödinger equation is:

$$i\frac{\partial}{\partial t}\psi(x,t)=-\frac{1}{2m}\frac{\partial^2}{\partial x^2}\psi(x,t) \tag{2}$$

This is a linear partial differential equation – if $\psi(x,t)$ has the form prescribed by Equation (1):

$$\psi(x,t)=\sum_{n,k}a_{nk}f_n(x)g_k(t) \tag{3}$$

it would satisfy Equation (2) when it is satisfied by each $f_n(x)g_k(t)$ term individually. Substituting a generic $f(x)g(t)$ product into Equation (2) yields:

$$i\frac{\partial}{\partial t}\left[f(x)g(t)\right]=-\frac{1}{2m}\frac{\partial^2}{\partial x^2}\left[f(x)g(t)\right] \tag{4}$$

The time derivative operator does not affect functions of x and the coordinate derivative operator does not affect functions of t, therefore:

$$f(x)i\frac{\partial}{\partial t}g(t)=-g(t)\frac{1}{2m}\frac{\partial^2}{\partial x^2}f(x) \tag{5}$$

Dividing this equation by the product $f(x)g(t)$ produces:

$$i\frac{1}{g(t)}\frac{\partial}{\partial t}g(t)=-\frac{1}{2m}\frac{1}{f(x)}\frac{\partial^2}{\partial x^2}f(x) \tag{6}$$

This is a peculiar relation – the left hand side only depends on time and the right hand side only depends on the coordinate. The two sides can only be equal for all values of x and t if they are both constant, meaning that the following two equations must simultaneously be true for some constant E:

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[1]The notion of "well-behaved" in this context is highly technical and will not be elaborated upon. See, for example, *"Partial Differential Equations"* by L.C. Evans for further information if you are interested.

$$\begin{cases} i\dfrac{1}{g(t)}\dfrac{\partial}{\partial t}g(t)=E \\ -\dfrac{1}{2m}\dfrac{1}{f(x)}\dfrac{\partial^2}{\partial x^2}f(x)=E \end{cases} \quad\Rightarrow\quad \begin{cases} \dfrac{\partial}{\partial t}g(t)=-iEg(t) \\ \dfrac{\partial^2}{\partial x^2}f(x)=-2mEf(x) \end{cases} \tag{7}$$

It is easy to recognize, in the first equation, the standard first-order ODE with exponentials as solutions and, in the second equation, the eigenvalue / eigenfunction problem for a particle in a box that we have already solved (and obtained infinitely many solutions) in the previous lecture:

$$E_n=\frac{\pi^2 n^2}{2ma^2},\quad f_n(x)=\sqrt{\frac{2}{a}}\sin\left(\frac{\pi n x}{a}\right),\quad n=1,2,3... \tag{8}$$

The time-dependent part has a different solution for each energy:

$$\frac{\partial}{\partial t}g(t)=-iE_n g(t) \quad\Rightarrow\quad g_n(t)=\exp(-iE_n t) \tag{9}$$

Note that in this case both sets of functions are numbered by the same index n. After plugging the two sets of functions into Equation (1), we obtain the general solution for the time-dependent Schrödinger equation describing a quantum mechanical particle in a box of size a:

$$\psi(x,t)=\sum_n \alpha_n \sin\left(\frac{\pi n x}{a}\right)\exp\left(-i\frac{\pi^2 n^2}{2ma^2}t\right) \tag{10}$$

where the coefficients α_n are determined by the initial condition (*i.e.* the starting state of the system). It is easy to verify by direct inspection that this solution satisfies Equation (2).

Variable separation 2: Laplace equation

In the absence of electric charges, the following equation describes the electrostatic potential inside a grounded metallic cuboid of dimensions $\{a,b,c\}$:

$$\left[\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right]\varphi(x,y,z)=0 \tag{11}$$

The boundary conditions at the edges of the cuboid shall be $\varphi=0$, except for one wall, where we will set some external potential $\varphi(x,y,c)=f(x,y)$. Because Equation (11) involves three independent coordinates, the product representation formula in Equation (1) should be modified:

$$\varphi(x,y,z)=\sum_{n,k,m}\alpha_{nkm}f_n(x)g_k(y)h_m(z) \tag{12}$$

and the generic term to be substituted into Equation (11) is therefore $f(x)g(y)h(z)$:

$$\left[\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right]f(x)g(y)h(z)=0 \tag{13}$$

After opening the brackets and moving out the terms that individual derivatives do not affect, we get:

$$g(y)h(z)\frac{\partial^2}{\partial x^2}f(x)+f(x)h(z)\frac{\partial^2}{\partial y^2}g(y)+f(x)g(y)\frac{\partial^2}{\partial z^2}h(z)=0 \tag{14}$$

After dividing this equation by $f(x)g(y)h(z)$, we obtain:

$$\frac{1}{f(x)}\frac{\partial^2}{\partial x^2}f(x)+\frac{1}{g(y)}\frac{\partial^2}{\partial y^2}g(y)+\frac{1}{h(z)}\frac{\partial^2}{\partial z^2}h(z)=0 \tag{15}$$

By the same argument as we had used for Equation (6), the three terms that depend on different variables can only sum up to a constant if they are constants themselves. We can therefore conclude that:

$$\begin{cases} \dfrac{\partial^2}{\partial x^2}f(x)=-\alpha^2 f(x), & f(0)=f(a)=0 \\ \dfrac{\partial^2}{\partial y^2}g(y)=-\beta^2 g(y), & g(0)=g(b)=0 \\ \dfrac{\partial^2}{\partial z^2}h(z)=\left(\alpha^2+\beta^2\right)h(z), & h(0)=0,\quad h(c)=1 \end{cases} \tag{16}$$

where the constants have been chosen so as to simplify the subsequent mathematics. The first and the second equations look exactly like Equation (7) that we have solved already, therefore:

$$\begin{aligned} f_n(x)&=\sqrt{\frac{2}{a}}\sin\left(\frac{\pi n x}{a}\right), \quad \alpha_n=\frac{\pi n}{a}, \quad n=1,2,3... \\ g_k(y)&=\sqrt{\frac{2}{b}}\sin\left(\frac{\pi k y}{b}\right), \quad \beta_k=\frac{\pi k}{b}, \quad k=1,2,3... \end{aligned} \tag{17}$$

And the final equation remains to be solved for each α_n and β_k:

$$\frac{\partial^2}{\partial z^2}h(z)=\left(\alpha_n^2+\beta_k^2\right)h(z), \qquad h(0)=0,\quad h(c)=1 \tag{18}$$

We do not have the time to go through the full procedure here, and so we would just guess the solution, which is simple enough to permit such liberties:

$$h_{nk}(z)=\xi_{nk}\exp\left[-\sqrt{\alpha_n^2+\beta_k^2}\,z\right]+\zeta_{nk}\exp\left[+\sqrt{\alpha_n^2+\beta_k^2}\,z\right] \tag{19}$$

the fact that this is the general solution may be verified by direct inspection. The values of the coefficients ζ and ξ will be determined below from the boundary conditions. What now remains is to assemble the final solution for the Laplace equation:

$$\varphi(x,y,z)=\sum_{n,k}\alpha_{nk}\sin\left(\frac{\pi n x}{a}\right)\sin\left(\frac{\pi k y}{b}\right)\left(\xi_{nk}\exp\left[-\sqrt{\alpha_n^2+\beta_k^2}\,z\right]+\zeta_{nk}\exp\left[+\sqrt{\alpha_n^2+\beta_k^2}\,z\right]\right) \tag{20}$$

in which the constants α_{nk} may be absorbed into ζ_{nk} and ξ_{nk}:

$$\varphi(x,y,z)=\sum_{n,k}\sin\left(\frac{\pi n x}{a}\right)\sin\left(\frac{\pi k y}{b}\right)\left(\xi_{nk}\exp\left[-\sqrt{\alpha_n^2+\beta_k^2}\,z\right]+\zeta_{nk}\exp\left[+\sqrt{\alpha_n^2+\beta_k^2}\,z\right]\right) \tag{21}$$

The values of ζ_{nk} and ξ_{nk} are constrained by the boundary conditions at $z=0$ and $z=c$:

$$\begin{cases} \displaystyle\sum_{n,k}\sin\left(\frac{\pi n x}{a}\right)\sin\left(\frac{\pi k y}{b}\right)\left(\xi_{nk}+\zeta_{nk}\right)=0 \\ \displaystyle\sum_{n,k}\sin\left(\frac{\pi n x}{a}\right)\sin\left(\frac{\pi k y}{b}\right)\left(\xi_{nk}\exp\left[-\sqrt{\alpha_n^2+\beta_k^2}\,c\right]+\zeta_{nk}\exp\left[+\sqrt{\alpha_n^2+\beta_k^2}\,c\right]\right)=f(x,y) \end{cases} \tag{22}$$

In which ζ_{nk} and ξ_{nk} are just 2D Fourier expansion coefficients for $f(x,y)$ that we have considered in the previous lectures – for lack of time, we will not go through the exercise of computing them here.

Week 31 workshop exercises

Steiner, 2nd edition: section 14.8, problems 1-5 (see the enclosed page from the book for the equations that problems 1-3 are referring to).

Monk and Munro, 2nd edition: chapter 22, problem 22.10 (the problem text contains multiple typos, what is required is to show that $\psi(\theta,\varphi)=\sin(\theta)\cos(\theta)e^{i\varphi}$ obeys the following differential equation:

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2\psi}{\partial\varphi^2}=\lambda\psi$$

Extra difficulty exercises for the brave

Steiner, 2nd edition: section 14.8, problems 6, 7, 10, 16-18.