CHEM2024 - Week 22 Lecture 1 - Line integrals

Sections 9.8-9.10 of Steiner, "The Chemistry Maths Book", 2nd edition.

Pages 376-382 of Monk and Munro, "Maths for Chemistry", 2nd edition.

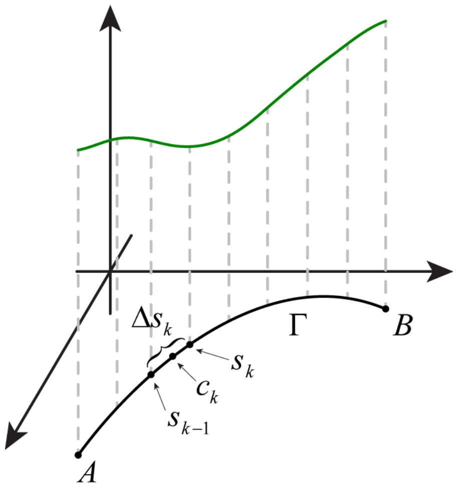
1. Line integrals over scalar fields

Let Γ be a continuous curve in $\mathbb{R}^N$ between points A and B, parameterised by a variable t:

$$\begin{cases} x = x(t) \\ y = y(t) \\ \ldots \end{cases} \tag{1}$$

and let $f(x, y, \ldots)$ be function that is defined on Γ. We need to define and evaluate an integral with the physical meaning of the area of the "fence" traced out by the function $f(x, y, \ldots)$.

Let us create a partitioning of the curve Γ: a set of points $A = s_0, s_1, \ldots, s_n = B$ and let the arc length between points s_k and s_{k-1} be Δs_k. Let us also choose a point c_k inside each arc.



The limit of the following sum, if it exists, is called a line integral:

$$\int_\Gamma f(x, y, \ldots)\, ds = \lim_{\Delta s_k \to 0} \sum_k f(c_k)\, \Delta s_k \tag{2}$$

Such integrals are taken by using the parameterisation in Equation (1) to obtain an explicit expression for the curve length element ds. For an infinitesimally small increment of each coordinate:

$$(ds)^2 = (dx)^2 + (dy)^2 + \ldots = \left(\frac{dx}{dt} dt\right)^2 + \left(\frac{dy}{dt} dt\right)^2 + \ldots \tag{3}$$

and therefore:

$$ds = dt \sqrt{\left(\frac{dx}{dt}\right)^2 + \left(\frac{dy}{dt}\right)^2 + \ldots} \tag{4}$$

The procedure for taking integrals of this type is therefore to use the parameterisation in Equation (1) to find the curve length element in Equation (4). After it is substituted into the integral, the integral reduces to the usual type.

Example 1: evaluate the following integral

$$\int_{\Gamma} xy^4 ds$$

where Γ is the curve given by $x(t)=4\cos t$ and $y(t)=4\sin(t)$ for $t\in[-\pi/2,+\pi/2]$.

Solution: using Equation (4) to obtain the expression for the curve length element, we get

$$\frac{dx}{dt}=-4\sin t \qquad \frac{dy}{dt}=4\cos t$$

$$ds=dt\sqrt{16\sin^2 t+16\cos^2 t}=4dt$$

Variable substitution then yields:

$$\int_{\Gamma} xy^4 ds=4096\int_{-\pi/2}^{\pi/2}\cos(t)\sin^4(t)dt=\ldots=\frac{8192}{5}$$

Example 2: evaluate the following integral

$$\int_{\Gamma} xyzds$$

where Γ is the helix given by $x(t)=\cos(t)$, $y(t)=\sin(t)$, and $z=3t$ with $t\in[0,4\pi]$.

Solution: using Equation (4) to obtain the expression for the curve length element, we get

$$ds=dt\sqrt{\sin^2 t+\cos^2 t+9}=dt\sqrt{10}$$

Variable substitution then yields:

$$\int_{\Gamma} xyzds=\sqrt{10}\int_{0}^{4\pi}3t\cos(t)\sin(t)dt=\ldots=-3\pi\sqrt{10}$$

2. Line integrals over vector fields

A problem that often occurs in physical sciences is the calculation of the work done by a force field as the system moves through it on a certain trajectory. A good example in the change in the internal energy of a chemical system when it moves along a curve C in $\{S,V\}$ coordinates:

$$dU=TdS-PdV \qquad \Rightarrow \qquad \Delta U=\int_{C}[TdS-PdV] \tag{5}$$

Another example is the work W done by the force acting on a particle that moves along a curve C in three dimensions:

$$\begin{gathered} dW=\vec{F}\cdot d\vec{l} \\ \Downarrow \\ W=\int_{C}\left[f_{\mathrm{X}}(x,y,z)dx+f_{\mathrm{Y}}(x,y,z)dy+f_{\mathrm{Z}}(x,y,z)dz\right] \end{gathered} \tag{6}$$

The integration curve is normally parameterised by some common variable, for example time:

$$x=x(t), \qquad y=y(t), \qquad a\le t\le b \tag{7}$$

In that case, $dx=x'(t)dt$ and $dy=y'(t)dt$, and the line integral is reduced to an ordinary integral:

$$\int_C \left[f(x,y)\,dx + g(x,y)\,dy \right] = \int_C \left[f(x,y)\,x'(t)\,dt + g(x,y)\,y'(t)\,dt \right] =$$
$$= \int_a^b \left[f\big(x(t),y(t)\big)\,x'(t) + g\big(x(t),y(t)\big)\,y'(t) \right] dt \tag{8}$$

After that is done, the integral may be taken in the standard way.

Example 3: evaluate the following integral

$$\int_C \left[yzdx + xzdy + xydz \right]$$

over the curve specified by $\begin{bmatrix} x(t) & y(t) & z(t) \end{bmatrix} = \begin{bmatrix} t & t^2 & t^3 \end{bmatrix}$ for $0 \le t \le 1$.

Solution: the differentials of the three Cartesian coordinates are

$$dx = dt, \quad dy = 2tdt, \quad dz = 3t^2 dt$$

Performing the corresponding substitution under the integral yields:

$$\int_C \left[yzdx + xzdy + xydz \right] = \int_0^1 \left[yzdt + 2xztdt + 3xyt^2 dt \right] = \int_0^1 6t^5 dt = 1$$

Example 4: by explicit integration of the following relation

$$dP = \left(\frac{\partial P}{\partial V} \right)_T dV + \left(\frac{\partial P}{\partial T} \right)_V dT$$

calculate the change in the pressure of one mole of an ideal gas when the system moves from the volume of 1 m^3 and the temperature of 300 Kelvin to the volume of 2 m^3 and the temperature of 400 Kelvin. Try at least two different trajectories.

Solution: the simplest trajectory is a straight line

$$V = 1 + t, \quad T = 300 + 100t, \quad 0 \le t \le 1$$

Performing the corresponding substitutions and using the ideal gas law to calculate the derivatives, we get:

$$\int \left[\frac{R}{V} dT - \frac{RT}{V^2} dV \right] = R \int_0^1 \left[\frac{100}{1+t} - \frac{300+100t}{(1+t)^2} \right] dt = \ldots = -100R$$

Picking a curved trajectory, for example

$$V = 1 + t, \quad T = 300 + 100t^2, \quad 0 \le t \le 1$$

ultimately yields exactly the same answer:

$$\int \left[\frac{R}{V} dT - \frac{RT}{V^2} dV \right] = R \int_0^1 \left[\frac{200t}{1+t} - \frac{300+100t^2}{(1+t)^2} \right] dt = \ldots = -100R$$

as of course it should.