1 Math Prerequisites

This chapter lists some of the mathematical concepts used in part 1 of this textbook. They are assumed to be covered in vector calculus and linear algebra. If any of these concepts look unfamiliar to the reader, it is crucial to review more elementary concepts. More thorough explanations can be found in standard mathematics textbooks about these topics.[1]

1.1 Matrices

Determinants.

$$det(A) = detA = \begin{vmatrix} a & b & c \\ d & e & f \\ g & h & i \end{vmatrix} = aei + bfg + cdh - afh - bdi - ceg$$

The Dot Product.

$$V \cdot V = V^T V = \begin{bmatrix} - & v & - \end{bmatrix} \begin{bmatrix} | \\ v \\ | \end{bmatrix} = \begin{bmatrix} a & b & c \end{bmatrix} \begin{bmatrix} a \\ b \\ c \end{bmatrix} = a^2 + b^2 + c^2$$

The Cross Product.

$$U \times V = \begin{vmatrix} \hat{\mathbf{i}} & \hat{\mathbf{j}} & \hat{\mathbf{k}} \\ u_x & u_y & u_z \\ v_x & v_y & v_z \end{vmatrix} = (u_y v_z - u_z v_y)\hat{\mathbf{i}} - (u_x v_z - u_z v_x)\hat{\mathbf{j}} + (u_x v_y - u_y v_x)\hat{\mathbf{k}}$$

The Del Operator.

$$\nabla = (\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z}) \leftarrow vectors$$
$$\nabla f = (\frac{\partial f}{\partial x}, \frac{\partial f}{\partial y}, \frac{\partial f}{\partial z}) \swarrow$$

The Laplacian Operator (Del Squared).

$$\Delta = \nabla^2 = \underset{\substack{\uparrow \\ \text{dot product}}}{\nabla \cdot \nabla} = \nabla^T \nabla = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \leftarrow \text{scalar}$$

[1] Textbooks such as "Advanced Engineering Mathematics" by Erwin Kreiszig provide a more rigorous review on these topics.

from physics: Angular Momentum (classical)

$\overrightarrow{L} = \overrightarrow{r} \times \overrightarrow{p}$

$$\begin{aligned}\overrightarrow{L} &= \begin{vmatrix} \hat{\mathbf{i}} & \hat{\mathbf{j}} & \hat{\mathbf{k}} \\ x & y & z \\ P_x & P_y & P_z \end{vmatrix} \\ &= (u_y v_z - u_z v_y)\hat{\mathbf{i}} \to L_x \\ &- (u_x v_z - u_z v_x)\hat{\mathbf{j}} \to L_y \\ &+ (u_x v_y - u_y v_x)\hat{\mathbf{k}} \to L_z\end{aligned}$$

- Operator in 3-D

$\hat{r} = \bar{r}(x, y, z)$

$\hat{p} = -i\hbar\big(\hat{\mathbf{i}}\frac{\partial}{\partial x} + \hat{\mathbf{j}}\frac{\partial}{\partial y} + \hat{\mathbf{k}}\frac{\partial}{\partial z}\big)$
where $\hat{\mathbf{i}}, \hat{\mathbf{j}}$, and $\hat{\mathbf{k}}$ are the unit vectors along the x, y, z axes, respectively.

$\hat{V}(x, y, z)$

$\hat{T} = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) = -\frac{\hbar^2}{2m}\nabla^2$

$\hat{H} = \hat{T} + \hat{V} = -\frac{\hbar^2}{2m}\nabla^2 + V(x, y, z)$

$\widehat{L_x} = -i\hbar\big(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\big)$

$\widehat{L_y} = -i\hbar\big(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\big)$

$\widehat{L_z} = -i\hbar\big(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\big)$

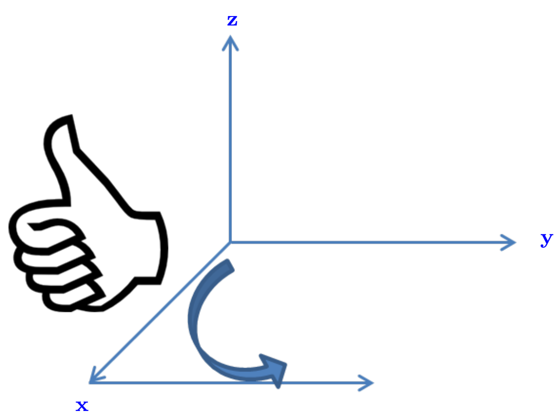


Figure 1: Right Hand Coordinate System

1.2 Vector Spaces

Let $\bar{x}$, $\bar{y}$, $\bar{z}$ denote vectors of vector space V,
and let r, s denote scalars in $\mathbb{R}$

We define a vector space to be a set satisfying the following properties:

- *Commutativity.* For all $\bar{x}$, $\bar{y}$ in the vector space V,

$$\bar{x} + \bar{y} = \bar{y} + \bar{x}$$

- *Associativity.* For all x, y, z in the vector space V,

$$(\bar{x} + \bar{y}) + \bar{z} = \bar{x} + (\bar{y} + \bar{z})$$

- *Additive identity.* There exists a vector $\bar{0}$ in V such that for all $\bar{x}$ in the vector space V,

$$\bar{0} + \bar{x} = \bar{x} + \bar{0}$$

- *Additive inverse.* For each $\bar{x}$ in the vector space V, There exists a vector $(-\bar{x})$ in V such that

$$\bar{x} + (-\bar{x}) = (-\bar{x}) + \bar{x} = \bar{(}0)$$

- *Associativity of scalar multiplication.*

$$r(s\bar{x}) = (rs)\bar{x}$$

- *Distributivity.*

$$r(\bar{x} + \bar{y}) = r\bar{x} + r\bar{y}$$

- *Scalar multiplicative identity.*

$$1 \cdot \bar{x} = \bar{x}$$

HW

Let V be the set of odd periodic functions composed of linear combinations of $\sin\left(\frac{n\pi x}{L}\right)$ whose domains consist of x such that $-L \leq x \leq L$. Show V is a vector space.
This HW problem can be easily generalized to any vector space V having periodic functions (both sine & cosine).

A set of vectors in a vector space is called **basis** if they are linearly independent and every vector in V is equal to a linear combination of the basis.
i.e. The unit vectors corresponding to the axes x, y, z form a basis of $\mathbb{R}^3$.
HW
Identify a basis set for the space V from the preceding problem.

Vectors.

$$\bar{v} = \begin{pmatrix} x \\ y \\ z \end{pmatrix} \qquad v^T = (x, y, z)$$

$$\hat{\mathbf{\imath}} = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} \qquad \hat{\mathbf{\imath}}^T = (1, 0, 0)$$

$$\hat{\mathbf{\jmath}} = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} \qquad \hat{\mathbf{\jmath}}^T = (0, 1, 0)$$

$$\hat{\mathbf{k}} = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} \qquad \hat{\mathbf{k}}^T = (0, 0, 1)$$

The dot product can be used to find the projection of v onto x:

$$\hat{\mathbf{\imath}}^T \cdot v = (1, 0, 0) \begin{pmatrix} x \\ y \\ z \end{pmatrix} = (x). \leftarrow \#$$

Similarly, you can find the projection of v onto y and z This is useful for finding $x, y,$ and z components of v and vector v can be expressed as a linear combination of basis vector $\hat{\mathbf{\imath}}$, $\hat{\mathbf{\jmath}}$, and $\hat{\mathbf{k}}$.

$$v = (\hat{\mathbf{\imath}}^T \cdot v)\hat{\mathbf{\imath}} + (\hat{\mathbf{\jmath}}^T \cdot v)\hat{\mathbf{\jmath}} + (\hat{\mathbf{k}}^T \cdot v)\hat{\mathbf{k}}$$

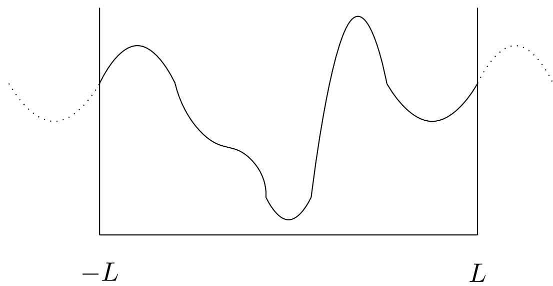
Note that the dot product involves the sum operation.

$$\hat{\mathbf{\imath}}^T \cdot v = 1 \cdot x + 0 \cdot y + 0 \cdot z = x$$

In an n dimensional space, the dot product of $a^T \cdot b$ is

$$a^T \cdot b = \sum_{i=1}^{n} a_i b_i$$

The Periodic Function



Mathematician Joseph Fourier stated that any periodic function is a linear combination of sine & cosine functions:

$$f(x) = a_0 + \sum_{n=1}^{\infty} b_n \sin\left(\frac{n\pi x}{L}\right) + \sum_{n=1}^{\infty} a_n \cos\left(\frac{n\pi x}{L}\right)$$

$$\begin{array}{l} \text{projection of} \\ f \text{ onto basis} \end{array} \quad \left\{ \begin{array}{l} a_n = \frac{1}{L}\int_{-L}^{L} f(x)\cos\left(\frac{n\pi x}{L}\right)dx \\ b_n = \frac{1}{L}\int_{-L}^{L} f(x)\sin\left(\frac{n\pi x}{L}\right)dx \end{array} \right. \quad \Bigg| \quad a_0 = \frac{1}{2L}\int_{-L}^{L} f(x)dx$$

The integration shown above is <u>similar to dot product</u>,
since

$$\frac{1}{L}\int_{-L}^{L} f(x)\cos\left(\frac{n\pi x}{L}\right)dx = \frac{1}{L}\lim_{n\to\infty}\sum_{i=1}^{n} \Delta x \cdot \overbrace{f(x_i)\cdot\cos\left(\frac{n\pi x}{L}\right)}$$

$$\text{where } \Delta x = \frac{L-(-L)}{n} = \frac{2L}{n}$$

In other words, the Fourier series decomposes functions f (vectors of the function space) to a linear combination of basis function vectors (sin and cos). At the same time, any periodic function can be approximated by a column vector of finite length as long as the function is sufficiently smooth.

<u>footnote</u>

Any integrable function will die out at large x. This means that any wave function associated with isolated molecules can be represented by periodic function by making the period arbitrarily large.

1.3 Birds-eye View of Physical Chemistry I

One of the main objectives of Physical Chemistry is to predict or explain a chemical process by studying molecular orbitals mathematically. Obviously, we can let all molecular orbitals be elements of the space of periodic functions, a vector space. Then, we can use sin and cos waves as bases, (i.e. plane wave basis set.) Alternatively, we can also use the set of atomic orbitals as a basis (as long as the period is large enough and that the orbitals contain all atomic nuclei well within their period and away from the boundary). The latter approach is common among chemists. We shall follow this traditional approach.

1.4 Linear Transformations

For vector spaces U and V, a linear transformation is a function
$T : U \to V$ satisfying the following properties:

① $T(x+y) = T(x) + T(y)$ for x, y in U
② $T(\alpha x) = \alpha T(x)$ $T(x)$, $T(y)$ in V
α in $\mathbb{R}$

We follow with a theorem from Linear Algebra:

Theorem

For any linear transformation $T : \mathbb{R}^n \to \mathbb{R}^m$,

There exists a unique matrix A such that

$$T(x) = Ax$$

We apply this theorem to spaces of periodic functions U and V, instead of $\mathbb{R}^n$ and $\mathbb{R}^m$, by swapping basis elements $x, y, z, \cdots$ to the $\sin\left(\frac{n\pi x}{L}\right)$ & $\cos\left(\frac{n\pi x}{L}\right)$ basis,

Thus the theorem should work with $T : U \to V$ where

U & V are spaces of periodic functions with dimension

n & m, respectively.

Consider a linear transformation $T : V \to V$ mapping a vector space into itself. Such a linear transformation is called a linear operator. It is essentially a mapping that acts on the elements of a space to produce another element of the same space. The linear transformation theorem holds for linear operators as well, where matrices are square matrices. During class, you will encounter many linear operators. They can be represented by $n \times n$ matrix.

1.5 Other Mathematical Concepts

1.5.1 Probablity (Review)

Probability is the measure of the likelihood that an event will occur.
It may be denoted a function, since if for event x, we have probability $P(x)$
It maps $x \to P(x)$

Properties.

$\int P(x)dx = 1$

$\int xP(x)dx = < x >$, the average value of x

Variance $Var(x)$ or σ^2

σ is the standard deviation about the mean, or the measure of uncertainty

$\sigma^2 = < x^2 > - < x >^2$

$= \int x^2 P(x)dx - \left(\int xP(x)dx \right)^2$

1.5.2 Ordinary Differential Equation (O.D.E. Review)

O.D.E. is a relation involving an independent variable x & a dependent variable $y(x)$ and its derivatives $y'(x)$, $y"(x)$, etc.

Linear ordinary differential equation:

$A_n(x)y^{(n)}(x) + A_{n-1}(x)y^{(n-1)}(x) + \cdots + A_1(x)y'(x) + A_0(x)y(x) = g(x)$
where $A_0(x), A_1(x), \cdots, A_n(x)$ are variables of x but not y.

A L.O.D.E.,(a Linear Ordinary Differential Equation,) is homogeneous if $g(x) = 0$ & inhomogeneous if $g(x) \neq 0$

Is the Shrödinger Equation homogeneous?

$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi + V(x)\psi = E\psi$

Example Consider the 2nd order L.O.D.E.:

$A_2(x)y" + A_1(x)y' + A_0(x)y = 0$

$$\downarrow$$

$y" + P(x)y' + Q(x)y = 0.$

Case $P(x)$ & $Q(x)$ are constant.

$y" + py' + qy = 0.$

By intuition, $y = e^{sx}$, and we have

$s^2y + psy + qy = 0$

$= (s^2 + ps + q)y = 0,$

$s^2 + ps + q = 0 \Rightarrow s_{1,2} = \frac{-p\pm\sqrt{p^2-4q}}{2}$

then for arbitrary constants C_1 and C_2,

$y = C_1e^{s_1x} + C_2e^{s_2x}$

is the solution. $\square$