1.2: Some Vectors and Dot Products

The concepts of **linear combinations** and **orthogonality** show up repeatedly in quantum chemistry. But these are generally not new concepts to students at this level, as the same concepts are used to describe forces and motions in a standard physics course in classical mechanics.

Consider a pair of vectors ($\mathbf{u}$ and $\mathbf{v}$) in three-dimensional space can be described as a linear combination of basis vectors in the x, y and z directions ($\mathbf{i}$, $\mathbf{j}$ and $\mathbf{k}$, respectively.)

$$\mathbf{u} = \mathrm{a}\mathbf{i} + \mathrm{b}\mathbf{j} + \mathrm{c}\mathbf{k}$$
$$\mathbf{v} = \mathrm{d}\mathbf{i} + \mathrm{e}\mathbf{j} + \mathrm{f}\mathbf{k}$$

The inner product of two vectors $\mathbf{u}$ and $\mathbf{v}$ is given the symbol $\langle \mathbf{u} \mid v \rangle$. There are many possible definitions for an inner product, but most students are familiar with the dot product. The dot product of these two vectors can be calculated by

$$\langle \mathbf{u} \mid \mathbf{v} \rangle = \mathbf{u} \cdot \mathbf{v} = (a \cdot d) + (b \cdot e) + (c \cdot f)$$

If the dot product is zero, the two vectors are said to be **orthogonal**. In three dimensional space, this is oftentimes interpreted as the vectors having a 90° angle between them as the dot product can also be calculated from

$$\mathbf{u} \cdot \mathbf{v} = \|\mathbf{u}\| \|\mathbf{v}\| \cos(\alpha)$$

where u indicates the magnitude of the vector $\mathbf{u}$ and α is the angle formed between the two vectors $\mathbf{u}$ and $\mathbf{v}$. Given this definition, the only way two vectors of non-zero magnitude can be orthogonal is if the $\cos(\alpha)$ term vanishes. In other words, the angle between them must be 90° or $\alpha/2$ radians.

The concept of orthogonality can also be extended to include functions. All that is necessary is a definition for an inner product for two functions. The definition that we will encounter most in quantum mechanics is the integral over all relevant space of the product of the two functions.

$$\langle f(x) \mid g(x) \rangle = \int f(x) \cdot g(x) \; dx$$

In the event that this integral is zero, the two functions are orthogonal in the same sense that two vectors whose dot product is zero are orthogonal.

In addition to being orthogonal, vectors can also be **normalized**. A vector is said to be normalized if it has a unit magnitude. The magnitude of a vector is determined by taking the square root of the dot product of the vector with itself.

$$\|\mathbf{u}\| = \sqrt{\langle \mathbf{u} \mid \mathbf{u} \rangle} = \sqrt{a^2 + b^2 + c^2}$$

The vector has unit magnitude and is normalized if its magnitude is unity.

In the case of vectors, $\mathbf{i}$, $\mathbf{j}$ and $\mathbf{k}$ form an **orthonormal set**. That is to say that each vector in the set is orthogonal to the other two and is normalized as each has a unit magnitude. This property can be defined for any set of vectors $\mathbf{e}_1, \mathbf{e}_2 \ldots \mathbf{e}_N$ by the following relationship

$$\langle \mathbf{e}_i \mid \mathbf{e}_j \rangle = \delta_{ij}$$

where δ_{ij} is a function called the **Kronecker Delta** and has the properties

$$\delta_{\mathrm{ij}} = \left| \begin{array}{ll} 1 & \text{if } \mathrm{i} = \mathrm{j} \\ 0 & \text{if } \mathrm{i} \neq \mathrm{j} \end{array} \right.$$

Similarly, functions ($f_1(x)$, $f_2(x) \ldots f_N(x)$) can form an orthonormal set if

$$\langle f_i(x) \mid f_j(x) \rangle = \int f_i(x) \cdot f_j(x) \; d\tau = \delta_{ij}$$

As we will see, this relationship is common in quantum mechanics, and has many useful properties which we will exploit as they make calculations simpler. This will be particularly evident when we discuss the **superposition theorem**.