CHEM2024 - Week 24 Lecture 1 - Algebraic foundations of quantum theory I

Sections 15.1-2, 16.10 of Steiner, "The Chemistry Maths Book", 2nd edition.

The unified mathematical framework of quantum mechanics has emerged as a generalisation of a large number of partially successful attempts at creating a physical theory of microscopic processes. At the time of writing, no violations of quantum mechanical equations of motion have ever been observed, although it is clear that quantum theory (in which space is a container) is fundamentally incompatible with the general theory of relativity (in which space is a participant).

1. Vector and function spaces

Previous lectures have introduced the concept of a *metric vector space* – a set of all vectors of a given dimension with addition, multiplication by a scalar, norm, and inner product defined. Formally speaking, a set $\mathcal{A}$ of vectors over a field $\mathbb{F}$ of scalars is called a metric space if:

1. The set is closed under addition: $\forall \vec{a},\vec{b} \in \mathcal{A} \quad \left(\vec{a}+\vec{b}\right) \in \mathcal{A}$.
2. The set is closed under multiplication by a scalar: $\forall \vec{a} \in \mathcal{A} \quad \forall c \in \mathbb{F} \quad \left(c\vec{a}\right) \in \mathcal{A}$.
3. There exists a unique zero vector: $\exists! 0 \in \mathcal{A}: \quad \forall \vec{a} \in \mathcal{A} \quad \vec{a}+0=\vec{a}$.
4. Each vector has a unique additive inverse: $\forall \vec{a} \in \mathcal{A} \quad \exists!\left(-\vec{a}\right) \in \mathcal{A}: \quad \vec{a}+\left(-\vec{a}\right)=0$
5. The usual bracket opening rules hold for addition and multiplication by a scalar.
6. There is a measure of distance, called *norm*.
7. There is a measure of angle, called *scalar product*.

It is easy to see that Properties 1-5 also apply to real and complex functions, because:

1. The sum of two functions is a function: $\forall f,g \in \mathcal{A} \quad \left(f+g\right) \in \mathcal{A}$.
2. A function times a scalar is a function: $\forall f \in \mathcal{A} \quad \forall \alpha \in \mathbb{F} \quad \left(\alpha f\right) \in \mathcal{A}$.
3. There exists a unique zero function: $\exists! 0 \in \mathcal{A}: \quad \forall f \in \mathcal{A} \quad f+0=f$.
4. Each function has a unique additive inverse: $\forall f \in \mathcal{A} \quad \exists!\left(-f\right) \in \mathcal{A}: \quad f+\left(-f\right)=0$
5. The usual bracket opening rules hold for addition and multiplication by a scalar.

This is the definition of a *function space*.

Examples (spaces):

1. All polynomials of the form $a_0+a_1x+a_2x^2+a_3x^3+a_4x^4+\ldots$
2. All general solutions to a linear homogeneous ordinary differential equation.

Examples (not spaces):

1. All concentration distributions across a three-dimensional chemical sample.
2. The set of all discontinuous functions of one argument.

2. Function norm and scalar product

Very roughly speaking, functions may be viewed as long and densely packed vectors. The metric on function spaces is then introduced by analogy with vector spaces – by replacing sums with integrals:

$$\begin{aligned} \|\vec{a}\| &= \sqrt{\sum_k a_k^* a_k} \quad \Rightarrow \quad \|f(x)\| = \sqrt{\int f^*(x) f(x)\,dx} \\ \langle \vec{a} | \vec{b} \rangle &= \sum_k a_k^* b_k \quad \Rightarrow \quad \langle f(x) | g(x) \rangle = \int f^*(x) g(x)\,dx \end{aligned} \tag{1}$$

where $\|f(x)\|$ is called the *norm* of the function $f(x)$, and $\langle f(x)|g(x)\rangle$ is called the *scalar product* of functions $f(x)$ and $g(x)$. The star denotes complex conjugation, and the integrals are taken over the domain that is relevant to the problem at hand, in the most general case from $-\infty$ to ∞. Norms and scalar products of multivariate functions are computed in a similar way, by integrating over all available variables. A function space equipped with a norm and a scalar product is called a *metric function space*. Pairs of functions that have a zero scalar product are called *orthogonal*. Functions with unit norm are called *normalised*. The norm of a function is always real and non-negative – only the zero function has a zero norm. Scalar products are, in general, complex numbers.

Example 1: calculate the norm of $f(x) = 2x + ix^2$ on the interval $x \in [0,1]$.

Solution: using the definition of the norm, we obtain

$$\|f(x)\| = \sqrt{\int_0^1 f^*(x) f(x)\,dx} = \sqrt{\int_0^1 (2x - ix^2)(2x + ix^2)\,dx} = \\ = \sqrt{\int_0^1 (4x^2 + x^4)\,dx} = \sqrt{\frac{23}{15}}$$

Example 2: calculate the scalar product of $\cos x$ and $\sin x$ on the interval $x \in [-\pi, \pi]$.

Solution: using the definition of the scalar product, we obtain

$$\langle \cos x | \sin x \rangle = \int_{-\pi}^{\pi} \cos(x)\sin(x)\,dx = \frac{1}{2}\int_{-\pi}^{\pi} \sin(2x)\,dx = 0$$

therefore, the two functions are orthogonal.

3. Linear combinations and linear independence

The algebraic equivalence of vector and function spaces means that all concepts we have previously seen for vectors are simply copied over to functions. In particular, a function f is called a *linear combination* of functions $\{g_1, g_2, g_3, \ldots\}$ if it can be expressed as

$$f = a_1 g_1 + a_2 g_2 + a_3 g_3 + \ldots \tag{2}$$

where $\{a_1, a_2, a_3, \ldots\}$ are real or complex numbers.

A set of functions $\{g_1, g_2, g_3, \ldots\}$ is called *linearly independent* if none of the functions can be expressed as a linear combination of other functions from the same set. If the set $\{g_1, g_2, g_3, \ldots\}$ is linearly independent, then the expansion in Equation (2) is unique.

4. Basis sets

A linearly independent set of functions is called a *basis set* of a space if any function in that space may be expressed as a linear combination of the elements of that set. If the functions in a basis set are mutually orthogonal and normalised

$$\langle g_k(x) | g_n(x) \rangle = \delta_{kn}, \quad \text{where} \quad \delta_{kn} = \begin{cases} 1 & \text{if} \quad k = n \\ 0 & \text{if} \quad k \neq n \end{cases}$$

then the basis set is called an *orthonormal basis set*. The symbol δ_{nk} is called *Kronecker symbol*, after Leopold Kronecker.

The number of functions in a linearly independent basis set (it is the same in all basis sets) is called the *dimension* of the space. Function spaces can be infinite-dimensional.

Example 3: demonstrate that the set of functions $g_n(x) = \cos(nx)/\sqrt{\pi}$, where n is a positive integer, is an orthonormal set on the interval $x \in [-\pi, \pi]$.

Solution: we can easily demonstrate normalization

$$\|g_n(x)\| = \left\| \frac{\cos(nx)}{\sqrt{\pi}} \right\| = \sqrt{\frac{1}{\pi} \int_{-\pi}^{\pi} \cos^2(nx)\, dx} =$$

$$= \sqrt{\frac{1}{2\pi} \int_{-\pi}^{\pi} [1 + \cos(2nx)]\, dx} = \sqrt{\frac{1}{2\pi} 2\pi} = 1$$

and orthogonality for the case when $n \neq k$

$$\langle g_n(x) | g_k(x) \rangle = \frac{1}{\pi} \int_{-\pi}^{\pi} \cos(nx) \cos(kx)\, dx =$$

$$= \frac{1}{2\pi} \int_{-\pi}^{\pi} \left(\cos[(n-k)x] + \cos[(n+k)x] \right) dx = \delta_{nk}$$

Orthonormal basis sets provide a way to express a function as a linear combination of other functions:

$$f(x) = a_1 g_1(x) + a_2 g_2(x) + a_3 g_3(x) + \ldots = \sum_{n=1}^{\infty} a_n g_n(x) \tag{3}$$

The coefficients $\{a_k\}$ are easy to find. We need to calculate the scalar product of both sides of Equation (3) with $g_k(x)$. Because the set $\{g_n(x)\}$ is orthonormal, only one term survives in the sum:

$$\langle g_k(x) | f(x) \rangle = \sum_{n=1}^{\infty} a_n \langle g_k(x) | g_n(x) \rangle = \sum_{n=1}^{\infty} a_n \delta_{nk} = a_k$$

This leads to an important conclusion – if a function $f(x)$ belongs to a particular function space and $\{g_n(x)\}$ is an orthonormal basis set of that space, then $f(x)$ may be expressed as a linear combination of the functions $\{g_n(x)\}$ as follows:

$$f(x) = \sum_{n=1}^{\infty} a_n g_n(x) \qquad a_n = \langle g_n(x) | f(x) \rangle \tag{4}$$

In the practical chemical context, $\{g_n(x)\}$ can be atomic orbitals, and $f(x)$ a molecular orbital in a LCAO method such as Hűckel theory.