CHEM2024 - Week 18 Lecture 2 - Linear expansions and basis sets

Sections 16.1-16.5, 16.10 of Steiner, "The Chemistry Maths Book", 2nd edition.

Linear combinations are important in physical sciences – it is often necessary to represent functions or vectors as linear combinations of other functions or vectors:

$$\begin{gathered} f(x)=\alpha_1 g_1(x)+\alpha_2 g_2(x)+\ldots+\alpha_n g_n(x) \\ \vec{y}=\alpha_1\vec{x}_1+\alpha_2\vec{x}_2+\ldots+\alpha_n\vec{x}_n \end{gathered} \tag{1}$$

examples are writing a vector as a combination of three principal direction orts $\vec{i},\vec{j},\vec{k}$, or representing a function as a combination of sine and cosine waves of different frequencies.

1. Linear expansions and basis sets

It is important to establish under what conditions the expansions shown in Equation (1) are unique, *i.e.* only one set of coefficients $\{\alpha_1,\alpha_2,\ldots,\alpha_n\}$ exists that satisfies Equation (1).

Theorem: let V be a vector space over a field $\mathbb{F}$, let $\vec{x}_1,\ldots,\vec{x}_n,\vec{y}\in V$, and let

$$\vec{y}=\alpha_1\vec{x}_1+\ldots+\alpha_n\vec{x}_n \tag{2}$$

where $\alpha_k\in\mathbb{F}$. This expansion of $\vec{y}$ in terms of $\vec{x}_1,\ldots,\vec{x}_n$ is unique if and only if the vectors $\vec{x}_1,\ldots,\vec{x}_n$ are linearly independent.

Proof: let us assume that another set of expansion coefficients $\beta_k\in\mathbb{F}$ exists for which also

$$\vec{y}=\beta_1\vec{x}_1+\ldots+\beta_n\vec{x}_n \tag{3}$$

Then the difference between Equations (2) and (3) will be:

$$\vec{0}=(\alpha_1-\beta_1)\vec{x}_1+\ldots+(\alpha_n-\beta_n)\vec{x}_n \tag{4}$$

which implies that the set $\{\vec{x}_1,\ldots,\vec{x}_n\}$ is not actually linearly independent, because for example $\vec{x}_1$ may now be expressed as a linear combination of $\vec{x}_2,\ldots,\vec{x}_n$. For linearly independent $\{\vec{x}_1,\ldots,\vec{x}_n\}$ we must therefore have $\alpha_k=\beta_k$ for all k.▪

A ***basis set*** of a vector space is a set of linearly independent vectors from that space, such that any vector of the space may be represented as a linear combination of basis vectors. In other words, if $\{\vec{x}_1,\ldots,\vec{x}_n\}$ is a basis set of V, then every element $\vec{y}\in V$ can be represented as

$$\vec{y}=\sum_k \alpha_k\vec{x}_k \tag{5}$$

This relation is called an ***expansion*** of $\vec{y}$ in the basis $\{\vec{x}_1,\ldots,\vec{x}_n\}$. As per the theorem above, this expansion is unique. Therefore, once a basis set is chosen, any vector in V can be represented by a string of numbers $\alpha_1,\ldots,\alpha_n$, which are called ***expansion coefficients***. The number of elements in the basis of a space is called the ***dimension*** of that space. All basis sets of a given space have the same number of vectors.

2. Finding expansion coefficients

The definitions given above do not provide a way of finding the expansion coefficients. We can, however, use the scalar products introduced in the previous lecture. Consider a particular expansion of some vector $|y\rangle$ *via* the basis vectors $\{|x_1\rangle,\ldots,|x_n\rangle\}$:

$$|y\rangle=\alpha_1|x_1\rangle+\ldots+\alpha_n|x_n\rangle \tag{6}$$

where we switched to Dirac notation for convenience. Let us take a scalar product of both sides of this expression with each vector $|x_k\rangle$ in turn:

$$\begin{cases} \langle x_1 | y \rangle = \alpha_1 \langle x_1 | x_1 \rangle + \ldots + \alpha_n \langle x_1 | x_n \rangle \\ \langle x_2 | y \rangle = \alpha_1 \langle x_2 | x_1 \rangle + \ldots + \alpha_n \langle x_2 | x_n \rangle \\ \cdots \\ \langle x_n | y \rangle = \alpha_1 \langle x_n | x_1 \rangle + \ldots + \alpha_n \langle x_n | x_n \rangle \end{cases} \tag{7}$$

In this system of equations, all angular brackets are just numbers. We therefore have a system of n equations for n unknown expansion coefficients; this system may be solved for $\alpha_1,\ldots,\alpha_n$.

Example 1: find the expansion of the vector $|y\rangle = (5 \quad 7)^{\mathrm{T}}$ in the basis set $\{|x_1\rangle, |x_2\rangle\}$, where $|x_1\rangle = (3 \quad 5)^{\mathrm{T}}$ and $|x_2\rangle = (1 \quad 1)^{\mathrm{T}}$.

Solution: in this case, the expansion contains two unknown coeficients

$$|y\rangle = \alpha_1 |x_1\rangle + \alpha_2 |x_2\rangle$$

Taking scalar products of this expression with $|x_1\rangle$ and then $|x_2\rangle$, we obtain:

$$\begin{cases} \langle x_1 | y \rangle = \alpha_1 \langle x_1 | x_1 \rangle + \alpha_2 \langle x_1 | x_2 \rangle \\ \langle x_2 | y \rangle = \alpha_1 \langle x_2 | x_1 \rangle + \alpha_2 \langle x_2 | x_2 \rangle \end{cases}$$

After calculating the scalar products, we obtain:

$$\begin{cases} 50 = 34\alpha_1 + 8\alpha_2 \\ 13 = 8\alpha_1 + 2\alpha_2 \end{cases}$$

from which we conclude that $\alpha_1 = 1$ and $\alpha_2 = 2$, and therefore:

$$|y\rangle = |x_1\rangle + 2|x_2\rangle$$

3. Orthonormal basis sets

Solving Equations (7) every time expansion coefficients are needed is cumbersome. Let us impose two further conditions on the basis set – that all its vectors have unit length, and are mutually orthogonal:

$$|\vec{x}_k| = 1 \quad \forall k, \quad \langle x_k | x_m \rangle = 0 \quad \text{when} \quad k \neq m \tag{8}$$

These conditions may be merged into the following more compact expression:

$$\langle x_k | x_m \rangle = \delta_{km} \tag{9}$$

where δ_{km} is *Kronecker symbol*, equal to 1 when $k = m$, and to zero otherwise. With this condition in place, Equation (7) simplifies because the brackets on the right hand side are either 0 or 1. Once those simplifications are applied, the expressions for the expansion coefficients become explicit:

$$\begin{cases} \langle x_1 | y \rangle = \alpha_1 \\ \langle x_2 | y \rangle = \alpha_2 \\ \cdots \\ \langle x_n | y \rangle = \alpha_n \end{cases} \tag{10}$$

Equation (10) may also be obtained by a more direct and general route. Let us assume that we have a general expansion for a vector $\vec{y}$ in an *orthonormal basis set* $\{\vec{x}_1,...,\vec{x}_n\}$ that satisfies Equation (9):

$$|y\rangle = \sum_k \alpha_k |x_k\rangle \tag{11}$$

Taking a scalar product on both sides of this expression with a specific basis vector $|x_m\rangle$, we get:

$$\langle x_m|y\rangle = \sum_k \alpha_k \langle x_m|x_k\rangle \tag{12}$$

where we now notice that all the brackets on the right hand side are zero, except for $\langle x_m|x_m\rangle$, which is equal to 1. This yields a very simple result:

$$\alpha_m = \langle x_m|y\rangle \tag{13}$$

Therefore, to find the expansion coefficient in an orthonormal basis set, it is sufficient to take a scalar product with the corresponding vector. The simplicity of Equation (13) is the principal reason why orthonormal basis sets are preferred in computational chemistry.

Example 2: demonstrate that the following basis set is orthornormal

$$\vec{x}_1 = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}, \quad \vec{x}_2 = \frac{1}{\sqrt{2}}\begin{pmatrix} 0 \\ -1 \\ +1 \end{pmatrix}, \quad \vec{x}_3 = \frac{1}{\sqrt{2}}\begin{pmatrix} 0 \\ +1 \\ +1 \end{pmatrix}$$

Solution: we can confirm by calculating the corresponding norms that $|\vec{x}_1| = |\vec{x}_2| = |\vec{x}_3| = 1$. The calculation of scalar products likewise yields $\langle x_1|x_2\rangle = \langle x_2|x_3\rangle = \langle x_3|x_1\rangle = 0$.

Example 3: the following basis occurs in nuclear magnetic resonance, and is known to be orthogonal, but not normalised

$$|\sigma_1\rangle = \begin{pmatrix} 0 \\ +1/2 \\ +1/2 \\ 0 \end{pmatrix}, \quad |\sigma_2\rangle = \begin{pmatrix} 0 \\ +i/2 \\ -i/2 \\ 0 \end{pmatrix}, \quad |\sigma_3\rangle = \begin{pmatrix} +1/2 \\ 0 \\ 0 \\ -1/2 \end{pmatrix}$$

Find the expansion of $|\rho\rangle = \begin{pmatrix} 0 & 0 & 1 & 0 \end{pmatrix}^{\mathrm{T}}$ in this basis.

Solution: it is clear that $|\sigma_3\rangle$ would not contribute because it has a zero in the third position. We are therefore looking at the following expansion:

$$|\rho\rangle = \alpha_1|\sigma_1\rangle + \alpha_2|\sigma_2\rangle$$

Taking scalar products of this with $|\sigma_1\rangle$ and $|\sigma_2\rangle$, we obtain:

$$\begin{cases} \langle\sigma_1|\rho\rangle = \alpha_1\langle\sigma_1|\sigma_1\rangle + \alpha_2\langle\sigma_1|\sigma_2\rangle \\ \langle\sigma_2|\rho\rangle = \alpha_1\langle\sigma_2|\sigma_1\rangle + \alpha_2\langle\sigma_2|\sigma_2\rangle \end{cases} \Rightarrow \begin{cases} \langle\sigma_1|\rho\rangle = \alpha_1\langle\sigma_1|\sigma_1\rangle \\ \langle\sigma_2|\rho\rangle = \alpha_2\langle\sigma_2|\sigma_2\rangle \end{cases}$$

where the expression simplifies because $\langle\sigma_1|\sigma_2\rangle = 0$ – the basis set is orthogonal. Therefore, the expressions for the coefficients are:

$$\alpha_1 = \frac{\langle \sigma_1 | \rho \rangle}{\langle \sigma_1 | \sigma_1 \rangle}, \qquad \alpha_2 = \frac{\langle \sigma_2 | \rho \rangle}{\langle \sigma_2 | \sigma_2 \rangle}$$

Simple arithmetic (not forgetting the conjugation in the scalar product) yields $\alpha_1 = 1$, and $\alpha_2 = i$, and therefore:

$$|\rho\rangle = |\sigma_1\rangle + i|\sigma_2\rangle$$