## Orthogonality

- orthogonality tells us something about the "space" that two orbitals (or more generally two functions) occupy
- if you take two functions, multiply them together ($f_1 \bullet f_2$) and then add up all the negative and positive areas (ie integrate $\int d\tau$) do they exactly balance, ie is the integral zero? If it is then the two functions are orthogonal, they occupy different areas in space, Figure 1

orthogonal:

$$\int \varphi_i \bullet \varphi_j d\tau = 0 \quad i \neq j$$

normalised:

$$\int \varphi_i \bullet \varphi_j d\tau = 1 \quad i = j$$

Figure 1 orthogonality and normalisation

- for example $\int \sin\theta d\theta = -\cos\theta$ and when integrated over a symmetric range the integral is zero (**Figure 2a**): $[-\cos\theta]_0^{2\pi} = [-\cos 2\pi] - [-\cos 0] = -1 + 1 = 0$

- for example consider $\int \sin\theta \bullet -\sin\theta d\theta$ (**Figure 2b**)
  - these two functions are not orthogonal, they are plotted to the left, their product is in **Figure 2c**

$$\int \sin\theta \bullet -\sin\theta d\theta$$
$$= -\int \sin^2\theta d\theta$$
$$\cos 2\theta = 1 - 2\int \sin^2\theta$$
$$= \int \frac{1}{2}(1+\cos 2\theta)d\theta = \int \frac{1}{2}d\theta + \int \frac{1}{2}\cos 2\theta d\theta$$
$$u = 2\theta \quad \frac{du}{d\theta} = 2 \quad d\theta = \frac{du}{2}$$
$$= \int \frac{1}{2}d\theta + \int \frac{1}{2}\cos u \frac{du}{2}$$
$$= \frac{\theta}{2} + \frac{1}{4}\sin u$$
$$= \frac{\theta}{2} + \frac{1}{4}\sin 2\theta$$

  - evaluate over a symmetric range

$$-\int_0^{2\pi} \sin^2\theta d\theta = \left[\frac{\theta}{2} + \frac{1}{4}\sin 2\theta\right]_0^{2\pi}$$
$$= \left[\frac{2\pi}{2} + \frac{1}{4}\sin 4\pi\right] - \left[\frac{0}{2} + \frac{1}{4}\sin 0\right]$$
$$= [\pi + 0] - [0 + 0]$$
$$= \pi$$

  - this is because if you multiply these two functions together, they are always negative and have no positive component to balance them (**Figure 2c**). You must consider the product of the individual functions!

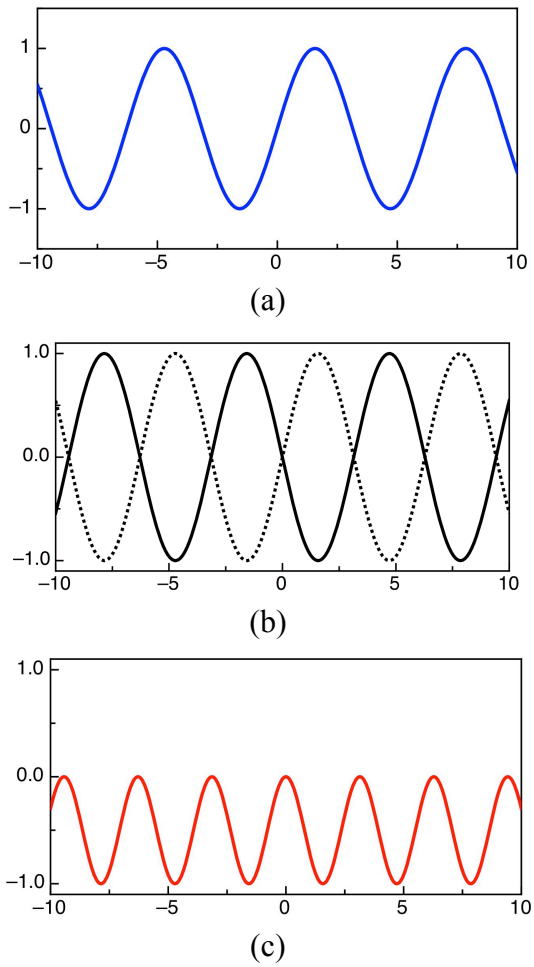



Figure 2 non-orthogonality of two functions

- there are two ways of representing orthogonality one is using an integral notation and the other is using a **Dirac notation** which uses two triangular brackets as shown below

$$\int f_1 \bullet f_2 d\tau = 0$$

$$\langle f_1 | f_2 \rangle = 0$$

- in addition if the integrated product of a function with itself is set to one (by altering coefficients in the function), then the functions are said to be normalised (Figure 3) you will meet this in your theoretical methods course.

orthogonal:

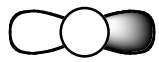
$$\int \varphi_i \bullet \varphi_j d\tau = 0 \quad i \neq j$$

normalised:

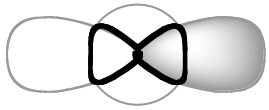
$$\int \varphi_i \bullet \varphi_j d\tau = 1 \quad i = j$$

Figure 3 orthogonality and normalisation

- as another example, think about the orthogonality of the s and p atomic functions
  - since we are multiplying two functions together, anywhere the s orbital is zero the product $\varphi_s \bullet \varphi_p$ will be zero, the same is true for anywhere the p orbital is zero, the product will be zero
  - this will leave only the portion where the s and p orbital overlap exactly that is non-zero (dark line in Figure 4)
  - the non-zero portion is 50% light and 50% dark, that is the positive and negative portions of the functions, which when summed together will exactly cancel
  - <u>atomic orbitals **on the same atom** are constructed to be orthogonal</u> to each other
  - the integral of two atomic orbitals on different centers is the overlap integral S
  - atomic orbitals are also normalised



$$\int \varphi_s \bullet \varphi_p d\tau = 0$$



$$\langle \varphi_s | \varphi_p \rangle = 0$$

Figure 4 atomic orbitals are orthogonal

- thus we don't need to explicitly evaluate rather horrible integrals to determine if it is zero or not, we have used *symmetry*. This pictorial tool of orthogonality is especially powerful as it tells us which integrals need to be evaluated in calculations, and which integrals we know "by symmetry" are zero. It has a very large impact, and is very important in theoretical chemistry, spectroscopy, and chemical reactivity.