

14.3: Wavefunctions

Laplace's wavefunctions are probably familiar to most physical chemistry students already. For example, the lowest energy solution $l = 0, m_l = 0$ has the solution: $Y_{l=0, m_l=0}(\phi, \theta) = \frac{1}{\sqrt{4\pi}}$

This lowest energy state is referred to as the s-state and it has no dependence on angle. To plot this wavefunction we will use what is called a "probability isosurface", which is a picture of where all the probabilities $|Y_{l,m_l}(\phi, \theta)|^2$ have a specific value, such as $|Y_{l,m_l}(\phi, \theta)|^2 = 0.95$. When applied to $Y_{0,0}$ we see a sphere as shown in Figure 14.5. What is interesting to note is that, while it is intuitive to describe a particle with a wavefunction as clearly circulating the origin this is in fact not the case as the rotational energy is:

$$E = l(l+1) \frac{\hbar^2}{2I} = 0 \text{ J}$$

The proper way to see this fact is that the wavefunction has no nodes, which is how quantum mechanics always imparts kinetic energy including rotational.

14.3.1. P- and d-states. Now let's climb the rotational kinetic energy ladder and examine the p-states. There must be three $l = 1$ wavefunctions given the m_l level degeneracy ($m_l = -1, 0, 1$), and they are plotted in Figure 14.6. We expect that we may see hydrogen-like p_z, p_x and p_y states, and in fact the $m_l = 0$ sure looks like p_z ! However, the two $m_l = \pm 1$ wavefunctions do not look anything like p_x or p_y !

The reason why you aren't seeing the expected p_x and p_y "dumbbells" is that the spherical harmonics with finite values of the m quantum number have $e^{\pm i m \phi}$ terms, which are complex (i.e. it contains real and imaginary numbers). Such functions are travelling waves; however, we would prefer stationary waves if possible. It turns out that we can remove the travelling wave components simply by making linear combinations of the spherical harmonics, which is valid because the sum of two Hamiltonian wavefunctions is still a valid wavefunction.

In this endeavor, let's see what happens if we do this: $Y_{1,1} + Y_{1,-1}$, which is an attempt to remove the m_l dependence. Looking up the functions from the table yields:

$$Y_{1,1} + Y_{1,-1} = \sqrt{\frac{3}{8\pi}} \sin(\theta) e^{i\phi} + \sqrt{\frac{3}{8\pi}} \sin(\theta) e^{-i\phi}$$

Next, collecting terms and using the identity $e^{-i\phi} + e^{i\phi} = 2 \cos(\phi)$ yields:

$$Y_{1,-1} + Y_{1,1} = 2 \sqrt{\frac{3}{8\pi}} \sin(\theta) \cos(\phi)$$

If we recall that, for spherical coordinates: $x = \sin(\theta) \cos(\phi)$, which makes $Y_{1,1} + Y_{1,-1}$ equal to the p_x orbital. Following the same idea we find that the difference of the two spherical harmonics $Y_{1,1} - Y_{1,-1}$ can be simplified using $e^{i\phi} - e^{-i\phi} = 2i \sin(\phi)$ to:

$$Y_{1,1} - Y_{1,-1} = 2i \sqrt{\frac{3}{8\pi}} \sin(\theta) \sin(\phi)$$

and since $y = \sin(\theta) \sin(\phi)$ then $(Y_{1,1} - Y_{1,-1})/2i$ is the p_y orbital. In fact, when we plot the isosurfaces of these functions in Figure 14.7 we see that is indeed the case.

Running through the same arguments for the five $l = 2$ d-states yields familiar hydrogen-like results as shown in Figure 14.8, and similarly for the seven f states. We will see these functions again when studying the hydrogen atom in the next chapter. Furthermore, the periodic table is arranged based on the l quantum number. Hopefully you learned in Freshman chemistry that $l = 1$ is the main block, $l = 2$ are for the transition metals and $l = 3$ are the trans-uranium elements.

This page titled 14.3: Wavefunctions is shared under a CC BY-NC 4.0 license and was authored, remixed, and/or curated by Preston Snee.