Quantum Mechanics: The Hydrogen Atom

20th April 2009

I. The Hydrogen Atom Wavefunctions: Orbital Building Blocks

1 The Radial Function

Let's consider $s-$, $p-$, and $d-$type orbitals and arrive at some general descriptions of the spatial variation of these functions.

If we consider Figure 20.6 in Engel and Reid, we note some qualities of the various wavefunctions (which we will now consider interchangeably as **orbitals**). Keep in mind that the x-axis is a reduced distance, but consider it a distance from the nucleus at $R = 0$. The figure shows the **Radial** part of the wavefunction:

- H-atom orbitals have a complex radial and angular dependence that is best discerned via 3-D visualizations; for the present purposes we consider various 2-D representations

- $s-orbitals$ are non-zero at $R = 0$. $p-orbitals$ and $d-orbitals$ are zero at $R = 0$. They have nodal points; in fact in 3-D space (where these functions live) they have **nodal planes**. s-orbitals have **spherical nodal surfaces**.

- For the radial part of the H-atom orbitals, the number of nodes (either planes or spherical surfaces) is equal to $n - l - 1$.

- For the angular functions, there are $(n-l)$ angular nodes. Figure 20.7 in Engel and Reid shows nicely the nodal planes for p and d orbitals.

2 The Radial Probability Distribution Function

We now ask about probabilities associated with the **Radial** part of the orbital. Since we are in 3-D space, working with spherical polar coordinates, we need to be careful when considering probabilities arising from the orbitals.

The probability of finding an electron at a point in 3-D space characterized by (r_0, ϕ_0, ψ_0) in a differential volume element given by $r^2 \, sin(\theta) \, drd\theta d\phi$ is :

$$
\begin{aligned}
P(r, \theta, \phi) r^2 sin(\theta) drd\theta d\phi &= \psi_{nlm}^* \psi_{nlm} r^2 sin(\theta) drd\theta d\phi \\
&= R_n^* R_n Y(\theta, \phi)_{nlm_l}^* Y(\theta, \phi)_{nlm_l} r^2 sin(\theta) drd\theta d\phi
\end{aligned}
$$

Now, if we average over the angular components (since the radial component only has meaning if we average over all the angles possible to sample at a particular radial position):

$$
P(r)dr = r^2 R_n(r)^* R_n(r) dr \left(\int_0^{2\pi} d\phi \int_0^{\pi} Y_{nlm_l}^*(\theta, \phi) Y_{nlm_l}(\theta, \phi) sin(\theta) d\theta \right)
\tag{1}
$$

Thus, as indicated in Engel and Reid, apart from a prefactor (that is simply multiplicative),

$$
\begin{aligned}
P(r)dr &= r^2 R_n(r)^* R_n(r) dr \\
&= r^2 \left[R(r) \right]^2 dr
\end{aligned}
$$

- The radial probability distribution function reconciles our intuition that the probability of finding an electron at the nucleus ($R = 0$) is zero since the electron and nucleus cannot occupy the same point in space at the same time.

- We also see that higher pricinpal quantum number orbitals have higher probability of being further from the nucleus; they are less strongly bound and can be further away. (Figure 20.2 in Engel and Reid)

- Subsidiary peaks emerge for all wavefunctions as the principal quantum number increases. This is a consequence of the wave nature of the particle (wave-particle duality)

- By considering the plots of the radial function and radial probability distribution function, we recover the wave-like property of the electron. Figure 20.10 in Engel and Reid is a nice depiction of this.