

15.3: Hydrogen Radial Wavefunctions

Before we study the wavefunctions, we will first make some approximations to the Hamiltonian that simulate the electron's behavior at short and long distances. For example, what does the radial Schrödinger equation say about the electron if it is highly displaced from the nucleus (at large r)? First, we can use the product rule to show that the kinetic energy operator $\frac{1}{r} \frac{\partial^2}{\partial r^2} r$ is equivalent to $\frac{1}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r}$ (you might demonstrate this as a homework assignment). We make this substitution in the kinetic energy operator because, when the Hamiltonian is multiplied by r :

$$\frac{-\hbar^2}{2\mu} \left(\frac{\partial^2}{\partial r^2} - \frac{l(l+1)}{r^2} - \frac{e^2}{4\pi\epsilon_0 r} \right) r \cdot R(r) = E \cdot r \cdot R(r)$$

This shows us that, if $r \rightarrow \infty$ we can remove the potential energy terms: $\frac{l(l+1)}{r^2} - \frac{e^2}{4\pi\epsilon_0 r}$ leaving:

$$\frac{-\hbar^2}{2\mu} \frac{\partial^2}{\partial r^2} r \cdot R(r) = E \cdot r \cdot R(r)$$

At long distances we can also make the approximation: $\frac{\partial^2}{\partial r^2} r \cdot R(r) \rightarrow r \frac{\partial^2 R(r)}{\partial r^2}$. Next we simply divide by r to find:

$$\frac{\partial^2}{\partial r^2} R(r) = \frac{-2\mu}{\hbar^2} E \cdot R(r)$$

The solution is $R(r) = e^{-c \cdot r}$, where $c = \sqrt{\frac{-2\mu E}{\hbar^2}}$ and has units of inverse length. It may appear that $\sqrt{\frac{-2\mu E}{\hbar^2}}$ should be imaginary; however, this isn't the case because the energies of the hydrogen atom are negative. What is important is that the wavefunction exponentially decays at large distance, which means that the electron very much wants to remain in proximity to the nucleus.

At short distances ($r \rightarrow 0$) we remove the $\sim r^{-1}$ Coulombic potential energy while retaining the angular momentum term $\frac{-\hbar^2}{2\mu} \frac{l(l+1)}{r^2}$ due to its $\sim r^{-2}$ dependence. Likewise we also make the approximation $E \cdot r \cdot R(r) \rightarrow 0$ to yield:

$$\frac{\partial^2}{\partial r^2} r \cdot R(r) - \frac{l(l+1)}{r} R(r) = 0$$

A solution is $R(r) = r^l$ as verified below:

$$\frac{\partial^2}{\partial r^2} r \cdot r^l - \frac{l(l+1)}{r} r^l = \frac{\partial^2}{\partial r^2} r^{l+1} - l(l+1) r^{l-1} = l(l+1) r^{l-1} - l(l+1) r^{l-1} = 0$$

What this means is that the radial wavefunctions have different behavior as a function of angular momentum. This is due to the increase in rotational kinetic energy as the electron approaches the nucleus. In fact it would gain infinite kinetic energy at $r = 0$, although at small distances the fact that $R(r) \approx r^l \rightarrow 0$ prevents this from happening.

The analysis above demonstrates that the radial wavefunctions must have short and long-distance components, with a mathematical entity that bridges the two:

$$R(r) \approx r^l \cdot (?) \cdot e^{-r}$$

This behavior is borne out from the “generalized Laguerre polynomials”; these are solutions to a related differential equation that were derived in 1880. In fact, it is the Laguerre polynomials that are responsible for the quantization of energy because, if the principal quantum number n wasn't an integer, then the wavefunctions wouldn't go to 0 at large distances. The complete radial wavefunctions are listed in Table 15.1.

15.3.1 Properties of the radial wavefunctions

The hydrogen atom's radial Schrödinger equation “controls” the energy via the principal quantum number n . As a result we can examine various features of the radial wavefunctions as they reveal the inner energetic workings of the simplest atom. This information can then be used to build up our knowledge of more complex (multielectron) atoms and eventually molecules. The most sensible organization scheme on hydrogen's electronic properties is based on the shell and angular momentum as characterized by the n and l quantum numbers; in fact the radial wavefunctions are labeled as $R_{n,l}(r)$.

15.3.1.1 The $l = 0$ states

Atomic states with no angular momentum are of the “s” type, and the radial wavefunctions for the first three s-state shells are shown in Figure 15.4 A, B. The 1s wavefunction $R_{1,0}(r) = N \cdot e^{-\frac{r}{a_0}}$ is a simple exponential decay from the origin. The 2s and 3s states are similar, although they have an increasing number of nodes that raises the energy and maintains orthogonality between different eigenstates. The most important feature of the s-states wavefunctions is that they are finite at the origin (i.e. $R_{n,l=0} > 0$ at $r = 0$). The reason that this is allowed is because there is no rotational kinetic energy: $\frac{\hbar^2}{2\mu \cdot r^2} l(l+1) = 0$ that would otherwise become infinitely high as $r \rightarrow 0$. Most interesting is the fact that the s-states are ostensibly degenerate with their higher angular momentum siblings within the same shell; however, as discussed later the phenomenon of shielding energetically favors the s-states.

15.3.1.2 Radial distribution functions

According to Coulomb’s Law if the electron “touches” the nucleus then an infinite amount of energy will be released that would destroy the Universe. The fact that the s-state wavefunctions are finite at $r = 0$ suggests this possibly; however, universal annihilation is thwarted because electron never “finds” the nucleus since it is a point particle. In more technical language, the probability that the electron resides exactly within the same volume as the nucleus is 0%. This fact reveals that it is desirable to represent this volume-probability relationship. To do so we simply multiply the volume-normalizing (Jacobian) $4\pi r^2$ factor times the absolute value of the radial wavefunctions $R_{n,l}^2$ as shown in Figure 15.4D. These are called radial distribution functions, and they provide a great way to communicate quantum information as one can now clearly see that the electron isn’t going to be found at the nucleus for any state. Furthermore, the radial separation between the various s-states due to the n-dependence of the wavefunctions $\sim e^{-\frac{r}{n \cdot a_0}}$ is more visible.

15.3.1.3 The $l > 0$ states

The fact that $R_{n,l>0} = 0$ at the origin is the most distinguishing feature of the higher angular momentum orbitals as seen in the 2p, 3p and 3d functions shown in Figure 15.4C. This is due to the $R(r) \approx r^l$ short length scale behavior originating from the rotational energy that is proportional to $\sim \frac{1}{r^2}$. This radial dependence means that, if the electron approaches the origin it will be spinning with near infinite energy; however, the suppression of wavefunction amplitude as $r \rightarrow 0$ prevents this. As seen in Figure 15.4C increasing the principal quantum number from the 2p to the 3p shell imparts a radial node that steps up the kinetic energy and maintains orthogonality. And while the 2p and 3p radial functions are clearly distinguished from each other, it is interesting to note that the 2p and 3d are similar in their overall shape due to a lack of nodes. The 4f state is similarly nodeless.

15.3.1.4 Degeneracies and magnetism

Due to the dependence of energy on the principal quantum number n one might ask, how do we even know that there are three p, five d and seven f m_l states? It’s because we can directly observe them, and to describe how we first note that an electron with angular momentum is a spinning charge. As such it creates its own magnetic field, the direction of which is proportional to $-m_l$ (the minus sign is a result of the negative charge of the electron). This is why m_l is often called the “magnetic quantum number”. Let’s analyze the 2p ($l = 1$) state’s three $m_l = -1, 0, 1$ sub-states. Since the $m_l = 1$ and $m_l = -1$ have opposing magnetic fields, an external field will interact to split their energies while the $m_l = 0$ state isn’t affected. As a result the m_l degeneracies are lifted which can be observed using fluorescence spectroscopy. Pieter Zeeman first did so in 1896 using sodium and lithium. The so-called Zeeman effect allowed Hendrik Lorentz to predict the properties electrons before the electron was even discovered, and as a result Lorentz and Zeeman won the Nobel Prize in 1902. Later m_l state splitting was observed due to the application of a strong electric field on hydrogen by Johannes Stark in 1913. This effect could only be accurately described using quantum theory which was considered one of the early validations of quantum mechanics, and Stark was awarded the Nobel Prize in 1919.

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