

15.2: The Hydrogen Schrödinger Equation

Concerning the energy of an atom, even a simple one as hydrogen, we must solve the wavefunction for both the electron and the proton. After all, light particle including protons may need to be described with wavefunctions. Electron must always be treated quantum mechanically due to their low mass. Thus, deriving a single wavefunction that describes both the electron and nucleus is unfortunately as complicated as it sounds. This problem can be circumvented using the concept of separability as described in Ch. 14. It was shown that a multidimensional wavefunction can be expressed as the product of smaller parts: $\psi_{total} = \psi_1 \psi_2$, which is possible so long as the Hamiltonian can be separated into terms that do not contain the same quantum operators. As it applies to the hydrogen atom, we can achieve separability by dividing the coupled motion of the proton and electron into relative and center of mass components. The center of mass is defined almost entirely by the proton, which means that the other component is for the electron. The total wavefunction can now be separated into two:

$$\psi_{total} \approx \psi_{electron} \cdot \psi_{proton}$$

Since the proton is $\sim 1800 \times$ heavier than the electron we can assume that it isn't moving, which allows us to simply ignore its wavefunction. The consequence for taking this approach is that the factor of mass in the electron's Hamiltonian is replaced with the proton / electron reduced mass:

$$\mu = \frac{m_p m_e}{m_p + m_e} \sim m_e$$

Due to the fact that a proton is $\sim 1836 \times$ heavier than the electron, the reduced mass is only 0.05% different from the electron mass.

Now that we have decided to focus solely on the electron with its reduced mass, we must define the Hamiltonian and then solve the wavefunction. To this end we will start with the kinetic energy operator. It must be three dimensional and use spherical coordinates since the hydrogen atom (and indeed all atoms) are round. As a result we expect it to be similar to that encountered for the 3D rigid rotor model from Chapter 14, although there is one correction. The radial component of the rigid rotor problem is a fixed quantity, making the radius (r) a parameter as opposed to an operator. This is not true for the hydrogen atom since the electron can approach (or move away) from the nucleus as much as it wants. As a result the correct form of the kinetic energy operator is:

$$\frac{-\hbar^2}{2\mu \cdot r^2} \cdot \left(\frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} + \frac{1}{\sin^2(\theta)} \frac{\partial^2}{\partial \phi^2} + \frac{1}{\sin(\theta)} \frac{\partial}{\partial \theta} \sin(\theta) \frac{\partial}{\partial \theta} \right)$$

Here we will drop the accent mark on the \hat{r} , $\hat{\theta}$ and $\hat{\phi}$ operators for clarity. Next we must tack on the Coulombic potential operator that describes the attraction between the nucleus and the electron:

$$\hat{V}(r) = \frac{e^2}{4\pi\epsilon_0 r}$$

With the addition of the electrostatic component we apply the wavefunction to the Hamiltonian operator into the standard eigenvalue form $\hat{H}\psi(r, \theta, \phi) = E \cdot \psi(r, \theta, \phi)$ as:

$$\frac{-\hbar^2}{2\mu \cdot r^2} \left(\frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} + \frac{1}{\sin^2(\theta)} \frac{\partial^2}{\partial \phi^2} + \frac{1}{\sin(\theta)} \frac{\partial}{\partial \theta} \sin(\theta) \frac{\partial}{\partial \theta} \right) \psi(r, \theta, \phi) + \frac{e^2}{4\pi\epsilon_0 r} \psi(r, \theta, \phi) = E \cdot \psi(r, \theta, \phi)$$

Real nightmare fuel, isn't it? Like Australian snakes, or pretty much any animal down under.

15.2.1. Separability

As with every multivariable quantum mechanical Hamiltonian the first thing to do is to check for separability, here between r , θ and ϕ . This is important because we can't solve the wavefunctions otherwise. Right out of the gate we can see that there may be a problem due to a single term with all three variables: $\frac{1}{r^2} \frac{1}{\sin^2(\theta)} \frac{\partial^2}{\partial \phi^2}$. However, we can make progress towards separability by first multiplying everything by $\frac{-2\mu}{\hbar^2} r^2$:

$$\left(\frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} + \frac{1}{\sin^2(\theta)} \frac{\partial^2}{\partial \phi^2} + \frac{1}{\sin(\theta)} \frac{\partial}{\partial \theta} \sin(\theta) \frac{\partial}{\partial \theta} \right) \psi(r, \theta, \phi) + \frac{e^2}{4\pi\epsilon_0 r} \psi(r, \theta, \phi) = E \cdot \psi(r, \theta, \phi)$$

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$$\sin^2(\theta) \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} \psi(r, \theta, \phi) + \frac{1}{\sin^2(\theta)} \frac{\partial^2}{\partial \phi^2} \psi(r, \theta, \phi) + \frac{1}{\sin(\theta)} \frac{\partial}{\partial \theta} \sin(\theta) \frac{\partial}{\partial \theta} \psi(r, \theta, \phi) + \frac{e^2}{4\pi\epsilon_0 r} \psi(r, \theta, \phi) = E \cdot \psi(r, \theta, \phi)$$

The next step is to insert the separated solution: $\psi(r, \theta, \phi) = R(r)Y(\theta, \phi)$ and divide out the same on the left as: $\frac{1}{R(r)Y(\theta, \phi)} \hat{H}R(r)Y(\theta, \phi)$:

$$\frac{1}{R(r)Y(\theta, \phi)} \left(\frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} \psi(r, \theta, \phi) + \frac{1}{\sin^2(\theta)} \frac{\partial^2}{\partial \phi^2} \psi(r, \theta, \phi) + \frac{1}{\sin(\theta)} \frac{\partial}{\partial \theta} \sin(\theta) \frac{\partial}{\partial \theta} \psi(r, \theta, \phi) + \frac{e^2}{4\pi\epsilon_0 r} \psi(r, \theta, \phi) \right) = E \cdot \frac{1}{R(r)Y(\theta, \phi)} \psi(r, \theta, \phi)$$

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$$\sin^2(\theta) \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} Y(\theta, \phi) + \frac{1}{\sin^2(\theta)} \frac{\partial^2}{\partial \phi^2} Y(\theta, \phi) + \frac{1}{\sin(\theta)} \frac{\partial}{\partial \theta} \sin(\theta) \frac{\partial}{\partial \theta} Y(\theta, \phi) + \frac{e^2}{4\pi\epsilon_0 r} Y(\theta, \phi) = E \cdot Y(\theta, \phi)$$

Now we group all the r terms on one side and the angular θ and ϕ on the other:

$$\frac{1}{R(r)} \left(\frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} R(r) + \frac{e^2}{4\pi\epsilon_0 r} R(r) \right) = E \cdot R(r) - \frac{1}{Y(\theta, \phi)} \left(\frac{1}{\sin^2(\theta)} \frac{\partial^2}{\partial \phi^2} Y(\theta, \phi) + \frac{1}{\sin(\theta)} \frac{\partial}{\partial \theta} \sin(\theta) \frac{\partial}{\partial \theta} Y(\theta, \phi) \right)$$

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$$\frac{1}{R(r)} \left(\frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} R(r) + \frac{e^2}{4\pi\epsilon_0 r} R(r) \right) = E \cdot R(r) - \frac{1}{Y(\theta, \phi)} \left(\frac{1}{\sin^2(\theta)} \frac{\partial^2}{\partial \phi^2} Y(\theta, \phi) + \frac{1}{\sin(\theta)} \frac{\partial}{\partial \theta} \sin(\theta) \frac{\partial}{\partial \theta} Y(\theta, \phi) \right)$$

We assume that the angular wavefunction $Y(\theta, \phi)$ is the same as encountered for the 3D rigid rotor, i.e. the spherical harmonics $Y_{l,m}$ discussed in Chapter 14, section 14.2.3. Based on the information derived from the 3D rigid rotor problem the right (angular) side of the expression $\frac{1}{Y_{l,m}} \hat{H}(\theta, \phi) Y_{l,m}$ is equal to $l(l+1)$, where the l quantum number is $l = 0, 1, 2$, etc. This leaves the radial part to solve as:

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

After some algebra and rearrangement we find:

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

To return the above into an eigenvalue form we simply multiply by $\frac{R(r)}{r^2}$ to reveal the radial Schrödinger equation:

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

This differential equation has to specify a value of the angular momentum quantum number l before solving it, which means that there will be an l dependence to the solutions as shown below. With the wavefunctions in hand the energy of the hydrogen atom can be determined:

$$E = -\frac{\mu \cdot e^4}{32\pi^2 \epsilon_0^2 \hbar^2} \frac{1}{n^2}$$

which is found to depend on a “principal” quantum number $n = 1, 2, 3$ etc. This quantum mechanical equation for energy is identical to that predicted by the Bohr model and conforms to the Balmer and Rydberg equation for spectroscopic transitions. The energies are negative due to the Coulomb potential as shown in Figure 15.2. As in all our previous examples the quantization occurs from a boundary condition, which for the hydrogen atom is that $R(r) \rightarrow 0$ as $r \rightarrow \infty$. Examination of the wavefunctions as discussed below reveal that n is related to the size of the orbital which we will now refer to as a “shell”. Degeneracies may be observed because, for any given principal quantum number n , there are $l = 0, 1, 2 \dots (n-1)$ solutions to the radial equation. In fact there are even more degeneracies due to the angular part of the Hamiltonian, as for each l there are $2l+1$ more states as defined by the $m_l = -l \dots 0 \dots l$ quantum number. Hence, it must be true that the first shell state ($n = 1$) has no angular momentum ($l = 0$) and is nondegenerate. In contrast, the $n = 2$ state has four degenerate wavefunctions characterized by $l = 0$ (2s orbitals) and $l = 1$ (2p orbitals). The 2p state has three wavefunctions that we know as p_x , p_y and p_z . The third and fourth shell can have $l = 2$ (d orbitals, describing transition metals) and $l = 3$ (f orbitals, characteristic of the actinides and lanthanides).

15.2.1. Quantum numbers and the periodic table

The dependencies of the various quantum numbers for the hydrogen atom are what give the periodic table its overall shape. Shown in Figure 15.3 is a representation based solely on quantum numbers; the rows are arranged according to the shell, which is the same thing as the principal quantum number n . The columns are arranged by the l quantum number, and each l block is $2l+1$ wide due to the m_l states. However, the overall arrangement of elements in Figure 15.3 is very different than the periodic table as you know it, which is arranged with the l blocks starting from s, f (tucked underneath) d, and finally p. This arrangement is due to the phenomenon of shielding that causes electrons to fill into orbitals according to that arrangement rather than monotonically with l as the atomic number Z increases. Shielding is discussed further below.

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