

Physics 438A – Lecture #9

The Hydrogen Atom

Aaron Wirthwein – wirthwei@usc.edu

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1 The Electrostatic Model

We shall use the *electrostatic model* for the hydrogen atom, in which the electron and proton interact by an electrostatic force determined by the instantaneous positions of the particles. The electrostatic model is an approximation to electrodynamics in which one neglects the delay in the communication between the particles, magnetic effects, and the effects of radiation. As a part of the electrostatic model we shall also assume the electron motion is non-relativistic, something that is justified in the case of hydrogen.

Under these assumptions, the potential energy of interaction between the electron and the proton is

$$V(r) = -\frac{e^2}{4\pi\varepsilon_0 r}$$

and the corresponding radial equation is

$$-\frac{\hbar^2}{2\mu} \frac{d^2u}{dr^2} + \left[\frac{\hbar^2}{2\mu} \frac{\ell(\ell+1)}{r^2} - \frac{e^2}{4\pi\varepsilon_0 r} \right] u = Eu$$

where μ is the reduced mass of the electron-proton system

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

To a good approximation, we could take $\mu = m_e$ since the proton is much heavier than the electron. In fact, the ratio of the proton mass to the electron mass is roughly 1836, which is suspiciously close to the pure number $6\pi^5$.

The Coulomb potential admits continuum states (in this case with $E > 0$) and discrete states (with $E < 0$). The Hamiltonian has a mixed spectrum, which implies the bound states are not complete on their own. For now, we are only interested in the bound states since they correspond to a stable hydrogen atom.

2 The Radial Equation

It is convenient to write the radial equation in terms of dimensionless energy and distance parameters. These parameters will give us a sense of scale. Define the characteristic length scale by introducing a change of variables

$$\rho = \frac{r}{a}$$

where a is the length scale to be determined. In terms of ρ , the radial equation becomes

$$-\frac{\hbar^2}{2\mu a^2} \frac{d^2 u}{d\rho^2} + \left[\frac{\hbar^2}{2\mu a^2} \frac{\ell(\ell+1)}{\rho^2} - \frac{e^2}{4\pi\varepsilon_0 a} \frac{1}{\rho} \right] u = Eu$$

After multiplying by $-2\mu a^2/\hbar^2$ and rearranging the expression,

$$\frac{d^2 u}{d\rho^2} + \left[\frac{2\mu a^2}{\hbar^2} E - \frac{\ell(\ell+1)}{\rho^2} + \frac{2\mu}{\hbar^2} \frac{e^2}{4\pi\varepsilon_0} \frac{a}{\rho} \right] u = 0$$

The term in square brackets must be dimensionless, so we're invited to define

$$a = \frac{4\pi\varepsilon_0 \hbar^2}{\mu e^2}$$

as the characteristic length scale for the hydrogen atom. From the first term in square brackets, we can identify $\hbar^2/2\mu a^2$ as the characteristic energy scale. We define

$$-\gamma^2 = \frac{E}{\hbar^2/2\mu a^2} \quad (E < 0)$$

With the dimensionless length and energy parameters, the radial equation becomes

$$\frac{d^2 u}{d\rho^2} + \left[\frac{2}{\rho} - \frac{\ell(\ell+1)}{\rho^2} - \gamma^2 \right] u = 0$$

2.1 Asymptotic Solutions

For large ρ , the terms involving ρ^{-1} and ρ^{-2} can be neglected, so we're left with

$$\frac{d^2 u}{d\rho^2} = \gamma^2 u$$

The general solution for large ρ is $u = A^{-\gamma\rho} + B^{\gamma\rho}$, but the wave function must vanish at $\rho \rightarrow \infty$, so we must choose $B = 0$. For large ρ , we find $u = Ae^{-\gamma\rho}$. Alternatively, when ρ is

small, the centrifugal term dominates, and the radial equation in this limit is

$$\frac{d^2u}{d\rho^2} = \frac{\ell(\ell+1)}{\rho^2}u$$

Monomial functions have the property that $(\rho^s)' = s\rho^{s-1}$, so with $u = \rho^s$,

$$s(s-1)u^{s-2} = \ell(\ell+1)u^{s-2} \rightarrow s(s-2) = \ell(\ell+1)$$

The general solution for small ρ is $u = C\rho^{\ell+1} + D\rho^{-\ell}$. The second term grows without bound for small ρ (assuming $\ell > 0$), so we must choose $D = 0$. The solution for small ρ is then $u = C\rho^{\ell+1}$. Now that we know the asymptotic solutions, we can find the solution for intermediate ρ by solving for a function $v(\rho)$ such that

$$u(\rho) = \rho^{\ell+1}e^{-\gamma\rho}v(\rho)$$

2.2 Series Solution to the Radial Equation

We substitute the equation $u(\rho) = \rho^{\ell+1}e^{-\gamma\rho}v(\rho)$ into the radial equation to obtain a differential equation for $v(\rho)$. After some lengthy calculations, we find

$$\rho \frac{d^2v}{d\rho^2} + 2(1+\ell-\gamma\rho) \frac{dv}{d\rho} + 2(1-\gamma-\gamma\ell)v = 0$$

We will use a power series expansion to solve the radial equation for $v(\rho)$. Assume

$$v(\rho) = \sum_{j=0}^{\infty} c_j \rho^j$$

where c_j are coefficients to be determined. After substituting the series solution,

$$\begin{aligned} & \sum_k k(k+1)c_{k+1}\rho^k + 2(\ell+1) \sum_k (k+1)c_{k+1}\rho^k \\ & - 2\gamma \sum_k kc_k\rho^k + 2(1-\gamma-\gamma\ell) \sum_k c_k\rho^k = 0 \end{aligned}$$

In order for all terms of the series to sum to zero for any and all values of ρ , the coefficient of each power of ρ must vanish. Hence,

$$k(k+1)c_{k+1} + 2(\ell+1)(k+1)c_{k+1} - 2\gamma kc_k + 2(1-\gamma-\gamma\ell)c_k = 0$$

or,

$$c_{k+1} = \frac{2\gamma(k + \ell + 1) - 2}{(k + 1)(k + 2\ell + 2)} c_k$$

This is a recurrence relation for the coefficients; the starting coefficient c_0 determines all of the remaining coefficients in the function $v(\rho)$. Ultimately, c_0 is determined by the normalization requirement. Observe that for large values of k ,

$$c_{k+1} \approx \frac{2\gamma k}{k^2} c_k = \frac{2\gamma}{k} c_k$$

which is precisely the recurrence relation for the exponential function, with series expansion

$$e^x = \sum_k \frac{1}{k!} x^k \rightarrow c_{k+1} = \frac{1}{k+1} c_k \approx \frac{1}{k} c_k$$

for large k . This implies for large ρ , $v(\rho) \approx A e^{2\gamma\rho}$, and furthermore

$$u(\rho) = A \rho^{\ell+1} e^{\gamma\rho}$$

which blows up for large ρ , and is therefore not a physical solution. We can eliminate the solution by forcing the series expansion of $v(\rho)$ to terminate at a finite value of k . The requirement that the wave function be normalizable and decay at infinity leads us to define a value k_{\max} such that the numerator of the recurrence relation vanishes. In other words,

$$\gamma(k_{\max} + \ell + 1) - 1 = 0$$

Since k and ℓ are integers, $k_{\max} + \ell + 1$ is also an integer, which we denote as n :

$$n = k_{\max} + \ell + 1$$

This new integer is the **principal quantum number** of the hydrogen atom. The definition of the principal quantum number n leads us immediately to three important conclusions.

1. The principle quantum number starts at 1 and goes to infinity:

$$n = 1, 2, \dots, \infty$$

2. Energy is quantized! Since $\gamma = 1/n$,

$$E = -\frac{\hbar^2}{2\mu a^2} \gamma^2 = -\frac{\hbar^2}{2\mu a^2} \frac{1}{n^2}$$

3. The angular momentum quantum number ℓ has a maximum value for every value of n . Notice that

$$\ell = n - k_{\max} - 1$$

is maximized when $k_{\max} = 0$, so

$$\ell_{\max} = n - 1$$

Thus, the radial eigenvalue solution places a new limit on the allowed values of the angular momentum quantum number.

$$\ell = 0, 1, 2, \dots, n - 1$$

2.3 The Radial Wave Function

The radial wave function with dimensions back in place is

$$\mathcal{R}_{n\ell}(r) = \left(\frac{r}{a}\right)^{\ell} e^{-r/na} v(r/a)$$

We label the radial wave functions with the two quantum numbers n and ℓ that affect the radial dependence. Now we're ready to use our knowledge of the allowed quantum numbers and the recurrence relation to find the polynomial $v(r/a)$ for each state. The polynomial terminates at the value

$$k_{\max} = n - \ell - 1$$

Let's start with the ground state (the state with lowest possible energy) labeled by the quantum numbers $n = 1$ and $\ell = 0$. The polynomial $v(r/a)$ terminates at $k_{\max} = 0$, so we simply have $v(r/a) = c_0$. The ground state radial wave function is

$$\mathcal{R}_{10}(r) = c_0 e^{-r/a}$$

where the constant c_0 is determined by normalization:

$$1 = \int_0^\infty r^2 dr |\mathcal{R}_{10}|^2 = \int_0^\infty dr r^2 |c_0|^2 e^{-2r/a} = |c_0|^2 \cdot \frac{a^3}{4}$$

$$c_0 = \frac{2}{a^{3/2}}$$

Hence,

$$\mathcal{R}_{10}(r) = \frac{2}{a^{3/2}} e^{-r/a}$$

Note that the coefficients for different sets of quantum numbers are not related to each other.

Consider the first excited state of hydrogen with $n = 2$. There are two possible values for ℓ (0 and 1) and three values for m (although the magnetic quantum number does not affect the radial wave function). There are four states with the same energy:

$$|n, \ell, m\rangle = \{ |2, 0, 0\rangle, |2, 1, -1\rangle, |2, 1, 0\rangle, |2, 1, 1\rangle \}$$

For the state $|2, 0, 0\rangle$, the polynomial $v(r/a)$ terminates at $k_{\max} = 1$, so

$$v(r/a) = c_0 + c_1(r/a)$$

where the coefficients are related by the recurrence relation such that $c_1 = -c_0/2$. Thus,

$$\mathcal{R}_{20}(r) = c_0 e^{-r/2a} (1 - r/2a)$$

and c_0 is determined by the normalization condition. For the states with $n = 2$ and $\ell = 1$, the polynomial $v(r/a)$ terminates at $k_{\max} = 0$, so $v(r/a) = c_0$ and

$$\mathcal{R}_{21}(r) = c_0 r e^{-r/2a}$$

It turns out that the radial wave functions can also be written in terms of a common set of functions known as the **associated Laguerre polynomials** $L_q^p(x)$, which are defined as

$$L_q^p(x) = \frac{d^p}{dx^p} L_q(x)$$

where $L_q(x)$ are the ordinary **Laguerre polynomials** defined as

$$L_q(x) = e^x \frac{d^q}{dx^q} (x^q e^{-x})$$

Using these definitions, the radial wave functions are

$$\mathcal{R}_{n\ell}(r) = - \left\{ \left(\frac{2}{na} \right)^3 \frac{(n - \ell - 1)!}{2n[(n + \ell)!]^3} \right\}^{1/2} e^{-r/na} \left(\frac{2r}{na} \right)^\ell L_{n+\ell}^{2\ell+1}(2r/na)$$

The associated Laguerre polynomial above is a polynomial of degree $(n + \ell) - (2\ell + 1) = n - \ell - 1$ as expected from the value of k_{\max} .

2.4 Hydrogen Energies and Spectrum

3 Hydrogen Wave Functions