

6 The hydrogen atom

Earlier in the course we used classical physics together with simple quantum arguments to study the Bohr model of the hydrogen atom. We will now apply the Schrödinger equation to the hydrogen atom in an attempt to derive a more complete quantum model. To do this we will

1. Consider the Schrödinger equation in three dimensions.
2. Describe the potential energy of the electron-proton system using Coulomb's law, i.e.

$$V(r) = -\frac{e^2}{4\pi\epsilon_0} \cdot \frac{1}{r}. \quad (1)$$

Using our previous experience of the time independent Schrödinger equation (TISE) in three dimensions we write the Schrödinger equation as

$$-\frac{\hbar^2}{2m} \frac{1}{\psi(x, y, z)} \left[\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} \right] = E - V(r). \quad (2)$$

A couple of modifications are required

1. We use μ , the reduced electron mass in the electron-proton system, rather than the electron mass, m .
2. If we modify the e^2 term in the potential to Ze^2 we can apply this model to any hydrogenic atom.

The electrostatic potential depends only upon the radial distance r between the electron and the proton. To exploit the radial symmetry of the potential we transform the Schrödinger equation from Cartesian to spherical polar coordinates (Figure 1), i.e.

$$x = r \sin \theta \cos \phi \quad (3)$$

$$y = r \sin \theta \sin \phi \quad (4)$$

$$z = r \cos \theta \quad (5)$$

where we define,

$$r = \sqrt{x^2 + y^2 + z^2}, \quad (6)$$

$$\theta = \cos^{-1} \left(\frac{z}{r} \right) \quad \text{as the polar angle} \quad (7)$$

$$\phi = \tan^{-1} \left(\frac{z}{r} \right) \quad \text{as the azimuthal angle.} \quad (8)$$

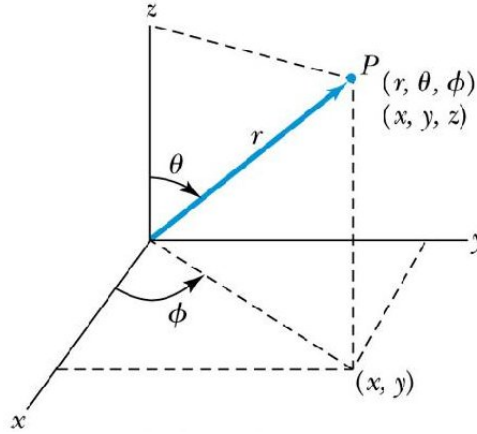


Figure 1: The relationship between polar and Cartesian coordinates.

The Laplacian operator, which in Cartesian coordinates takes the form

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}, \quad (9)$$

is now written as

$$\nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2}. \quad (10)$$

We now re-write the Schrödinger equation as

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \psi}{\partial \phi^2} + \frac{2\mu}{\hbar^2} [E - V(r)] \psi = 0 \quad (11)$$

This equation does not contain any cross-terms of the form $\partial/\partial r \times \partial/\partial \theta$ etc., and we can look for a solution of the form

$$\psi(r, \theta, \phi) = R(r)f(\theta)g(\phi). \quad (12)$$

We will substitute this equation into the Schrödinger equation and solve for the appropriate boundary conditions in each dimension. In the process we will require three quantum numbers – one for each direction of motion available to the electron – in order to describe the system.

Computing solutions to the Schrödinger equation will allow us to understand the electron “structure” (in reality a probability density function) of the hydrogen atom – in both the ground and excited states. Using Equation 12 we derive the following quantities

$$\frac{\partial \psi}{\partial r} = fg \frac{\partial R}{\partial r}, \quad \frac{\partial \psi}{\partial \theta} = Rg \frac{\partial f}{\partial \theta}, \quad \frac{\partial^2 \psi}{\partial \phi^2} = Rf \frac{\partial^2 g}{\partial \phi^2}. \quad (13)$$

Substituting these terms into the Schrödinger equation, we obtain

$$\frac{fg}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial R}{\partial r} \right) + \frac{Rg}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial f}{\partial \theta} \right) + \frac{Rf}{r^2 \sin^2 \theta} \frac{\partial^2 g}{\partial \phi^2} + \frac{2\mu}{\hbar^2} [E - V(r)] Rfg = 0. \quad (14)$$

Multiplying both sides by $(r^2 \sin^2 \theta)/Rfg$, we obtain

$$-\frac{\sin^2 \theta}{R} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) - \frac{\sin \theta}{f} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial f}{\partial \theta} \right) - \frac{2\mu}{\hbar^2} r^2 \sin^2 \theta [E - V(r)] = \frac{1}{g} \frac{\partial^2 g}{\partial \phi^2}. \quad (15)$$

As we have seen before, this equation must hold simultaneously for all r, θ, ϕ . The RHS contains only terms involving ϕ whereas the LHS contains only terms involving r, θ . Therefore, each side must be equal to some constant value. We let this constant equal $-m_l^2$ and consider the RHS of the above equation, i.e.

$$\frac{1}{g} \frac{d^2 g}{d\phi^2} = -m_l^2 \quad \text{or} \quad \frac{d^2 g}{d\phi^2} = -m_l^2 g. \quad (16)$$

This is referred to as the **Azimuthal** equation (ϕ represents the azimuth). This equation describes a harmonic oscillator and solutions for $g(\phi)$ will take the general form $e^{im_l \phi}$.

The appropriate boundary condition we apply here is that $g(\phi)$ must be single valued. This means that

$$\begin{aligned} g(\phi) &= g(\phi + 2\pi) \\ g(0) &= g(2\pi) \\ e^0 &= e^{2\pi im_l}. \end{aligned} \quad (17)$$

This condition is satisfied for all ϕ if m_l is restricted to being equal to zero or either a positive or negative integer.

We now turn to the LHS of Equation 15. Setting this equal to $-m_l^2$ and re-arranging, we obtain

$$\frac{1}{R} \frac{\partial}{\partial r} \left(r^2 \frac{\partial R}{\partial r} \right) + \frac{2\mu r^2}{\hbar^2} [E - V(r)] = \frac{m_l^2}{\sin^2 \theta} - \frac{1}{f \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial f}{\partial \theta} \right), \quad (18)$$

and note that we have now separated the functions R and f representing the variables r and θ . As before, we set each side of this equation equal to a constant, i.e. $l(l+1)$. Re-arranging each side of the equation in turn generates

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \frac{2\mu}{\hbar^2} \left[E - V(r) - \frac{\hbar^2 l(l+1)}{2\mu r^2} \right] R = 0, \quad (19)$$

which defines the **Radial** equation, and

$$\frac{1}{\sin \theta} \frac{d}{d\theta} \left(\sin \theta \frac{df}{d\theta} \right) + \left[l(l+1) - \frac{m_l^2}{\sin^2 \theta} \right] f = 0, \quad (20)$$

which defines the **Angular** equation. Our analysis of the Schrödinger equation has generated three ordinary second order differential equations which can be solved in turn.

6.1 The Radial equation

The form of the Radial equation has been known to mathematicians since long before the advent of quantum mechanics as the **associated Laguerre equation**. The solutions R to this equation that satisfy the appropriate boundary conditions are known as associated Laguerre functions. It turns out that the ground state wave function of the hydrogen atom is characterised by the quantum numbers $l = 0$ and $m_l = 0$. Under these conditions, the Radial equation takes the relatively simple form

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \frac{2\mu}{\hbar^2} [E - V(r)] R = 0. \quad (21)$$

Expanding out both the differential term and the Coulomb potential we obtain

$$\frac{d^2 R}{dr^2} + \frac{2}{r} \frac{dR}{dr} + \frac{2\mu}{\hbar^2} \left(E + \frac{e^2}{4\pi\epsilon_0 r} \right) R = 0. \quad (22)$$

The solution to this equation takes the form $R = Ae^{-r/a_0}$ where A is a normalisation constant and a_0 is a length scale associated with the electron ground state. We insert our trial solution into the ground state radial equation, noting that the terms

$$\frac{dR}{dr} = -\frac{1}{a_0} R \quad \text{and} \quad \frac{d^2 R}{dr^2} = \frac{R}{a_0^2}, \quad (23)$$

to obtain

$$\left(\frac{1}{a_0^2} + \frac{2\mu E}{\hbar^2} \right) + \frac{1}{r} \left(\frac{2\mu e^2}{4\pi\epsilon_0 \hbar^2} - \frac{2}{a_0} \right) = 0. \quad (24)$$

Using the same reasoning that we applied to the separation of variables, the only way that this equation can hold for all r is if each term in parentheses is equal to zero. Looking at the second set of parentheses we have

$$a_0 = \frac{4\pi\epsilon_0 \hbar^2}{\mu e^2} \quad (25)$$

which is equal to the **Bohr radius**. Looking at the first set of parentheses we have

$$E = -\frac{\hbar^2}{2\mu a_0^2} = -E_0, \quad (26)$$

where $E_0 = 13.6$ eV is the ground state energy of the electron. These relationships are valid for the ground state hydrogen atom only. Given that the wave functions of the excited states depend upon the associated Laguerre functions we will discuss excited states in qualitative form only.

6.2 Quantum numbers and excited states

The full solution of the Radial equation involves the introduction of the quantum number n . The associated energy states are

$$E_n = -\frac{E_0}{n^2}, \quad (27)$$

the same as we obtained for the Bohr model. The quantum numbers are named as follows:

n	Principal quantum number	$n > 0$	positive integer
l	Orbital angular momentum quantum number	$l < n$	zero or positive integer
m_l	Magnetic quantum number	$ m_l \leq l$	zero, positive or negative integer

where the restrictions on the values of quantum numbers are derived from the application of the boundary conditions to the wave function $\psi(r, \theta, \phi)$. For example, the permitted quantum numbers describing the $n = 4$ state are

n	l	m_l
4	0	0
4	1	-1,0,1
4	2	-2,-1,0,1,2
4	3	-3,-2,-1,0,1,2,3

The $n = 4$ state is degenerate (in the absence of an electric or a magnetic field) with each of the sixteen possible states possessing the same energy. However, each state is described by a different wave function.

Due to the form of the Radial equation the radial wave functions depend upon the quantum numbers n and l . Solutions are labeled R_{nl} . Both the Angular and Azimuthal equations depend upon the quantum number m_l (with the Angular equation also displaying a l dependence). Solutions to the Angular and Azimuthal equations are grouped together into a spherical harmonic series of the form

$$Y_{lm_l}(\theta, \phi) = f_{lm_l}(\theta)g_{m_l}(\phi). \quad (28)$$

Solutions to $R_{nl}(r)$ and $Y_{lm_l}(\theta, \phi)$ are shown in T-Rex Tables 7.1 and 7.2

T-Rex Example 7.2: Show that the hydrogen wave function ψ_{211} is normalised.

To normalise the wave function in three dimensions we form the expression

$$\int \psi_{nlm_l}^* \psi_{nlm_l} d\tau = \int_0^\infty \int_0^\pi \int_0^{2\pi} \psi_{211}^* \psi_{211} r^2 \sin \theta dr d\theta d\phi = 1, \quad (29)$$

where $d\tau = r^2 \sin \theta dr d\theta d\phi$ is the spherical polar volume element. The wave function may be written as

$$\psi_{211} = R_{21} Y_{11} = \left[\frac{r}{a_0} \frac{e^{-r/2a_0}}{\sqrt{3}(2a_0)^{3/2}} \right] \left[\frac{1}{2} \sqrt{\frac{3}{2\pi}} \sin \theta e^{i\phi} \right], \quad (30)$$

and the probability term

$$\psi_{211}^* \psi_{211} = \frac{1}{64\pi a_0^5} r^2 e^{-r/a_0} \sin^2 \theta. \quad (31)$$

The normalisation condition then becomes

$$\begin{aligned} \int \psi_{nlm_l}^* \psi_{nlm_l} d\tau &= \frac{1}{64\pi a_0^5} \int_0^\infty r^4 e^{-r/a_0} dr \int_0^\pi \sin^3 \theta d\theta \int_0^{2\pi} d\phi \\ &= \frac{1}{64\pi a_0^5} [24a_0^5][4/3][2\pi] \\ &= 1. \end{aligned} \quad (32)$$

Therefore the wave function is normalised.

6.3 The electron probability density function

In the Bohr model of the atom, the electron was visualised as a particle travelling about the proton on a circular (or elliptical) orbit with a well-defined position vector \vec{r} . However, using our wave description of matter, we know that the position of the electron is no longer a well-defined property and instead we must use a probability distribution function which gives the probability to find the electron in a volume element $d\tau$ as

$$dP = \psi^*(r, \theta, \phi) \psi(r, \theta, \phi) d\tau. \quad (33)$$

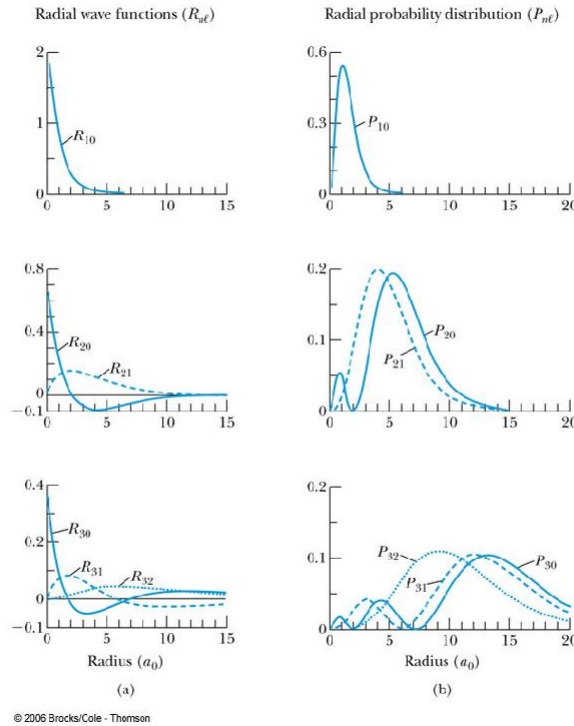
If we choose to look at the radial probability density, i.e. the probability to locate the electron within a radius r to $r + dr$, we must integrate over θ and ϕ to determine the average radial dependence, i.e.

$$P(r)dr = r^2 R^*(r) R(r) dr \int_0^\pi |f(\theta)|^2 \sin^2 \theta d\theta \int_0^{2\pi} |g(\phi)|^2 d\phi. \quad (34)$$

If the Angular and Azimuthal wave functions are already normalised, this expression reduces to

$$P(r)dr = r^2|R(r)|^2dr. \quad (35)$$

Radial probability density functions are displayed in Figure 2.



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Figure 2: Radial wave functions and their associated radial probability distributions.

Finally, we compare the most probable and the average expected position in the ground state hydrogen atom. For the most probable location we set $dP(r)/dr = 0$ and solve for r , i.e.

$$\begin{aligned} P(r) &= r^2|R(r)|^2 \\ &= r^2 \left(\frac{2}{a_0^{3/2}} e^{-r/a_0} \right)^2 \\ &= \frac{4r^2}{a_0^3} e^{-2r/a_0} \\ \frac{dP(r)}{dr} &= \frac{4}{a_0^3} \left(-\frac{2}{a_0} + 2r \right) e^{-2r/a_0} \end{aligned}$$

$$\begin{aligned}\frac{2r^2}{a_0} &= 2r \\ r &= a_0,\end{aligned}\tag{36}$$

is the most probable radius.

To compute the average value we must compute the expectation value of the electron position given the wave function.

$$\begin{aligned}\langle r \rangle &= \int \psi^*(r, \theta, \phi) r \psi(r, \theta, \phi) d\tau \\ &= \int r P(r) dr,\end{aligned}\tag{37}$$

having integrated over θ and ϕ . Therefore

$$\begin{aligned}\langle r \rangle &= \int_0^\infty \frac{4}{a_0^3} r^2 e^{-2r/a_0} dr \\ &= \frac{4}{a_0^3} \left[\frac{3a_0^4}{8} \right]\end{aligned}\tag{38}$$

$$= \frac{3}{2} a_0,\tag{39}$$

i.e. the average radius is larger than the most probable value of the radius – a result that can be understood noting the long tail in $P(r)$ with increasing r with respect to the maximum.