

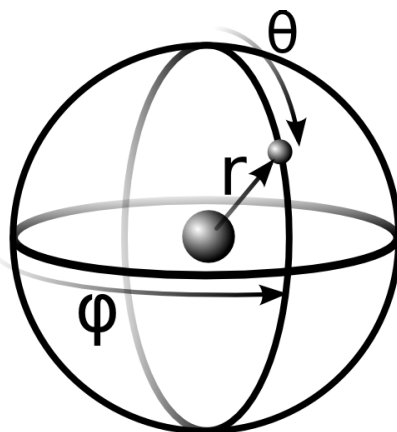
# The Spectrum of the Hydrogen Atom

*By*

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## Abstract

This article reviews the method of separation of variables and some of the basic results of quantum theory in order to derive the energy levels of a hydrogen atom, explaining the cause for the observed spectrum of the hydrogen atom.

The hydrogen atom is modelled in spherical polar coordinates as an electron orbiting a proton due to an electric Coulomb potential. The time independent Schrödinger equation for hydrogen, a three variable partial differential equation, is then solved using the method of separation of variables to find the radial, azimuthal and polar normalised functions; and these are recombined to find the total wavefunction describing the quantum states of the hydrogen atom.

During the process it is found that the states of a hydrogen atom are described by three integer quantum numbers —  $l$ ,  $m$  and  $n$  — and that the energy levels of the hydrogen atom —  $E_n$  — are only dependant on  $n$ . It is explained that the result of an electron moving from an energy level  $E_p$  in an excited hydrogen atom to a lower energy level  $E_q$  results in the release of a photon with energy  $E = E_p - E_q$ , and this fact is used to derive the possible frequencies of light given off by an excited hydrogen atom — the spectrum of hydrogen.

## Contents

<b>1</b>	<b>Introduction</b>	<b>3</b>
1.1	Aim of this Article . . . . .	3
1.2	Approach . . . . .	3
1.3	Main Conclusions . . . . .	4
1.4	Overview . . . . .	4
<b>2</b>	<b>Quantum Mechanics and the Schrödinger Equation</b>	<b>4</b>
2.1	The Founders of Quantum Mechanics . . . . .	4
2.2	Wavefunctions . . . . .	5
2.2.1	Heisenberg's Uncertainty Principle . . . . .	6
2.2.2	Normalisation . . . . .	6
2.2.3	Wavefunctions Are Single Valued . . . . .	6
2.2.4	Eigenstates and Eigenvalues . . . . .	6
2.3	Schrödinger Equation . . . . .	7
2.4	Time Independent Schrödinger Equation (TISE) . . . . .	7
2.5	TISE in Spherical Polar Coordinates . . . . .	8
2.6	Schrödinger Equation for the Hydrogen Atom . . . . .	9
<b>3</b>	<b>Separation of Variables</b>	<b>10</b>
3.1	Explanation . . . . .	10
3.2	An Example: The Schrödinger Equation for Hydrogen . . . . .	11
<b>4</b>	<b>Solving the TISE for the Hydrogen Atom</b>	<b>12</b>
4.1	Solution for $\Phi$ . . . . .	12
4.2	Solution for $\Theta$ . . . . .	13
4.3	Solution for $R$ . . . . .	13
4.4	The Final Wavefunction . . . . .	16
<b>5</b>	<b>Energy Levels in the Hydrogen Atom</b>	<b>16</b>
5.1	Absorption and Emission Spectra . . . . .	17
<b>6</b>	<b>Discussion</b>	<b>19</b>
6.1	Conclusion . . . . .	20
<b>A</b>	<b>Associated Legendre Equation</b>	<b>20</b>
A.1	The Legendre Equation . . . . .	20
A.2	The Associated Legendre Equation . . . . .	22
	<b>Glossary</b>	<b>22</b>
	<b>References</b>	<b>24</b>

## List of Figures

1	Simplified model of the hydrogen atom. . . . .	9
2	Emission spectrum of hydrogen. . . . .	18

## List of Tables

1	The first 20 energy levels of the hydrogen atom. . . . .	18
2	A sample of the wavelengths of light emitted from a hydrogen atom. . . . .	19

## 1 Introduction

Newton introduced his Laws of Motion in the 18<sup>th</sup> century, which at the time appeared to explain all visible motions (those of apples, planets, stars...). However, with more and more powerful telescopes, astronomers began to notice that something was amiss. Around the beginning of the 20<sup>th</sup> century, Einstein introduced his controversial theories of relativity. This theory gave more accurate predictions for the motions of extremely massive objects, whilst remaining accurate for smaller masses.

However, Einstein's theory of relativity, was not perfect: it did not explain motion on the atomic scale. At the beginning of the 20<sup>th</sup> century, many scientists including the likes of Bohr, Born, de Broglie, Compton, Dirac, Einstein, Heisenberg, von Neumann, Pauli, Planck, Schrödinger and Weyl helped work on the theory of Quantum Mechanics, which helps explain the motion and mechanics of very small entities, allowing for the discrete nature of energy. Quantum mechanics has become the predominant theory for atomic and sub-atomic motion, due to how well it explains many observed phenomena which cannot be explained with classical mechanics.

Currently, one of the biggest problems in physics is trying to reconcile quantum mechanics with relativity, in order to form a Grand Unified Theorem (GUT), also known as a Theory of Everything.

### 1.1 Aim of this Article

This article intends to outline some of the very basic features of quantum mechanics, and apply them to the problem of the hydrogen atom, in order to derive the energy levels inherent therein, and apply this information to the problem of atomic spectra.

The article will also recap the method of separation of variables in order to solve a three variable partial differential equation, expressed in spherical polar coordinates.

### 1.2 Approach

We will quote the Schrödinger equation and the Coulomb potential for an electron orbiting a proton. We will then separate out the Schrödinger equation's time dependence (as the Coulomb potential is static for a stationary proton), and thus we will deduce the time-independent Schrödinger equation (TISE) for the hydrogen atom.

Using the mathematical method of separation of variables, we will solve the TISE for the hydrogen atom. We will also derive the energy levels of the hydrogen atom, and use these levels to explain the observed spectra of the hydrogen atom.

### 1.3 Main Conclusions

We will find that the predicted energy levels of the hydrogen atom agree with the observed data, and find that the energy levels of the hydrogen atom depend solely on the *principal quantum number*,  $n$ .

### 1.4 Overview

The article starts with an introduction to *quantum mechanics*, giving a little background on a few of the main contributors to the theory. We go on to explain what *wavefunctions* are, and define the Schrödinger equation, which we then simplify for hydrogen into a time-independent form.

In order to solve this equation, we review the method of *separation of variables*, using the time-independent Schrödinger equation for hydrogen as an example.

After separating this partial differential equation into three separate ordinary differential equations, we solve and normalise them, and then amalgamate them into the final *wavefunction* for hydrogen.

We then study one of the results of the previous derivation, an equation relating the energy of the system,  $E$ , to the *principal quantum number*,  $n$ , an integer. We use this to deduce that the energy levels of the hydrogen atom are discrete, and we use this to explain the emission spectra of the hydrogen atom.

Finally, there is a discussion of the article, followed by a brief conclusion. We also cover the *Legendre equation* and the *associated Legendre equation* and their solutions, in order to supplement the article's main derivation.

A brief glossary can be found at the end of the article explaining many of the terms found in *italics*.

## 2 Introduction to Quantum Mechanics and the Schrödinger Equation

In classical mechanics, electro-magnetic energy (that from radiation of visible light, x-rays, radiowaves, ...) is seen as being continuous. However, early in the 19<sup>th</sup> century, Max Planck and others started to think that it was actually discrete. Quantum mechanics was a theory introduced to try and model the physics of these discrete energy “quanta”, which are called “photons” in the case of electro-magnetic radiation (EM-radiation). Quantum mechanics deals with very small scale problems: those of an atomic or sub-atomic nature.

### 2.1 The Founders of Quantum Mechanics

There were many people involved in the initial theorisation of quantum mechanics. Here are just a few of the contributors, and an example of their contributions:

- **Niels Bohr** developed the model of the atom now called the *Bohr atom*.
- **Max Born** introduced the current interpretation of the squared amplitude of the wavefunction  $\psi^*\psi$  in the Schrödinger equation: a probability density function.

- **Louis de Broglie** introduced the *de Broglie wavelength*: the theory that matter has wavelike properties, with a wavelength proportional to its momentum.
- **Arthur Compton** discovered the phenomena now known as *Compton scattering*, and wrote the paper *A Quantum Theory of the Scattering of X-Rays by Light Elements*.
- **Paul Dirac** did a lot of work in *quantum mechanics* and relativity, and proposed an equation of motion for an electron, taking into consideration relativistic effects.
- **Albert Einstein** did a lot of work in order to explain the photoelectric effect, but did not like the path the new *quantum mechanics* was following, famously saying in a letter to Max Born in 1926 that he was “convinced that He [the Old One, God] does not throw dice.”
- **Werner Heisenberg** is well known for the *Heisenberg uncertainty principle*: that an object’s position and momentum cannot both be known accurately simultaneously. He also introduced the *matrix mechanical formulation* of *quantum mechanics*.
- **John von Neumann** introduced the idea of linear *operators* for *quantum mechanics* whilst he was giving the theory rigour by assigning it axioms.
- **Wolfgang Pauli** is known for the *Pauli exclusion principle*: that two fermions (for example, electrons) cannot occupy the same quantum state at the same time. He also used *quantum mechanics* to predict the existence of *neutrinos*.
- **Max Planck**, whilst studying *black-body radiation*, theorised that electromagnetic radiation could only be released in small “packets” with energy given by  $E = hf$ , where  $f$  is the frequency of the radiation, and  $h$  is *Planck’s constant*.
- **Erwin Schrödinger** was responsible for the *wave mechanical formulation*, and introduced the famous *Schrödinger equation*, which describes how a *wavefunction* evolves with time.
- **Hermann Weyl** introduced the theory of compact groups, which is used to understand the symmetry inherent in the theory of quantum mechanics. (Dirac, 1958)

## 2.2 Wavefunctions

In Schrödinger’s interpretation of *quantum mechanics*, a system is described by a *wavefunction*,  $\psi$ , which contains “all the information we have about the state of a physical system” (Schrödinger and Bitbol, 1995, page 70). A *wavefunction* is given by the *superposition* of the *eigenstates* for an *operator* of the system (see section 2.2.4).  $\psi$  itself is not physically important, instead  $\psi^*\psi$  (where  $\psi^*$  is the *complex conjugate* of  $\psi$ ) is the physically important quantity: it is a probability density function, detailing the probability of finding the system in a particular state.

### 2.2.1 Heisenberg's Uncertainty Principle

Heisenberg theorised that it is not possible to know the exact location of a particle and know its exact momentum at the same time, as measurement of one will change the other. This theory is known as *Heisenberg's uncertainty principle*.

For example, using light to measure the position of a small particle will let us know where it was at a certain time to an accuracy in the order of the wavelength of the light. In order to make the measurement more precise, we use light with a smaller wavelength  $\lambda$  which thus has a higher frequency  $f$  by the relation  $c = f\lambda$ , where  $c$  is the *speed of light*. The energy of a *photon* is given by  $E = hf$  where  $h$  is *Planck's constant*, so the more precisely we measure the position of the particle, the more energy the photon has. Photons with this energy which collide with the particle (they make the shadow which we observe, and use to locate the particle), will give the particle their energy, adjusting the particles momentum unpredictably.

This principle is reflected very accurately in the methods of determining position and momentum inherent in *quantum mechanics*.

### 2.2.2 Normalisation

For a system of one particle, described by the quantum wavefunction  $\psi(\mathbf{x}, t)$ , the probability of finding a particle at position  $\mathbf{x}$  at time  $t$  is given by  $P(\mathbf{x}, t) = \psi^*(\mathbf{x}, t)\psi(\mathbf{x}, t)$  and is infinitesimal (by Heisenberg's uncertainty principle). Working now in 1 dimension for clarity, the probability of finding the particle in a range  $x_0 < x < x_1$  at time  $t$  is given by

$$\int_{x_0}^{x_1} P(x, t) dx = \int_{x_0}^{x_1} \psi^*(x, t)\psi(x, t) dx$$

Now, the probability of finding the particle **somewhere** has to be 1: the particle has to have a position! Thus we require that:

$$\int_{-\infty}^{\infty} P(x, t) dx = \int_{-\infty}^{\infty} \psi^*(x, t)\psi(x, t) dx = 1 \quad (2.1)$$

A wavefunction that satisfies this requirement is said to be *normalised*. The process of turning a prototype wavefunction into a *normalised* wavefunction is known as *normalisation*. All *wavefunctions* must be *normalisable*. Note that in order to be *normalisable*, a *wavefunction* must be continuous.

### 2.2.3 Wavefunctions Are Single Valued

It does not make sense for a particle described by  $\psi(x, t)$  to have two or more different probabilities of being found at a specified place  $x_0$  at time  $t_0$ , and for this reason we say that *wavefunctions* must be single valued.

### 2.2.4 Eigenstates and Eigenvalues

In order to introduce some more vocabulary, we will consider a rather cruel example, very similar to Schrödinger's cat. We place a cat in a box. Inside the box, there is a sealed poison container, and a radioactive atom, which acts as

a random trigger of the poison release. When the atom decays, the poison is released into the box killing the cat. Before the atom decays, the cat is alive. The box is totally sealed, and there is no way of knowing whether the cat inside the box is alive or dead.

One *operator* for this system could be called  $\hat{L}$  for *Look*, where we open the box five minutes after the cat was placed in it, and see whether the cat is alive or dead. This operator has (assuming instant death from the release of the poison) two possible *eigenstates*: one describing an alive cat,  $u_A$ , and one describing a dead cat,  $u_D$ . These *eigenstates* have associated *eigenvalues*: alive ( $A$ ) and dead ( $D$ ) respectively.

In quantum mechanical terms, the system is described by the total *wavefunction*,  $\psi$ , which is a *superposition* of the *eigenstates* of one of the *operators* of the system, with adjusted amplitudes,  $c_A$  and  $c_D$ , where  $c_A^2$  is the probability of finding the cat alive, and  $c_D^2$  is the probability of finding the cat dead. Then the equation for the total *wavefunction* is

$$\psi = c_A u_A + c_D u_D$$

Were we now to perform the operation  $\hat{L}$ , on the system, we would find out if the cat was alive or dead, and the *wavefunction* describing the system would collapse into the associated *eigenfunction*. Performing this operation would look like this:

$$\hat{L}\psi = L\psi$$

where  $L$  takes the value of either  $A$  for alive, or  $D$  for dead. Let us assume that performing the operator found that the cat was alive. Then, we know that  $L$  has the value  $A$ , and  $\psi$  has collapsed into the alive *eigenstate*:  $\psi = u_A$ . Were we to perform this operator again on  $\psi$ , we would still find the cat to be alive, as “alive” is the only outcome for the collapsed *wavefunction*: it is the only *eigenstate*.

### 2.3 Schrödinger Equation

The *Schrödinger equation* governs how a *wavefunction* evolves with time. The *Schrödinger equation* for a particle of mass  $m$  in a potential  $V$  described by a *wavefunction*  $\psi$  is:

$$-\frac{\hbar^2}{2m}\nabla^2\psi + V\psi = i\hbar\frac{\partial\psi}{\partial t} \quad (2.2)$$

where  $\nabla^2$  is the *Laplacian operator* and  $i = \sqrt{-1}$ . As was commented before,  $\psi^*\psi$  is physically significant, whilst  $\psi$  itself is not. This can be seen by looking at the equation above:  $\psi$  is a *complex number*, but by the definition of the *complex conjugate*,  $\psi^*\psi$  is a real number, and we expect things we observe to be real.

### 2.4 Time Independent Schrödinger Equation (TISE)

For systems which have a static potential  $V(\mathbf{r}, t) = V(\mathbf{r})$ , we can write the much simpler *time-independent Schrödinger equation (TISE)* by employing the method of *separation of variables* (for a more detailed description of *separation of variables*, please see section 3). Let us assume that  $\psi$  has the form:

$\psi(\mathbf{r}, t) = u(\mathbf{r})f(t)$ , then substitution into equation (2.2) and division by  $\psi$  gives the separated Schrödinger equation:

$$\frac{1}{u(\mathbf{r})} \left( -\frac{\hbar^2}{2m} \nabla^2 u(\mathbf{r}) + V u(\mathbf{r}) \right) = E = \frac{1}{f(t)} \left( i\hbar \frac{\partial f(t)}{\partial t} \right) \quad (2.3)$$

where  $E$  is the *separation constant*.

Studying just the right hand side of the separated Schrödinger equation (2.3), we see that:

$$\frac{d}{dt} f(t) + i\frac{E}{\hbar} f(t) = 0 \quad \Rightarrow \quad f(t) = A \exp\left(-\frac{iEt}{\hbar}\right) \quad (2.4)$$

Studying the left hand side of the separated Schrödinger equation (2.3), we find the TISE (as displayed in Davies and Betts, 1994, equation (2.2)):

$$-\frac{\hbar^2}{2m} \nabla^2 u(\mathbf{r}) + V(\mathbf{r})u(\mathbf{r}) = Eu(\mathbf{r}) \quad (2.5)$$

So, the dependence of  $\psi$  on  $t$  when  $V$  is static is lost when we find the probability distribution, because:

$$\begin{aligned} \psi^* \psi &= \left[ u(\mathbf{r}) \exp\left(-\frac{iEt}{\hbar}\right) \right]^* \left[ u(\mathbf{r}) \exp\left(-\frac{iEt}{\hbar}\right) \right] \\ &= [u(\mathbf{r})]^2 \left[ \exp\left(\frac{iEt}{\hbar} - \frac{iEt}{\hbar}\right) \right] \\ &= [u(\mathbf{r})]^2 \end{aligned}$$

which is independent of  $t$ .

## 2.5 TISE in Spherical Polar Coordinates

We can substitute the spherical polar definition of the *Laplacian operator*  $\nabla^2$  (Bethe and Salpeter, 1977, equation (1.2)):

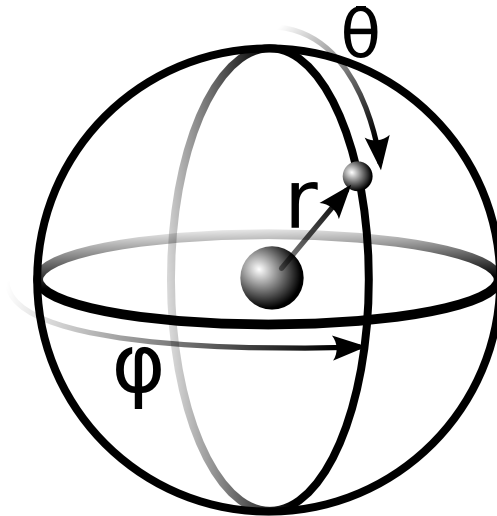
$$\nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \quad (2.6)$$

in to the TISE (2.5), to give us (after re-arranging) the TISE in *spherical polar coordinates*  $\mathbf{r} = (r, \theta, \phi)$  (Osborn, 1988, equation (1.38)):

$$-\frac{\hbar^2}{2m} \frac{1}{r^2 \sin \theta} \left[ \sin \theta \frac{\partial}{\partial r} \left( r^2 \frac{\partial u}{\partial r} \right) + \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial u}{\partial \theta} \right) + \frac{1}{\sin \theta} \frac{\partial^2 u}{\partial \phi^2} \right] + Vu = Eu \quad (2.7)$$

where  $u = u(r, \theta, \phi)$  and  $V = V(r, \theta, \phi)$ . Note that the following limits are placed on spherical polars coordinates:

$$\begin{aligned} 0 &\leq r \\ 0 &\leq \theta < \pi \\ 0 &\leq \phi < 2\pi \end{aligned} \quad (2.8)$$



**Figure 1:** Simplified model of the hydrogen atom, showing a proton at the centre ( $r = 0$ ), with an electron orbiting it, currently located at spherical polar coordinates  $(r, \theta, \phi)$  (illustration copyright © Benjamin Gillam, 2007).

## 2.6 Schrödinger Equation for the Hydrogen Atom

In order to solve the Schrödinger equation for hydrogen, we must first simplify it. We model the hydrogen atom as shown in Figure 1. We see the electron, of mass  $m_e$ , orbiting the nucleus of the atom, a proton with mass  $m_p$ . To simplify the situation mathematically, we fix the position of the nucleus, by endowing it with infinite inertia. This results in a modification of the mass of the electron to compensate. We call this new mass the *reduced mass*,  $\mu$ , and it is given by

$$\mu = \frac{m_e m_p}{m_e + m_p} \quad (2.9)$$

We see the electron as orbiting the central proton at a distance  $r$ , moving under the influence of a central potential,  $V(r)$ , defined in many text books (such as Tipler and Mosca, 2004, equation 36-26; and Bethe and Salpeter, 1977, equation (1.1)):

$$V(r) = -\frac{e^2}{4\pi\epsilon_0 r} \quad (2.10)$$

where  $e$  is the charge on the electron, and  $\epsilon_0$  is the *permittivity of free space* (a constant attained from observational evidence).

We can now substitute these two facts into the *TISE* (2.5), to give the *TISE* for hydrogen:

$$-\frac{\hbar^2}{2\mu} \nabla^2 u - \frac{e^2}{4\pi\epsilon_0 r} u = Eu \quad (2.11)$$

We can write this using spherical polar coordinates,  $(r, \theta, \phi)$ , so that the  $r$  in the *TISE* for hydrogen (2.11) is one of the coordinates, by using the definition of the *Laplacian operator*  $\nabla^2$  in *spherical polar coordinates* (2.6):

$$\begin{aligned}
-\frac{\hbar^2}{2\mu} \frac{1}{r^2 \sin \theta} \left[ \sin \theta \frac{\partial}{\partial r} \left( r^2 \frac{\partial u(r, \theta, \phi)}{\partial r} \right) + \right. \\
\left. \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial u(r, \theta, \phi)}{\partial \theta} \right) + \right. \\
\left. \frac{1}{\sin \theta} \frac{\partial^2 u(r, \theta, \phi)}{\partial \phi^2} \right] - \frac{e^2}{4\pi\epsilon_0 r} u(r, \theta, \phi) = Eu(r, \theta, \phi)
\end{aligned} \tag{2.12}$$

Note that the potential energy of the electron must vanish as  $r \rightarrow \infty$ , as at  $\infty$  the proton should have no physical effect on the electron whatsoever.

We now use separation of variables to solve the problem.

### 3 Separation of Variables

It is sometimes possible to simplify partial differential equations into ordinary differential equations. One method which follows this route is called *separation of variables*, and it tries to reduce a partial differential equation of  $n$  variables into a collection of  $n$  ordinary differential equations. It then restricts the form of the solution into separate factors, each dependent on just one variable, which are all multiplied together.

#### 3.1 Explanation

As just noted, the basic idea behind *separation of variables* is that, for an target function of  $n$  variables, we assume that it takes the form of the product of  $n$  single variable functions (one for each variable in the original function). For example, for the *wavefunction* discussed in section 2.5, we would look for a solution of the form

$$u(r, \theta, \phi) = R(r)\Theta(\theta)\Phi(\phi) \tag{3.1}$$

We would then substitute this solution form into the partial differential equation, and attempt to separate it so that one side is dependant on one variable only, and the other side is independent of that same variable. Then, we would know that both sides must be equal to a constant, generally called the *separation constant* (Street, 1973), and so we can separate the equation into two equations that are both equal to this constant. We would then repeat this process on any of these resulting equations which are dependant on more than one variable.

### 3.2 An Example: The Schrödinger Equation for Hydrogen

We substitute the assumed form of  $u$  (3.1) into our partial differential equation, the *TISE* for hydrogen (2.12), to give:

$$\begin{aligned}
 -\frac{\hbar^2}{2\mu} \frac{1}{r^2 \sin \theta} \left[ \sin \theta \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \{R(r)\Theta(\theta)\Phi(\phi)\} \right) + \right. \\
 \left. \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \{R(r)\Theta(\theta)\Phi(\phi)\} \right) + \right. \\
 \left. \frac{1}{\sin \theta} \frac{\partial^2}{\partial \phi^2} \{R(r)\Theta(\theta)\Phi(\phi)\} \right] - \\
 \frac{e^2}{4\pi\epsilon_0 r} R(r)\Theta(\theta)\Phi(\phi) = ER(r)\Theta(\theta)\Phi(\phi)
 \end{aligned} \tag{3.2}$$

The next step is to perform the derivatives, and to divide by the product  $R(r)\Theta(\theta)\Phi(\phi)$ . I will omit the dependence of the variables now for brevity. After a little rearranging, we can write the result as the separated *TISE* for hydrogen:

$$\begin{aligned}
 \frac{\mu e^2 r}{2\pi\epsilon_0} + \frac{\hbar^2}{R} \frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) + 2\mu E r^2 = \hbar^2 \lambda = \\
 -\hbar^2 \left[ \frac{1}{\Theta \sin \theta} \frac{d}{d\theta} \left( \sin \theta \frac{d\Theta}{d\theta} \right) + \frac{1}{\Phi \sin^2 \theta} \frac{d^2 \Phi}{d\phi^2} \right]
 \end{aligned} \tag{3.3}$$

Notice that the left hand side of equation (3.3) only depends on  $r$ , and the right hand side is independent of  $r$ . As  $r$  can vary, this means that each side of the equation must equal a constant (the *separation constant*), labelled  $\lambda$  in equation (3.3) above.

By rearranging the right hand side of the separated *TISE* for hydrogen (3.3), we get a separated equation for  $\theta$  and  $\phi$ :

$$\frac{\sin \theta}{\Theta} \frac{d}{d\theta} \left( \sin \theta \frac{d\Theta}{d\theta} \right) + \frac{\lambda \sin^2 \theta}{\hbar^2} = b^2 = -\frac{1}{\Phi} \frac{d^2 \Phi}{d\phi^2} \tag{3.4}$$

Applying the same logic again, we notice that the left hand side of the separated equation for  $\theta$  and  $\phi$  (3.4) depends only on  $\theta$ , whilst the right hand side depends only on  $\phi$ . So, both sides must be equal to another *separation constant*, which has been labelled  $b^2$  (note that at this point  $b$  can, in general, be a *complex number*).

Studying just the right hand side of the separated equation for  $\theta$  and  $\phi$  (3.4), we find the ordinary differential equation for  $\Theta$ :

$$\frac{d^2 \Phi}{d\phi^2} + b^2 \Phi = 0 \tag{3.5}$$

From the left hand side of the separated equation for  $\theta$  and  $\phi$  (3.4), we find the differential equation for  $\Phi$ :

$$\frac{\sin \theta}{\Theta} \frac{d}{d\theta} \left( \sin \theta \frac{d\Theta}{d\theta} \right) + \frac{\lambda \sin^2 \theta}{\hbar^2} = b^2 \tag{3.6}$$

Finally, we recall the left hand side of the separated *TISE* for hydrogen (3.3), extracting the differential equation for  $R$ :

$$\frac{\mu e^2 r}{2\pi\epsilon_0} + \frac{\hbar^2}{R} \frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) + 2\mu E r^2 = \hbar^2 \lambda \quad (3.7)$$

So, you can see that the *TISE* for hydrogen (3.2), a partial differential equation in three variables, has been reduced to three ordinary differential equations, each of just one variable. We must now solve these.

## 4 Solving the TISE for the Hydrogen Atom

Now that we have reduced the *TISE* for hydrogen into three ordinary differential equations, we must solve them.

### 4.1 Solution for $\Phi$

The differential equation for  $\Phi$  (3.5) has the following standard solutions:

$$\Phi = Ae^{ib\phi} \quad (4.1)$$

$$\Phi = Be^{-ib\phi} \quad (4.2)$$

By the symmetry of our model, we realise that these two solutions for  $\Phi$  just involve the atom moving in opposite directions about the proton. We thus arbitrarily choose to only use the first solution (4.1).

From the section 2.2.3, we know that the wave function must be single valued at every point. As  $\phi = \phi_0$  and  $\phi = \phi_0 + 2\pi$  represent the same physical point for arbitrary  $\phi_0$ , we must have that  $\Phi(\phi) = \Phi(\phi + 2\pi)$  for all  $\phi$ :

$$\begin{aligned} Ae^{ib\phi} &= Ae^{ib(\phi+2\pi)} \\ &= Ae^{ib\phi} e^{i2b\pi} \\ \Rightarrow e^{i2b\pi} &= 1 \end{aligned}$$

It follows that  $b$  must be a real integer, which we label  $m$ , the *magnetic quantum number*. We now normalise  $\Phi$  (see section 2.2.2), in order to find the value of the constant  $A$  (remembering that the complex conjugate of  $e^{im\phi}$  is  $e^{-im\phi}$ ):

$$\begin{aligned} \int_0^{2\pi} (Ae^{im\phi})^* (Ae^{im\phi}) d\phi &= 1 \\ A &= \frac{1}{\sqrt{2\pi}} \end{aligned}$$

So, substituting this value of  $A$  into the standard solution for  $\Phi$  (4.1), we find that the normalised solution for  $\Phi$  is:

$$\Phi_m(\phi) = \frac{1}{\sqrt{2\pi}} e^{im\phi} \quad (4.3)$$

## 4.2 Solution for $\Theta$

To solve the left hand side of the differential equation for  $\Theta$  (3.4), we introduce a substitution: let  $\alpha = \cos \theta$ . Then we have the following relations:

$$\frac{d}{d\theta} = \frac{d\alpha}{d\theta} \frac{d}{d\alpha} = -\sin \theta \frac{d}{d\alpha} \quad (4.4)$$

$$\sin^2 \theta = 1 - \cos^2 \theta = 1 - \alpha^2 \quad (4.5)$$

Upon substitution of the first (4.4) and then the second (4.5) of these relations into the left hand side of the differential equation for  $\Theta$  (3.4), and rearranging, we find:

$$\frac{-\sin^2 \theta}{\Theta} \frac{d}{d\alpha} \left( -\sin^2 \theta \frac{d\Theta}{d\alpha} \right) + \lambda \sin^2 \theta = m^2 \quad (4.6)$$

$$\implies \frac{d}{d\alpha} \left( (1 - \alpha^2) \frac{d\Theta}{d\alpha} \right) + \left( \lambda - \frac{m^2}{(1 - \alpha^2)} \right) \Theta = 0 \quad (4.7)$$

Equation (4.7) is known as the *associated Legendre equation*. This is covered in further detail in Appendix A. It only has solutions when:

$$\lambda = l(l + 1) \quad l = 0, 1, 2, \dots \quad (4.8)$$

where we call  $l$  the *angular momentum quantum number* (Bethe and Salpeter, 1977, equation (1.6)) with normalised solutions:

$$\Theta_{lm}(\theta) = \sqrt{\frac{(l - m)!}{(l + m)!} \frac{2l + 1}{2}} P_l^m(\cos \theta) \quad (4.9)$$

(Bethe and Salpeter, 1977, equation (1.7); Geremia, 2006, equation (42); Davies and Betts, 1994, equation 7.23) where  $P_l^m(\cos \theta)$  are the associated Legendre solutions written in terms of  $\cos \theta$  as defined in appendix A in equations (A.11) and (A.12).  $m$  is an integer in the range  $-l, \dots, l$  (see appendix section A.2 for more details). Thus for every value of  $l$ , there are  $2l + 1$  choices for  $m$ , and thus  $2l + 1$  solutions.

## 4.3 Solution for $R$

Recalling the differential equation for  $R$  (3.7) (and substituting  $\lambda = l(l + 1)$ ), we have that:

$$\frac{\mu e^2 r}{2\pi\epsilon_0} + \frac{\hbar^2}{R} \frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) + 2\mu E r^2 = \hbar^2 l(l + 1) \quad (4.10)$$

This can be written as the following ordinary differential equation:

$$\frac{d^2 R}{dr^2} + \frac{2}{r} \frac{dR}{dr} + \left[ \frac{2\mu E}{\hbar^2} + \frac{\mu e^2}{2\pi\epsilon_0 \hbar^2 r} - \frac{l(l + 1)}{r^2} \right] R = 0 \quad (4.11)$$

For the electron to be orbiting the proton, it must never reach  $r = \infty$ . We can impose this condition by giving the particle negative kinetic energy at infinity, and we know that at infinity the potential energy is zero, and thus

the particle must have negative total energy,  $E$ . We first study this ordinary differential equation (4.11) under the condition  $r \rightarrow \infty$ :

$$\frac{d^2 R}{dr^2} + \frac{2\mu E}{\hbar^2} R = 0 \quad (4.12)$$

This has the standard solutions:

$$R(r) = \exp\left(\frac{\sqrt{-2\mu E}}{\hbar} r\right) = e^{\beta r} \quad (4.13)$$

$$R(r) = \exp\left(-\frac{\sqrt{-2\mu E}}{\hbar} r\right) = e^{-\beta r} \quad (4.14)$$

where  $\beta = \frac{\sqrt{-2\mu E}}{\hbar}$  is a constant. We must choose the second solution (4.14), as the first solution (4.13) diverges as  $r \rightarrow \infty$ , which does not allow *normalisation*.

In order to expand the second solution (4.14) to work for finite  $r$ , we multiply it by a polynomial in  $r$  (Dirac, 1958, equation (74), page 157; Davies and Betts, 1994, page 42), which I shall denote  $F(r)$ . Thus we try the solution  $R(r) = F(r)e^{-\beta r}$ . We substitute this into the ordinary differential equation (4.11) to get (after rearranging) the following constraint on  $F$ :

$$\frac{d^2 F}{dr^2} + \left(\frac{2}{r} - 2\beta\right) \frac{dF}{dr} - \left(\frac{2\beta}{r} + \frac{\beta^2 e^2}{4\pi\epsilon_0 E r} + \frac{l(l+1)}{r^2}\right) F = 0 \quad (4.15)$$

On normalisation grounds, we know that  $F(r)$  must have a highest order term, so we let  $k$  be the order of this term. We now insert just this term, into the constrain on  $F$  (4.15):

$$k(k-1)r^{k-2} + \left(\frac{2}{r} - 2\beta\right) kr^{k-1} - \left(\frac{2\beta}{r} + \frac{\beta^2 e^2}{4\pi\epsilon_0 E r} + \frac{l(l+1)}{r^2}\right) r^k = 0 \quad (4.16)$$

$$(k(k+1) - l(l+1))r^{k-2} - \left(2\beta k + 2\beta + \frac{\beta^2 e^2}{4\pi\epsilon_0 E}\right) r^{k-1} = 0 \quad (4.17)$$

The lead term is  $-(2\beta k + 2\beta + \frac{\beta^2 e^2}{4\pi\epsilon_0 E})r^{k-1}$ , which cannot be cancelled with any lower order terms from the polynomial (because they would have a lower order of  $r$ ). For this reason, we require that the coefficient vanishes:

$$-\left(2\beta k + 2\beta + \frac{\beta^2 e^2}{4\pi\epsilon_0 E}\right) = 0 \quad (4.18)$$

or, by rearranging:

$$k + 1 = -\frac{\beta e^2}{8\pi\epsilon_0 E} = -\frac{e^2}{8\pi\epsilon_0 \hbar} \sqrt{\frac{-2\mu}{E}} = n \quad (4.19)$$

where we have introduced  $n = k + 1$ .

By its definition, we know that  $k$  is an integer, and thus  $k + 1$  is an integer also, so by the previous equation (4.19),  $n$  must also be an integer. We call this value  $n$  the *principal quantum number*. Also, note that  $k = n - 1$ , so the highest order term in the polynomial  $F(r)$  is  $r^{n-1}$ .

Similarly, let  $g$  be the order of the lowest order term in the polynomial  $F(r)$ . Inserting this term into the constraint on  $F$  (4.15), we get:

$$(g(g+1) - l(l+1))r^{g-2} - \left(2\beta g + 2\beta + \frac{\beta^2 e^2}{4\pi\epsilon_0 E}\right)r^{g-1} = 0 \quad (4.20)$$

We are interested in the lowest order term,  $r^{g-2}$ , as it cannot be cancelled with any higher order terms from the polynomial. Thus, we have that its coefficient,  $(g(g+1) - l(l+1))$ , must be equal to 0. From this we deduce:

$$g(g+1) = l(l+1) \implies \begin{cases} \text{either: } & g = l \\ \text{or: } & g = -(l+1) \end{cases} \quad (4.21)$$

If we were to let  $g = -(l+1)$ , then there would be negative powers of  $r$ , meaning that as  $r \rightarrow 0$ ,  $P(r) \rightarrow \infty$ . This cannot be true, as the wavefunction needs to be normalisable; we must therefore have that  $g = l$ , and thus the lowest term in the polynomial  $P(r)$  is  $r^l$ . We also know that  $0 \leq l \leq n-1$ .

We can now write the equation for  $F_{l,n}(r)$ :

$$F_{l,n}(r) = \sum_{s=l}^{n-1} a_{l,n,s} r^s \quad (4.22)$$

where  $a_{l,n,s}$  are constants. The functions  $F(r)$  are known as ‘‘associated Laguerre polynomials’’ (Davies and Betts, 1994, page 111).

The equation for  $R_{l,n}(r)$  is:

$$R_{l,n}(r) = \left( \sum_{s=l}^{n-1} a_{l,n,s} r^s \right) \exp\left(-\frac{\sqrt{-2\mu E_n} r}{\hbar}\right) \quad (4.23)$$

(note that, as  $E_n$  is negative, the parameter of the exponential function is a real, negative value).

If we substitute  $n = 1$  into the equation for  $F_{l,n}(r)$  (4.22), we get that  $l = 0$  (as  $n - 1 = 0$ ) and thus  $m = 0$ ; and also that  $F(r) = a_{1,0,0}$ . We require  $R_{l,n}(r)$  to be *normalised*, giving a value for  $a_{1,0,0}$ :

$$\begin{aligned} 1 &= \int_0^\infty (R_{l,n}(r)^* R_{l,n}(r)) dr \\ &= a_{1,0,0}^2 \int_0^\infty (e^{-2\beta_n r}) dr \\ &= a_{1,0,0}^2 \left[ \frac{1}{-2\beta_n} e^{-2\beta_n r} \right]_0^\infty \\ &= \frac{a_{1,0,0}^2 \hbar}{2\sqrt{-2\mu E_n}} \\ a_{1,0,0} &= \sqrt[4]{\frac{-8\mu E_n}{\hbar^2}} \end{aligned}$$

Substituting  $n = 2$  into the equation for  $F_{l,n}(r)$  (4.22), tells us that  $F(r) = a_{2,l,0} + a_{2,l,1}r$ , and that  $l = 0$  (which implies  $m = 0$ ), or  $l = 1$  (which implies  $m = -1, 0, 1$ ). We would use the same method as above to get an expression for the normalisation constants  $a_{2,l,0}$  and  $a_{2,l,1}$ ; and for the normalisation constants for other values of  $n$  and  $l$ .

#### 4.4 The Final Wavefunction

Now we can substitute the normalised solutions for  $R_{l,n}(r)$  (4.23),  $\Theta_{l,m}(\theta)$  (4.9) and  $\Phi_m(\phi)$  (4.3) into the assumed form of  $\Psi_{l,m,n}(r, \theta, \phi)$  (3.1) to give the normalised solution:

$$\Psi_{l,m,n}(r, \theta, \phi) = \sqrt{\frac{(l-m)! 2l+1}{(l+m)! 4\pi}} \left( \sum_{s=l}^{n-1} a_{n,l,s} r^s \right) \exp\left(-\frac{\sqrt{-2\mu E}}{\hbar} r\right) P_l^m(\cos\theta) e^{im\phi} \quad (4.24)$$

The first few normalised solutions of which are given by:

$$\begin{aligned} \Phi_{1,0,0} &= \frac{1}{\sqrt{\pi a_0^3}} \exp\left(-\frac{r}{a_0}\right) \\ \Phi_{2,0,0} &= \frac{1}{\sqrt{8\pi a_0^3}} \left(1 - \frac{r}{2a_0}\right) \exp\left(-\frac{r}{2a_0}\right) \\ \Phi_{2,1,0} &= \frac{1}{\sqrt{8\pi a_0^3}} \left(\frac{r}{2a_0}\right) \cos\theta \exp\left(-\frac{r}{a_0}\right) \\ \Phi_{2,1,\pm 1} &= \frac{1}{\sqrt{\pi a_0^3}} \left(\frac{r}{8a_0}\right) \sin\theta \exp(\pm i\phi) \exp\left(-\frac{r}{a_0}\right) \\ \Phi_{3,0,0} &= \frac{1}{\sqrt{27\pi a_0^3}} \left(1 - \frac{2r}{3a_0} + \frac{2r^2}{27a_0^2}\right) \exp\left(-\frac{r}{3a_0}\right) \\ \Phi_{3,1,0} &= \frac{2}{27} \sqrt{\frac{2}{\pi a_0^3}} \left(\frac{r}{a_0}\right) \left(1 - \frac{r}{6a_0}\right) \cos\theta \exp\left(-\frac{r}{3a_0}\right) \end{aligned}$$

(Davies and Betts, 1994, Table 8.1). where

$$a_0 = \frac{4\pi\epsilon_0\hbar^2}{\mu e^2} \quad (4.25)$$

is a constant called the ‘‘Bohr radius’’ (Davies and Betts, 1994, page 43).

Note that the time dependence can be added to these equations simply by multiplying them by

$$\exp\left(-\frac{iEt}{\hbar}\right)$$

as previously calculated in equation (2.4).

## 5 Energy Levels in the Hydrogen Atom

Rearranging the equation relating  $n$  to  $E$  (4.19), we find:

$$E_n = -\frac{1}{n^2} \frac{\mu}{32} \left(\frac{e^2}{\pi\epsilon_0\hbar}\right)^2 = \frac{1}{n^2} E_1 \quad (5.1)$$

where the first energy level,  $E_1$ , is given by:

$$E_1 = -\frac{\mu}{32} \left(\frac{e^2}{\pi\epsilon_0\hbar}\right)^2$$

which implies that the energy levels for hydrogen (the feasible values of  $E_n$ , the total energy) are discrete.

Using the fundamental physical constants from Mohr and Taylor (2002), we can calculate  $E_1$ . I will use the following constants:

$$\begin{aligned} m_e &= 9.1093826 \times 10^{-31} \text{ kg} \\ m_p &= 1.67262171 \times 10^{-27} \text{ kg} \\ e &= 1.60217653 \times 10^{-19} \text{ C} \\ \varepsilon_0 &= 8.854187817 \times 10^{-12} \text{ F m}^{-1} \\ \pi &= 3.14159265 \\ \hbar &= 1.05457148 \times 10^{-34} \text{ m}^2 \text{ kg s}^{-1} \end{aligned}$$

to give a value of  $E_1 = -2.1786864 \times 10^{-18} \text{ J} = -13.598292 \text{ eV}$  (where  $eV$  stands for *electron-volts*). So the energy levels of the hydrogen atom, according to *quantum mechanics*, are given by the following formula:

$$E_n = -\frac{13.598292}{n^2} \text{ eV} \quad (5.2)$$

A few things worth noting about this formula:

1. As discussed previously (in section 4.3) the total energy of the system,  $E_n$ , is negative.
2. The lowest energy level,  $E_1 \approx -13.6 \text{ eV}$ , is known as the *ionisation energy* of hydrogen. This value has been confirmed by experimental evidence (such as the limit of the *Lyman series*) (Davies and Betts, 1994, page 43; Dirac, 1958, page 158; Bethe and Salpeter, 1977, page 9).
3. There are an infinite number of energy levels, with  $E_\infty = 0$
4. As  $n \rightarrow \infty$ ,  $(E_n - E_{n-1}) \rightarrow 0$ , i.e. the energy levels get closer together as  $n$  increases.
5. Hydrogen is special, in that its energy levels do not depend on any other *quantum numbers*, such as  $l$  and  $m$ . This is related to the fact that there is just 1 proton and 1 electron: they have equal and opposite charges, with no other charges interfering.

The first 20 of these energy levels are shown in Table 1.

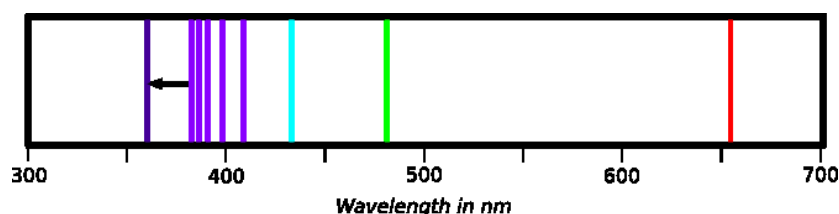
## 5.1 Absorption and Emission Spectra

When a photon hits a hydrogen atom, if it has the right amount of energy, then it may be absorbed by an electron, and excite it to a higher energy level. When the electron returns from a higher energy state,  $n_1$ , to a lower energy state,  $n_2$ , the change in energy,  $E$ , is released in the form of a photon. A photon of this energy may be absorbed by an electron in energy level  $n_2$  of another hydrogen atom, exciting the electron to energy level  $n_1$ . Photons have well defined frequency,  $f$ , proportional to their energy,  $E$ , defined by Planck's relation:

$$E = hf = \frac{hc}{\lambda}$$

n	$E_n$ in eV	n	$E_n$ in eV
1	-13.598291697575	11	-0.112382576013
2	-3.399572924394	12	-0.094432581233
3	-1.510921299731	13	-0.080463264483
4	-0.849893231098	14	-0.069379039273
5	-0.543931667903	15	-0.060436851989
6	-0.377730324933	16	-0.053118326944
7	-0.277516157093	17	-0.047052912448
8	-0.212473307775	18	-0.041970036104
9	-0.167880144415	19	-0.037668398054
10	-0.135982916976	20	-0.033995729244

**Table 1:** The first 20 energy levels of the hydrogen atom, in electron-volts, calculated using the values of the fundamental constants from section 5.



**Figure 2:** Diagram showing the wavelengths of light emitted from electrons moving from energy states with  $n > 2$  to the  $n = 2$  energy state in a hydrogen atom (an emission spectrum). The left of the diagram is the limit of the series as  $n \rightarrow \infty$  ( $\lambda \approx 365$  nm), the right of the diagram is the emission from an electron moving from  $n = 3$  to  $n = 2$  ( $\lambda \approx 657$  nm). The colours of the diagram reflect the fact that most of the wavelengths are visible light. The wavelengths of these lines can be looked up in the  $n = 2$  column of Table 2. This diagram is copyright © Benjamin Gillam, 2007.

(where  $h$  is Planck's constant,  $c$  is the speed of light, and  $\lambda$  is the wavelength of the photon).

If a photon of energy  $E = 2.54968$  eV is released from a hydrogen atom (such as the green line in Figure 2 with wavelength  $\lambda \approx 486$  nm), we would know that the electron which produced it dropped from level  $n_1 = 4$  with  $E_4 = -0.84989$  eV to level  $n_2 = 2$  with  $E_2 = -3.39957$  eV. Similarly a photon caused by an electron in a hydrogen atom dropping from state  $n_1 = 2$  to state  $n_2 = 1$  would have an energy given by  $E = E_2 - E_1 = (-3.39957) - (-13.59829) = 10.19872$  eV.

For the case of absorption, we could shine a wide range of wavelengths of electro-magnetic radiation through a cloud of hydrogen, and some of these wavelengths might not make it through, as they may have been absorbed by electrons in the hydrogen. The absorption and emission frequencies are the same, and these energies can be measured extremely accurately. This gives each element a unique fingerprint in the form of *emission and absorption spectra*, which can be thought of as the complete set of wavelengths (and thus energies) that photons given off by and absorbed by that atom may have.

By calculating the energy difference between pairs of quantum states in atoms, we can calculate and catalogue the list of possible wavelengths (and thus

frequencies) of *electro-magnetic radiation* that each atom may emit/absorb. The beginnings of one such table, displaying some of the possible wavelengths of light that may be emitted by a hydrogen atom, is shown in Table 2. We can then monitor the wavelengths of photons emitted from an object, and use our catalogue to deduce the object's atomic composition.

<b>n</b>	<b>N = 1</b>	<b>N = 2</b>	<b>N = 3</b>	<b>N = 4</b>
2	79.54	—	—	—
3	74.75	656.92	—	—
4	70.50	486.61	1876.92	—
5	66.71	434.47	1283.05	4055.08
6	63.31	410.58	1094.87	2627.69
7	60.23	397.40	1005.91	2167.63
8	57.44	389.29	955.53	1946.44
9	54.90	383.92	923.80	1819.17
10	52.58	380.16	902.37	1737.89
⋮	⋮	⋮	⋮	⋮
∞	91.24	364.96	821.15	1459.83

**Table 2:** Table showing a sample of the wavelengths (in nm) of light emitted from a hydrogen atom when an electron moves from an energy level  $E_n$  with  $n > N$  to energy level  $E_N$ .

For example, sodium lamps (such as many street lamps in the UK) give out a characteristic orange-yellow glow, which actually comprises a relatively small number of discrete wavelengths. By looking up these wavelengths in our catalogue, we would see that they correspond to the differences between some of the energy levels in a sodium atom.

If we were to use a device to monitor the energies of photons being emitted from the sun, we would see many spectral lines which correspond to the energy levels in hydrogen and helium atoms. There would also be traces of spectral lines corresponding to heavier atoms: “hydrogen comprises about 94% of the atoms in the solar atmosphere [...] Helium is the next most abundant [...] All the other elements are present only in trace amounts.” (Celarier and Hollandsworth, 2004, section 3.2)

## 6 Discussion

In this article, we have discussed some of the basic formulae and ideas of *quantum mechanics*, and have gone on to form the Schrödinger equation for the hydrogen atom. We found that the hydrogen atom's energy levels are dependant solely on the principal quantum number  $n$  (they are independent of  $l$  and  $m$ ), in a form that  $E_n \propto -n^{-2}$ :

$$E_n = -\frac{1}{n^2} \frac{\mu}{32} \left( \frac{e^2}{\pi \epsilon_0 \hbar} \right)^2 = -\frac{13.598292}{n^2} eV$$

We have found that the lowest energy level,  $E_1 \approx -13.6 eV$ , corresponds with the observational evidence for the ionisation energy of hydrogen. We then

went on to discuss how an electron moving from a higher energy level to a lower one releases the difference in energy as a photon, and how a photon may be absorbed by an electron to raise the electron from a lower energy level to a higher one. We discussed monitoring the frequency of photons received from a source to find their energy, and thus the energy difference through which an electron has moved; and finally how this can be used to identify the source atom.

This article is only meant as an introduction to the subject. It does not cover isotopes of hydrogen, such as Deuterium, nor does it cover larger atoms. It also does not allow for relativistic effects. The *quantum mechanics* of larger atoms gets quite complicated, as we would have to allow for many different charges orbiting the centre, and have to consider their interactions. If you want to learn more on the subject of *quantum mechanics* of atoms, you could start with the book *Quantum Mechanics of One- and Two-Electron Atoms* by Bethe and Salpeter, 1977 (see references).

## 6.1 Conclusion

We conclude that the method of separation of variables can be applied successfully to the Schrödinger equation, a physical partial differential equation of three variables, and have used this to derive that the energy levels of the hydrogen atom are given by

$$E_n = -\frac{13.598292}{n^2} \text{ eV}$$

We also note that electrons moving between different energy levels absorb or emit photons of well defined frequencies, allowing us to fingerprint the source atom if we know all the differences between energy levels for all atoms. This method is important as it can be used to deduce the atomic composition of even the most distant (visible) stars.

## A Associated Legendre Equation

We will now look at solving the *associated Legendre equation*. The results of this section are used in section 4.2. For convenience, we repeat the *associated Legendre equation* (4.7) here:

$$\frac{d}{d\alpha} \left( (1 - \alpha^2) \frac{d\Theta}{d\alpha} \right) + \left( \lambda - \frac{m^2}{(1 - \alpha^2)} \right) \Theta = 0 \quad (\text{A.1})$$

In order to solve this equation, I will be following a method based on those followed by Geremia (2006, section 28.1) and Davies and Betts (1994, Appendix B). I have also used information from Bethe and Salpeter (1977, pp. 344-346).

### A.1 The Legendre Equation

First, we let  $m = 0$  to give us the *Legendre equation*:

$$\frac{d}{d\alpha} \left( (1 - \alpha^2) \frac{d\Theta}{d\alpha} \right) + \lambda \Theta = 0 \quad (\text{A.2})$$

We now look for a solution in the form of an infinite power series, with lowest order term  $\alpha^c$ :

$$\Theta(\alpha) = \sum_{k=0}^{\infty} d_k \alpha^{c+k} \quad (\text{A.3})$$

Substituting this power series into into the equation of the Legendre equation (A.2), we obtain:

$$\begin{aligned} & \frac{d}{d\alpha} \left( \sum_{k=0}^{\infty} (c+k) d_k (\alpha^{c+k-1} - \alpha^{c+k+1}) \right) + \lambda \sum_{k=0}^{\infty} d_k \alpha^{c+k} = 0 \\ & \sum_{k=0}^{\infty} d_k ((c+k)(c+k-1)\alpha^{c+k-2} - [(c+k)(c+k+1) - \lambda] \alpha^{c+k}) = 0 \end{aligned}$$

By splitting this sum into two, changing the index on the first half so that the terms have order  $c+k$  instead of  $c+k-2$ , extracting the first two terms, and recombining the sums, we obtain:

$$\begin{aligned} & d_0(c(c-1))\alpha^{c-2} + d_1((c+1)c)\alpha^{c-1} + \\ & \sum_{k=0}^{\infty} [(d_{k+2}(c+k+2)(c+k+1) - d_k [(c+k)(c+k+1) - \lambda]) \alpha^{c+k}] = 0 \end{aligned} \quad (\text{A.4})$$

For this to be true, the coefficient of each order of  $\alpha$  must be zero. From the lowest order term, we find:

$$d_0(c(c-1)) = 0 \quad (\text{A.5})$$

By our assumption that the lowest order term in  $\Theta(\alpha)$  is  $\alpha^c$ , we know that  $d_0 \neq 0$ . Thus either  $c = 0$  or  $c = 1$ .

For the coefficient of  $\alpha^{c+k}$  to be zero, we require that:

$$\begin{aligned} d_{k+2}(c+k+2)(c+k+1) &= d_k [(c+k)(c+k+1) - \lambda] \\ \Rightarrow d_{k+2} &= \frac{[(c+k)(c+k+1) - \lambda]}{(c+k+2)(c+k+1)} d_k \end{aligned}$$

and so:

$$\text{(for } c = 0) \quad d_{k+2} = \frac{k(k+1) - \lambda}{(k+2)(k+1)} d_k \quad (\text{A.6})$$

$$\text{(for } c = 1) \quad d_{k+2} = \frac{(k+1)(k+2) - \lambda}{(k+3)(k+2)} d_k \quad (\text{A.7})$$

From this *recurrence relation*, we know all of the even coefficients in the power series (A.3) for  $c = 0$  and all of the odd coefficients for  $c = 1$ .

If we look back at the power series (A.3), in order for it to be normalisable, the coefficients  $d_k$  must vanish at some point. So let us label the order of the highest order term in the power series (A.3) as  $l - c$ . We thus deduce:

$$\text{(for } c = 0) \quad d_{l+2} = 0 = \frac{l(l+1) - \lambda}{(l+2)(l+1)} d_l \quad (\text{A.8})$$

$$\text{(for } c = 1) \quad d_{l+1} = 0 = \frac{l(l+1) - \lambda}{(l+2)(l+1)} d_{l-1} \quad (\text{A.9})$$

For this to be true,  $\lambda = l(l + 1)$ , where  $l \geq c$ . As the coefficients obey a linear recurrence relation, we only have two coefficients to determine:  $d_0$  (non-zero only for  $c = 0$ ) and  $d_1$  (non-zero only for  $c = 1$ ).

The solutions to the Legendre equation are called the *Legendre polynomials* and they are given by:

$$P_l(\alpha) = \frac{1}{2^l l!} \frac{d^l[(\alpha^2 - 1)^l]}{d\alpha^l} \quad (\text{A.10})$$

(Bethe and Salpeter, 1977, page 344).

## A.2 The Associated Legendre Equation

It is very difficult to solve the *associated Legendre equation* directly, however there is simple formula in terms of the Legendre polynomials for  $m \geq 0$ :

$$P_l^m(\alpha) = (1 - \alpha^2)^{\frac{m}{2}} \frac{d^m P_l(\alpha)}{d\alpha^m} \quad (\text{A.11})$$

and for  $m < 0$  we have a solution in terms of the  $m \geq 0$  solutions:

$$P_l^{-m}(\alpha) = (-1)^m \left[ \frac{(l - m)!}{(l + m)!} \right] P_l^m(\alpha) \quad (\text{A.12})$$

It is worth noting at this point that this only gives a non-zero solution when  $m$  is in the range  $-l \leq m \leq l$ . The reason for this is that the  $(l + 1)^{\text{th}}$  derivative of  $P_l(\alpha)$  is zero, as its highest order term is  $\alpha^l$  ( $c = 0$ ) or  $\alpha^{l-1}$  ( $c = 1$ ).

## Glossary

A brief description of many of the terms that are *italicised* in the main text.

**angular momentum quantum number** the quantum number related to the total angular momentum of the electron about the nucleus

**black-body radiation** the *electro-magnetic radiation* from a hot body which absorbs all incoming light

**Bohr atom** the model of the atom suggested by Bohr; wherein electrons orbit a central nucleus much like the planets about the sun

**complex conjugate** the term by which a complex number can be multiplied in order to get a product which is both real and has the square of the initial modulus

**complex numbers** numbers which have imaginary components; those of the form  $z = a + ib$  where  $a$  and  $b$  are real numbers, and  $i = \sqrt{-1}$

**Compton scattering** the decrease in energy of an X-ray when it interacts with matter

- de Broglie wavelength** the wavelength of a particle of momentum  $p$  is said to have de Broglie wavelength  $\lambda = h/p$  where  $h$  is *Planck's constant*
- eigenfunctions** see section 2.2.4
- eigenstates** see section 2.2.4
- eigenvalues** see section 2.2.4
- electro-magnetic radiation** radiation that travels through space, having the form of a coupled magnetic and electric disturbance; examples include visible light, X-rays, microwaves, ...
- electron-volts** a unit of energy; the amount of energy required to accelerate an electron through a potential of 1 volt
- Heisenberg uncertainty principle** a particles position and momentum cannot both be known to arbitrary precision simultaneously
- ionisation energy** the lowest amount of energy that has to be given to an atom in its lowest energy state in order to allow the escape of an electron
- (associated) Legendre equation** partial differential equations related to spherical harmonics, see appendix A
- (associated) Legendre solutions** solutions to the (associated) Legendre equation, see appendix A
- Laplacian operator** the partial differential operator  $\nabla^2$
- Lyman series** the series of emission lines caused by an electron in a hydrogen atom moving from a quantum state with  $n > 1$  to the quantum state with  $n = 1$
- magnetic quantum number** the coordinate-specific quantum number related to the component of the electrons angular momentum about the z axis
- matrix mechanical formulation** a definition of quantum mechanics which utilises matrices for the storage of the properties of the components of a system; this was introduced by Werner Heisenberg
- neutrinos** chargeless, extremely low mass, fundamental particles created during some types of radioactive decay
- operators** see section 2.2.4
- permittivity of free space** the ability of free space to transmit an electric field; a fundamental constant
- photoelectric effect** the effect wherein electrons are ejected from matter under a particular wavelength of light; giving evidence for wave-particle duality

- photon** the quantum of *electro-magnetic radiation*; a particle of light
- Planck's constant** the constant  $h$  that relates the energy and frequency of *electro-magnetic radiation* in the equation  $E = hf$ ; it has value  $h \approx 6.626 \text{ m}^2 \text{ kg s}^{-1}$
- principal quantum number** the quantum number in hydrogen related to the atoms total energy
- quantum** (plural: quanta) the smallest piece of energy of a particular form: for example a photon is the quantum of *electro-magnetic radiation*
- quantum mechanics** a theory describing the motion and state of very small particles; such as those on the atomic and sub-atomic scales
- quantum numbers** the numbers describing the state of a quantum system
- recurrence relation** the equation defining a recursive sequence, that is, a sequence for which later terms depend on previous terms
- reduced mass** an adjusted mass  $\mu$  which allows physicists to treat one of the masses in a system of two masses  $m_1$  and  $m_2$  as stationary, by setting its mass to  $\infty$ ; given by  $\mu = \frac{m_1 m_2}{m_1 + m_2}$
- relativity** a catch-all term for Einstein's theories of general relativity and special relativity
- Schrödinger's equation** a partial differential equation which governs the evolution of a *wavefunction* in time and space
- separation constant** the constant both sides of a differential equation are set to once the equation has undergone *separation of variables*
- separation of variables** a method used to solve partial differential equations by reducing them to ordinary differential equations (see section 3)
- speed of light** literally the speed at which light travels through empty space: a value around  $3 \times 10^8 \text{ m s}^{-1}$
- sub-atomic** entities which are smaller than the size of an atom; electrons, protons, neutrons, neutrinos and so on
- superposition** the process by which a new solution to a linear differential equation may be obtained by adding together two other solutions to the equation with arbitrary constant coefficients
- TISE** time independent Schrödinger equation; the equation describing the wavefunction a particle in a static potential (that is, a potential with no dependence on time)
- wave mechanical formulation** a definition of quantum mechanics which uses the theory of waves to describe the properties of the components of a system; this was introduced by Erwin Schrödinger
- wavefunction** a function used in quantum mechanics to store all of the information about a system's state

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