Schrödinger's Equation

MAP372 Project

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Contents

Chapter 1

Why do we need quantum mechanics?

To understand Schrödinger's wave mechanics, we must firstly explore the history of quantum mechanics. This chapter will underline the key theories on this relatively new field. The sources of history in this chapter are based on [1], [2] and [3].

1.1 Introduction

Definition 1. Classical Mechanics can be described as the motion of a body according to Newton's Laws.

Classical mechanics was developed in the 18^{th} and 19^{th} centuries. It consists of defined mathematical laws, so it is possible to accurately calculate what will happen when the body is well-defined. It succeeds to describe the behaviour of macroscopic bodies, but it fails to describe the behaviour of microscopic bodies. So how can we describe the behaviour of a microscopic body?

Definition 2. Quantum Mechanics can be described as the principles relating to the behaviour of energy and matter in an atomic and subatomic scale.

Quantum mechanics was discovered at the start of the 20^{th} century. Electromagnetic radiation was the area in which quantum theory was first developed. As the theory developed, so did the understanding of the microscopic system. Although there were difficulties in visualisation, the gains proved the theory effective. The laws of planetary motion or motion of a projectile could also determine the shape of molecules and the energy of chemical reaction. Such inventions like the laser and transistor were inspired by quantum theory.

1.2 Quanta

Definition 3. A black body is a body which absorbs all the radiation it receives.

The black body case was a study in the spectral distribution of electromagnetic radiation in thermodynamic equilibrium with matter. This experiment caused disagreement with classical mechanics because general thermodynamics shows that the radiation emitted by the black body is only a function of temperature (figure 1.1).

In 1900, Planck provided a solution to the problem. He suggested that energy exchanges between matter and radiation are not continuous, but can be emitted or absorbed in discrete and individual amounts. These packets of energy are called quanta.

Einstein expanded on the theory of quanta in 1905 with the Photoelectric effect.

Black-Body Radiation

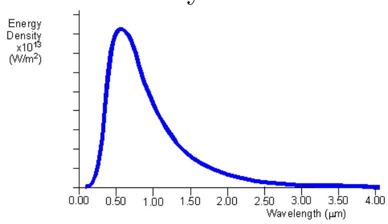

Figure 1.1: The distribution of radiation emitted according to its wavelength. [4]

1.3 Photoelectric effect

Definition 4. The photoelectric effect is the theory that when radiation of sufficiently short wavelength interacts with matter, electrons are emitted.

In 1905, Einstein postulated that quanta are not a feature of atoms but a feature of light itself. He viewed light as streams of quanta, where the energy of the quanta was proportional to their frequency.

Experiments showed that by increasing the frequency of light the number of electrons remained unchanged. However it increased the energy of the electrons. Whilst increasing the intensity of the light affected the number of electrons; it did not increase the energy. The emissions of the electrons begin immediately but below a certain light frequency, no electrons were emitted at all.

A practical example of this theory is with solar panels. They show the way in which light striking certain materials can emit electrons causing a current to flow.

In concluding Einstein's Photoelectric effect, energy in each quanta is related to the wave length, hence the frequency of the radiation. The equation

$$E = \hbar v, \tag{1.1}$$

can be derived, where v is the frequency and $\hbar = \frac{h}{2\pi}$, where h is Planck's constant.

The Photoelectric effect can be explained using Planck's law and the principle of energy conservation. We know below a certain frequency no electrons are emitted. If we call ϕ, the minimum energy to emit electrons then

$$E_{max} = \hbar v - \phi \tag{1.2}$$

if each photon transmits its energy to just one electron.

Einstein then went on to discover the theory of relativity.

1.4 Wave-particle duality

Definition 5. Wave-Particle Duality describes the theory that a microscopic body can possess both wave and particle-like properties.

In 1923, de Broglie suggested that as light can exhibit both wave and particle properties, particles such as electrons might show wave-like properties. De Broglie showed that Einstein's theory of relativity provided a unique, consistent procedure for associating a wave to a particle.

Using the analogy with photons, he proposed that the wavelength of the particle was proportional to the momentum giving

$$\lambda = \frac{\hbar}{p} \tag{1.3}$$

where λ is the wavelength and p is its momentum.

De Broglie's hypothesis on wave-particle duality formed the basis for Schrödinger's wave equation.

1.5 Diffraction of matter waves

The first diffraction experiments were performed by Davisson and Germer (1927).

The experiment shows diffraction of electrons by a polycrystalline foil. The electron beam originating at the source is collimated by the diaphragm and then diffracted by the polycrystalline foil. The diffracted pattern then appears on a screen (figure 1.2).

The beam passes through the foil, it splits into a transmitted and a diffracted wave forming interference patterns. The observed pattern on the screen is made up of a succession of well-localized impacts. If the intensity of the waves are decreased then the number of impacts decreases proportionately. Eventually with a very low intensity, a single impact would appear either on the centre spot or on one of the diffracted rings.

The experiment gives a statistical interpretation. The intensity of the wave at each point of the screen, gives the probability of occurrence of an impact at that point.

Diffraction of Matter Waves

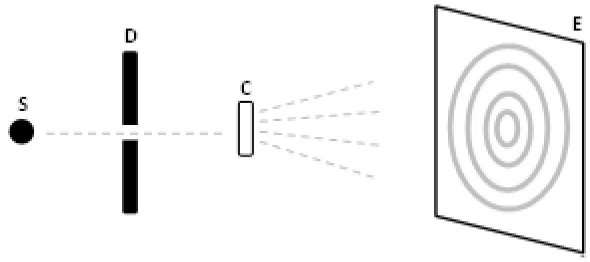

Figure 1.2: Source S, monoërgic cathode rays, behind a diaphragm D with fixed shutter. A polycrystalline foil C diffracts electrons onto a screen E.

1.6 Low energy electron diffusion

LEED experiment is one of surface diffraction used to investigate the arrangements of atoms on surface. Electrons have low penetration power, so the diffraction effects observed with electrons reflect back from the crystalline surface (figure 1.3).

As the electrons are light, their wave properties are easy to detect. The experiment conclusively shows that the beams of electrons do have wave-like properties.

Low-Energy Electron Diffraction

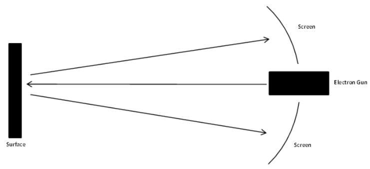

Figure 1.3: Electron diffraction reflected onto two screens.

1.7 Double slit experiment

Young's double slit experiment contains light from a source passing through a very narrow slit s_1 in the first screen. The light then passes through two closely spaced, also narrow slits s_2 and s_3. When it reaches the third screen, it does not irradiate equally but produces an interference pattern (figure 1.4). If, for example one of the slits were closed, then there would be no interference pattern as a result.

If the dimensions of the apparatus are known, then the distance between the light and dark regions on the screen can be determined. But measuring the particles travelling through a slit cannot be achieved, since the particles used to measure will interfere with the light passing through the slit.

If the light source was swapped with a low intensity light, individual photons could be measured as long as the screen was replaced with photosensitive microcrystal, an instrument that can detect individual photons. When this is used each photon appears to be unpredictable. We can say that the probability of a photon arriving at a particular point is proportional to the wave intensity

When the experiment is using massive numbers of photons, the number of photons arriving at any point must be proportional to the wave intensity.

Double Slit Experiment

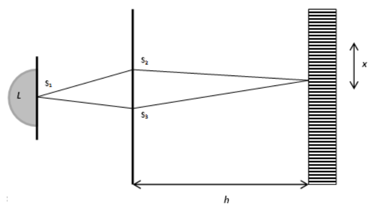

Figure 1.4: Interference pattern on a screen produced by light passing through narrow slits.

Chapter 2

The Schrödinger Equation

2.1 Introduction

The focus of this chapter is to evaluate examples of the Schrödinger equation from [2] Chapter 2. The Schrödinger equation is used to describe the nature of the waves.

2.2 Time-dependent equation

The time-dependent Schrödinger equation will be accepted as

$$i\hbar\frac{\partial\psi}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\psi + V\psi. \tag{2.1}$$

ψ represents a wave function associated to a quantum particle of mass m moving under a force $-\nabla v$ where $v =$ potential and $\psi = \psi(x,t)$, a function of space and time. ∇^2 represents the Laplacian, this operator depends on whether the particle is moving in one or two dimensions. In one dimension it takes the form, $\frac{\partial^2\psi}{\partial x^2}$. In two dimensions it takes the form $\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2}$.

The space and time variables, $T(t)$ and $\psi(x)$ are separable. Substituting $\psi = T\Psi$ into the equation and dividing by $T\Psi$ gives

$$i\hbar\frac{dT\Psi}{dt}/T\Psi = \left(\frac{-\hbar^2}{2m}\nabla^2\Psi T + VT\Psi\right)/T\Psi$$

$$= i\hbar\frac{dT}{dt}/T = \left(\frac{-\hbar^2}{2m}\nabla^2\Psi + V\Psi\right)/\Psi,$$

where the left side is dependent on t and the right side dependent on x.

$$E = \left(\frac{-\hbar^2}{2m} \nabla^2 \Psi + V\Psi \right) / \Psi$$
$$E = i\hbar \frac{dT}{dt} / T.$$

Therefore this gives the equations,

$$i\hbar \frac{dT}{dt} = ET \tag{2.2}$$

and

$$\frac{-\hbar^2}{2m} \nabla^2 \Psi + V\Psi = E\Psi. \tag{2.3}$$

As

$$\psi(t, x) = T(t)\Psi(x)$$

$$\psi(t, x) = T(t)\Psi(x) = e^{\frac{-iEt}{\hbar}} T(0) E\Psi,$$

therefore

$$T(t) = e^{\frac{-iEt}{\hbar}} T(0).$$

At $t = 0$ we get

$$\psi(0, x) = E\Psi.$$

$$\psi(t, x) = e^{\frac{-iEt}{\hbar}} T(0)\psi(0, x),$$

which gives

$$\psi(t, x) = e^{\frac{-iEt}{\hbar}} \psi(0, x).$$

Next we multiply 2.2 and 2.3 equation by Ψ and T respectively, gives

$$i\hbar \frac{dT}{dt} \Psi = E\Psi T = i\hbar \frac{\partial \psi}{\partial t}$$

and

$$-\frac{\hbar^2}{2m} \nabla^2 \Psi = E\Psi T = -\frac{\hbar^2}{2m} \nabla^2 \psi + V\psi,$$

where

$$E\Psi T = E\psi.$$

So therefore

$$-\frac{\hbar^2}{2m} \nabla^2 \psi + V\psi = E\psi. \tag{2.4}$$

2.3 Time-independent equation

The equation

$$-\frac{\hbar^2}{2m}\nabla^2\psi + V\psi = E\psi.$$

is known as Schrödinger's time-independent equation.

2.4 The square well

Consider the square well example [2]. The example consists of a particle moving within the interval $[0, a]$ on the x-axis, under the influence of the potential $V(x) = 0$. A zero potential allows it to move freely within the interval. Modifying the Laplacian in Schrödinger's time-independent equation for a particle moving in one-dimension gives,

$$-\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\delta x^2} + V\psi = E\psi. \tag{2.5}$$

Potential equalling zero gives,

$$-\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\delta x^2} = E\psi. \tag{2.6}$$

For $x \in (0, a)$, the boundary conditions, $\psi(0) = 0 = \psi(a)$.

Next we find the general solution of the differential equation using the discriminants.

$$\psi(a) = \begin{cases} Ae^{\alpha t} + Be^{\beta t}, & D > 0, \\ (A + Bx)e^{\alpha t}, & D = 0, \\ e^{\alpha t}\left(A\cos(\beta t) + B\sin(\beta t)\right), & D < 0. \end{cases}$$

Where α is the real part and β is the imaginary part.

$$\begin{aligned} -\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} &= E\psi \\ -\frac{\hbar^2}{2m}\lambda &= E \\ -\hbar\lambda &= \sqrt{2mE}. \end{aligned}$$

$$\psi(x) = \begin{cases} A\cosh(\lambda x) + B\sinh(\lambda x), & D > 0, \\ (A + Bx)e^{\lambda x} = A + Bx, & D = 0, \\ A\cos(\lambda x) + B\sin(\lambda x), & D < 0. \end{cases}$$

Using Boundary conditions, ψ is continuous as it cannot jump.

$$\psi(0) = \begin{cases} A, \ \psi(0) = 0 = A, \\ A, \ \psi(0) = 0 = A, \\ A, \ \psi(0) = 0 = A. \end{cases}$$

$$\psi(a) = \begin{cases} B\sinh(\sqrt{2mEa/\hbar}) & D > 0, \\ Ba & D = 0, \\ B\sin(\sqrt{2mEa/\hbar}) & D < 0. \end{cases}$$

$\psi(a) = 0 = Ba$, therefore $B = 0$ which is trivial.

$$\psi(a) = 0 = B\sin(\sqrt{2mEa}/\hbar),$$

$$\sin b = 0, \text{if } b = \frac{n\pi}{a}, \text{for any } n \in \mathbb{N}.$$

This gives

$$\psi(x) = \psi_n(x) = B\sin(n\pi x/a) \tag{2.7}$$

for positive E, the boundary condition can be satisfied if $\sqrt{2mE}/\hbar = n\pi/a$.

$$\sqrt{2mE}/\hbar = n\pi/a$$

$$E = \frac{n^2\pi^2\hbar^2}{2ma^2}.$$

Therefore the energy can take only certain discrete values.

The square well example shows that the quantization of energy is not a direct prediction of Schrödinger's equation, but is a consequence of the boundary conditions imposed on the wave function.

Definition 6. The ground state energy is the lowest possible energy when the energies of the system are discrete and bounded.

Higher energies known in increasing order as the first excited state energy, second excited state energy and so on.

Let

$$\int |\psi(x)|^2 dx = 1 \tag{2.8}$$

$\psi(x) = B\sin(n\pi x/a)$, where B is an arbitrary constant.

$$\int |B\sin(n\pi x/a)|^2 dx = 1.$$

The wave function is normalized. Conditions then give

$$\begin{aligned} 1 &= \int_0^a |B\sin(n\pi x/a)|^2 dx \\ &= |B|^2 \int_0^a \sin^2 n\pi x/a dx \\ &= |B|^2 \int_0^a \frac{1}{2} - \frac{\cos(\frac{2n\pi x}{a})}{2}\, dx, \end{aligned}$$

$$\int_0^a \frac{1}{2} - \frac{\cos(\frac{2n\pi x}{a})}{2} dx = \frac{x}{2} - \frac{n\pi}{a}\frac{\sin 2n\pi x}{a}$$

$$\left[\frac{x}{2} - \frac{n\pi}{a}\frac{\sin 2n\pi x}{a}\right]_b^a = \frac{a}{2} - \frac{n\pi}{a}\frac{\sin 2n\pi a}{a}$$

For all values of a, $\sin 2n\pi a = 0$. So

$$\int_0^a \sin^2 n\pi x/a dx = \frac{a}{2},$$

therefore

$$\frac{a}{2}|B|^2 = 1.$$

$$|B|^2 = \frac{2}{a}, \qquad |B| = \sqrt{\frac{2}{a}}.$$

So

$$\sqrt{\frac{2}{a}}\sin(n\pi x/a) = \psi_n(x)$$

Combine with the time development to arrive at,

$$\begin{aligned} \psi_n(t,x) &= e^{-iE_n t/\hbar\psi}(0,x) \\ &= \sqrt{\frac{2}{a}} e^{\frac{-iE_n t}{\hbar}} \sin\frac{n\pi x}{a} \\ &= \sqrt{\frac{2}{a}} e^{\frac{-in^2\pi\hbar t}{2ma^2}} \sin\frac{n\pi x}{a}. \end{aligned}$$

2.5 The time evolution of the wave function

We now expand the wave function as an infinte sum of separable solutions.

Take

$$
\begin{aligned}
\psi(t,x) &= \sum_{n=1}^{\infty} C_n \psi_n(t,x) \\
&= \sqrt{\frac{2}{a}} \sum_{n=1}^{\infty} C_n e^{\frac{-in^2\pi\hbar t}{2ma^2}} \sin\frac{n\pi x}{a}.
\end{aligned}
$$

$$
\psi(0,x) = f(x), \text{when } t = 0, e^{\frac{-in^2\pi\hbar t}{2ma^2}} = 1,
$$

So

$$
f(x) = \sqrt{\frac{2}{a}} \sum_{n=1}^{\infty} C_n \sin\frac{n\pi x}{a}. \tag{2.9}
$$

The Fourier coefficients are then given by,

$$
\begin{aligned}
\sqrt{\frac{2}{a}} C_n &= \frac{2}{a} \int_0^a f(x) \sin\frac{n\pi x}{a} dx \\
C_n &= \sqrt{\frac{2}{a}} \int_0^a f(x) \sin\frac{n\pi x}{a} dx. \\
&= \int_0^a f(x) \sqrt{\frac{2}{a}} \sin\frac{n\pi x}{a} \\
&= \int_0^a f(x) \psi_n(x) dx.
\end{aligned}
$$

2.6 The interpretation of the wave function

Max Born modified suggestions of de Broglie and Schrödinger. Born's interpretation states that the square of the wave function at any point gives the probability of finding the particle at that point.

$$
\mathbb{P}(\text{particle is in } A \text{ at time } t) = \int_A |\psi(x,t)|^2 \, dx. \tag{2.10}
$$

where $\rho(x) = |\psi(x)|^2$ gives the probability density for the position of the particle.

Normalising the function gives,

$$
\int_{\mathbb{R}} |\psi(x,t)|^2 \, dx = 1.
$$

From Probability theory, the probability of a particle being in the whole of space must be one.

For the square well example, this gives the probability density as

$$f_n(x) = \frac{2}{a}\sin^2\frac{n\pi x}{a} = \frac{1}{a}\left(1 - \cos\frac{2n\pi x}{a}\right).$$

To obtain the distribution function the density must be integrated, which gives

$$\begin{aligned} F_n(x) &= \int_0^x f_n(x)\,dx = \left[\frac{x}{a} - \frac{a}{2n\pi a}\sin\frac{2n\pi x}{a}\right]_0^x \\ &= \left(\frac{x}{a} - \frac{a}{2n\pi a}\sin\frac{2n\pi x}{a}\right). \end{aligned}$$

This shows that the distribution oscillates between $[0, a]$, arising from interference effects for the wave function.

An example from [2] will now show us how this works in practice.

Let us calculate the probability that the particle confined in the box $[0, a]$ is within $\frac{1}{4}a$ of the centre of the box, so the probability is within $[\frac{a}{4}, \frac{3a}{4}]$. Using the distribution function and the wave function ψ_n, the probability is

$$\int_{\frac{a}{4}}^{\frac{3a}{4}} |\psi_n(x)|^2\,dx = \int_{\frac{a}{4}}^{\frac{3a}{4}} f_n(x)\,dx$$

$$= F_n(\frac{3a}{4}) - F_n(\frac{a}{4}) = \left[\frac{3}{4} - \frac{1}{2n\pi}\left(\sin\frac{3n\pi}{2}\right)\right] - \left[\frac{1}{4} - \frac{1}{2n\pi}\left(\sin\frac{n\pi}{2}\right)\right].$$

$$\sin\frac{3n\pi}{2} = -\sin\frac{n\pi}{2}$$

To give

$$\begin{aligned} &= \frac{3}{4} - \frac{1}{4} + \frac{1}{2n\pi}\sin\frac{n\pi}{2} + \frac{1}{2n\pi}\sin\frac{n\pi}{2} \\ &= \frac{1}{2} + \frac{1}{n\pi}\sin\frac{n\pi}{2}, \end{aligned}$$

if n is even, $\sin\frac{n\pi}{2} = 0$, if n is odd, $\sin\frac{n\pi}{2} = (-1)^{\frac{1}{2}(n-1)}$. To give

$$\frac{1}{2} + \frac{1}{n\pi}\sin\frac{n\pi}{2} = \begin{cases} \frac{1}{2}, & \text{if } n \text{ is even,} \\ \frac{1}{2} + (-1)^{\frac{1}{2}(n-1)}/n\pi, & \text{if } n \text{ is odd.} \end{cases}$$

To find the mean of the particle's position, we use integration by parts,

$$\int_0^a x\, f_n(x)\, dx = [x\, F_n(x)]_0^a - \int_0^a F_n(x),$$

$$\begin{aligned}
&= \left[x\left(\frac{x}{a} - \frac{1}{2n\pi}\sin\frac{2n\pi x}{a}\right)\right]_0^a - \int_0^a \left(\frac{x}{a} - \frac{1}{2n\pi}\sin\frac{2n\pi x}{a}\right) dx, \\
&= a - \left[\frac{x^2}{2a} + \frac{a}{4n^2\pi^2}\cos\frac{2n\pi x}{a}\right]_0^a \\
&= a - \frac{a^2}{2a} + \frac{a}{4n^2\pi^2} - \frac{a}{4n^2\pi^2}.
\end{aligned}$$

as $\cos 2n\pi = 1 \quad \text{and} \quad \cos 0 = 1.$

$$= a - \frac{a}{2} = \frac{a}{2}.$$

This result shows the mean is about the midpoint.

To calculate the variance of the distribution we must first integrate

$$\int_0^a x^2 f_n(x)\, dx = \left[x^2 F_n(x)\right]_0^a - 2\int_0^a x F_n(x)\, dx.$$

We can see from calculating the mean that $[x^2 F_n(x)]_0^a = a^2$.
Now integrate by parts

$$-2\int_0^a x F_n(x)\, dx,$$

$$\begin{aligned}
&= -2\left(\left[\frac{x^3}{2a} + \frac{xa}{4n^2\pi^2}\cos\frac{2n\pi x}{a}\right]_0^a - \int_0^a \left(\frac{x^2}{2a} + \frac{a}{4n^2\pi^2}\cos\frac{2n\pi x}{a}\right) dx\right), \\
&= -2\left(\left[\frac{x^3}{2a} + \frac{xa}{4n^2\pi^2}\cos\frac{2n\pi x}{a}\right]_0^a - \left[\frac{x^3}{6a} + \frac{a^2}{8n^3\pi^3}\sin\frac{2n\pi x}{a}\right]_0^a\right), \\
&= -2\left(\frac{a^3}{2a} + \frac{a^2}{4n^2\pi^2} + \frac{a^3}{6a}\right).
\end{aligned}$$

Put together with first part to get

$$= a^2 - a^2 - \frac{a^2}{2n^2\pi^2} - \frac{a^2}{3}.$$

Now subtract the mean squared to get

$$= \frac{a^2}{3} - \frac{a^2}{2n^2\pi^2} - \left(\frac{a}{2}\right)^2 = \frac{a^2}{12} - \frac{a^2}{2n^2\pi^2}.$$

When n is large the variance approximates to $\frac{1}{12}a^2$, which is the classical uniform distribution.

Definition 7. When the quantum number is large and the quantum mechanical formulae tends to that of classical mechanics it is called the *correspondence principle.*

2.7 Currents and probability conservation

If we take

$$\int_{\mathbb{R}^3} |\psi(t,x)|^2 \, d^3x = 1,$$

does the equation hold as the wave function evolves for all values of t? This must be true for the statistical interpretation to hold as probability must be conserved.

Since

$$|\psi_n(t,x)|^2 = |e^{-iE_nt/\hbar}\psi_n(0,x)|^2 = |\psi_n(0,x)|^2,$$

probability is conserved for stationary states.

Using $\frac{\partial|\psi_t|^2}{\partial t} = \frac{\partial}{\partial t}(\overline{\psi_t}\psi_t)$, where $\overline{\psi}$ is the complex conjugate.
We arrive at

$$\frac{\partial}{\partial t}|\psi(t,x)|^2 = \frac{\partial}{\partial t}\overline{(\psi(t,x))}\,\psi(t,x) + \overline{\psi(t,x)}\,\frac{\partial}{\partial t}\psi(t,x),$$

from using the product rule. Then by substituting in Schrödinger's equation,

$$\begin{aligned}
&= \overline{\left[-\frac{i}{\hbar}\left(-\frac{\hbar^2}{2m}\nabla^2\psi + V\psi\right)\right]}\,\psi + \overline{\psi}\left[-\frac{i}{\hbar}\left(-\frac{\hbar^2}{2m}\nabla^2\psi + V\psi\right)\right] \\
&= \left[\frac{i}{\hbar}\left(-\frac{\hbar^2}{2m}\nabla^2\overline{\psi} + V\overline{\psi}\right)\right]\,\psi + \overline{\psi}\left[-\frac{i}{\hbar}\left(-\frac{\hbar^2}{2m}\nabla^2\psi + V\psi\right)\right].
\end{aligned}$$

The potential cancels to give

$$= \frac{i\hbar}{2m}(\overline{\psi}\nabla^2\psi - \psi\nabla^2\overline{\psi})$$

as $\nabla \cdot \nabla\psi = \nabla^2\psi,$ we conclude

$$\frac{\partial}{\partial t}|\psi(t,x)|^2 = \frac{i\hbar}{2m}\text{div}\left(\overline{\psi}\text{grad}\psi - \psi\text{grad}\overline{\psi}\right).$$

Definition 8. The probability current $\mathbf{j}$, is defined by

$$\mathbf{j}(t,x) = \frac{\hbar}{2mi}\left(\overline{\psi}\text{grad}\psi - \psi\text{grad}\overline{\psi}\right) \tag{2.11}$$

The probability density and probability current then satisfy the continuity equation

$$\frac{\partial\rho}{\partial t} + \text{div}\mathbf{j} = 0.$$

This equation leads to the probability conservation law.

Suppose that for all t the probability current $\mathbf{j}(t,x)$ tends to 0 faster than $|x|^{-2}$ as $|x| \to \infty$. Then

$$\int_{\mathbb{R}^3} \rho(t,x)d^3x$$

is independent of t.

Proof. If D is the volume enclosed by a surface S then for suitably well-behaved functions ψ.

$$\frac{\partial}{\partial t}\int_D \rho\; d^3x = \int_D \frac{\partial\rho}{\partial t}d^3x = \int_D(-\text{div}\mathbf{j})d^3x.$$

By the divergence theorem

$$= -\int_S \mathbf{j}\cdot\underline{n}\,ds.$$

Considering a sphere S of radius R we can see from spherical polars that

$$\int_0^\pi\int_0^{2\pi}\mathbf{j}\cdot\underline{n}\;R^2\sin\theta\,d\phi d\theta,$$

where $R^2\sin\theta$ are scale factors h_θ and h_ϕ.

So if $\mathbf{j}$ tends to 0 faster that $1/R^2$ for large R then the surface integral tends to 0 as $R \to \infty$.

Giving

$$\frac{\partial}{\partial t}\int_{\mathbb{R}^3}\rho\; d^3x = 0.$$

Hence,

$$\int_{\mathbb{R}^3} \rho(t,x)\, d^3x \tag{2.12}$$

is independent of t. $\square$

If for example,

$$\int_{\mathbb{R}^3} \rho(0,x)\ d^3x = 1,$$

then it is 1 for all values of t.

2.8 Statistical distribution of energy

In the time evolution of the wave function section we achieved,

$$\psi(t,x) = \sum C_n \psi_n(t,x) = \sqrt{\frac{2}{a}} \sum C_n \sin\frac{n\pi x}{a}.$$

$\partial\psi/\partial t$ is no longer in the form $E\psi$ so that the energy is no longer explicitly defined.

Heisenberg and Born proposed the probability of measuring value E_n is $|C_n|^2$.

Parseval's theorem for the Fourier series gives

$$\frac{2}{a}\int_0^a |\psi(t,x)|^2\, dx = \sum_{n=1}^{\infty} |\sqrt{\frac{2}{a}} C_n|^2 \tag{2.13}$$

since ψ is normalised, we have

$$\sum |C_n|^2 = 1.$$

Shows there is a zero probability of finding an energy other than E_n.

Suppose that the wave function ψ inside the square well is just the constant $\frac{1}{\sqrt{a}}$, example 2.6.1 [2], $\frac{1}{\sqrt{a}}$ ensures ψ is normalised. Then

$$\begin{aligned}
C_n &= \sqrt{\frac{2}{a}} \int_0^a \sqrt{\frac{1}{a}} \sin \frac{n\pi x}{a}\, dx, \\
&= \sqrt{\frac{2}{a}} \sqrt{\frac{1}{a}} \int_0^a \sin \frac{n\pi x}{a}\, dx, \\
&= \frac{\sqrt{2}}{a} \left[-\frac{a}{n\pi} \cos \frac{n\pi x}{a} \right]_0^a \\
&= \frac{\sqrt{2}}{a} \left(-\frac{a}{n\pi} \cos n\pi + \frac{a}{n\pi} \right) \\
&= \frac{\sqrt{2}}{n\pi} \left(1 - (-1)^n \right).
\end{aligned}$$

If n is even, the probability of measuring the energy E_n is zero if n is odd,

$$E_n = \left(\frac{2\sqrt{2}}{n\pi} \right)^2 = \frac{8}{n^2\pi^2}. \tag{2.14}$$

Chapter 3

The Hydrogen Atom

3.1 Introduction

This chapter follows the examples and cases from [2], Chapter 4. In 1912, Rutherford formulated a planetary model of the atom where negatively charged electrons orbit a positively charged nucleus from electrostatic interaction. The effect of the force acting on the nucleus is neglected as its mass is almost 2000 times heavier than the electrons.

This causes the centre of mass to be located almost at the centre of the nucleus.

Consider the simple hydrogen atom containing 1 electron orbiting 1 proton in the nucleus. Assuming the nucleus is fixed, the electrostatic potential energy is

$$V = -\frac{Ze^2}{4\pi\epsilon_0 r}. \tag{3.1}$$

where Ze is the positive nucleus charge, ϵ_0 is the dielectric constant of the vacuum and r is the radius between electron and nucleus. Putting the potential into Schrödinger's equation gives

$$-\frac{\hbar^2}{2m}\nabla^2\psi - \frac{Ze^2}{4\pi\epsilon_0 r}\psi = E\psi. \tag{3.2}$$

3.2 Central force problems

To consider this problem we need to rewrite the Laplacian in spherical polar coordinates (r, θ, ϕ) to give

$$-\frac{\hbar^2}{2m}\left(\frac{1}{r}\frac{\partial^2 r\psi}{\partial r^2} + \frac{1}{r^2 \sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}\right) + V(r)\psi = E\psi.$$

Next we use separation of variables. Assume that $\psi(r,\theta,\phi) = R(r)\Theta(\theta)\Phi(\phi)$. Substituting the wave function into the equation gives

$$\left(\frac{1}{r}\frac{\partial^2 r}{\partial r^2}\left(rR\Theta\Phi\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}R\Phi\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2\Phi}{\partial\phi^2}R\Theta\right)$$

$$+V(r)R\Theta\Phi = ER\Theta\Phi.$$

Differentiating with respects to r, θ and ϕ gives

$$\left(\frac{1}{r}\Theta(\theta)\Phi(\phi)\frac{\partial^2 r}{\partial r^2}\left(rR\right) + \frac{1}{r^2\sin\theta}R(r)\Phi(\phi)\left(\cos\theta\Theta'(\theta) + \sin\theta\Theta''(\theta)\right) + \frac{R(r)\Theta(\theta)}{r^2\sin^2\theta}\Phi''(\phi)\right)$$

$$+V(r)R(r)\Theta(\theta)\Phi(\phi) = ER(r)\Theta(\theta)\Phi(\phi).$$

Next we divide by $R(r)\Phi(\phi)\Theta(\theta)$ and multiply by r^2.

$$= \frac{r}{R(r)}\frac{d^2}{dr^2}(rR) + \frac{1}{\Theta(\theta)\sin\theta}\left(\cos\theta\Theta'(\theta) + \sin\theta\Theta''(\theta)\right)$$

$$+\frac{1}{\Phi(\phi)\sin^2\theta}\Phi''(\phi) + r^2V(r) = r^2E.$$

Therefore

$$-\frac{\hbar^2}{2m}\left(\frac{r}{R}\frac{d^2}{dr^2}(rR) + \frac{1}{\Theta\sin\theta}\Big(\cos\theta\frac{d\Theta}{d\theta} + \sin\theta\frac{d^2\Theta}{d\theta^2}\Big) + \frac{1}{\Phi\sin^2\theta}\frac{d^2\Phi}{d\phi^2}\right)$$

$$+r^2V = r^2E.$$

Only the second and third variables depend on angular variables. The others only depend on r. So when r is fixed

$$-\frac{\hbar^2}{2m}\Big(\frac{r}{R}\frac{d^2}{dr^2}(rR) - \lambda\Big) + r^2V = r^2E. \tag{3.3}$$

where λ is a constant.

$$-\lambda = \frac{1}{\Theta\sin\theta}\Big(\cos\theta\frac{d\Theta}{d\theta} + \sin\theta\frac{d^2\Theta}{d\theta^2}\Big) + \frac{1}{\Phi\sin^2\theta}\frac{d^2\Phi}{d\phi^2}.$$

The variables can be further separated. Multiplying the angular equation by $sin^2\theta$ gives

$$-\lambda \sin^2 \theta = \frac{sin\theta}{\Theta} \left(\cos\theta \frac{d\Theta}{d\theta} + \sin\theta \frac{d^2\Theta}{d\theta^2} \right) + \frac{1}{\Phi} \frac{d^2\Phi}{d\phi^2}.$$

Φ''/Φ only depends on ϕ therefore $\Phi''/\Phi = -\mu^2$, where μ is a constant and

$$-\lambda \sin^2 \theta = \frac{sin\theta}{\Theta} \left(\cos\theta \frac{d\Theta}{d\theta} + \sin\theta \frac{d^2\Theta}{d\theta^2} \right) - \mu^2.$$

From before we have $\Phi'' = -\mu^2\Phi$, which equals $\quad \Phi'' + \mu^2\Phi = 0$.

From this equation we get the characteristic polynomial $p^2 + \mu^2 = 0$.

Since $\Phi(\phi + 2\pi) = \Phi(\phi)$, μ must be a real integer. When $\mu = 0$ only the constant solution is periodic.

Therefore

$$\Phi = e^{i\mu\phi}, \qquad \mu \in \mathbb{Z}.$$

Now the angular equation can be re-written in terms of $\cos(\theta)$, which will be denoted by c.

$$-\lambda \sin^2 \theta = \frac{sin\theta}{\Theta} \left(\cos\theta \frac{d\Theta}{d\theta} + \sin\theta \frac{d^2\Theta}{d\theta^2} \right) - \mu^2.$$

$$\frac{\sin\theta}{\Theta} \frac{d}{d\theta} \left(\sin\theta \frac{d\Theta}{d\theta} \right),$$

Using trigonometric identities

$$sin\theta \frac{d}{d\theta} = \sin\theta \frac{dc}{d\theta} \frac{d}{dc} = \sin^2\theta \frac{d}{dc} = (c^2 - 1)\frac{d}{dc}.$$

We then from this now obtain Legendre's equation

$$(c^2 - 1)\frac{d}{dc} \left((c^2 - 1)\frac{d\Theta}{dc} \right) - \mu^2\Theta + \lambda(c^2 - 1)\Theta = 0. \tag{3.4}$$

The solutions to the equations are at $c = \pm 1$ unless $\lambda = l(l+1)$ where $l \in \mathbb{N} \geq |\mu|$.

When $\lambda = l(l+1)$ there exists a unique solution P_l^μ which is continuous between the interval [-1,1].

When $\mu = 0$ the solution is P_l which is called a *Legendre polynomial*. We now arrive at the full angular term

$$\Theta\Phi = P_l^\mu(\theta)e^{i\mu\phi}.$$

This is called a *spherical harmonic* of degree l, we denote this $Y_l^\mu(\theta,\phi)$.

We now go back and look at the radial equation 3.3. Firstly we multiply by R and divide by r to get

$$-\frac{\hbar^2}{2m}\left(\frac{d^2}{dr^2}(rR) - \frac{l(l+1)}{r}R\right) + VrR = ErR.$$

$$\frac{d^2}{dr^2}(rR) - \frac{l(l+1)}{r}R + VrR = -\frac{2mE}{\hbar^2}rR.$$

If $r \to \infty$ then $V(r)$ tends to 0 as well as $\frac{l(l+1)}{r}$. This means the equation can be re-written as

$$\frac{d^2}{dr^2}(rR) \sim -\frac{2mE}{\hbar^2}(rR).$$

$$\frac{d^2}{dr^2}(rR) + \frac{2mE}{\hbar^2}(rR) \sim 0$$

$$\lambda^2 + r^2\frac{2mE}{\hbar^2} \sim 0$$

$$\lambda = r\frac{\sqrt{-2mE}}{\hbar}.$$

Therefore the solutions are

$$rR \sim e^{(\pm r\sqrt{-2mE}/\hbar)}. \tag{3.5}$$

If E is positive the argument becomes imaginary. We should have $|rR| = 1$. This would mean that R is not normalizable since

$$\int_{\mathbb{R}^3} |R|^2 d^3r = \int_{\mathbb{R}} |R|^2 r^2 \sin\theta dr d\theta d\phi = 4\pi \int_0^\infty |rR|^2 dr. \tag{3.6}$$

rR must be less singular than $r^{-\frac{1}{2}}$ or the integral will diverge. Therefore E must be negative. Take $E = -\hbar^2\kappa^2/2m$, with $\kappa > 0$, so that

$$rR(r) \sim e^{-r\sqrt{-2m(-\hbar^2\kappa^2/2m)}/\hbar}$$

$$rR(r) \sim e^{-\kappa r}.$$

We will now try to find an exact solution in the form

$$R(r) = \frac{f(r)}{r} e^{-\kappa r}.$$

Firstly we will calculate the differentiation in the equation

$$\begin{aligned}
\frac{d^2}{dr^2}(rR) = \frac{d^2}{dr^2} rR(r) &= \frac{d^2}{dr^2} f(r) e^{-\kappa r} \\
&= f'(r)e^{-\kappa r} - f(r)\kappa e^{-\kappa r} \\
&= f''(r)e^{-\kappa r} - f'(r)\kappa e^{-\kappa r} + f(r)\kappa^2 e^{-\kappa r} - f'(r)\kappa e^{-\kappa r} \\
&= f''(r)e^{-\kappa r} - 2f'(r)\kappa e^{-\kappa r} + f(r)\kappa^2 e^{-\kappa r}.
\end{aligned}$$

Now we put this into the equation and simplify

$$-\frac{\hbar^2}{2m}\left(f''(r)e^{-\kappa r} - 2f'(r)\kappa e^{-\kappa r} + f(r)\kappa^2 e^{-\kappa r} - \frac{l(l+1)}{r} R \right) + VrR = ErR.$$

$e^{-\kappa r}$ cancels to give

$$-\frac{\hbar^2}{2m}\left(f'' - 2f'\kappa + f\kappa^2 - \frac{l(l+1)}{r^2} f \right) + Vf = Ef.$$

Substitute $E = -\hbar^2\kappa^2/2m$ and divide by $-\hbar^2/2m$ to arrive at

$$f'' - 2f'\kappa + f\kappa^2 - \frac{l(l+1)}{r^2} f - \frac{2mV}{\hbar^2} f = \kappa^2 f$$

$$f'' - 2f'\kappa - \frac{l(l+1)}{r^2} f - \frac{2mV}{\hbar^2} f = 0.$$

3.3 The spectrum of the hydrogen atom

The *Bohr radius* will now be introduced as $a = 4\pi\epsilon_0\hbar^2/me^2$. Now the term $2mV/\hbar^2$ can be written as $-2Z/ar$.

For the equation

$$-\frac{\hbar^2}{2m}\nabla^2\psi - \frac{Ze^2}{4\pi\epsilon_0 r}\psi = E\psi.$$

the permissible bound state energies are

$$E_n = -\frac{1}{2n^2} \cdot \frac{Z^2e^2}{4\pi\epsilon_0 a},$$

for $n = l+1, l+2, ...$ The corresponding wave functions take the form

$$\psi_{nlm}(r) = \text{constant} \cdot r^l L_n^l (Zr/a) e^{-zr/na} Y_l^m(\theta,\phi)$$

where L_n^l is a polynomial of degree $n-l$. In particular, the normalized ground state wave function maybe written as

$$\psi_{100}(r) = (Z^3/\pi a^3)^{\frac{1}{2}} e^{Zr/a}. \qquad [2] \tag{3.7}$$

Proof. Using the radial equation and substituting $-2Z/ar$ we get

$$\left(f''2\kappa f' - \frac{l(l+1)}{r^2} f \right) + \left(\frac{2Z}{ar} \right) f = 0 \tag{3.8}$$

Next we change the variable to $\rho = Zr/a$. This gives us

$$\frac{d^2 f}{d\rho^2} - \frac{2a\kappa}{Z} \frac{df}{d\rho} - \frac{l(l+1)}{\rho^2} f + \frac{2}{\rho} f = 0. \tag{3.9}$$

If f is holomorphic it has a series expansion. We will use the series solution

$$f(\rho) = \sum_{k=0}^{\infty} a_k \rho^{k+c} \tag{3.10}$$

The series expansion is unique. With$a_0 \neq 0$ we get

$$f'(\rho) = \sum_{k=0}^{\infty} a_k (k+c) \rho^{k+c-1}$$

and

$$f''(\rho) = \sum_{k=0}^{\infty} a_k (k+c)(k+c-1) \rho^{k+c-2}.$$

Therefore substituting the series into the equation gives

$$\sum_{k=0}^{\infty} a_k (k+c)(k+c-1) \rho^{k+c-2} - \frac{2a\kappa}{Z} \sum_{k=0}^{\infty} a_k (k+c) \rho^{k+c-1}$$
$$-l(l+1) \sum_{k=0}^{\infty} a_k \rho^{k+c-2} + 2 \sum_{k=0}^{\infty} a_k \rho^{k+c-1} = 0.$$

Now we take out the first terms to give

$$a_0\, c(c-1)\rho^{c-2} + \sum_{k=1}^{\infty} a_k(k+c)(k+c-1)\rho^{k+c-2} - a_0\, l(l+1)\rho^{c-2}$$

$$-l(l+1)\sum_{k=1}^{\infty} a_k\rho^{k+c-2} - \sum_{k=0}^{\infty}\rho^{k+c-1}\left(\frac{2a\kappa}{Z}a_k(k+c) - 2a_k\right) = 0.$$

Next we collect the terms

$$\rho^{c-2}\left(a_0\, c(c-1) - a_0\, l(l+1)\right) + \sum_{k=0}^{\infty} a_{k+1}(k+c+1)(k+c)\rho^{k+c-1}$$

$$-l(l+1)\sum_{k=0}^{\infty} a_{k+1}\rho^{k+c-1} - \sum_{k=0}^{\infty}\rho^{k+c-1}\left(\frac{2a\kappa}{Z}a_k(k+c) - 2a_k\right).$$

This then equals

$$\rho^{c-2}\left(a_0\, c(c-1) - a_0\, l(l+1)\right)$$

$$+\sum_{k=0}^{\infty}\rho^{k+c-1}\left(a_{k+1}(k+c+1)(k+c) - 2a_k\left(\frac{2a\kappa}{Z}a_k(k+c)+1\right) - l(l+1)a_{k+1}\right). \tag{3.11}$$

We can see that each part equals 0. So from this we get

$$a_0\left(c(c-1) - l(l+1)\right). \tag{3.12}$$

Because $a_0 \neq 0$ we get $c(c-1) = l(l+1)$ therefore $c = l+1$ or $c = -l$

To ensure a normalizable wave function, $|rR|^2$ must have a finite integral near $r = 0$, which is only possible if $2c > -1$, so we must take $c = l+1$.

We also get from 3.11

$$a_{k+1}(k+c+1)(k+c) - 2a_k\left(\frac{\kappa a}{Z}(k+c)+1\right) - l(l+1)a_{k+1} = 0. \tag{3.13}$$

Substituting $c = l+1$ then gives us the recurrence relation for the coefficients for $k \geq 1$

$$(k+2l+1)ka_k = 2\left[(a\kappa/Z)(k+l) - 1\right]a_{k-1}. \tag{3.14}$$

Now we need to force the series to terminate. If $k = h$ and the term equals 0, then the term $k = h+1$ will equal 0 causing the series to terminate. If $a_k = Z/n \quad$ for $\quad n = (k+l) > l$, then

$$2\left[\frac{1}{k+l}(k+l) - 1\right] a_{k-1}$$

will cause the series to terminate.

Definition 9. The positive integer n is called the *principal quantum number.*

We can now substitute $\kappa = Z/na$ to deduce the Energy.

$$E_n = \frac{-\hbar^2\kappa^2}{2m} = \frac{-Z^2\hbar^2}{2mn^2a^2}$$

then by using the definition of a we get

$$\begin{aligned} E_n &= -\frac{1}{2n^2} \cdot \frac{Z^2e^2}{4\pi\epsilon_0 a} \\ E_n &= -\frac{Z^2e^2}{8\pi\epsilon_0 n^2 a}. \end{aligned}$$

In the ground state $n = 1$, both l and μ must vanish and the series terminates after the first term to give

$$\psi(r) = a_0 e^{-\kappa r}$$

for $n = 1, \qquad \kappa = Z/a$ so

$$\psi(r) = a_0 e^{-Zr/a}.$$

To find a_0 we must normalize the ground state wave function which requires

$$1 = \int_{\mathbb{R}^3} |\psi(r)|^2 \, r^2 sin\theta dr d\theta d\phi$$

from 3.6 we get

$$\begin{aligned} &= 4\pi \int_0^\infty |r^2\psi(r)|^2 \, dr \\ &= 4\pi|a_0|^2 \int_0^\infty r^2 e^{-\kappa r} \, dr \\ &= 4\pi|a_0|^2 \frac{d^2}{d\kappa^2} \int_0^\infty e^{-Zr/a} \, dr \end{aligned}$$

$$\begin{aligned}&= 4\pi|a_0|^2\frac{d^2}{d\kappa^2}2\kappa^{-1}\\&= 4\pi|a_0|^2 \cdot 4\kappa^{-3}\\&= \pi a^3|a_0|^2/Z^3.\end{aligned}$$

This then gives the normalized ground state wave function 3.7

$$\psi_{100}(r) = (Z^3/\pi a^3)^{\frac{1}{2}}e^{Zr/a}.$$

□

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