The
Wilsonian
Flux

Issue 3 / March 2025 - Physics

Welcome to Issue 3 - I hope your exams went swimmingly. We've decided to expand horizons to both maths and physics, and so it makes more sense to have separate maths and physics articles. This month, we focus on quantum physics; this might be slightly less relevant to an engineer and slightly more relevant to a physicist - but should be interesting nonetheless. Most of the articles are quite mathematically rigorous, and so being comfortable with linear algebra and differential equations would be extremely helpful, alongside other concepts such as partial derivatives as well as Taylor and Fourier series. Most of these should be familiar either through A-Level maths or through previous issues.

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Figure 1: Bohr and Heisenberg meet in a Nazi-occupied Copenhagen in September 1941 [1]

1 An introduction to quantum mechanics

Written by **Christian, Year 13**

1.1 Introduction

At the end of the 20th century, many physicists were of the opinion that almost all major physics had been discovered. However, a few unexplainable problems, such as the ultraviolet catastrophe and Max Planck's discovery of energy quanta, would soon overturn that belief and open the eyes of physicists, showing them just how little they really knew at the time. What I want to achieve in this very brief introduction to quantum theory is to show you the foundations on which the theory rests and to show you how they can lead you to one of the most important results in quantum mechanics - the wavefunction of the electron in the hydrogen atom. Quantum mechanics is very often regarded as a counter-intuitive subject which is difficult to grasp, but I find many of its concepts rather elegant and the tools for understanding them are quite versatile, and so I believe that there is worth in knowing at least a bit about the subject at this stage.

1.2 The Wavefunction and the Statistical Interpretation

In classical (Newtonian) mechanics, the problem to be solved in order to describe the evolution of a system is to find solutions to the equation $F = ma$. Once we have armed ourselves with the acceleration of the object of interest, we can use basic calculus to find its velocity and displacement as functions of time as well as parameters such as its kinetic energy and momentum. Another way of writing Newton's second law is as follows; the acceleration of an object is equivalent to the second derivative of its displacement with respect to time, and the force on an object (for conservative systems, which are the only kind that we will explore at the microscopic level) is equivalent to the negative of the partial derivative of its potential energy with respect to displacement, so $F = ma$ becomes:

$$-\frac{\partial V}{\partial x} = m\frac{d^2x}{dt^2}$$

This much more general formulation of Newton's second law, along with initial conditions, such as the position and velocity of the object at $t = 0$ allows us to solve for the displacement of an object as a function of time, and so all other parameters of interest of the system.

Quantum mechanics approaches the same problem, but in quite a different way. The equation of interest in quantum mechanics, developed in 1926 by Erwin Schrödinger, aptly named after him, solves for something called the wavefunction of the particle, $\Psi(x,t)$, and is given by:

$$\boxed{i\hbar\frac{\partial\Psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2\Psi}{\partial x^2} + V\Psi} \tag{2.1}$$

Here, i is the square root of -1, and $\hbar$ is Planck's constant divided by 2π:

$$\hbar = \frac{h}{2\pi} = 1.054573 \times 10^{-34}\,\mathrm{J\,s} \tag{2.2}$$

The Schrödinger equation plays a role analogous to Newton's second law: Given suitable initial conditions (typically $\Psi(x,0)$), the Schrödinger equation determines $\Psi(x,t)$ for all future time, just as how, in classical mechanics, Newton's law determines $x(t)$ for all future time. Schrödinger developed his equation based on principles related to the wave equation, since its goal was to describe the wave properties of matter. Unfortunately, I do not have time to go into its derivation, so I refer you to Phillip's section of this Flux issue. I definitely encourage you to look at it, considering the incredible appearance of an imaginary number in such a fundamental equation of nature!

Now you may ask, what exactly *is* the wavefunction? The answer is given by Max Born's statistical interpretation, which tells you that $|\Psi(x,t)|^2$ gives you the probability of finding the particle at a point x, at a time t. More precisely:

$$\boxed{\int_a^b |\Psi(x,t)|^2\,dx = \left\{\begin{array}{l}\text{probability of finding the particle}\\ \text{between } a \text{ and } b, \text{ at time } t.\end{array}\right.} \tag{2.3}$$

As $\Psi(x,t)$ is a complex function, $|\Psi|^2 = \Psi^*\Psi$ (where Ψ^* is the complex conjugate of Ψ). A key feature of the wavefunction is something known as wavefunction collapse. If you measure a particle, its wavefunction collapses to a particular value, such that an immediate re-measurement of the particle will yield exactly the same values of position, momentum, etc. as the initial measurement. The phenomenon by which the wavefunction collapses is still not exactly known, and is one of the most important unanswered questions in quantum mechanics. Another key feature of the wave function is that:

$$\boxed{\int_{-\infty}^{+\infty} |\Psi(x,t)|^2\,dx = 1} \tag{2.4}$$

This must obviously be true as the total probability must always equal 1 - the particle must be *somewhere*. What this means is that we have to multiply the wavefunction by some (complex) constant such that the above condition always holds - this process is called normalizing the wavefunction. Normalizing the wavefunction at $t = 0$ ensures that it remains normalized for all future t, although the proof of this is not something I will go into.

1.3 Operators and Heisenberg's Uncertainty Principle

From the properties of continuous random variables in statistics, we know that the expectation value of a variable, x, is given by:

$$\langle x\rangle = \int_{-\infty}^{+\infty} x\rho(x)\,dx \tag{3.1}$$

Where $\rho(x)$ is the probability density of x. However, we have just learned that the probability density of x for a quantum mechanical object is given by $|\Psi(x,t)|^2$, so we can write:

$$\langle x \rangle = \int_{-\infty}^{+\infty} x|\Psi(x,t)|^2 \, dx \tag{3.2}$$

Logically, what the above equation means is that if you prepare a whole ensemble of particles, each in the same state Ψ, and measure the positions of all of them, $\langle x \rangle$ is the average of *these* results. Be careful - this is different from saying that this is the average result you get when measuring the position of one particle over and over again. On the contrary, the first measurement would cause the wavefunction to collapse, so all subsequent measurements would return the same result!

What if we wanted to find the expectation value of some other variable of the system? We use the appropriate **operator** for that variable, by "sandwiching" the operator between Ψ^* and Ψ and integrating as we did above. For example, the expectation value for the momentum of a particle (the derivation of this is encouraged as an exercise for the reader - consider the rate of change of position) is given by:

$$\langle p \rangle = \int_{-\infty}^{+\infty} \Psi^* \left[-i\hbar \frac{\partial}{\partial x} \right] \Psi \, dx \tag{3.3}$$

And the expectation value for the position of a particle is given by:

$$\langle x \rangle = \int_{-\infty}^{+\infty} \Psi^* \left[x \right] \Psi \, dx \tag{3.4}$$

We say that the operator x "represents" position, and the operator $-i\hbar(\partial/\partial x)$ "represents" momentum. In general, operators are mathematical objects that act on quantum states to return the value of a variable of that quantum state, and are represented using hats on top of the letter representing the operator. For position and momentum, these are:

$$\boxed{\hat{x} = x} \tag{3.5}$$

$$\boxed{\hat{p} = -i\hbar \frac{\partial}{\partial x}} \tag{3.6}$$

Furthermore, *all* classical variables can be expressed in terms of position and momentum, so to calculate the expectation of any such quantity, $Q(x,p)$, we simply replace every p by $-i\hbar(\partial/\partial x)$, then insert the resulting operator between Ψ^* and Ψ and integrate (I am removing the bounds of integration to avoid too much cluttering):

$$\boxed{\langle Q(x,p) \rangle = \int \Psi^* \left[Q(x, -i\hbar\partial/\partial x) \right] \Psi \, dx} \tag{3.7}$$

Before we proceed, there is a very important condition that measured variables must satisfy, which you should be aware of. This is the very famous **Heisenberg Uncertainty Principle** and it goes as follows:

$$\boxed{\sigma_x \sigma_p \geq \frac{\hbar}{2}} \tag{3.8}$$

What this is saying is that the standard deviation in the measured position of a particle, multiplied by the standard deviation in the measured momentum of that particle, must always be greater than or equal to the above value (where the standard deviations are calculated in the usual way, using expectation values). In other words, you can never exactly know both the momentum and position of a particle, and the more precisely you know one, the less precisely you know the other. The proof for this uncertainty principle comes from a derivation of the general uncertainty principle, which is covered in Phillip's part of this Flux issue, so please refer to that if interested!

1.4 The Time-Independent Schrödinger Equation and Stationary States

Now that we have the basic preliminaries to understand the meaning behind the Schrödinger equation, let us try solving it. To get $\Psi(x,t)$, we need to solve the Schrödinger equation for a specific potential, $V(x)$ (all potentials I will cover are assumed to be independent of time). As the Schrödinger equation is something known as a partial differential equation, we can use a special method for solving it known as **separation of variables**. This is when we look for solutions which are *products*:

$$\Psi(x,t) = \psi(x)\varphi(t) \tag{4.1}$$

If you aren't convinced that this is a solution, feel free to manually check that the solutions obtained at the end satisfy the Schrödinger equation. At first glance, it may seem like there is no way that this gives us all possible solutions to the Schrödinger equation - all I ask is that you be patient and prepare to have your minds blown. For these separable solutions:

$$\frac{\partial \Psi}{\partial t} = \psi \frac{d\varphi}{dt}, \quad \frac{\partial^2 \Psi}{\partial x^2} = \frac{d^2\psi}{dx^2}\varphi$$

So the Schrödinger equation reads:

$$i\hbar\psi\frac{d\varphi}{dt} = -\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2}\varphi + V\psi\varphi$$

Dividing through by $\psi\varphi$:

$$i\hbar\frac{1}{\varphi}\frac{d\varphi}{dt} = -\frac{\hbar^2}{2m}\frac{1}{\psi}\frac{d^2\psi}{dx^2} + V \tag{4.2}$$

Now, here is the important bit. The left hand side is a function of t alone, and the right side is a function of x alone. The only way that this could be true is if both sides are in fact *constant* - otherwise, by varying t, I could change the left side without touching the right side, and the two would no longer be equal. I will choose to call this separation constant E for reasons that will become apparent soon. Then,

$$i\hbar\frac{1}{\varphi}\frac{d\varphi}{dt} = E$$

or

$$\frac{d\varphi}{dt} = -\frac{iE}{\hbar}\varphi \tag{4.3}$$

and

$$-\frac{\hbar^2}{2m}\frac{1}{\psi}\frac{d^2\psi}{dx^2} + V = E$$

or

$$\boxed{-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V\psi = E\psi} \tag{4.4}$$

The first of these equations is easy to solve, and the general solution (for simplicity, I will absorb the constant factor in front of the solution into ψ, since the quantity of interest is the product $\psi\varphi$) is:

$$\varphi(t) = e^{-iEt/\hbar} \tag{4.5}$$

The second, and more significant equation is called the **time-independent Schrödinger equation**, and we cannot solve it until we are given a specific potential $V(x)$. It is important to distinguish between this and $\Psi(x,t)$, which is the **time-dependent Schrödinger equation**.

Before I continue, there are three important features of the above separable solutions which I will mention, but not prove here:

1. They are **stationary states**. Although the wave function itself,

$$\Psi(x,t) = \psi(x)e^{-iEt/\hbar} \tag{4.6}$$

does obviously depend on t, the *probability density*,

$$|\Psi(x,t)|^2 = \Psi^*\Psi = \psi^* e^{+iEt/\hbar}\psi e^{-iEt/\hbar} = |\psi(x)|^2 \tag{4.7}$$

does *not* - the time dependence cancels out. The same thing happens in calculating the expectation value of any dynamical variable of interest; Equation 3.7 reduces to:

$$\langle Q(x,p)\rangle = \int \psi^* \left[Q\left(x, -i\hbar\frac{d}{dx}\right)\right]\psi\, dx \tag{4.8}$$

Every expectation value is constant in time, so we might as well drop the factor $\varphi(t)$ altogether, and simply use ψ instead of Ψ - remember, though, that the full solution to the Schrödinger equation will be the function Ψ and not ψ; this is just for our convenience when calculating things such as expectation values. In particular $\langle x\rangle$ is constant, and hence $\langle p\rangle = 0$. Nothing ever *happens* in a stationary state, hence the name.

2. They are states of *definite total energy*. In classical mechanics, the total energy (kinetic plus potential) is called the **Hamiltonian**:

$$H(x,p) = \frac{p^2}{2m} + V(x) \tag{4.9}$$

The corresponding Hamiltonian *operator* is therefore:

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x) \tag{4.10}$$

Thus the time-independent Schrödinger equation can be written:

$$\hat{H}\psi = E\psi \tag{4.11}$$

Those of you proficient at linear algebra may recognise this as an eigenvalue equation - if interested, please look at Vivaan's section on linear algebra. Using this result, it is quite trivial to prove that:

$$\sigma_H = 0 \tag{4.12}$$

This means that, for separable solutions (in a stationary state), every measurement of the total energy is certain to return the value E, hence why I chose that letter for the separation constant earlier.

3. The general solution of the time-dependent Schrödinger equation is a **linear combination** of separable solutions. As we are about to see, the time-independent Schrödinger equation yields an infinite collection of solutions ($\psi_1(x),\ \psi_2(x),\ \psi_3(x),\ \ldots$), each with its associated separation constant ($E_1,\ E_2,\ E_3,\ \ldots$), thus there is a different wavefunction for each allowed energy:

$$\Psi_1(x,t) = \psi_1(x)e^{-iE_1t/\hbar}, \quad \Psi_2(x,t) = \psi_2(x)e^{-iE_2t/\hbar}, \quad \ldots$$

Now, (as you can easily check yourself) the time-dependent Schrödinger equation has the property that any linear combination of solutions is itself a solution. This means that once we have found the separable solutions, we can immediately construct a much more general solution, of the form:

$$\Psi(x,t) = \sum_{n=1}^{\infty} c_n\psi_n(x)e^{-iE_nt/\hbar} \tag{4.13}$$

> It so happens that *every* solution to the time-dependent Schrödinger equation can be written in this form, as long as you find the right (complex) constants ($c_1,\ c_2,\ \ldots$) so as to fit the initial conditions for the problem at hand. Look! We've achieved what we set out to do (partly) - evidently, all we need to do to find the solution to the time dependent Schrödinger equation is to solve the time-*in*dependent Schrödinger equation, followed by a couple of extra steps I will explain later on.

To summarise, here's the generic problem we need to solve in quantum mechanics: You are given a (time-independent) potential $V(x)$, along with the starting wavefunction (initial conditions) $\Psi(x,0)$ and have to find the wavefunction $\Psi(x,t)$ for any subsequent time t. To do this, you have to solve the time-*in*dependent Schrödinger equation, which yields an infinite set of solutions $\{\psi_n(x)\}$, each with its own associated energy, $\{E_n\}$. To fit $\Psi(x,0)$, you write down the general linear combination of these solutions:

$$\Psi(x,0) = \sum_{n=1}^{\infty} c_n \psi_n(x) \tag{4.14}$$

The important point to note is that you can *always* match the specified initial state by an appropriate choice of the constants $\{c_n\}$. To construct $\Psi(x,t)$ you simply tack onto each term its characteristic time dependence (often called its "wiggle factor" - don't ask me why physicists chose to name it that), exp$(-iE_nt/\hbar)$:

$$\boxed{\Psi(x,t) = \sum_{n=1}^{\infty} c_n \psi_n(x) e^{-iE_nt/\hbar} = \sum_{n=1}^{\infty} c_n \Psi_n(x,t)} \tag{4.15}$$

The separable solutions themselves,

$$\Psi_n(x,t) = \psi_n(x) e^{-iE_nt/\hbar} \tag{4.16}$$

are *stationary* states, in the sense that all probabilities and expectation values are independent of time (a property which is *not* shared by the general solution (Equation 4.15)).

To finish off, let us ask the question: what do the coefficients $\{c_n\}$ represent *physically*? The answer (which I once again do not have time to prove here) is that:

$$\boxed{|c_n|^2 \begin{cases} \text{is the } \textit{probability} \text{ that a measurement of the} \\ \text{energy would return the value } E_n. \end{cases}} \tag{4.17}$$

Naturally, the sum of these probabilities should be 1:

$$\boxed{\sum_{n=1}^{\infty} |c_n|^2 = 1} \tag{4.18}$$

and the expectation value of the energy must be:

$$\boxed{\langle H \rangle = \sum_{n=1}^{\infty} |c_n|^2 E_n} \tag{4.19}$$

1.5 The Infinite Square Well

Let us now look at the simplest example of a potential "well" that exists, to reinforce these new concepts that we have learned and to smoothen the transition into the hydrogen atom. Suppose we have a potential (Figure 5.1):

$$V(x) = \begin{cases} 0, & 0 \le x \le a \\ \infty, & \text{otherwise} \end{cases} \tag{5.1}$$

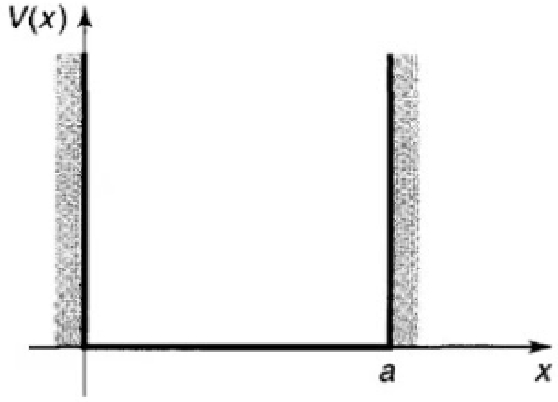

Figure 5.1: The infinite square well potential (Equation 5.1).

Outside the well, $\psi(x) = 0$, as the particle cannot have the infinite energy required to escape the well, and so the probability of finding it there is 0. However, *inside* the well, where $V = 0$, the time-independent Schrödinger equation becomes:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = E\psi \tag{5.2}$$

or

$$\frac{d^2\psi}{dx^2} = -k^2\psi, \quad \text{where } k \equiv \frac{\sqrt{2mE}}{\hbar} \tag{5.3}$$

(I have assumed that $E \geq 0$, since $E < 0$ won't work here. Think about why this is, but I'll give you a hint; E must exceed $V(x)$ for every normalizable solution to the time-independent Schrödinger equation - try to show this).

Those of you who have studied **simple harmonic motion** will instantly recognise the general solution to this equation as:

$$\psi(x) = A\sin(kx) + B\cos(kx) \tag{5.4}$$

where A and B are arbitrary constants. Typically, these constants are fixed by the **boundary conditions** of the problem, but what *are* the boundary conditions for $\psi(x)$? The short answer is that both $\psi(x)$ and $d\psi/dx$ are *continuous*, but where the potential goes to infinity, only the first of these applies, and so that is the appropriate boundary condition to use in this case.

Therefore, continuity of $\psi(x)$ requires that:

$$\psi(0) = \psi(a) = 0 \tag{5.5}$$

so that the solution inside the well is "joined" to the solution outside the well (remember that $\psi(x) = 0$ outside the well). Using this, we can find A and B as follows:

$$\psi(0) = A\sin(0) + B\cos(0) = B$$

so B = 0 and hence:

$$\psi(x) = A\sin(kx) \tag{5.6}$$

Then $\psi(a) = A\sin(ka)$, so either $A = 0$ (in which case we are left with the trivial (non-normalizable) solution $\psi(x) = 0$), or else $\sin(ka) = 0$, which means that:

$$ka = 0,\ \pm\pi,\ \pm 2\pi,\ \pm 3\pi,\ \ldots \tag{5.7}$$

However, $k = 0$ is no good (since that again implies that $\psi(x) = 0$), and the negative solutions give nothing new, since $\sin(-\theta) = -\sin(\theta)$ and we can absorb the minus sign into the constant A. Therefore, the *distinct* solutions are:

$$k_n = \frac{n\pi}{a}, \quad \text{with } n = 1,\ 2,\ 3,\ \ldots \tag{5.8}$$

But wait, we have determined possible values of k, not A! Don't worry, we can now just use normalization to find it. However, let us first find the possible values of E from these values of k. From Equation 5.3, we obtain:

$$\boxed{E_n = \frac{\hbar^2 k_n^2}{2m} = \frac{n^2\pi^2\hbar^2}{2ma^2}} \tag{5.9}$$

This result demonstrates a key concept in **quantum** mechanics. The energies of a particle in the infinite square well cannot have just *any* energy - it has to be one of these special "allowed" energies. We say that the energies are **quantized**.

Now, to find A, we simply *normalize* ψ (technically we should be normalizing $\Psi(x,t)$, but remember that for stationary states the "wiggle factor" cancels out, so normalizing $\psi(x)$ is sufficient):

$$\int_0^a |A|^2 \sin^2(kx)\,dx = |A|^2 \frac{a}{2} = 1, \quad \text{so} \quad |A|^2 = \frac{2}{a}$$

This only determines the *magnitude* of A , but it is simplest to pick the positive real root: $A = \sqrt{2/a}$, since the phase of A carries no physical significance anyway. This finally gives us the solutions to the time-independent Schrödinger equation for the infinite square well:

$$\boxed{\psi_n(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a} x\right)} \tag{5.10}$$

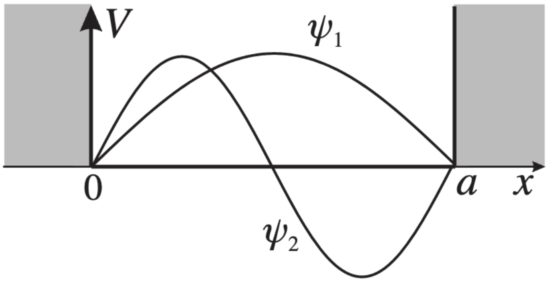

Figure 5.2: An infinite square well with the ground state and first excited state wavefunctions, ψ_1 and ψ_2 (Equation 5.10).

Just as I mentioned above, we have gotten an infinite collection of solutions to the time-independent Schrödinger equation (one for each positive integer n), each with its own associated energy. What you may notice is that these solutions look like standing waves on a string of length a; ψ_1, which carries the lowest energy, is called the **ground state**. The others, whose energies increase in proportion to n^2, are called **excited states** (Figure 5.2). As a collection, the functions $\psi_n(x)$ have some interesting and important properties that you should be aware of:

1. They are alternately **even** and **odd**, with respect to the centre of the well: ψ_1 is even, ψ_2 is odd, ψ_3 is even, and so on.

2. As you go up in energy, each successive state has one more **node** (zero-crossing): ψ_1 has none (the end points don't count), ψ_2 has one, ψ_3 has two, and so on.

3. They are mutually orthogonal, in the sense that:

$$\int \psi_m(x)^* \psi_n(x)\, dx = 0, \quad (m \neq n) \tag{5.11}$$

   I encourage the reader to try and prove this. Note that this does *not* work if $m = n$. In that case normalization tells us that the integral is 1. In fact, we can combine orthogonality and normalization into a single statement:

$$\boxed{\int \psi_m(x)^* \psi_n(x)\, dx = \delta_{mn}} \tag{5.12}$$

   where δ_{mn} is the **Kronecker delta function** (you should recognise this from the previous issue of the Wilsonian Flux), and is defined by:

$$\delta_{mn} = \begin{cases} 0, & m \neq n \\ 1, & m = n \end{cases} \tag{5.13}$$

   We say that the ψs are **orthonormal**.

4. They are **complete**, in the sense that any *other* function, $f(x)$, can be expressed as a linear combination of them:

$$f(x) = \sum_{n=1}^{\infty} c_n \psi_n(x) = \sqrt{\frac{2}{a}} \sum_{n=1}^{\infty} c_n \sin\left(\frac{n\pi}{a} x\right) \tag{5.14}$$

   I'm definitely **not** going to prove the completeness of the functions here, but you should recognise the above equation as nothing but the **Fourier series** for $f(x)$ (see previous issue of the Wilsonian Flux for Fourier series and transforms). The fact that "any" function can be expanded in this way is sometimes called **Dirichlet's theorem**.

   The coefficients c_n can be evaluated - for a given $f(x)$ - by a method known as **Fourier's trick**, which, in the words of David Griffiths, "beautifully exploits the orthonormality of $\{\psi_n\}$": Multiply both sides of Equation 5.14 by $\psi_m(x)^*$, and integrate:

$$\int \psi_m(x)^* f(x)\, dx = \sum_{n=1}^{\infty} c_n \int \psi_m(x)^* \psi_n(x)\, dx = \sum_{n=1}^{\infty} c_n \delta_{mn} = c_m \tag{5.15}$$

   (Notice how the Kronecker delta kills every term in the sum except the one for which $n = m$.) Thus, the nth coefficient in the expansion of $f(x)$ is:

$$\boxed{c_n = \int \psi_n(x)^* f(x)\, dx} \tag{5.16}$$

These four properties are extremely powerful, and they are not specific to the infinite square well. The first is true whenever the potential itself is a symmetric function; the second is universal, regardless of the shape of the potential. Orthogonality is also quite general, and completeness holds for all of the potentials you are likely to encounter.

The stationary states (Equation 4.16) of the infinite square well are:

$$\Psi_n(x,t) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a} x\right) e^{-i(n^2\pi^2\hbar/2ma^2)t} \tag{5.17}$$

Remember that the most general solution to the time-dependent Schrödinger equation is a linear combination of stationary states (Equation 4.15):

$$\boxed{\Psi(x,t)=\sum_{n=1}^{\infty}c_n\sqrt{\frac{2}{a}}\sin\left(\frac{n\pi}{a}x\right)e^{-i(n^2\pi^2\hbar/2ma^2)t}} \tag{5.18}$$

The last thing left to do is to demonstrate that you can fit any prescribed initial wave function, $\Psi(x,0)$ by appropriate choice of the coefficients c_n. The completeness of the ψs guarantees that I can always express $\Psi(x,0)$ as I have in Equation 4.14, and their orthonormality licences the use of Fourier's trick to determine the actual coefficients:

$$c_n=\sqrt{\frac{2}{a}}\int_0^a\sin\left(\frac{n\pi}{a}x\right)\Psi(x,0)\,dx \tag{5.19}$$

So, the final solution to the time-dependent Schrödinger equation for the infinite square well is:

$$\boxed{\Psi(x,t)=\frac{2}{a}\sum_{n=1}^{\infty}\left[\int_0^a\sin\left(\frac{n\pi}{a}x\right)\Psi(x,0)\,dx\right]\sin\left(\frac{n\pi}{a}x\right)e^{-i(n^2\pi^2\hbar/2ma^2)t}} \tag{5.20}$$

And that's *it*. Given an initial wavefunction, $\Psi(x,0)$, along with the size of the well, a, and the mass of the particle of interest, m, we can calculate all values of interest of the system for all future times, using the appropriate operators. We have effectively solved $F=ma$, but for the quantum case! It is important to note, however, that the infinite square well is an artificial potential - it doesn't really exist in nature, but the results we have obtained so easily due to its simplicity are of great importance. To finish off, we now move onto one of the "simplest" and few real-life systems that can be solved exactly - the hydrogen atom. Prepare yourselves, because it will be a **very** bumpy ride.

1.6 Quantum Mechanics in Three Dimensions

Until now, we have only been working with the Schrödinger equation in 1 dimension, $\Psi(x,t)$, and everything has been relatively simple. Thankfully, the generalization to 3 dimensions, $\Psi(x,y,z,t)$ is also relatively simple - it's what comes after that is the difficult bit. In 3 dimensions, we need to consider all components of momentum, in the x, y and z directions, so the Hamiltonian operator becomes:

$$\hat{H}=\frac{1}{2m}\left(\hat{p}_x^2+\hat{p}_y^2+\hat{p}_z^2\right)+V$$

Where:

$$\hat{p}_x\to-i\hbar\frac{\partial}{\partial x},\quad \hat{p}_y\to-i\hbar\frac{\partial}{\partial y},\quad \hat{p}_z\to-i\hbar\frac{\partial}{\partial z} \tag{6.1}$$

or

$$\boxed{\mathbf{p}\to-i\hbar\nabla} \tag{6.2}$$

for short. (The upside down triangle is called **nabla**, for those interested.) Thus,

$$\boxed{i\hbar\frac{\partial\Psi}{\partial t}=-\frac{\hbar^2}{2m}\nabla^2\Psi+V\Psi} \tag{6.3}$$

where

$$\nabla^2\equiv\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2} \tag{6.4}$$

is called the **Laplacian**, in Cartesian coordinates.

The potential energy V and the wave function Ψ are now functions of $\mathbf{r} = (x, y, z)$ and t. The probability of finding the particle in the infinitesimal volume $d^3\mathbf{r} = dx\,dy\,dz$ is $|\Psi(\mathbf{r}, t)|^2 d^3\mathbf{r}$, and the normalization condition reads:

$$\boxed{\int |\Psi|^2\, d^3\mathbf{r} = 1} \tag{6.5}$$

with the integral taken over all space. If V is independent of time (as it is in what comes next), there will be a complete set of stationary states:

$$\Psi_n(\mathbf{r}, t) = \psi_n(\mathbf{r}) e^{-iE_n t/\hbar} \tag{6.6}$$

where the spatial wave function ψ_n satisfies the time-*independent* Schrödinger equation:

$$\boxed{-\frac{\hbar^2}{2m}\nabla^2\psi + V\psi = E\psi} \tag{6.7}$$

The general solution to the time-*dependent* Schrödinger equation is:

$$\Psi(\mathbf{r}, t) = \sum c_n \psi_n(\mathbf{r}) e^{-iE_n t/\hbar} \tag{6.8}$$

with the constants c_n determined by the initial wave function, $\Psi(\mathbf{r}, 0)$, in the usual way. (If the potential admits continuum states, then the sum in Equation 6.8 becomes an integral.)

However, for **spherically symmetric (central) potentials** such as that of the hydrogen atom, where V is a function only of the distance from the origin, $V(\mathbf{r}) \to V(r)$, it is much easier and simpler to work with **spherical coordinates**, (r, θ, ϕ) (Figure 6.1).

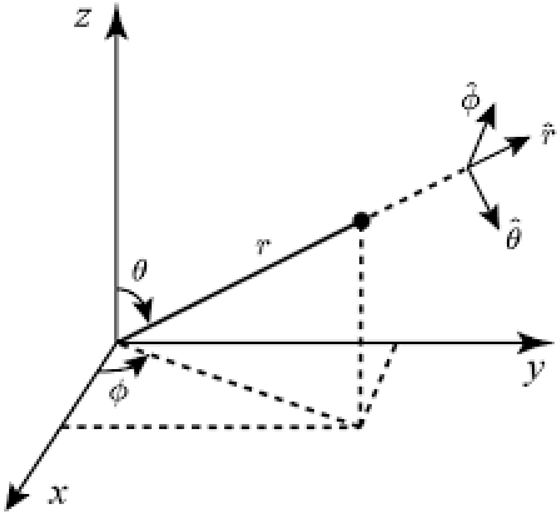

Figure 6.1: Spherical coordinates: radius r, polar angle θ, and azimuthal angle ϕ.

In spherical coordinates the Laplacian takes the form:

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin(\theta)}\frac{\partial}{\partial\theta}\left(\sin(\theta)\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2(\theta)}\left(\frac{\partial^2}{\partial\phi^2}\right) \tag{6.9}$$

Therefore, in spherical coordinates, the time-independent Schrödinger equation reads:

$$-\frac{\hbar^2}{2m}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2\sin(\theta)}\frac{\partial}{\partial\theta}\left(\sin(\theta)\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{r^2\sin^2(\theta)}\left(\frac{\partial^2\psi}{\partial\phi^2}\right)\right] + V\psi = E\psi \tag{6.10}$$

This might look like a crazy equation to try and solve at first, and I don't blame you for thinking that, considering that I literally had to make the text smaller to fit it on the page! But trust me, you can definitely solve it. Let us proceed as we did with the time-dependent Schrödinger equation and use separation of variables. Let's assume a solution of the form:

$$\psi(r,\theta,\phi) = R(r)Y(\theta,\phi) \tag{6.11}$$

Plugging this into Equation 6.10, we get:

$$-\frac{\hbar^2}{2m}\left[\frac{Y}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{R}{r^2\sin(\theta)}\frac{\partial}{\partial\theta}\left(\sin(\theta)\frac{\partial Y}{\partial\theta}\right) + \frac{R}{r^2\sin^2(\theta)}\frac{\partial^2 Y}{\partial\phi^2}\right] + VRY = ERY$$

Dividing by YR and multiplying by $-2mr^2/\hbar^2$:

$$\left\{\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) - \frac{2mr^2}{\hbar^2}\left[V(r)-E\right]\right\} + \frac{1}{Y}\left\{\frac{1}{\sin(\theta)}\frac{\partial}{\partial\theta}\left(\sin(\theta)\frac{\partial Y}{\partial\theta}\right) + \frac{1}{\sin^2(\theta)}\frac{\partial^2 Y}{\partial\phi^2}\right\} = 0$$

The term in the first curly bracket depends only on r, whereas the remainder depends only on θ and ϕ, so, as before, each must be a constant. I will call this separation constant $\ell(\ell+1)$, for reasons which go way beyond what I am covering here, and which depend on a property of the particle known as its **angular momentum**. Therefore:

$$\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) - \frac{2mr^2}{\hbar^2}\left[V(r)-E\right] = \ell(\ell+1) \tag{6.12}$$

$$\frac{1}{Y}\left\{\frac{1}{\sin(\theta)}\frac{\partial}{\partial\theta}\left(\sin(\theta)\frac{\partial Y}{\partial\theta}\right) + \frac{1}{\sin^2(\theta)}\frac{\partial^2 Y}{\partial\phi^2}\right\} = -\ell(\ell+1) \tag{6.13}$$

Notice how the second equation (known as the **angular equation**) does *not* depend on the potential, and so must be the same for **all** spherically symmetric (central) potentials. That means that, in 3 dimensions, the main problem is solving the first equation (known as the **radial equation**).

As the angular equation is the same for all spherically symmetric potentials, and in the interest of saving time, I will just give you the solution to it (since the main course is the radial equation anyway). If you are interested in how you solve the angular equation, we approach it in the exact same way, by using separation of variables and letting:

$$Y(\theta,\phi) = \Theta(\theta)\Phi(\phi) \tag{6.14}$$

We then plug this into the angular equation, rearrange, and solve the two resulting equations, one of which requires a special function (described below) to be solved. Normalizing the resultant 'angular wave functions', this ultimately gives us:

$$\boxed{Y_\ell^m(\theta,\phi) = \sqrt{\frac{(2\ell+1)}{4\pi}\frac{(\ell-m)!}{(\ell+m)!}}\,e^{im\phi}\,P_\ell^m(\cos(\theta))} \tag{6.15}$$

These beautiful equations are given an equally beautiful name - **spherical harmonics**. m is another separation constant, introduced by the second round of separation of variables which I mentioned above, and P_ℓ^m is known as the **associated Legendre function**, defined by (strictly, this is only for $m \geq 0$, and for $m < 0$ a different formula for the associated Legendre functions needs to be used, but for our purposes this isn't important, so I will just stick to this one):

$$\boxed{P_\ell^m(x) \equiv (-1)^m\left(1-x^2\right)^{m/2}\left(\frac{d}{dx}\right)^m P_\ell(x)} \tag{6.16}$$

and $P_\ell(x)$ is the ℓth **Legendre polynomial**, defined by the **Rodrigues formula**:

$$\boxed{P_\ell(x) \equiv \frac{1}{2^\ell \ell!}\left(\frac{d}{dx}\right)^\ell \left(x^2-1\right)^\ell} \tag{6.17}$$

As mentioned before, ℓ and m both depend on the **angular momentum** properties of the particle of interest, so we will just take them to be constants that are given to us. These constants can only take the following values for the formulae above to make any sense:

$$\boxed{\ell = 0,\ 1,\ 2,\ \ldots; \quad m = -\ell,\ -\ell+1,\ \ldots,\ -1,\ 0,\ 1,\ \ldots,\ \ell-1,\ \ell} \tag{6.18}$$

Now onto the radial equation. We can significantly simplify the radial equation if we change variables: Let

$$u(r) \equiv rR(r) \tag{6.19}$$

so that $R = u/r$, $dR/dr = [r(du/dr) - u]/r^2$, $(d/dr)[r^2(dR/dr)] = rd^2u/dr^2$, and hence:

$$\boxed{-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2} + \left[V + \frac{\hbar^2}{2m}\frac{\ell(\ell+1)}{r^2}\right]u = Eu} \tag{6.20}$$

Notice how this is identical to the one-dimensional Schrödinger equation (Equation 4.4), except that the **effective potential**,

$$V_{\text{eff}} = V + \frac{\hbar^2}{2m}\frac{\ell(\ell+1)}{r^2} \tag{6.21}$$

contains an extra piece called the **centrifugal term**, $(\hbar^2/2m)[\ell(\ell+1)/r^2]$. It is so called because it tends to throw the particle outward (away from the origin), just like the centrifugal (pseudo-)force in classical mechanics.

This is as far as we can go until a specific potential $V(r)$ is provided, so it is time to use all of the tools we have built up until now to finally confront the **hydrogen atom**.

1.7 The Hydrogen Atom

Enough procrastination - let's now solve the Schrödinger equation for the electron in the hydrogen atom. As you know, the hydrogen atom consists of a proton of charge e, and an electron of charge $-e$ and mass m_e, with the mass of the proton being roughly $1836\times$ larger than that of the electron. For that reason, we will treat the proton as being essentially motionless. From Coulomb's law, the potential energy of the electron is:

$$V(r) = -\frac{e^2}{4\pi\epsilon_0}\frac{1}{r} \tag{7.1}$$

and the radial equation (Equation 6.20) becomes:

$$\boxed{-\frac{\hbar^2}{2m_e}\frac{d^2u}{dr^2} + \left[-\frac{e^2}{4\pi\epsilon_0}\frac{1}{r} + \frac{\hbar^2}{2m_e}\frac{\ell(\ell+1)}{r^2}\right]u = Eu} \tag{7.2}$$

The Coulomb potential admits *continuum* states (with $E > 0$), describing electron-proton scattering (I have not explained continuum states here, but they aren't of interest anyway so it's fine), as well as discrete *bound* states (with $E < 0$), representing the hydrogen atom - we will confine our attention to the latter.

The first thing we should do is tidy up the notation. Let

$$\kappa \equiv \frac{\sqrt{-2m_eE}}{\hbar} \tag{7.3}$$

(Remember that E is negative for bound states, as I mentioned above, so κ is *real*.) Dividing Equation 7.2 by E, we have:

$$\frac{1}{\kappa^2}\frac{d^2u}{dr^2} = \left[1 - \frac{m_ee^2}{2\pi\epsilon_0\hbar^2\kappa}\frac{1}{(\kappa r)} + \frac{\ell(\ell+1)}{(\kappa r)^2}\right]u$$

Introducing the variables:

$$\rho \equiv \kappa r \quad \text{and} \quad \rho_0 \equiv \frac{m_ee^2}{2\pi\epsilon_0\hbar^2\kappa} \tag{7.4}$$

We obtain:

$$\frac{d^2u}{d\rho^2} = \left[1 - \frac{\rho_0}{\rho} + \frac{\ell(\ell+1)}{\rho^2}\right]u \tag{7.5}$$

Now here comes a devilishly clever trick to solving differential equations such as these - we perform a technique called "stripping off asymptotic behaviour". In other words, we look at what form the solution must take when approaching limits such as 0 or infinity, and we 'pull' those factors out of the solution so that we end up with an equation which we hope is easier to solve than the original. If you are still a bit confused by what this means, it will become clear in a moment.

As $\rho \to \infty$, the constant term in the brackets dominates (since the other two go to 0), so approximately:

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

The general solution is:

$$u(\rho) = Ae^{-\rho} + Be^{\rho} \tag{7.6}$$

but e^{ρ} blows up (as $\rho \to \infty$), which would make the solution non-normalizable, so $B = 0$. Evidently,

$$u(\rho) \sim Ae^{-\rho} \tag{7.7}$$

for large ρ. On the other hand, as $\rho \to 0$ the centrifugal term dominates; approximately then:

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

The general solution is:

$$u(\rho) = C\rho^{\ell+1} + D\rho^{-\ell}$$

but, once again, $\rho^{-\ell}$ blows up (as $\rho \to 0$), so $D = 0$. Thus,

$$u(\rho) \sim C\rho^{\ell+1} \tag{7.8}$$

for small ρ.

Now, stripping off the asymptotic behaviour and introducing the new function $v(\rho)$, we get:

$$u(\rho) = \rho^{\ell+1}e^{-\rho}v(\rho) \tag{7.9}$$

in the hope that $v(\rho)$ will turn out to be simpler than $u(\rho)$. At first, this doesn't look to be the case:

$$\frac{du}{d\rho} = \rho^{\ell}e^{-\rho}\left[(\ell+1-\rho)v + \rho\frac{dv}{d\rho}\right]$$

and

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

In terms of $v(\rho)$, then, the radial equation (Equation 7.5) reads:

$$\rho\frac{d^2v}{d\rho^2} + 2(\ell+1-\rho)\frac{dv}{d\rho} + [\rho_0 - 2(\ell+1)]v = 0 \tag{7.10}$$

To finish off, we employ another method for solving differential equations called the **power series method**. To do this, we assume that the solution, $v(\rho)$, can be expressed as a power series in ρ:

$$v(\rho) = \sum_{j=0}^{\infty} c_j \rho^j \tag{7.11}$$

The problem that we need to solve is to determine the coefficients (c_0, c_1, c_2, $\ldots$). Differentiating term by term:

$$\frac{dv}{d\rho} = \sum_{j=0}^{\infty} j c_j \rho^{j-1} = \sum_{j=0}^{\infty}(j+1)c_{j+1}\rho^j$$

(In the second summation I have renamed the "dummy index": $j \to j+1$. Check that this indeed doesn't change the value of the summation.) Differentiating again:

$$\frac{d^2v}{d\rho^2} = \sum_{j=0}^{\infty} j(j+1)c_{j+1}\rho^{j-1}$$

Inserting these back into Equation 7.10:

$$\sum_{j=0}^{\infty} j(j+1)c_{j+1}\rho^j + 2(\ell+1)\sum_{j=0}^{\infty}(j+1)c_{j+1}\rho^j$$
$$-2\sum_{j=0}^{\infty} j c_j \rho^j + [\rho_0 - 2(\ell+1)]\sum_{j=0}^{\infty} c_j\rho^j = 0$$

This equation can only be true if the coefficient of *each power* of ρ vanishes, so, exploiting the linearity of the summation operator, and equating the coefficients of like powers yields:

$$j(j+1)c_{j+1} + 2(\ell+1)(j+1)c_{j+1} - 2jc_j + [\rho_0 - 2(\ell+1)]c_j = 0$$

or:

$$c_{j+1} = \left\{\frac{2(j+\ell+1) - \rho_0}{(j+1)(j+2\ell+2)}\right\}c_j \tag{7.12}$$

This recursion formula determines the coefficients, and hence the function $v(\rho)$, which in turn determines the function $u(\rho)$, which in turn determines the function $u(r)$, which in turn determines the function $R(r)$, which, when combined with the spherical harmonics $Y_\ell^m(\theta, \phi)$, determines the function $\psi(r, \theta, \phi)$, which in turn determines the function $\Psi(r, \theta, \phi, t)$ - quite a journey! It is quite easy to lose sight of the end goal when solving difficult differential equations such as these, so it is good to keep reminding yourselves by asking the question - what am I actually trying to find? Let us proceed.

To determine these coefficients, we start with c_0, and the above equation gives us c_1. We then use c_1 to find c_2, and so on. Let us examine what the coefficients look like for large j (which corresponds to large ρ, where the higher powers dominate). In this case the recursion formula says:

$$c_{j+1} \approx \frac{2j}{j(j+1)}c_j = \frac{2}{j+1}c_j$$

(The $+1$ in the denominator makes no difference apart from making the following argument a little cleaner, so I have decided to keep it, despite dropping the other constant terms. You are welcome to try and do it without the $+1$ if you are not convinced). So:

$$c_j \approx \frac{2^j}{j!} c_0 \tag{7.13}$$

Suppose for a moment that this were the *exact* result. Then:

$$v(\rho) = c_0 \sum_{j=0}^{\infty} \frac{2^j}{j!} \rho^j = c_0 e^{2\rho}$$

(The second formula comes from the Taylor series expansion of e^x). Hence,

$$u(\rho) = c_0 \rho^{\ell+1} e^{\rho} \tag{7.14}$$

which blows up at large ρ. This is precisely the asymptotic behaviour we *didn't* want, in Equation 7.6. The only escape from this dilemma is this: *The series must terminate.* There must occur some integer N such that:

$$c_{N-1} \neq 0 \quad \text{but} \quad c_N = 0 \tag{7.15}$$

(Beyond this all coefficients vanish automatically, from the recursion formula above, and so all large powers of ρ vanish, preventing a non-normalizable solution). In that case Equation 7.12 states that:

$$2(N+\ell) - \rho_0 = 0$$

As N and ℓ are both constants, we can define a new constant, n, for simplicity:

$$n \equiv N + \ell \tag{7.16}$$

This gives us:

$$\rho_0 = 2n \tag{7.17}$$

But ρ_0 determines E, from Equations 7.3 and 7.4, so:

$$E = -\frac{\hbar^2 \kappa^2}{2m_e} = -\frac{m_e e^4}{8\pi^2 \epsilon_0^2 \hbar^2 \rho_0^2} \tag{7.18}$$

so the allowed energies (Figure 7.1) are:

$$\boxed{E_n = -\left[\frac{m_e}{2\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2\right]\frac{1}{n^2} = \frac{E_1}{n^2}, \quad n = 1, 2, 3, \ldots} \tag{7.19}$$

This is the famous **Bohr formula**, regarded as *"the most important result in all of quantum mechanics, by any measure."* What just happened?! It seemed like we weren't anywhere close to finishing, yet we suddenly obtained this result! I told you that being patient was worth it - we are nearing the end now.

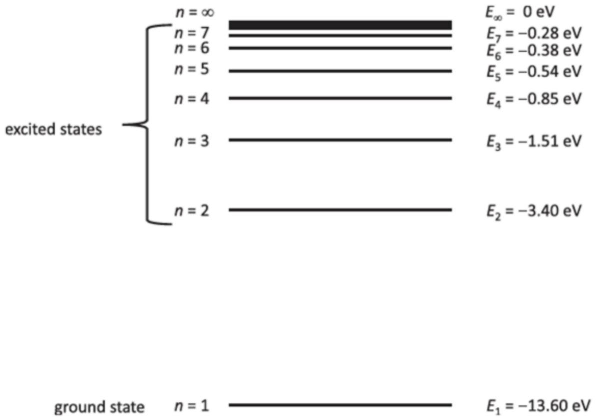

Figure 7.1: The ground state and excited state energies of the electron in hydrogen for increasing values of n (Equation 7.19).

Combining Equations 7.4 and 7.17, we find that:

$$\boxed{\kappa = \left(\frac{m_e e^2}{4\pi\epsilon_0\hbar^2}\right)\frac{1}{n} = \frac{1}{an}} \tag{7.20}$$

where

$$\boxed{a \equiv \frac{4\pi\epsilon_0\hbar^2}{m_e e^2} = 0.529 \times 10^{-10}\,\mathrm{m}} \tag{7.21}$$

is the so-called **Bohr radius**. It follows, from Equation 7.4 again, that:

$$\boxed{\rho = \frac{r}{an}} \tag{7.22}$$

The spatial wavefunctions for the electron in the hydrogen atom are therefore labelled by three **quantum numbers** (n, ℓ, and m, where n is called the **principal quantum number** and tells you the energy of the electron, from Equation 7.19, ℓ is called the **azimuthal quantum number** and m is called the **magnetic quantum number**. As mentioned before, ℓ and m are related to the angular momentum of the electron):

$$\psi_{n\ell m}(r,\theta,\phi) = R_{n\ell}(r)Y_\ell^m(\theta,\phi) \tag{7.23}$$

where (from Equations 6.19 and 7.9):

$$R_{n\ell}(r) = \frac{1}{r}\rho^{\ell+1}e^{-\rho}v(\rho) \tag{7.24}$$

where $v(\rho)$ is a polynomial of degree $n-\ell-1$ in ρ, whose coefficients are determined (up to an overall normalization factor) by the recursion formula from before:

$$c_{j+1} = \frac{2(j+\ell+1-n)}{(j+1)(j+2\ell+2)}c_j \tag{7.25}$$

The polynomial $v(\rho)$, defined by this recursion formula, is a function well known to applied mathematicians; apart from the normalization, it can be written as:

$$v(\rho) = L_{n-\ell-1}^{2\ell+1}(2\rho) \tag{7.26}$$

where

$$\boxed{L_q^p(x) \equiv (-1)^p \left(\frac{d}{dx}\right)^p L_{p+q}(x)} \tag{7.27}$$

is known as the **associated Laguerre polynomial**, and

$$\boxed{L_q(x) \equiv \frac{e^x}{q!} \left(\frac{d}{dx}\right)^q \left(e^{-x} x^q\right)} \tag{7.28}$$

is the qth **Laguerre polynomial**. Therefore, the complete radial equation for the electron in the hydrogen atom (apart from the normalization constant out front) is:

$$\boxed{R_{n\ell}(r) = \frac{1}{r} \left(\frac{r}{na}\right)^{\ell+1} e^{-r/na}\, L_{n-\ell-1}^{2\ell+1}\left(\frac{2r}{na}\right)} \tag{7.29}$$

Now, the moment you've all been waiting for - upon combining this radial equation with the spherical harmonic equation and normalizing appropriately (the normalization is **not** something I encourage you to try, but if you'd like to suffer a bit please by all means go ahead) we finally obtain the normalized hydrogen wavefunctions:

$$\boxed{\psi_{n\ell m}(r,\theta,\phi) = \sqrt{\left(\frac{2}{na}\right)^3 \frac{(n-\ell-1)!}{2n(n+\ell)!}}\, e^{-r/na} \left(\frac{2r}{na}\right)^\ell \left[L_{n-\ell-1}^{2\ell+1}\left(\frac{2r}{na}\right)\right] Y_\ell^m(\theta,\phi)} \tag{7.30}$$

They may not look pretty, but don't complain - as I mentioned before, this is one of the very few realistic systems that can be solved at all, in exact closed form. The fact that we have managed to find exact solutions to this problem is an incredible feat in itself!

To find the time-dependent wavefunction, we apply the exact same procedure that we have until now, and since usually the spacial wavefunctions are the main point of interest, as we want to *visualise* what the wavefunctions look like in space, I will not bother with the time-dependent general solution (you can have a go at it yourself if you want to). To give you some idea of what the wavefunctions look like, let me show you the **ground state** wavefunction, which corresponds to $n = 1$ and $\ell = m = 0$, and is the state the electron in hydrogen is usually found in (and is also the simplest one, of course). Substituting the relevant values of n, ℓ, and m:

$$\boxed{\psi_{100}(r,\theta,\phi) = \frac{1}{\sqrt{\pi a^3}} e^{-r/a}} \tag{7.31}$$

Much nicer to look at, wouldn't you agree? The corresponding energy level of the electron, which also happens to be the **binding energy** (energy required to ionise the atom in its ground state) of hydrogen, is:

$$\boxed{E_1 = -\left[\frac{m_e}{2\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2\right] = -13.6\,\mathrm{eV}} \tag{7.32}$$

There we go - we have built our way up from the very basics and have managed to obtain the most important result in quantum mechanics, and now possess the ability to explain phenomena such as the **blackbody emission and absorption spectra**, **atomic orbitals**, the shapes of **electron clouds** in atoms, and much more!

I hope that on this journey you have gained at least some appreciation for the elegance of quantum theory, along with an appreciation of just how incredible physicists are, to have been able to come up with such a theory and reach this same conclusion a century ago!

2 Canonically quantizing a single mode of radiation

Written by **Philip, Year 12**

2.1 Introduction

Initially looking at this title, one may think to themselves, "what is canonical quantization"? Simply put, this is the procedure in which we convert a classical system into a quantum system. But why do we need this, you might ask? With classical and semi-classical quantizations, we can describe most phenomena within optics, such as interference, or diffraction. However, this fails to describe the process of spontaneous emission, in which an atom eventually emits a photon, when in an excited state, or squeezed states of light (I will not get into this now, though feel free to research this, perhaps as an exercise for the reader). In this article, I will present to you the general form of canonical quantization, and then show the application of it to the most basic mode of light, a simple, plane-polarised, propogating wave. Before we begin, I would like to introduce two things, a notation many of you are likely unfamiliar with, known as Dirac notation, and also what we call states of a quantum system.

2.1.1 Dirac Notation

This is a notation that allows us to demonstrate vectors and their complex conjugates, and what is known as an adjoint. It is also known as bra-ket notation, bra and ket being the actual brackets that surround our vectors.
The general form of a simple column vector is shown with the ket brackets surrounding it, as follows:

$$\varphi = \begin{bmatrix} x_1 \\ x_2 \\ \vdots \\ x_n \end{bmatrix} = |\varphi\rangle \tag{1}$$

The bra notation is used for the hermitian adjoint of φ - a combination of its complex conjugate and conjugate transpose. We denote a complex conjugate as $\overline{\varphi}$, that if there is some element which is a complex number in the vector, say $a + bi$, its complex conjugate is $a - bi$. The conjugate transpose for a column vector, is converting it into a row vector:

$$\overline{\varphi^T} = \begin{bmatrix} \overline{x_1} & \overline{x_2} & \cdots & \overline{x_n} \end{bmatrix} = \langle\varphi| \tag{2}$$

Using this notation, we can show the inner product (another term for the more commonly known dot product), as $\langle\varphi|\varphi\rangle$, producing a scalar, but also the outer product:

$$|\phi\rangle = \begin{bmatrix} \phi_1 \\ \phi_2 \end{bmatrix} \tag{3}$$

$$\langle\psi| = \begin{bmatrix} \psi_1 & \psi_2 \end{bmatrix} \tag{4}$$

$$|\phi\rangle \langle\psi| = \begin{bmatrix} \phi_1\psi_1 & \phi_1\psi_2 \\ \phi_2\psi_1 & \phi_2\psi_2 \end{bmatrix} \tag{5}$$

The outer product is generally used in accompany with tensors, for combining sub-vector spaces, however I will not get into that now, though we will see an application of it soon.

2.1.2 States

States of a quantum system are sort of an expression for its behaviour. One example is its polarisation - we can describe the state of a photon by what axis it is polarised in. To show this, we use the Dirac notation $|\psi\rangle$ to represent a state of wavefunction ψ:

$$|\psi\rangle = |H\rangle \tag{6}$$

This example is where our photon ψ is polarised in the horizontal direction H. In this basis, known as the canonical basis, we label the vertical direction V. You can think of it as your $\boldsymbol{i}$ and $\boldsymbol{j}$ vectors, if you wish, the canonical basis being the simple x,y coordinate basis. Of course, there are different basis, where the coordinate system is transformed, think of it how the x,y, plane changes when you transform sets of points by a matrix, such as a matrix that rotates it by $180°$. But this is not all there is to it. In quantum systems, we can have our photon in a superposition of polarisations, such that when we measure it in the canonical basis, there is a chance that we measure it to be in state $|H\rangle$ or in state $|V\rangle$:

$$|\phi\rangle = \frac{1}{\sqrt{2}}(|H\rangle + |V\rangle) \tag{7}$$

Notice the $\frac{1}{\sqrt{2}}$ at the beginning. This is here since we always keep our states to be normalised, of magnitude 1 (you can check this with normal Pythagoras). This keeps our magnitudes always the same within basis, and also makes our calculations a lot easier, as it means that $\langle\varphi|\varphi\rangle = 1$, for example. Armed with this knowledge, I will now take you through the rather long journey of canonically quantising a single mode of light.

2.2 Canonical Quantization

We can define canonical quantization as taking some classical Hamiltonian conjugate variables (pairs of variables, that help us to express the energy – the Hamiltonian – of a classical system), say q_j and p_j, denoting a coordinate in space and momentum respectively, and then transform them into $\hat{q_j}$ and $\hat{p_j}$, such that:

$$[\hat{q_j}, \hat{p_j}] = i\hbar \tag{8}$$

Where:

$$[\boldsymbol{A}, \boldsymbol{B}] = \boldsymbol{AB} - \boldsymbol{BA} \tag{9}$$

For some A,B.

We use $\hbar$, the Reduced Planck constant, i.e. $\hbar = \frac{h}{2\pi}$.We can do this more generally with any Classical Matrix, quantizing it into a Quantum Matrix, that contains pairs of these canonically conjugate variables. We find that if variables are not of the same pair, (e.g. some q_i and some p_j, where $i \neq j$), we define them as being commutative, and so their commutator is 0. Hence we find:

$$\mathbf{A} = (q_1, ...q_j, ...; p_1, ...p_j, ...) \Rightarrow \hat{\mathbf{A}} = (\hat{q}_1, ...\hat{q}_j, ...; \hat{p}_1, ...\hat{p}_j, ...) \tag{10}$$

Where:

$$[\hat{q}_i, \hat{p}_j] = i\hbar\delta_{ij} \tag{11}$$

Note that we use the Kronecker delta symbol δ_{ij}, which shows that when $i \neq j$, they commute (i.e. their commutator is 0), and when $i = j$, the two canonically conjugate variables commute, having a commutator of $i\hbar$.

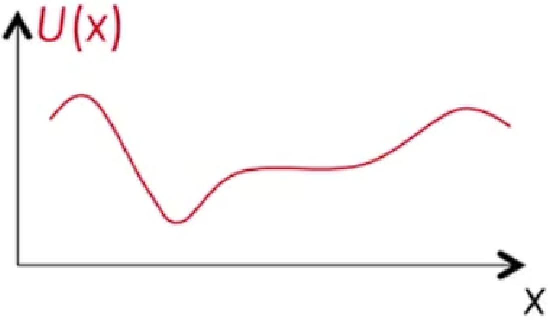

Figure 2: Potential Energy of a particle (U(x)) against it's position (x)

2.3 Finding pairs of Canonically Conjugate Variables

However, one may ask how we can actually find and recognize these pairs of canonically conjugate variables? Well, we go through a procedure of applying it to the classical Hamiltonian equations, which are equations based on the classical Hamiltonian expression of energy - we define the Hamiltonian of a system (H), to equal the potential energy, summed with the kinetic energy ($H = U(x) + \frac{p^2}{2m}$). We also define the Hamiltonian, as having an eigenvalue of E - energy (E being some scalar), essentially that $H\left|\psi\right\rangle = E\left|\psi\right\rangle$.These allow us to find a link between these pairs of variables, and the evolution of them as a system progresses (e.g. momentum progressing with space). First, we are presented with the Hamiltonian equations below, linking the evolution of both variables.

$$\begin{aligned} \dot{q} &= \frac{\partial H}{\partial p} \\ \dot{p} &= -\frac{\partial H}{\partial q} \end{aligned} \tag{12}$$

In order to see their mechanics, let us take an example. This is a material particle of mass m, evolving in a potential U(x), where we define $q = x$ and $p = m\frac{\mathrm{d}x}{\mathrm{d}t}$. And Thus we outlay the equations:

$$\begin{aligned} \frac{\mathrm{d}x}{\mathrm{d}t} &= \frac{p}{m} \\ \frac{\partial H}{\partial p} &= \frac{p}{m} \end{aligned} \tag{13}$$

And so as these yield the same result, so far we view them as canonically conjugate variables (since for this to be true, we require $\frac{\mathrm{d}x}{\mathrm{d}t} = \frac{\partial H}{\partial p}$). Now we must check this to be true by applying it similarly to the derivative of momentum:

$$\begin{aligned} \frac{\mathrm{d}p}{\mathrm{d}t} &= -\frac{\partial U}{\partial x} \\ -\frac{\partial H}{\partial q} &= -\frac{\partial U}{\partial x} \end{aligned} \tag{14}$$

Hence, we confirm our first pair of canonically conjugate variables.

2.3.1 A short detour to Schödinger's equation

Now, we canonically quantise this pair of variables in $\hat{x}$ and $\hat{p}$, getting the Quantum Hamiltonian, such that:

$$\hat{H} = U(\hat{x}) + \frac{\hat{p}^2}{2m} \tag{15}$$

Where:

$$[\hat{x}, \hat{p}] = i\hbar \tag{16}$$

And we define:

$$\hat{p} = \frac{\hbar}{i}\frac{\partial}{\partial x} \tag{17}$$

I will now present to you how we use this in order to derive a version of Schödinger's famed wave equation. Initially, consider a classical EM plane-polarised wave that propogates along the space **r**, with an angular frequency ω, the phase of the electric field being φ (distributed into φ_H and φ_V for the horizontal and vertical components of the field, respectively), and a wavenumber $\boldsymbol{k} = \frac{\omega}{c}$, where c is the speed of light. Do not worry if you don't recognise this, it is just simply another quantity that we consider for the wave. We know that the EM wave is transverse, so we define its electric field as follows:

$$\mathbf{E}(\mathbf{r}, t) = A_H \hat{\imath} \cos(\boldsymbol{k}\mathbf{r} - \omega t + \phi_H) + A_V \hat{\jmath} \cos(\boldsymbol{k}\mathbf{r} - \omega t + \varphi_V) \tag{18}$$

Where A_H and A_V are the horizontal and vertical components of the real amplitude, respectively, and $\hat{\imath}$ and $\hat{\jmath}$ being the unit vectors of the x-y plane we all know about. Putting this into complex form, knowing our identity of $\cos(\theta) = \frac{e^{i\theta} + e^{-i\theta}}{2}$, and $e^{i\theta} = \cos(\theta) + i\sin(\theta)$, we find:

$$\mathbf{E}(\mathbf{r}, t) = Re[A_H e^{i\varphi_H} \hat{\imath} + A_v e^{i\varphi_V} \hat{\jmath}) e^{i\boldsymbol{k}\mathbf{r} - i\omega t}] \tag{19}$$

Remember that we take the real part of the complex form, for we only care about expressing the real part of the field for now. We can now proceed to use this to define the state $|\psi\rangle$ of the electric field (note that it doesn't care about where the field is in space, just its 'state'), and now we use the normalised states $|H\rangle$ and $|V\rangle$ instead of our $\hat{\imath}$ and $\hat{\jmath}$ vectors respectively , to stick with our Dirac notation. We make the state $|\psi\rangle$ normalised, having a magnitude of 1, since this will make our calculations much easier:

$$|\psi\rangle = \frac{1}{\sqrt{A_H^2 + A_V^2}} \Big(A_H e^{i\phi_H} |H\rangle + A_V e^{i\phi_V} |V\rangle \Big) e^{-i\omega t} \tag{20}$$

From this, by inspection we see that we can define the state $|\psi(t)\rangle$ at a time t as a function of its initial state, $|\psi(0)\rangle$:

$$|\psi(t)\rangle = |\psi(0)\rangle e^{-i\omega t} \tag{21}$$

We know of the equation showing the energy of a photon, $E = hf$. We can rearrange this as follows:

$$\begin{aligned} E &= hf \\ &= h\frac{1}{T} \\ &= \frac{h}{2\pi}\frac{2\pi}{T} \\ &= \hbar\omega \end{aligned} \tag{22}$$

Where T is the time period, the time it takes to complete one oscillation, $\frac{1}{f}$. And so we can substitute this into our equation, eliminating ω:

$$|\psi(t)\rangle = |\psi(0)\rangle e^{-\frac{i}{\hbar}Et} \tag{23}$$

In Quantum Mechanics, we define the Quantum Hamiltonian as such:

$$\begin{aligned}\hat{H} &= \begin{bmatrix} E_1 & 0 & \cdots & 0 \\ 0 & E_2 & & 0 \\ \vdots & & \ddots & \vdots \\ 0 & 0 & \cdots & E_m \end{bmatrix} \\ &= \sum_j E_j \left|E_j\right\rangle \left\langle E_j\right| \end{aligned} \tag{24}$$

Where m is some positive integer. We use $\hat{H}$ rather than H, since we now are describing the quantum states of the electric field, not its classical description anymore. We must add the scalar E_j at the front, since we take all states to be normalised (in this case, $|E_j\rangle$). From this, we are able to get a complete orthonormal basis to work in, and so we can describe any quantum state as a linear combination/superposition of these eigenstates $|E_j\rangle$. And so we define the initial state $|\psi(0)\rangle$ as follows:

$$|\psi(0)\rangle = \sum_j \psi_j \left|E_j\right\rangle \tag{25}$$

ψ_j being a scalar coefficient of each eigenstate that makes up our initial state (how 'much' each energy eigenstate makes up the state). Hence, we can define the state $|\psi(t)\rangle$ at a time t as shown:

$$|\psi(t)\rangle = \sum_j \psi_j \left|E_j\right\rangle e^{-\frac{i}{\hbar}E_j t} \tag{26}$$

Due to the nature of a diagonalised matrix, we can define $\hat{H}^n$ as such:

$$\hat{H}^n = \begin{bmatrix} E_1 & 0 & \cdots & 0 \\ 0 & E_2 & & 0 \\ \vdots & & \ddots & \vdots \\ 0 & 0 & \cdots & E_m \end{bmatrix}^n = \begin{bmatrix} E_1^n & 0 & \cdots & 0 \\ 0 & E_2^n & & 0 \\ \vdots & & \ddots & \vdots \\ 0 & 0 & \cdots & E_m^n \end{bmatrix} \tag{27}$$

Using the Taylor expansion for e^x (if you haven't met this before, it is a way of approximating functions in terms of polynomials), we find that:

$$e^x = 1 + x + \frac{x^2}{2} + \frac{x^3}{6} + ... = \sum_{n=0}^{\infty} \frac{x^n}{n!} \tag{28}$$

$$\begin{aligned}\therefore e^{-\frac{i}{\hbar}E_j t} &= 1 + -\frac{i}{\hbar}E_j t + \frac{(-\frac{i}{\hbar}E_j t)^2}{2} + \frac{(-\frac{i}{\hbar}E_j t)^3}{6} + ... \\ &= \sum_{n=0}^{\infty} \frac{(-\frac{i}{\hbar}E_j t)^n}{n!} = \sum_{n=0}^{\infty} \frac{(-\frac{i}{\hbar}t)^n}{n!} E_j^n \end{aligned} \tag{29}$$

And so we proceed as follows:

$$\begin{aligned}|\psi(t)\rangle &= \sum_j \psi_j \left|E_j\right\rangle e^{-\frac{i}{\hbar}E_j t} \\ &= \sum_j \psi_j \left|E_j\right\rangle \sum_{n=0}^{\infty} \frac{(-\frac{i}{\hbar}t)^n}{n!} E_j^n \\ &= \sum_j \sum_{n=0}^{\infty} \psi_j \frac{(-\frac{i}{\hbar}t)^n}{n!} E_j^n \left|E_j\right\rangle \end{aligned} \tag{30}$$

Since:

$$\hat{H}^n |E_j\rangle = \sum_j E_j^n |E_j\rangle \tag{31}$$

We find:

$$\begin{aligned} |\psi(t)\rangle &= \sum_j \sum_{n=0}^{\infty} \psi_j \frac{(-\frac{i}{\hbar}t)^n}{n!} \hat{H}^n |E_j\rangle \\ &= \sum_j \sum_{n=0}^{\infty} \frac{(-\frac{i}{\hbar}\hat{H}t)^n}{n!} \psi_j |E_j\rangle \\ &= e^{-\frac{i}{\hbar}\hat{H}t} |\psi(0)\rangle \end{aligned} \tag{32}$$

Now, we have successfully found a relation between the state $|\psi\rangle$ at any particular time, in terms of the initial state, a constant. This allows us to therefore find the relation between the rate of change of the state at a time t and the initial state:

$$\begin{aligned} \frac{\partial}{\partial t} |\psi(t)\rangle &= -\frac{i\hat{H}}{\hbar} e^{-\frac{i}{\hbar}\hat{H}t} |\psi(0)\rangle \\ \frac{\partial}{\partial t} |\psi(t)\rangle &= -\frac{i\hat{H}}{\hbar} |\psi(t)\rangle \end{aligned} \tag{33}$$

Since we take the partial derivative of time, we generalise it to a state $|\psi\rangle$:

$$\begin{aligned} \frac{\partial}{\partial t} |\psi\rangle &= -\frac{i\hat{H}}{\hbar} |\psi\rangle \\ i\hbar\frac{\partial}{\partial t} |\psi\rangle &= \hat{H} |\psi\rangle \end{aligned} \tag{34}$$

And so we have arrived at Schödinger's wave equation, relating the Quantum Hamiltonian of a state to its rate of change. We can further substitute our known expression for the Quantum Hamiltonian, getting:

$$\begin{aligned} i\hbar\frac{\partial}{\partial t} |\psi\rangle &= \left(U(\hat{x}) + \frac{\hat{p}^2}{2m}\right) |\psi\rangle \\ i\hbar\frac{\partial}{\partial t} |\psi\rangle &= \left(U(\hat{x}) + \frac{(\frac{\hbar}{i}\frac{\partial}{\partial x})^2}{2m}\right) |\psi\rangle \\ i\hbar\frac{\partial}{\partial t} |\psi\rangle &= \left(U(\hat{x}) - \frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\right) |\psi\rangle \end{aligned} \tag{35}$$

And so we find this form of Schrödinger's wave equation. You have already seen two applications of it within the previous section of the article, but you are free to search for more if you'd like. Fascinating, isn't it!

2.4 Material Harmonic Oscillators

Now, we will see how quantised radiation can be described by a set of quantised harmonic oscillators. To do this, we will solve the Schrödinger equation associated to this classical system, which will then be quantized. For our solution, we will use Dirac's method of formalism, which can be applied to any vibrating system that can be modelled as a harmonic oscillator, such as the electromagnetic field.

First, we define a system of particle mass m, which moves along the x axis, attracted towards the origin by a force proportional to its distance, that is defined as $F = -\sqrt{m}\omega x$, such as

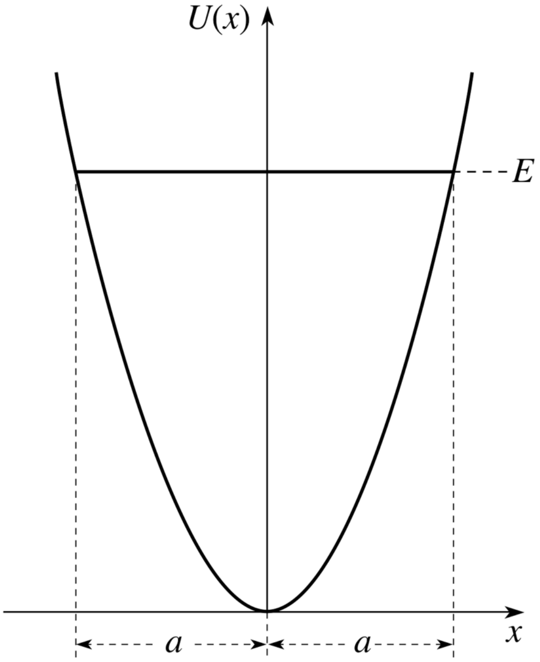

Figure 3: U(x) of a material particle in a harmonic oscillator against its space

the equation of elastic force for $F = -kx$ that I'm sure you're all aware of. From this, we can derive the following equations depicting the potential and Hamiltonian of the system.

$$\hat{H} = \frac{1}{2}m\omega^2\hat{x}^2 + \frac{\hat{p}^2}{2m} \tag{36}$$

$$\hat{H}\left|\phi\right\rangle = E\left|\phi\right\rangle \tag{37}$$

We look for a solution to this equation, where $\left|\phi\right\rangle$ is simply a vector within the space, describing the state of the system. The first step of Dirac's method to proceed solving this, is to introduce two new dimensionless operators, $\hat{X}$ and $\hat{P}$, such that:

$$\begin{aligned} \hat{X} &= \sqrt{\frac{m\omega}{\hbar}}\hat{x} \\ \hat{P} &= \sqrt{\frac{1}{m\omega\hbar}}\hat{p} \end{aligned} \tag{38}$$

By a simple calculation, we find that:

$$\begin{aligned} [\hat{X}, \hat{P}] &= i \\ \hat{H} &= \frac{\hbar\omega}{2}(\hat{X}^2 + \hat{P}^2) \end{aligned} \tag{39}$$

We introduce two further operators, the annihilation operator $\hat{a}$, and its Hermitian conjugate (essentially its complex conjugate $\overline{\hat{a}}$, followed by its conjugate transpose, $\hat{a}^T$, making $\overline{\hat{a}^T}$), the creation operator $\hat{a}^\dagger$, where:

$$\begin{aligned} \hat{a} &= \frac{1}{\sqrt{2}}(\hat{X} + i\hat{P}) \\ \hat{a}^\dagger &= \frac{1}{\sqrt{2}}(\hat{X} - i\hat{P}) \end{aligned} \tag{40}$$

Following from this, we find:

$$\begin{aligned}[\hat{a}, \hat{a}^\dagger] &= \hat{a}\hat{a}^\dagger - \hat{a}^\dagger\hat{a} \\ &= \frac{1}{2}((\hat{X} + i\hat{P})(\hat{X} - i\hat{P}) - (\hat{X} - i\hat{P})(\hat{X} + i\hat{P})) \\ &= \frac{1}{2}((\hat{X}\hat{X} - i\hat{X}\hat{P} + i\hat{P}\hat{X} + \hat{P}\hat{P}) - (\hat{X}\hat{X} + i\hat{X}\hat{P} - i\hat{P}\hat{X} + \hat{P}\hat{P})) \\ &= i(\hat{P}\hat{X} - \hat{X}\hat{P})\end{aligned} \tag{41}$$

Since we know that $[\hat{X}, \hat{P}] = \hat{X}\hat{P} - \hat{P}\hat{X} = i$, we can deduce:

$$[\hat{a}, \hat{a}^\dagger] = i(\hat{P}\hat{X} - \hat{X}\hat{P}) = 1 \tag{42}$$

Moreover, we can express $\hat{P}$ and $\hat{X}$ as functions of $\hat{a}$ and $\hat{a}^\dagger$, easily done using simultaneous equations or the inner product:

$$\begin{aligned}\hat{X} &= \frac{1}{\sqrt{2}}(\hat{a} + \hat{a}^\dagger) \\ \hat{P} &= \frac{-i}{\sqrt{2}}(\hat{a} - \hat{a}^\dagger)\end{aligned} \tag{43}$$

Using this, we find a new expression of the Quantum Hamiltonian, as a function of the annihilation and creation operators:

$$\begin{aligned}\hat{H} &= \frac{\hbar\omega}{2}(\hat{X}^2 + \hat{P}^2) \\ &= \frac{\hbar\omega}{4}((\hat{a}^\dagger\hat{a}^\dagger + \hat{a}^\dagger\hat{a} + \hat{a}\hat{a}^\dagger + \hat{a}\hat{a}) - (\hat{a}^\dagger\hat{a}^\dagger - \hat{a}^\dagger\hat{a} - \hat{a}\hat{a}^\dagger + \hat{a}\hat{a})) \\ &= \frac{\hbar\omega}{2}(\hat{a}^\dagger\hat{a} + \hat{a}\hat{a}^\dagger) \\ &= \hbar\omega\left(\hat{a}^\dagger\hat{a} + \frac{1}{2}\right)\end{aligned} \tag{44}$$

And now we have successfully described the Quantum Hamiltonian as a function of the creation and annihilation operators. If you are unsure where the final step came from, I would suggest looking over the commutator of $\hat{a}^\dagger$ and $\hat{a}$. I would also like you to take note of the ordering of the operators $\hat{a}$ and $\hat{a}^\dagger$, the latter coming first. This is known as normal ordering. Although its use is not particularly apparent at this stage, if you choose to further research this topic of Quantum Optics, this knowledge may prove useful to you later on.

2.5 Number States and Heisenberg's Uncertainty Limit

We now have more weapons in our arsenal to help us solve the equation $\hat{H}\left|\phi\right\rangle = E\left|\phi\right\rangle$. What I will also introduce now, are known as Number States of a mode of radiation, also known as Fock States. Dirac reasoned that using these, we can solve the slightly simpler equation below, which can then lead us to the answer of the original equation. I cannot however mention this without showing the derivation of Heisenberg's Uncertainty Limit for our case of momentum and space, for it will help with understanding how there are always fluctuations, even in a vacuum.

By simple calculation, we see that:

$$\begin{aligned}[\hat{H}, \hat{a}] &= -\hbar\omega\hat{a} \\ [\hat{H}, \hat{a}^\dagger] &= \hbar\omega\hat{a^\dagger}\end{aligned} \tag{45}$$

We take that $\hat{H}|\phi\rangle = E|\phi\rangle$ for some scalar E. Letting $|\phi'\rangle = \hat{a}|\phi\rangle$, we find that:

$$\begin{aligned} \hat{H}|\phi'\rangle &= \hat{H}\hat{a}|\phi\rangle \\ &= (\hat{a}\hat{H} - \hbar\omega\hat{a})|\phi\rangle \\ &= (E\hat{a} - \hbar\omega\hat{a})|\phi\rangle \\ &= (E - \hbar\omega)|\phi'\rangle \end{aligned} \tag{46}$$

Similarly, taking $|\phi''\rangle = \hat{a}^\dagger|\phi\rangle$, we show:

$$\begin{aligned} \hat{H}|\phi''\rangle &= \hat{H}\hat{a}^\dagger|\phi\rangle \\ &= (\hat{a}^\dagger\hat{H} + \hbar\omega\hat{a})|\phi\rangle \\ &= (E\hat{a}^\dagger + \hbar\omega\hat{a})|\phi\rangle \\ &= (E + \hbar\omega)|\phi''\rangle \end{aligned} \tag{47}$$

And so we see the creation and annihilation effects, of these creation and annihilation operators. We know that the energy of a photon can be defined as $\hbar\omega$. This is derived from the more familiar expression hf most of you have learnt, as $hf = \frac{h}{2\pi}2f\pi = \frac{h}{2\pi}\frac{2\pi}{T} = \hbar\omega$, ω being its angular velocity. From these equations, we notice that when the annihilation operator is applied to a state $|\phi\rangle$ with a well defined energy E, the final energy is equal to $E - \hbar\omega$, the previous energy, but now subtracting one photon from the system. Similarly, there is a complementary effect for the creation operator $\hat{a}^\dagger$. Therefore we find that there must be a state $|0\rangle$, where when $\hat{a}$ is applied, it returns a result of null, there is no longer anything within the system, and this is what is known as the ground state.

Just as in statistics, we describe the variance as the root mean square - arithmetic mean inequality, such that:

$$\sigma_x^2 = \sum_i^n \frac{(x_i - \overline{x})^2}{n} \tag{48}$$

(In this sole equation, $\overline{x}$ represents the mean, not the conjugate, to clear up any confusion). We can do just the same with an observable, $\hat{V}$, in which we find the variance in what we could measure from it:

$$\begin{aligned} \langle\Delta\hat{V}^2\rangle &= \langle\psi|(\hat{V} - \langle\hat{V}\rangle)^2|\psi\rangle \\ &= \langle\psi|\hat{V}^2 - 2\hat{V}\langle\hat{V}\rangle + \langle\hat{V}\rangle^2|\psi\rangle \\ &= \langle\hat{V}^2\rangle - 2\langle\hat{V}\rangle\langle\hat{V}\rangle + \langle\hat{V}\rangle^2 \\ &= \langle\hat{V}^2\rangle - 2\langle\hat{V}\rangle^2 + \langle\hat{V}\rangle^2 \\ &= \langle\hat{V}^2\rangle - \langle\hat{V}\rangle^2 \end{aligned} \tag{49}$$

We now define a new relation, between operators A and B, where:

$$\{A, B\} = AB + BA \tag{50}$$

We will proceed to prove a very useful inequality, and then use that to determine Heisenberg's uncertainty principle for our case of momentum and space operators $\hat{p}$ and $\hat{x}$. For two operators, A and B, and where $\operatorname{Im}\{x\}, \operatorname{Re}\{x\}$ denote the imaginary and real parts of some complex number x respectively we find:

$$\begin{aligned}|\langle AB\rangle|^2 &= \langle AB\rangle\overline{\langle AB\rangle}\\ &= \mathsf{Re}\,\{\,\langle AB\rangle\,\}^2+\mathsf{Im}\,\{\,\langle AB\rangle\,\}^2\\ &= \frac{1}{4}((2\mathsf{Re}\,\{\,\langle AB\rangle\,\})^2+(2\mathsf{Im}\,\{\,\langle AB\rangle\,\})^2)\\ &= \frac{1}{4}((\langle AB\rangle+\overline{\langle AB\rangle})^2+(\langle AB\rangle-\overline{\langle AB\rangle})^2)\\ &= \frac{1}{4}((\langle AB\rangle+\langle BA\rangle)^2+(\langle AB\rangle-\langle BA\rangle)^2)\\ &= \frac{1}{4}(|\langle\{\,A,B\,\}\rangle|^2+|\langle[A,B]\rangle|^2)\\ &\therefore |\langle AB\rangle|^2\geq\frac{1}{4}|\langle[A,B]\rangle|^2\end{aligned}\tag{51}$$

Equality is achieved when $AB=-BA$, so when two operators are anti-commutative.
The Cauchy-Schwarz Inequality states that:

$$|\langle a|b\rangle|^2\geq|a|^2|b|^2\tag{52}$$

This can be easily be proved when thinking of the dot product as $\boldsymbol{a}\cdot\boldsymbol{b}=|a||b|\cos\theta$, and so equality is proved when $\theta=0$. Using this, we can prove that the expected values of 2 operators squared multiplied together is greater than or equal the square of the expected value of them multiplied, as follows:

$$\langle\hat{A}^2\rangle\langle\hat{B}^2\rangle\geq|\langle\hat{A}\hat{B}\rangle|^2\tag{53}$$

Letting $|x\rangle=\hat{A}\,|\psi\rangle$ and $|y\rangle=\hat{B}\,|\psi\rangle$, we find:

$$\langle\hat{x}|\hat{x}\rangle\,\langle\hat{y}|\hat{y}\rangle\geq\langle\hat{x}|\,\hat{y}\rangle\tag{54}$$

Which we see follows the Cauchy-Schwarz Inequality. In the case where $\langle\hat{A}\rangle=\langle\hat{B}\rangle=0$, using our newly derived relations, we hence find that:

$$\begin{aligned}\langle\Delta\hat{A}^2\rangle\langle\Delta\hat{B}^2\rangle=\langle\hat{A}^2\rangle\langle\hat{B}^2\rangle\geq|\langle AB\rangle|^2 &\geq\frac{1}{4}|\langle[A,B]\rangle|^2\\ \langle\Delta\hat{A}^2\rangle\langle\Delta\hat{B}^2\rangle &\geq\frac{1}{4}|\langle[A,B]\rangle|^2\end{aligned}\tag{55}$$

Thus proving Heisenberg's Uncertainty. We will now show this for the case of our space and momentum operators. Since:

$$\begin{aligned}\hat{x}&=\frac{\sqrt{\hbar}}{\sqrt{2m\omega}}(\hat{a}+\hat{a}^\dagger)\\ \hat{p}&=-i\frac{\sqrt{m\omega\hbar}}{\sqrt{2}}(\hat{a}-\hat{a}^\dagger)\end{aligned}\tag{56}$$

Using this, we find the expectation values of our two variables when in the ground state:

$$\begin{aligned}
\langle\hat{x}\rangle &= \frac{\sqrt{\hbar}}{\sqrt{2m\omega}}\langle 0|\,(\hat{a}+\hat{a}^{\dagger})\,|0\rangle \\
&= \frac{\sqrt{\hbar}}{\sqrt{2m\omega}}(\langle 0|\,\hat{a}\,|0\rangle + \langle 0|\,\hat{a}^{\dagger}\,|0\rangle) \\
&= \frac{\sqrt{\hbar}}{\sqrt{2m\omega}}(\langle 0|\,\hat{a}\,|0\rangle + \overline{\hat{a}\,|0\rangle}\,|0\rangle) \\
&= \frac{\sqrt{\hbar}}{\sqrt{2m\omega}}(0\,\langle 0| + 0\,\langle 0|) \\
&= 0 \\
\langle\hat{p}\rangle &= -i\frac{\sqrt{m\omega\hbar}}{\sqrt{2}}\langle 0|\,(\hat{a}-\hat{a}^{\dagger})\,|0\rangle \\
&= -i\frac{\sqrt{m\omega\hbar}}{\sqrt{2}}(\langle 0|\,\hat{a}\,|0\rangle - \langle 0|\,\hat{a}^{\dagger}\,|0\rangle) \\
&= -i\frac{\sqrt{m\omega\hbar}}{\sqrt{2}}(\langle 0|\,\hat{a}\,|0\rangle - \overline{\hat{a}\,|0\rangle}\,|0\rangle) \\
&= -i\frac{\sqrt{m\omega\hbar}}{\sqrt{2}}(0\,\langle 0| - 0\,\langle 0|) \\
&= 0
\end{aligned} \tag{57}$$

And so we see their expected value is 0. Therefore, we can apply it to our Heisenberg uncertainty inequality, finding:

$$\begin{aligned}
\Delta\hat{x}^2\Delta\hat{p}^2 &\geq \frac{1}{4}|\langle[x,p]\rangle|^2 \\
\Delta\hat{x}^2\Delta\hat{p}^2 &\geq \frac{1}{4}|i\hbar|^2 \\
\Delta\hat{x}^2\Delta\hat{p}^2 &\geq \frac{1}{4}\hbar^2 \\
\Delta\hat{x}\Delta\hat{p} &\geq \frac{\hbar}{2}
\end{aligned} \tag{58}$$

This tells us that even in the ground state, for the case of light a vacuum, there are quantum fluctuations, leading to a energy state that is greater than 0. In this case, it is $\frac{\hbar\omega}{2}$. Therefore, we can express the Hamiltonian of a state $|n\rangle$, applying it to the state, as:

$$\hat{H}\,|n\rangle = \hbar\omega\left(n+\frac{1}{2}\right)|n\rangle \tag{59}$$

Solving our desired equation, and where $n \in \mathbb{N}\cup\{0\}$. One can also show this, using our equation of the Hamiltonian in terms of $\hat{a}^{\dagger},\hat{a}$ and applying it to the state $|0\rangle$. I will show you something further now: how we can construct any state of light, which contains n photons, using our creation and annihilation operators:

We are aware of the expression $\hat{H} = \hbar\omega\left(\hat{a}^{\dagger}\hat{a}+\frac{1}{2}\right)$, and so can rearrange it to: $\frac{1}{\hbar\omega}\hat{H}-\frac{1}{2} = \hat{a}^{\dagger}\hat{a}$.

We will now proceed to solve the equation:

$$\hat{a}\,|n\rangle = \alpha\,|n-1\rangle \tag{60}$$

Where α is some unknown constant to be solved for.

$$\begin{aligned}
\hat{a}\left|n\right\rangle &= \alpha\left|n-1\right\rangle \\
\left|\hat{a}\left|n\right\rangle\right|^2 = \left\langle n\right|\hat{a}^\dagger\hat{a}\left|n\right\rangle &= |\alpha|^2\left\langle n-1|n-1\right\rangle = |\alpha|^2 \\
\frac{1}{\hbar\omega}\left\langle n\right|\hat{H}\left|n\right\rangle - \frac{1}{2}\left\langle n|n\right\rangle &= |\alpha|^2 \\
\left\langle n\right|(n+\frac{1}{2})\left|n\right\rangle - \frac{1}{2}\left\langle n|n\right\rangle &= |\alpha|^2 \\
n\left\langle n|n\right\rangle &= |\alpha|^2 \\
n &= |\alpha|^2 \\
\alpha &= \sqrt{n}
\end{aligned} \tag{61}$$

We are able to perform a similar equation, using the creation operator, to find that $\hat{a}^\dagger\left|n\right\rangle = \sqrt{n+1}\left|n\right\rangle$. Indeed, these show us that using the two operators, we are able to generate any state of n photons from just the ground state.

2.6 A Single Mode of Radiation

We are all aware of the electromagnetic fields that are everywhere in our day-to-day life. I will now introduce Maxwell's equations, which are those that govern the behaviour of the fields, and then we will go through the classical calculations to obtain the dynamics of our known field, which will then be quantized to receive our final expression of the Quantum Hamiltonian in this mode of light. Below are the simplest form of Maxwell's equations, without source terms of charges or currents.

$$\begin{aligned}
\nabla\cdot\mathbf{E}(\mathbf{r},t) &= 0 \\
\nabla\cdot\mathbf{B}(\mathbf{r},t) &= 0 \\
\nabla\times\mathbf{E}(\mathbf{r},t) &= -\frac{\partial\mathbf{B}}{\partial t} \\
\nabla\times\mathbf{B}(\mathbf{r},t) &= \frac{1}{c^2}\frac{\partial\mathbf{E}}{\partial t}
\end{aligned} \tag{62}$$

Where $\mathbf{r}$ represents the vector in space of a point in the field, and $\nabla = \frac{\partial}{\partial x}\mathbf{e}_x + \frac{\partial}{\partial y}\mathbf{e}_y + \frac{\partial}{\partial z}\mathbf{e}_z$, $\mathbf{e}$ denoting the orthonormal basis vectors of our space.

To define a field in a volume that we are interested in, in this case our quantization volume, one only needs to know the values at the boundary of said volume, which these equations will help us with. The most elementary solution of Maxwell's equations is what is known as a mode; simply a field that oscillates at a well defined frequency. Due to the oscillation, we can now proceed to quantize it as a harmonic oscillator.

We find that one solution of this set of equations is as of the following, provided that it follows a few rules:

$$\mathbf{E}(\mathbf{r},t) = \boldsymbol{\epsilon}_l\mathcal{E}_l(t)e^{i(\boldsymbol{k}_l\cdot\mathbf{r})} + c.c. \tag{63}$$

You may recall seeing a similar equation to this earlier on within the article, when we derived Schrödinger Wave equation, and that it was slightly different. Do not worry, we are simply expressing virtually the same equation, but with some different coefficients for ease and the different conditions (such as no sources). Perhaps you can take the fulfilment of these conditions as a further proof towards Schrödinger's equation working, if you'd like. The first condition that must be met, for this to be a functioning equation is that the unit vector $\boldsymbol{\epsilon}_l$, denoting the direction, or polarisation of the electric field, must be perpendicular to $\boldsymbol{k}_l$, the vector defining the direction of propagation. This is needed to confirm that the divergence,

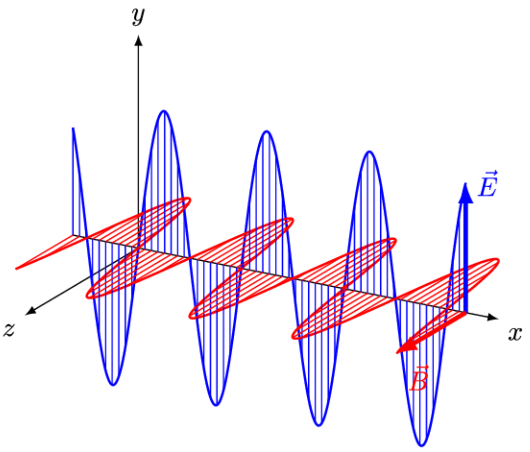

Figure 4: An EM Field obeying Maxwell's Equations

$\nabla \cdot \mathbf{E}$, of the electric field is null (none of the field is 'flowing in or out' of our quantization volume, as there are no sources).
The second condition is that the amplitude of the field, $\mathcal{E}_l(t)$, oscillates at a well-defined angular frequency of ω_l ($\mathcal{E}_l(t) = \mathcal{E}_l(0)e^{-i\omega_l t}$, where $\omega_l = c||\boldsymbol{k}_l|| = ck_l$.
We define this mode l of polarisation $\boldsymbol{\epsilon}_l$ and direction of propagation $\boldsymbol{k}_l$ as a 'polarised plane travelling monochromatic wave'. However, this alone is not enough to entirely determine the mode, it only describes its structure. We must also know our complex amplitude, $\mathcal{E}_l$, which characterizes the state of the field in this mode. This is affected by two real variables, such as its real and imaginary parts, or its modulus/magnitude and phase. Take instance an example of the pendulum. To fully know its behaviour, one must know the amplitude and phase of its oscillation, akin to the modulus and phase of this mode l. We will now proceed to confirm that this equation works within well within the conditions, and retreive a set of dynamic variables to use in order to describe the system.

2.7 Canonically Conjugate Dynamic Variables of the Field

To begin finding this pair of dynamic variables, we present ourselves with one of Maxwell's equations again.

$$\begin{gathered}\nabla \cdot \mathbf{E}(\mathbf{r}, t) = 0 \\ \mathbf{E}(\mathbf{r}, t) = \boldsymbol{\epsilon}_l \mathcal{E}_l(t) e^{i(\boldsymbol{k}_l \cdot \mathbf{r})} + c.c.\end{gathered} \tag{64}$$

We know that when applying ∇ to our electric field equation, we find that it results in the direction of propagation, as it has the effect of taking a derivative: $\nabla \mathbf{E}(\mathbf{r}, t) = i\boldsymbol{k}_l \boldsymbol{\epsilon}_l \mathcal{E}_l(t) e^{i(\boldsymbol{k}_l \cdot \mathbf{r})} + c.c.$. And so we get

$$\nabla \cdot \mathbf{E}(\mathbf{r}, t) = i\boldsymbol{k}_l \cdot \boldsymbol{\epsilon}_l \mathcal{E}_l(t) e^{i(\boldsymbol{k}_l \cdot \mathbf{r})} + c.c. = 0 \tag{65}$$

Hence $\boldsymbol{k}_l \cdot \boldsymbol{\epsilon}_l = 0$, so $\boldsymbol{k}_l$ must be perpendicular to $\boldsymbol{\epsilon}_l$. Using the third Maxwell equation, we find that:

$$\nabla \times \mathbf{E}(\mathbf{r}, t) = i\boldsymbol{k}_l \times \boldsymbol{\epsilon}_l \mathcal{E}_l(t) e^{i(\boldsymbol{k}_l \cdot \mathbf{r})} + c.c. = -\frac{\partial \mathbf{B}}{\partial t} \tag{66}$$

Therefore, as a rate of change of the magnetic field, $\frac{\partial \mathbf{B}}{\partial t}$, is in the direction of the cross product of $\boldsymbol{k}_l$ and $\boldsymbol{\epsilon}_l$, we find that the magnetic field, electric field, and direction of propagation are three perpendicular vectors, forming a right-handed set. Using the fourth Maxwell equation, we obtain the following description of our magnetic field:

$$\begin{aligned} \nabla\times\mathbf{B}(\mathbf{r},t) &= \frac{1}{c^2}\frac{\partial \mathbf{E}}{\partial t}\\ \nabla\times(\nabla\times\mathbf{B}(\mathbf{r},t)) &= \nabla\times(\frac{1}{c^2}\frac{\partial\mathbf{E}}{\partial t}) \end{aligned} \tag{67}$$

The Vector Triple Product Identity states that: $\boldsymbol{A}\times(\boldsymbol{B}\times\boldsymbol{C}) = (\boldsymbol{A}\cdot\boldsymbol{C})\boldsymbol{B} - (\boldsymbol{A}\cdot\boldsymbol{B})\boldsymbol{C}$. We can use this to our advantage in solving for the magnetic field; in this case, since ∇ and $\mathbf{B}(\mathbf{r},t)$ are orthogonal, we get that $\nabla\times(\nabla\times\mathbf{B}(\mathbf{r},t)) = i^2(\boldsymbol{k}_l\times(\boldsymbol{k}_l\times\mathbf{B}(\mathbf{r},t))) = |\boldsymbol{k}_l|^2\mathbf{B}(\mathbf{r},t)$. Substituting this in, we get:

$$\begin{aligned} &\nabla\times(\nabla\times\mathbf{B}(\mathbf{r},t)) = \nabla\times(\frac{1}{c^2}\frac{\partial\mathbf{E}}{\partial t})\\ &-\boldsymbol{k}_l\times(\boldsymbol{k}_l\times\mathbf{B}(\mathbf{r},t)) = i\boldsymbol{k}_l\times(\frac{1}{c^2}\frac{\partial\mathbf{E}}{\partial t})\\ &|\boldsymbol{k}_l|^2\mathbf{B}(\mathbf{r},t) = i\boldsymbol{k}_l\times(\frac{1}{c^2}\frac{\partial\mathbf{E}}{\partial t})\\ &\mathbf{B}(\mathbf{r},t) = \frac{i}{|\boldsymbol{k}_l|^2}\boldsymbol{k}_l\times(\frac{1}{c^2}\frac{\partial\mathbf{E}}{\partial t})\\ &\mathbf{B}(\mathbf{r},t) = \frac{i}{c^2k_l^2}\boldsymbol{k}_l\times\boldsymbol{\epsilon}_l\frac{\mathrm{d}\mathcal{E}_l(t)}{\mathrm{d}t}e^{i(\boldsymbol{k}_l\cdot\mathbf{r})} + c.c.\\ &\mathbf{B}(\mathbf{r},t) = \frac{i}{\omega_l^2}\boldsymbol{k}_l\times\boldsymbol{\epsilon}_l\frac{\mathrm{d}\mathcal{E}_l(t)}{\mathrm{d}t}e^{i(\boldsymbol{k}_l\cdot\mathbf{r})} + c.c. \end{aligned} \tag{68}$$

And we see that it has the same form with the same complex exponential, $e^{i(\boldsymbol{k}_l\cdot\mathbf{r})}$, as the electric field. Taking the derivative with respect to time of this equation, combined with the third Maxwell equation, we find a second order differential equation:

$$\begin{aligned} \nabla\times\mathbf{E}(\mathbf{r},t) &= -\frac{\partial\mathbf{B}}{\partial t} = -\frac{i}{\omega_l^2}\boldsymbol{k}_l\times\boldsymbol{\epsilon}_l\frac{\mathrm{d}^2\mathcal{E}_l(t)}{\mathrm{d}t^2}e^{i(\boldsymbol{k}_l\cdot\mathbf{r})} + c.c.\\ i\boldsymbol{k}_l\times\boldsymbol{\epsilon}_l\mathcal{E}_l(t)e^{i(\boldsymbol{k}_l\cdot\mathbf{r})} + c.c. &= -\frac{1}{\omega_l^2}i\boldsymbol{k}_l\times\boldsymbol{\epsilon}_l\frac{\mathrm{d}^2\mathcal{E}_l(t)}{\mathrm{d}t^2}e^{i(\boldsymbol{k}_l\cdot\mathbf{r})} + c.c.\\ -\omega_l^2\mathcal{E}_l(t) &= \frac{\mathrm{d}^2\mathcal{E}_l(t)}{\mathrm{d}t^2} \end{aligned} \tag{69}$$

Since this equation is linear (as $\mathcal{E}_l$ is proportional to this second-order derivative, and vice versa), we expect the solution to be of the form e^{rt}

Hence $\frac{\mathrm{d}\mathcal{E}_l}{\mathrm{d}t} = re^{rt}$, and $\frac{\mathrm{d}^2\mathcal{E}_l}{\mathrm{d}t^2} = r^2e^{rt}$

So we get that $r^2e^rt + \omega^2e^{rt} = 0$

As we know $e^{rt} \neq 0$ for all values of r, we can simply cancel it out.

This gets $r^2 = -\omega^2$, and so $r = \pm i\omega$.

Therefore $\mathcal{E}_l(t) = \mathcal{E}_l(0)e^{\pm i\omega t}$.

However, this gives two solutions - one where the wave travels along the propagation vector $\boldsymbol{k}_l$, and one against it. Since we are only looking at a single mode, we only keep on solutions, and simply omit the other. In this case, we omit the solution of the wave travelling against $\boldsymbol{k}_l$, keeping the solution $\mathcal{E}_l(t) = \mathcal{E}_l(0)e^{-i\omega t}$

And so we rewrite our equations for the electric and magnetic fields, substituting in this new known variable:

$$\begin{aligned}\mathbf{E}(\mathbf{r},t) &= \boldsymbol{\epsilon}_l\mathcal{E}_l(0)e^{i(\boldsymbol{k}_l\cdot\mathbf{r}-\omega_l t)} + c.c.\\ \mathbf{B}(\mathbf{r},t) &= \frac{\boldsymbol{k}_l\times\boldsymbol{\epsilon}_l}{\omega_l}\mathcal{E}_l(t)e^{i\boldsymbol{k}_l\cdot\mathbf{r}} + c.c\\ &= \frac{\boldsymbol{k}_l\times\boldsymbol{\epsilon}_l}{\omega_l}\mathcal{E}_l(0)e^{i(\boldsymbol{k}_l\cdot\mathbf{r}-\omega_l t)} + c.c.\end{aligned} \tag{70}$$

From this we notice again that the direction of propagation, and polarisation of electric and magnetic fields form an orthogonal/perpendicular set. Moreover, We further notice that the magnetic field is in phase with the electric, and that its complex amplitude is equal to that of the electric field divided by the speed of light, c. And so we can describe entirely the dynamics of this field by the equation:

$$\frac{\mathrm{d}\mathcal{E}_l(t)}{\mathrm{d}t} = -i\omega_l\mathcal{E}_l(t) \tag{71}$$

2.8 Canonical Quantization of a Single Mode

We are on the final stretch now of quantizing this mode. Now to show we have confirmed its dynamics, we will show that the real and imaginary parts of the complex amplitude $\mathcal{E}_l(t)$ are a pair of canonically conjugate variables. Initially we introduce a normal variable (having a magnitude of 1), $\alpha_l(t)$, such that:

$$\mathcal{E}_l(t) = i\mathscr{E}_l^{(1)}\alpha_l(t) \tag{72}$$

We take $\mathscr{E}_l^{(1)}$ as some constant in the dimensions of an electric field, that we will calculate, and so it is easy to see that the evolution of $\alpha_l(t)$ is the same as that of the complex amplitude, and that our normal variable is dimensionless.
As we see that the evolution of the two is the same, we get that:

$$\frac{\mathrm{d}\alpha_l(t)}{\mathrm{d}t} = -i\omega_l\alpha_l(t) \tag{73}$$

And this equation also fully determines the dynamics of our field in mode l. We now introduce the real and imaginary parts of alpha, as follows:

$$\begin{aligned}\alpha_l(t) &= \frac{1}{\sqrt{2\hbar}}(Q_l + iP_l)\\ \overline{\alpha_l}(t) &= \frac{1}{\sqrt{2\hbar}}(Q_l - iP_l)\end{aligned} \tag{74}$$

Again, by inner product or substitutions, we find:

$$\begin{aligned}Q_l &= \sqrt{\frac{\hbar}{2}}(\alpha_l(t) + \overline{\alpha_l}(t))\\ P_l &= -i\sqrt{\frac{\hbar}{2}}(\alpha_l(t) - \overline{\alpha_l}(t))\end{aligned} \tag{75}$$

Now to find the Classical Hamiltonian of the system, we apply the following integral defining **E** and **B** to be the strengths of the electric and magnetic fields respectively:

$$H_l = \frac{\varepsilon_0}{2}\int\limits_{V_l} d^3r(\mathbf{E}^2 + c^2\mathbf{B}^2) \tag{76}$$

This is becuase the energy of a field can be defined as the energy density of a field integrated over its quantization volume, where the energy density for an electric field is equal to the half of the permittivity of free space (essentially how 'easy' it is for an electric field to pass through a vacuum, where $\varepsilon_0 \approx 8.854 \times 10^{-12}$m^{-3}kg^{-1}s^{4}A^2), multiplied by the square of the field, $U_E = \frac{1}{2}\varepsilon_0 \mathbf{E}^2$. Since we know the relation of the magnetic complex amplitude to that of the electric field, we can equate $c^2\mathbf{B}^2$ to $\mathbf{E}^2$, and can define $\mathbf{E}^2$ to be directly proportional to the square of the complex amplitude, $|\mathcal{E}_l(t)|^2$. You can check this yourself - if you return to the original equation describing the electric field, and multiply it by it's complex conjugate, you will find that it is equal to twice the square of the magnitude of the complex amplitude: $\mathbf{E}(\mathbf{r},t)\overline{\mathbf{E}(\mathbf{r},t)} = |\mathbf{E}(\mathbf{r},t)|^2 = \mathbf{E}^2 = 2|\mathcal{E}_l(t)|^2$.

$$\begin{aligned} H_l &= \varepsilon_0 \int\limits_{V_l} d^3r \mathbf{E}^2 \\ &= 2\varepsilon_0 \int\limits_{V_l} d^3r |\mathcal{E}_l(t)|^2 \\ &= 2\varepsilon_0 V_l |\mathcal{E}_l(t)|^2 \\ &= 2\varepsilon_0 V_l |\mathscr{E}_l^{(1)}|^2 |\alpha_l|^2 \end{aligned} \tag{77}$$

Now we choose to define $\mathscr{E}_l^{(1)}$ as such:

$$\mathscr{E}_l^{(1)} = \sqrt{\frac{\hbar\omega}{2\varepsilon_0 V_l}} \tag{78}$$

We choose this formula, since it will make the calulation simpler when we quantize this equation to retrieve our Quantum Hamiltonian of this mode of light. Indeed, this constant actually represents the one-photon amplitude of mode l. Using this notation, we find a familiar expression for our Hamiltonian:

$$\begin{aligned} H_l &= \hbar\omega_l |\alpha_l(t)|^2 \\ &= \frac{\omega_l}{2}(Q_l^2 + P_l^2) \end{aligned} \tag{79}$$

But what exactly is our quantization volume, you may have been asking? Well, it is simply the volume in which we define our wave, in this case defined to be a cubic box of length L.

For this to work, we require our box to fufill a few conditions. Since the wave obviously will continue to propogate outside of the box, we require that the length L is of sufficient length to capture the full dynamics of one period, since the wave is periodic in all directions of space.

$$\begin{aligned} k_{lx}L &= 2\pi n_{lx} \\ k_{ly}L &= 2\pi n_{ly} \\ k_{lz}L &= 2\pi n_{lz} \end{aligned} \tag{80}$$

Where n_l is some integer for this mode, and k_l the magnitude of the propogation vector in a specific direction.

Finally, before we proceed with our quantization of this light, we will first show our dynamic variables Q_l and P_l are canonically conjugate. We apply the Hamiltonian equations again to obtain the evolution of these two dynamic variables, so that we can then obtain the

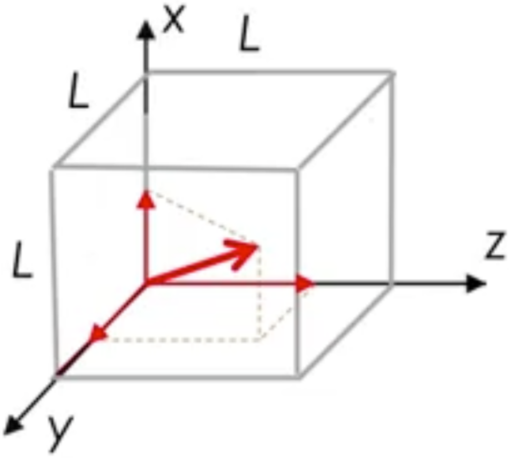

Figure 5: Volume of Quantization

evolution of $\alpha(t)$:

$$\begin{aligned}\frac{\mathrm{d}Q_l}{\mathrm{d}t} &= \frac{\partial H}{\partial P_l} = \omega_l P_l \\ \frac{\mathrm{d}P_l}{\mathrm{d}t} &= -\frac{\partial H}{\partial Q_l} = -\omega_l Q_l \\ \frac{\mathrm{d}}{\mathrm{d}t}\alpha(t) &= -i\omega_l(Q_l + iP_l)\end{aligned} \tag{81}$$

Indeed, this is exactly the result we obtained from using Maxwell's equations, our known dynamics, and so we conclude that Q_l and P_l are canonically conjugate. Undergoing the process of canonical quantization, and using it to obtain the Quantum Hamiltonian, we conclude:

$$\begin{aligned}[Q_l, P_l] &= i\hbar \\ \hat{H}_l &= \frac{\omega_l}{2}(Q_l^2 + P_l^2)\end{aligned} \tag{82}$$

We thus obtain our quantized relations for $\alpha(t)$ and its conjugate, getting:

$$\begin{aligned}\alpha(t) \Rightarrow \hat{a} &= \frac{1}{\sqrt{2\hbar}}(\hat{Q}_l + i\hat{P}_l) \\ \overline{\alpha(t)} \Rightarrow \hat{a}^\dagger &= \frac{1}{\sqrt{2\hbar}}(\hat{Q}_l - i\hat{P}_l) \\ [\hat{a}, \hat{a}^\dagger] &= 1\end{aligned} \tag{83}$$

And so we finally get the equation for our Quantum Hamiltonian for this mode of light, yielding:

$$\hat{H} = \hbar\omega\Big(\hat{a}^\dagger\hat{a} + \frac{1}{2}\Big) \tag{84}$$

We have finally canonically quantized a single mode of light. What a journey, wasn't it? Perhaps you weren't expecting such a simple result as this, perhaps it was anticlimactic as we saw it earlier within the article. However, I find beauty in that. How amazing it is that we can apply such a simplified to approach to this complex process, everything tying together nicely, making our lives so much easier in the calculations. Do not worry though if this result disappointed you. Of course there are more difficult quantizations of fields in Quantum Optics; if you are curious, looking at a standing wave would be a great start.

3 Problems

Introduction to Quantum Mechanics

1. (4 marks) Prove that normalizing the wavefunction at $t = 0$ ensures that it stays normalized for all future t.
   (Hint: Consider the following - if the solution is the same for all future time, what must the integral below be?
   $$\frac{d}{dt}\int_{-\infty}^{+\infty} |\Psi(x,t)|^2 \, dx = ?$$
   Show this, and then use the product rule, along with the (time-dependent) Schrödinger equation and the property that the wavefunction must go to 0 at $-\infty$ and $+\infty$ for the solution to be normalizable, to prove the above statement.)
2. (3 marks) Prove that:
   $$\hat{p} = -i\hbar\frac{\partial}{\partial x}$$
   (Hint: Consider $\langle v\rangle = d\langle x\rangle/dt$ and use some of the equations established in Question 1.)
3. (5 marks) (**Problem 1.7** in Griffiths' "Introduction to Quantum Mechanics"). Show that:
   $$\frac{d\langle p\rangle}{dt} = \left\langle -\frac{\partial V}{\partial x}\right\rangle$$
   This is an instance of **Ehrenfest's theorem**, which asserts that *expectation values obey the classical laws*.
4. (3 marks) Use the fact that $\hat{H}\psi = E\psi$ to show that $\sigma_H = 0$ in a stationary state.
5. (10 marks) (**Problem 4.20** in Griffiths' "Introduction to Quantum Mechanics" - also one of my favourites). Consider the earth-sun system as a gravitational analogue to the hydrogen atom.
   (a) What is the potential energy function (replacing Equation 7.1)? (Let m_E be the mass of the earth, and M the mass of the sun).
   (b) What is the "Bohr radius", a_g, for this system? Work out the actual number.
   (c) Write down the gravitational "Bohr formula", and, by equation E_n to the classical energy of a planet in a circular orbit of radius r_o, show that $n = \sqrt{r_o/a_g}$. From this, estimate the quantum number n of the earth.
   (d) Suppose the earth made a transition to the next lower level $(n-1)$. How much energy (in Joules) would be released? What would the wavelength of the emitted photon (or, more likely, graviton) be? (Express your answer in light years - is the remarkable answer a coincidence?)

Canonically quantising a single mode of radiation

1. Are x (space), and v (velocity) canonically conjugate variables?
2. Apply the Hamiltonian to the ground state $|0\rangle$ to show that its energy is $\frac{\hbar\omega}{2}$
3. Find the general expression of a state $|n\rangle$, in terms of the creation operator and the ground state $|0\rangle$

4 Solutions

An introduction to AC circuits

1. **Q: Explain why at high frequencies a capacitor acts as an AC short, whereas an inductor acts as an open circuit.**

   This behaviour comes from the definition of the impedance of a capacitor. We know that a capacitor has an impedance $Z = 1/i\omega C$, and so Z is inversely proportional to ω. As ω increases, Z decreases, meaning that at very high frequences, Z approaches 0, meaning the capacitor acts as a short circuit, allowing AC to flow with almost no resistance.

   Similarly, we can apply this logic to an inductor. The impedance of an inductor is given by $Z = i\omega L$. As ω increases, the impedance increases, meaning at very high frequencies, the impedance is effectively infinite, blocking AC flow, mimicking an open circuit.

2. **Q: In an RLC series circuit, can the voltage measured across the capacitor be greater than the voltage of the source? Answer the same question for the voltage across the inductor.**

   Yes, this is possible, when **resonance** occurs, and this phenomenon is commonly exploited in RF circuits for signal amplification. At resonance, the inductive and capacitive reactances are largest in magnitude but out of phase. This causes an extremely large current to flow in the circuit, potentially causing the voltage across components to be much greater than the source voltage.

3. **An RLC series circuit with $R = 600\Omega$, $L = 30$mH and $C = 0.050\mu$F is driven by an AC source whose frequency and voltage amplitude are 500Hz and 50V, respectively, so: (a) what is the impedance of the circuit, (b) what is the amplitude of the current in the circuit and (c) what is the phase angle between the emf of the source and the current?**

   (a) Using the method outlined in the article, we see that

   $$\begin{aligned} Z &= \sqrt{R^2 + (X_L - X_C)^2} \\ &= \boxed{6300\Omega} \end{aligned}$$

   (b) Using Ohm's Law for AC circuits

   $$I = \frac{V}{Z} = \boxed{7.94\text{mA}}$$

   (c) We can calculate the phase angle using

   $$\begin{aligned} \phi &= \arctan \frac{X_L - X_C}{R} \\ &= \boxed{-84.5^\circ} \end{aligned}$$

   Since the phase angle is negative, the circuit is capacitive, meaning the current leads the voltage.

Solutions to the problems from this issue will feature in the next issue!

Credits

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