

# Chapter 3

## Light and Atoms

Lovingly brought to you by Ervin Chia, Chua Wei Hong, Hillson Hung and Nemo Chen

### Learning objectives

By the end of this chapter, you should be familiar with the concept of quantum mechanics and light, the history of the various atomic models proposed and the reasons propelling them. You will also be introduced to the field of spectroscopy as means to study light and atoms together. Finally, a mention about the modern interpretation of quantum mechanics with wavefunctions and probabilities is made.

### Learning flow

This chapter will span 2 weeks.

Before week 3 lecture, do the pre-lecture homework and briefly read through sections 3.2–3.4.

During week 3 lecture, we will discuss the topics of light, spectroscopy and early atomic models in 3.2–3.4. The content is heavy and possibly dry. Hence we intend to deliver the content via the associated lecture activities, which are more hands-on and visual. That is the plan, at least.

Before week 4 lecture, no pre-lecture homework. Just briefly read through sections 3.4 and 3.6.

During week 4 lecture we will go explore some aspects of modern quantum mechanics.

In week 4 IS, we will do discussion questions 1-6.

In week 5 IS, we will fully understand the quantum mechanics of a particle in a box through questions 7 and 8.

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## 3.1 Pre-Lecture Homework

### 3.1.1 Some mathy stuffs

Graph

$$y = A \sin(kx + \omega t + \phi)$$

on Desmos and investigate how  $k$ ,  $\omega$ ,  $\phi$  and  $A$  affect the shape of the wave. Also identify which variable relates to the wavelength,  $\lambda$  and frequency,  $f$  of the wave.

Google Euler's formula and complete the equation below

$$e^{i(kx - \omega t)} =$$

Read Ervin's article on Fourier Representation. Find in the Canvas  $\rightarrow$  SP3176  $\rightarrow$  Files  $\rightarrow$  Lecture Notes.

### 3.1.2 Force and potential

Force is a vector quantity. Sometimes it is tricky to find the force (both magnitude and direction) at all positions. Fortunately there is a scalar quantity known as Potential Energy  $V$  that is closely related to force  $\mathbf{F}$  via

$$\mathbf{F} = \begin{pmatrix} F_x \\ F_y \\ F_z \end{pmatrix} = - \begin{pmatrix} \frac{\partial V}{\partial x} \\ \frac{\partial V}{\partial y} \\ \frac{\partial V}{\partial z} \end{pmatrix}$$

Consider a force

$$\mathbf{F}_E = \frac{1}{4\pi\epsilon_0} \frac{qq_2}{(x^2 + y^2 + z^2)^{3/2}} \begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

Verify that

$$V = \frac{1}{4\pi\epsilon_0} \frac{q_1q_2}{(x^2 + y^2 + z^2)^{1/2}}$$

is the potential energy for  $\mathbf{F}_E$ . (Do feel free to use Wolfram Alpha to help with the differentiation.)

The mechanics of a system of particles can be equivalently studied using either forces or energy. Often the latter is preferred as the expression for potential energy is simpler. Applying the **conservation of energy** also allows us intuitively understand the behaviour of a closed system.

## 3.2 Light

### 3.2.1 From the *Optica* to the electromagnetic spectrum

The study of light can be traced back 2500 years. People attempted to study and understand how light came to be: it was often the case that the Sun was the only natural source of light and thus revered then. The earliest known work on light was *Optica* by Euclid, studying the nature of light and how it behaved both qualitatively and quantitatively. Over the years, our understanding of light has vastly changed, especially so during the Scientific Revolution. Models of light have come and gone but most remain in one way or another due to its relevance in nature or practicality.

The nature of light was a contentious issue before the 1700s. The two leading theories of light's nature were particle-like (or corpuscular) and wave-like. In 1690, Christiaan Huygens published a work that would set in motion the victory of the wave theory, the *Traité de la Lumière*<sup>1</sup>. Summarily, his treatise put forth that light was best described by waves. This was primarily because of the following three phenomenon unique to *transverse* waves:

1. Diffraction
2. Refraction
3. Polarization

Light was found to be capable of exhibiting all three properties and Huygens mathematically proved the first two so. Although not widely accepted during its time of publication, contributions by several others such as Augustin-Jean Fresnel, Denis Poisson and Léon Foucault expanded on Huygens's work or proved the corpuscular theory otherwise, leading to the eventual acceptance of light as a wave in the mid-1800s.

In 1862, James Clerk Maxwell brought together several empirical laws that described electric fields  $\mathbf{E}$  and magnetic field  $\mathbf{B}$  and compiled them into a set of equations known (today) as the Maxwell's equations. By further combining the equations, he found that the  $\mathbf{E}$  and  $\mathbf{B}$  fields in vacuum obey

$$\frac{\partial^2 \mathbf{E}}{\partial x^2} + \frac{\partial^2 \mathbf{E}}{\partial y^2} + \frac{\partial^2 \mathbf{E}}{\partial z^2} = \mu_0 \epsilon_0 \frac{\partial^2 \mathbf{E}}{\partial t^2} \quad (3.1)$$

$$\frac{\partial^2 \mathbf{B}}{\partial x^2} + \frac{\partial^2 \mathbf{B}}{\partial y^2} + \frac{\partial^2 \mathbf{B}}{\partial z^2} = \mu_0 \epsilon_0 \frac{\partial^2 \mathbf{B}}{\partial t^2} \quad (3.2)$$

Equations that look like the above are well studied: they are known as wave equations because solutions to this class of equations are of the form of waves. Through theory, he found that electromagnetic waves travelled at the speed of light, which had been fairly accurately measured by then. Additionally, treating light as an electromagnetic phenomenon would also solve the final piece of the puzzle; polarization of light. However, light was seen as entirely unrelated to electromagnetism then; thus this finding had stirred the whole scientific community as either proof of a new revolutionary theory or an amazing coincidence in nature.

Heinrich Hertz, in 1882, experimentally generated electromagnetic waves and showed that they travelled through space at the speed of light. Essentially he created the first radio 'antenna' and 'generator'. His work proved Maxwell's equations, which were not widely accepted then, as well as unified the study of light, electricity and magnetism into the same concept. Funnily enough, when asked about the practical importance of radio waves,

*"It's of no use whatsoever[...] this is just an experiment that proves Maestro Maxwell was right—we just have these mysterious electromagnetic waves that we cannot see with the naked eye. But they are there."*

and when asked for potential uses of his antenna contraption, he said

*"Nothing, I guess."*

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<sup>1</sup>in full; *Treatise on Light: In Which Are Explained the Causes of That Which Occurs in Reflection & Refraction.*

We'll leave it at that, I guess.

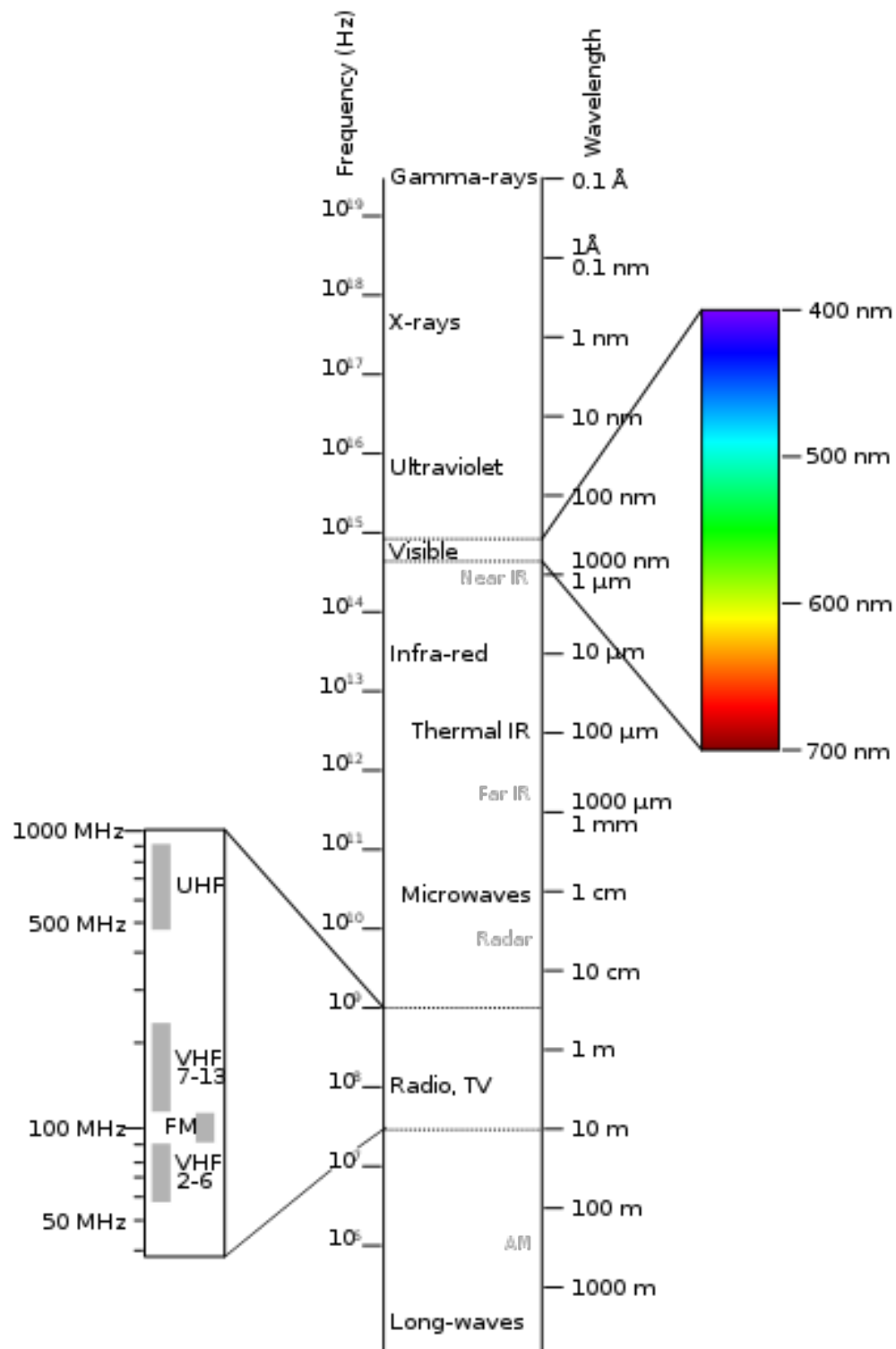


Figure 3.1: The electromagnetic spectrum. Image credit: Victor Blacus CC BY-3.0

### 3.2.2 The wave nature

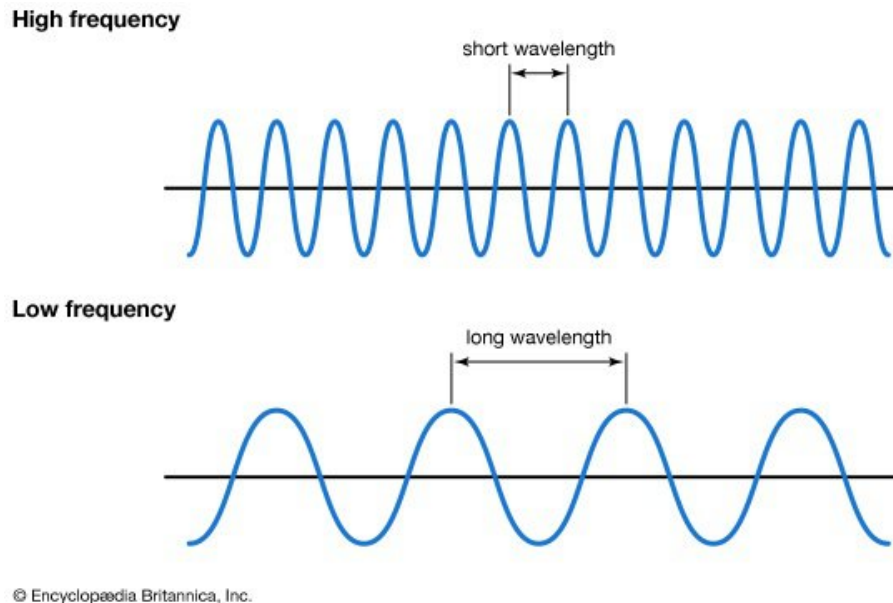


Figure 3.2: Key descriptors of a periodic wave. Credits: *Encyclopedia Britannica*.

Intuitively, a periodic wave can be described with three properties: frequency  $f$ , wavelength  $\lambda$  and its speed,  $v$ . The wavelength of a wave tells us how far, physically, does a wave extend before it repeats again. The frequency tells us how rapidly, in time, does a wave repeat itself. Finally, these two properties are related to the speed at which the wave travels by

$$v = f\lambda \quad (3.3)$$

In the case of light,  $v$  is a famously known value: the speed of light. This quantity is conventionally denoted as  $c$ , and has the value  $c = 299792458 \text{ ms}^{-1}$ . Since the speed of light does not change at all (bar some circumstances), light can be entirely (and is often the case) described with only one of the two variables; application of equation 3.3 would govern the other. The wave-like nature of light motivates us to mathematically describe light in the form of a wave. In its most general form, the equation of a periodic wave looks like:

$$y = A \sin(kx + \omega t + \phi) \quad (3.4)$$

where  $A$ ,  $k$ ,  $\phi$  and  $\omega$  are constants that influence the way the function behaves. As a result, investigating light and its properties translates, mathematically, to solving for these 4 variables.  $x$  represents position in the x-axis and  $t$  represents time, which are typically the variables which we cannot control. In nomenclature,  $A$  is known as the amplitude,  $\phi$  the phase of the wave,  $k$  the angular wavenumber and  $\omega$  the angular frequency.  $k$  and  $\omega$  are related to wavelength and frequency via the following equations;

$$k = 2\pi/\lambda \quad (3.5)$$

$$\omega = 2\pi f \quad (3.6)$$

### 3.2.3 Optics

Optics is the study of behaviour and properties of light and its interactions. We must therefore venture into the field of optics to understand how to measure the properties of light.

## Ray optics

In earlier education, you may have come across a simple treatise in optics. Light is treated as rays, and lenses serve to bend the path of light. From this, we are able to predict how light would travel. The assumption that light can be treated as simple linear rays is known as the paraxial ray theory, and hinges on the key assumption in its namesake:

*Light must travel at an angle that is small when measured from the optical axis of the system.*

In any optical system that we study, we must first define a principal axis. The principal axis is an imaginary line that is drawn, such that if light would approach the system nearly parallel to this axis, it would interact the same regardless of position around the principal axis. This is known as having some degree of rotational symmetry; were you to rotate around the optical axis, the system would look the same to you. If one approaches the lens from above the optical axis, it must be affected in the same way as it would if it approaches from below the optical axis; in this case, they both converge to the same spot F in the diagram.

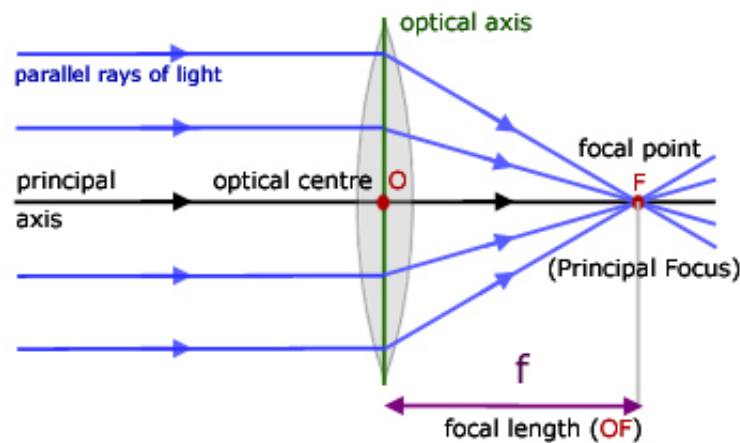
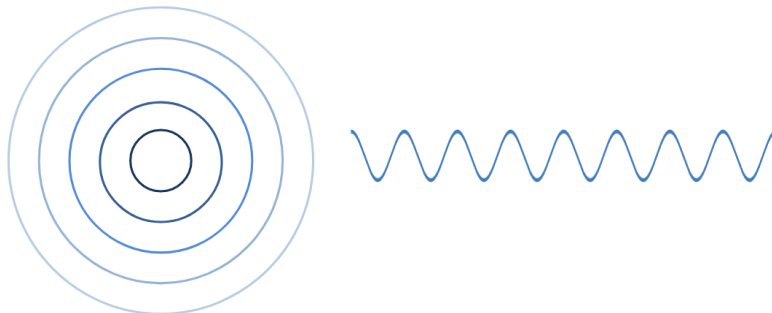


Figure 3.3: A labelled example of a typical optical diagram.

## Diffraction

As much as we would like to treat light as rays for their simplicity, ray optics is extremely limited in explaining what light can do. If we wish to study the properties of light, then we must rely on a theory or method that hinges on the behaviour of light. The paraxial theory makes no concession for its wavelength; it is after all one of the earliest models of light. The ideas behind Huygen's *Treatise* are discussed from here on. To measure the wavelength of light, we must accept the behaviour of light as a wave, and as such treat it accordingly. Diffraction is one such phenomenon that is related to waves.

To understand diffraction, let us first take a step back to visualize a water wave. Imagine you throw a stone into a pond of water. What will you see?



We should see something that looks like the picture on the left, but intuitively we know that the pattern is made up of water waves that looks like the picture on the right.

The lines in picture on the left is what we call circular wavefronts. They are formed by (water) waves coming from the point source (your stone). Each line/wavefront represent a set of points at which the waves are in-phase (same  $\phi$  angle in the sinusoidal wave). If the light source comes from very far, the circularity of the wavefronts begin to become insignificant and instead appear parallel.

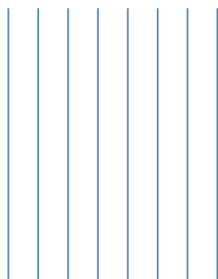


Figure 3.4: Parallel wavefronts from a light source far away. Each line represents a top down view of waves; the lines connect waves at their maxima together.

Diffraction is a phenomenon which occurs when waves meets an obstacle in the form of aperture (hole) or edge. The Huygens-Fresnel principle states that every point on a wavefront can be treated as a source of a circular wave. When the waves travel parallel, each point on a wavefront emits its own circular wavefront, and cancel out because of *superposition* (discussed right after this.), remaining parallel. However, if the parallel wavefronts are blocked by any opaque material, some sections of a parallel wavefront can no longer cancel each other out. As such one can have a diffraction phenomenon as such:

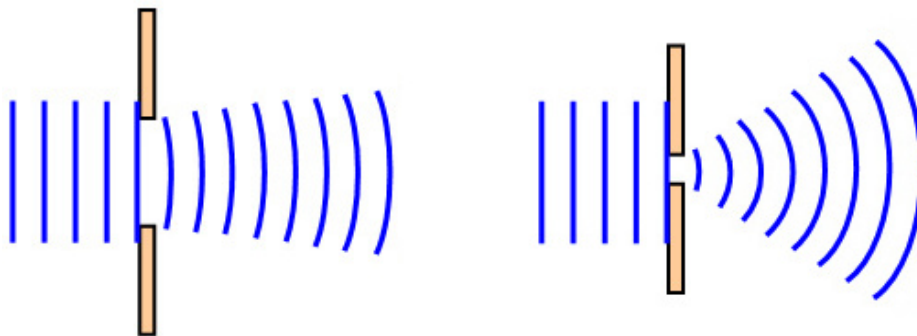


Figure 3.5: Diffraction through slits of different sizes.

## Superposition

The superposition principle tells us that when waves physically overlap, their amplitudes can be added up. As such, the phases of the waves are important when superposing them; it can determine the amplitude of the individual waves at that point.

When two waves are in phase, such that their phase *differences* are even multiples of  $\pi$ , then they are said to constructively interfere and will add up. On the other hand, if they are odd integer multiples of  $\pi$ , then they destructively interfere with each other and results in a minimum. It is from the superposition principle that the Huygens-Fresnel principle explains and accounts for diffraction.

**Go to Activity 1.**



## Diffraction Pattern

Since every gap can allow for the wave to act as a point source, then a series of gaps can be treated as a series of point sources at different fixed positions. This sets up a very interesting situation, as we are in position to consider what happens between the path differences between two sources. This is known as the double-slit diffraction problem, and is easily extendable to many arbitrary slits, or equivalent sources.

Light from two (or more) slits travel a different distance to the same point on a screen. Due to the path difference, there will be phase differences and constructive/destructive interference will occur. The condition for maximum constructive interference is

$$d \sin \theta = m\lambda$$

where  $m$  is an integer. As a result, we see alternating bright and dark spots on the screen as the angle  $\theta$  varies, due to constructive and destructive interference respectively.

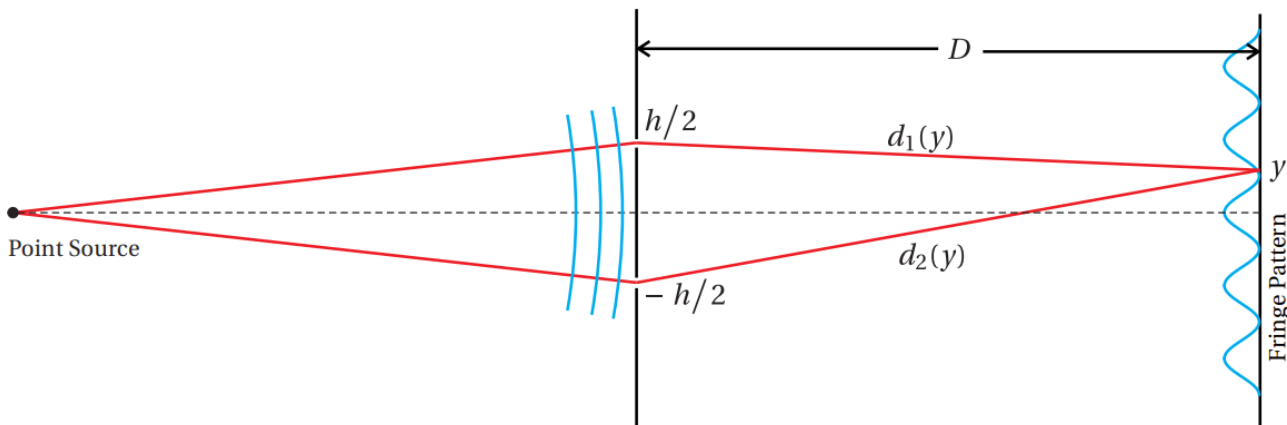


Figure 3.6: Diagram of the double slit setup. Adapted from Peatross & Ware, *Physics of Light and Optics*.

We arrive at a phenomenon that depends on the wavelength of the light that we are observing: the maxima at which the interference pattern occurs depends on the wavelength. Light of different wavelengths will have maxima at different distances from the central maxima, which is denoted by  $y$  here. It was also found that the more slits there are, the sharper and clearer these maxima become. Thus, we employ diffraction gratings which have many grooves or gaps to allow light through, or reflect them, periodically across very small distances. Diffraction gratings can arise from (regular) imperfections on a surface; a metal ruler or even your phone screen can serve as a diffraction grating.

**Go to Activity 2.**

## Wave-Particle duality of Light

Occurring in the early 1900s was the ultraviolet catastrophe, an observation that was irreconcilable with the wave theory of light. Max Planck proposed a solution to this problem by unwillingly assuming that energy carried by light had to be quantized. The quantization of light was so successful in solving the problem that it even accurately predicted the entire emission spectrum of objects. This problem will be revisited later.

The success of quantization and particle-like light as a concept did not stop there. In 1905, Albert Einstein's Nobel prize winning work on the photoelectric effect was also evidence of light quantization. In his experiment, he showed that by shining light of low frequency, no matter how intense, could not generate electrical current from a polished metal surface, indicating an insufficiency of energy to do so. However, once the frequency was raised past a certain value, an electrical current was observed, regardless of how strong the light was. This pointed towards some form of quantization with regards to the frequency (or equivalently, wavelength) of light. These successes reinvigorated the corpuscular theory of light.

In modern physics, we also treat light as quantized particles, capable of many things a classical particle could do such as carry momentum. Today, we understand that in the quantum regime, light exhibits both particle and wave nature, famously known as the *wave-particle duality*. The Planck-Einstein concept of light as a particle states that a single light particle known as the photon, carries a packet of energy  $E$  equivalent to

$$E = hf = h\frac{c}{\lambda} \quad (3.7)$$

Where  $h$  is the Planck's constant,  $6.626 \times 10^{-34} \text{ Js}^{-1}$  and the last equality holds from substitution using equation 3.3. This extended further meaning of a wave's properties into its particulate nature: the frequency of light not only denotes the rate at which it repeats, but also the energy it carries.

**Go to Activity 3.**

### 3.3 Spectroscopy

We rounded off the section on optics with a very important property of light: diffraction patterns through gratings. By employing diffraction gratings, light of **different wavelengths are distributed differently across space**. This is instrumental because it allows us to break down incoming light into its constituents; you may think of it as reverse superposition across space. The technique and field of splitting light into different wavelengths and observing its interactions with other matter is known as spectroscopy. A famous and early example of spectroscopy is Newton's prism where Sir Isaac Newton was able to split light from a pinhole into its constituent colours using a glass prism. The image formed as a result of performing spectroscopy is known as a spectrum, detailing the presence of the constituents of the light measured. Over the years, new methods and equipment were developed to split light more effectively and precisely.

#### Emission spectra

Optics and spectroscopy has had a long runway to develop; even in the 1800s, the spectra of all kinds of light sources were investigated. An emission spectra is one type of spectrum, by which an object is allowed to emit light. This light is then collected and split into its constituents. For many sources such as fire, light bulbs and even the sun, a continuous spectrum was observed. However, when elements were heated and allowed to emit or excited through electrical means, scientists observed that their emission spectra were discrete and not continuous. No one was able to explain why, even though many empirical observations and formulae were written. One famous example is the Rydberg formula by Johannes Rydberg:

$$\frac{1}{\lambda} = RZ^2 \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \quad (3.8)$$

The Rydberg formula originally describes the relationship between the discrete emission lines observed and their wavelengths. It was eventually found to be extendable to certain specific elements such as sodium and lithium. Discreteness of the emission is captured by number  $n$ : these values are only allowed to take integer values, and emissions are described from a higher integer  $n_2$  to a lower  $n_1$ .

As heavier elements were investigated, the emission spectra quickly become very complicated; some having very fine differences as well as having many more emissions. Compare the complexity of Hydrogen's spectra to that of Iron:

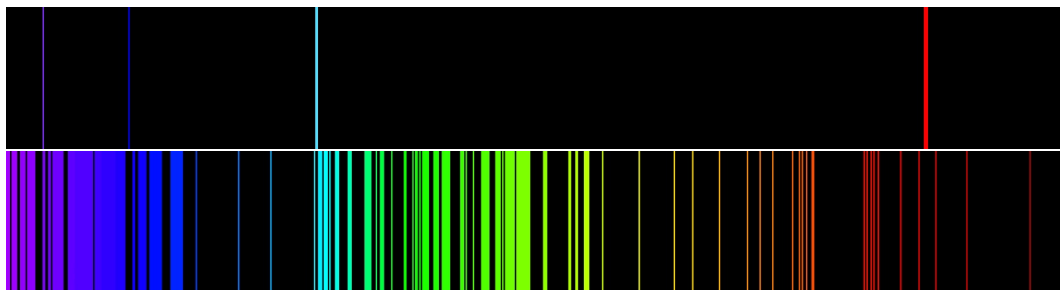


Figure 3.7: Emission Spectra of Hydrogen (top) and Iron (bottom)

This then became a huge problem that physicists were unable to solve for a long time: What governed these emissions, and why were they unique to each element? Even after repeating spectroscopy on materials under different conditions such as temperature or pressure, the emission spectra remained the same. As a result, emission spectras of atoms could be used as a elemental "fingerprint": if one had a catalog of individual spectrum of elements, then given an unknown spectrum, one can find what elements are found in the source of the emission! This is known as *atomic emission spectroscopy* and is highly useful in probing materials at very low quantities. Therefore, despite the puzzling nature of the discreteness of emissions from elements, they were very useful.

**Go to Activity 4.**

## Blackbody radiation

When we have an object made up of a dense collection of particles in motion, the distribution of kinetic energies give rise to a measurable macroscopic quantity called temperature<sup>2</sup>. Any object with a non-zero temperature will give out light in the form of blackbody radiation. This form of light has a continuous distribution of wavelengths. The key differences between blackbody radiation and atomic emissions are summarised in the table below.

Atomic emission	Blackbody radiation
Discrete lines	Continuous band
Dilute samples. Little or no interaction between particles	Collective effect of many particles that interact
Highly sensitive to chemical composition	Only depends on temperature
<i>Intrinsic</i> property	<i>Extrinsic</i> property

Earlier, we discussed the successes of the particulate nature of light in the late 1800/early 1900s. The problem faced by Max Planck, known as the ultraviolet catastrophe, is exactly this phenomenon of blackbody radiation. Consequentially, this broad and continuous distribution of radiation emitted by hot objects is known as the Planck distribution. We will not dwell too long with blackbody radiation as we will save the more in-depth discussions on this topic in a later chapter. In the meantime, to get a better understanding of blackbody radiation, **go to Activity 5**.

Are there any light emission that is a combination of both blackbody and discrete transitions? Study the spectrum of a galaxy (SDSS object 582093484903825431) below.

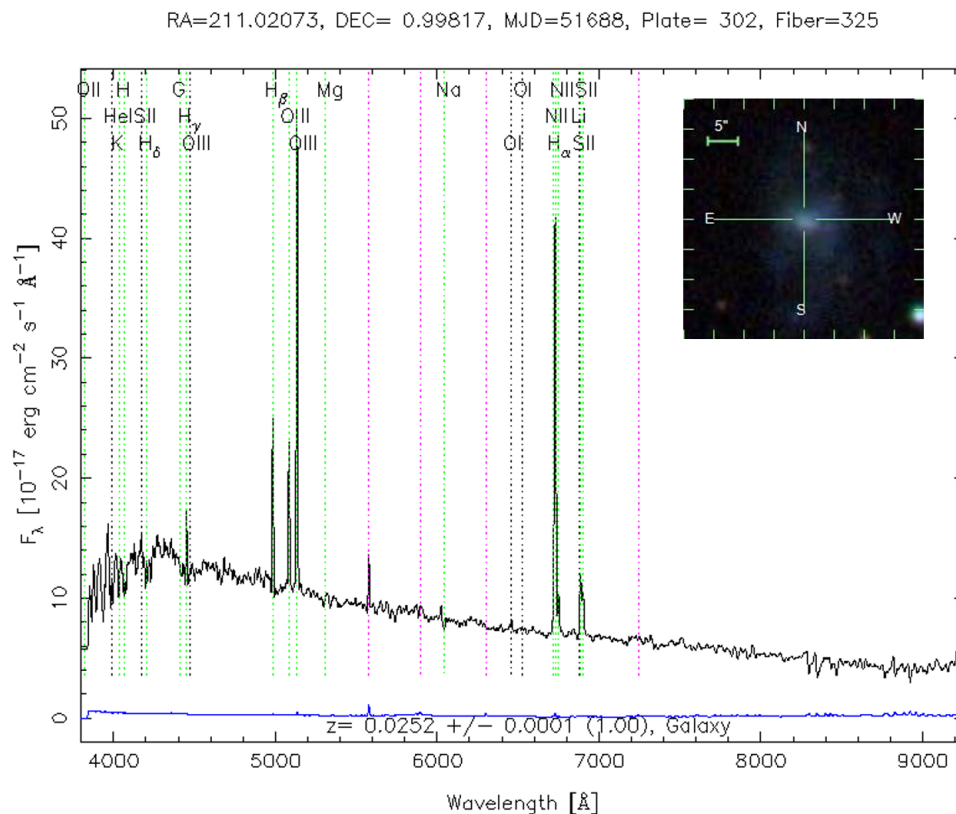


Figure 3.8: Spectrum of a galaxy showing both continuous blackbody and discrete atomic emission peaks. Image credit: SDSS

<sup>2</sup>Apologies for the high number of technical terms in this one statement! Each term is not hard. The difficulty is understanding their relation to each other.

## Absorption spectra

Another method to probe a sample's constituent elements is to perform the opposite of an emission spectra: an absorption spectra. As it turns out, just as specific wavelengths of light is emitted by an element, shining light with those same wavelengths will result in absorption; collecting the light that passes through and splitting it is known as an absorption spectra.

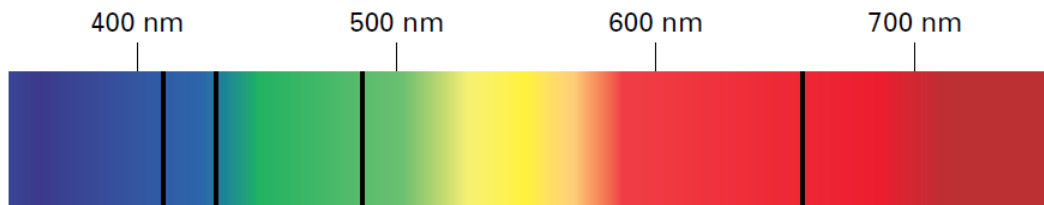


Figure 3.9: Absorption spectra of hydrogen. Credit: Chemblog, *Atomic Theories*

A typical setup for absorption spectroscopy is shown below. The sample is illuminated by a broadband light source. Certain wavelengths of light will be absorbed by the sample. The light that passes through the sample is split by a diffraction grating or prism and the spectrum is collected by photodetectors or a camera for analysis. Absorption spectroscopy is probably the most commonly used spectroscopic technique used in research and industrial labs.

Additionally, spectroscopy has proven exceptionally useful in probing things that are (i) delicate and precious or (ii) hard to access, which categorically encompass many things such as dinosaur fossils, artwork, new materials, and of course celestial objects.

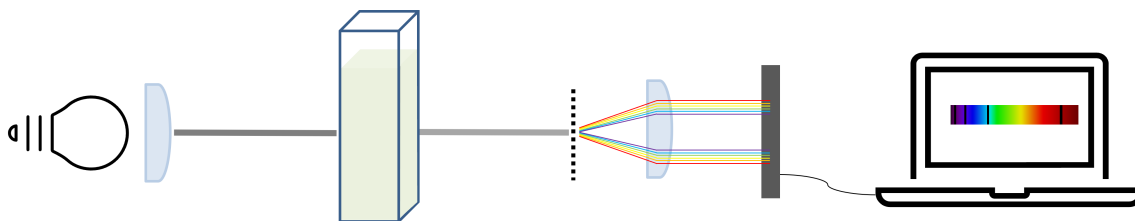


Figure 3.10: A typical setup for absorption spectroscopy.

### 3.3.1 Stellar Spectroscopy

In 1802, the spectrum of our very own star was studied, and was found to have interesting properties and dark fringes. In 1814, Joseph von Fraunhofer studied the wavelengths at which these dark fringes occurred and classified them, giving rise to the eponymous Fraunhofer lines. The Fraunhofer lines give us insight to both the solar and planetary atmospheres, since light from the sun must have interacted with both before reaching the surface of Earth.

In more modern times, one can efficiently collect light from other stellar sources to analyse their spectra. The figure below shows a spectrum of a star (SDSS object 75094094052851712).

RA=145.44053, DEC=-0.72904, MJD=51630, Plate= 266, Fiber=259

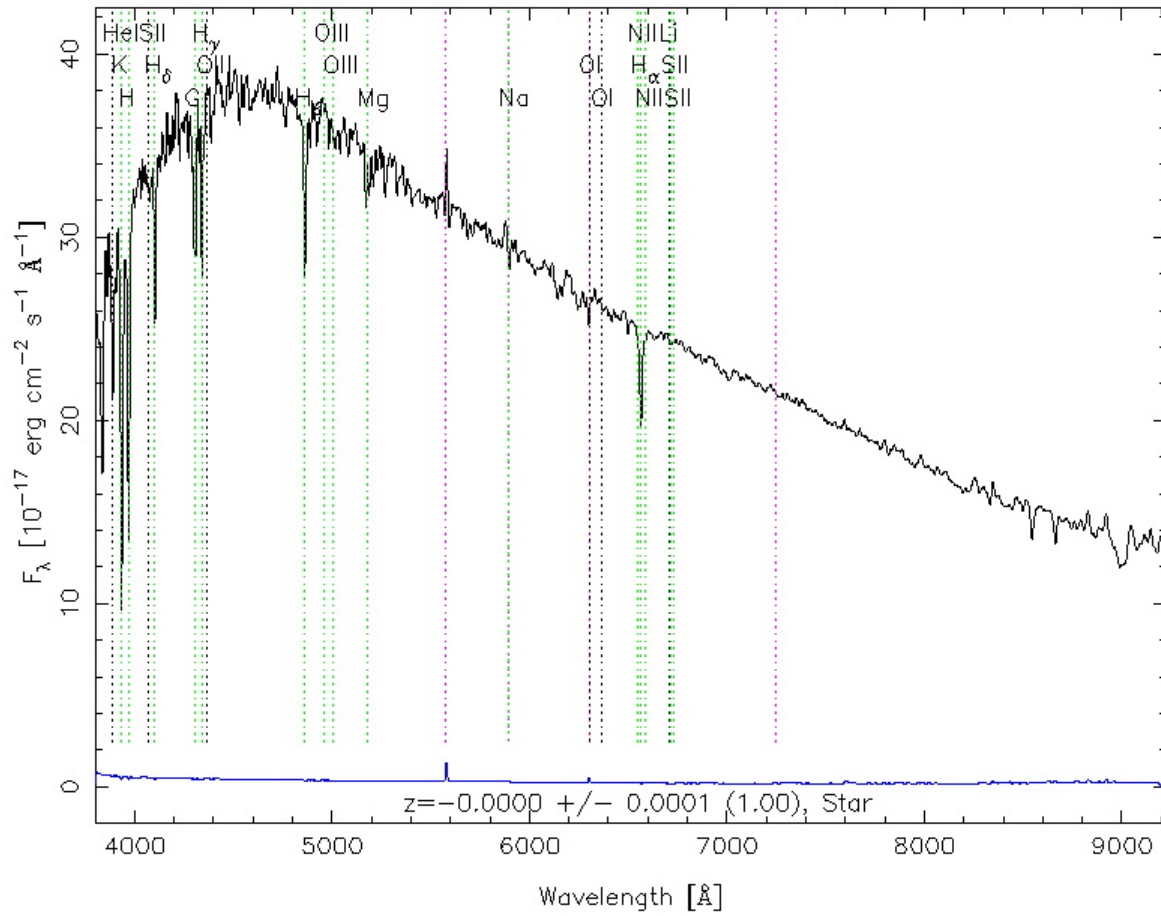


Figure 3.11: Spectrum of a star showing both continuous blackbody and discrete atomic absorption peaks. Image credit: SDSS.

Through spectroscopy, we are able to identify what stars are actually made of, and with that, we are able to build an understanding of the cosmos.

In summary, the light being absorbed and emitted by elements encodes information about the atoms themselves. The principle is straightforward, and a wide variety of problems can be solved by this technique. However, at this stage, we are unsure of how the atom is able to accept and emit very specific wavelengths of light. To understand how it does so, we must travel back in time once again to follow the models that tried to explain what the enigmatic atom is.

**Go to Activity 6.**

## 3.4 Atomic Models Throughout History

Towards the end of the 1800s, most problems in classical physics were considered solved; they were either solved ingeniously or were decided that they had too much computational cost. The problems left, in principle, were solvable, given enough time to calculate (back then, by hand). People widely thought that physics was nearing its limit. However, it was eventually to be found that classical theories failed to account for various phenomena in atomic physics.

The atomic model was a huge point of debate for scientists back then; only the most creative of methods would allow them to investigate something smaller than any microscope could hope to see. First, a quick summary of what an atom has:

- Protons: particles with a small unit positive electrical charge, known as an elementary charge  $+e$ .
- Neutrons: particles with a very similar mass to a proton, carries no electrical charge.
- Electrons: particles with a *negative* electric charge,  $-e$ . Also significantly lighter than protons and neutrons.

### Plum Pudding model, 1904

The plum pudding model was proposed by J.J. Thompson in 1904, in which the discovery of electrons, which are very small particles that carry a singular unit of negative charge, led him to envisage atoms as negatively charged electron particles held together by a cloud of positive charge. Protons and neutrons were not discovered yet.

### Rutherford model, 1911

Ernest Rutherford investigated the Plum pudding model and quickly realised that it was wrong; the famous Rutherford Scattering experiment showed that the atom had to be composed of an extremely dense nucleus surrounded by a sea of electrons. Scientists were largely satisfied with the Rutherford model based on whatever experiments they could do with an atom, albeit for a gap in understanding of how the electrons behave in the atom.

Consider just one of the electron. Since the nucleus is positively charged with  $+Ze$ , and the electron is negatively charged with  $-e$ , there is an attractive Coulomb force  $\mathbf{F}_E$  between them given by

$$\mathbf{F}_E = -\frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r^2} \hat{\mathbf{r}} \quad (3.9)$$

where  $\epsilon_0 = 8.854 \times 10^{-12} \text{m}^{-3} \text{kg}^{-1} \text{s}^4 \text{A}^2$  is a constant,  $r$  is the distance between the nucleus and the electron, and  $\hat{\mathbf{r}}$  is the radial unit vector. With this attractive force, shouldn't the electron fall into the nucleus? Not necessarily! Recall how planets orbit around a star under the influence of an attractive gravitational force. Motivated by the planetary model, Rutherford suggested that the electron is to orbit around the nucleus under the influence of the Coulomb force.

There is however something peculiar about charges (that do not apply for uncharged masses such as planets): When charges accelerate, they emit radiation (light) and lose energy. This means that the electron will lose energy (continuously) during the orbit and will spiral into the nucleus. A planetary model atom should not even last for a second!

Enter Niels Bohr. He knew of Planck's and Einstein's new idea of a quantised light particle (didn't quite like the idea though), and also Rutherford's new planetary atom (this idea he loved!). He did not regard the abovementioned shortcoming of Rutherford's model as a no-go. His intuition led him to believe that the workings of the subatomic world should not be ruled by classical theories. Through a series of educated guesses, Bohr then assumed that when electrons orbited around the nucleus, not any kind of orbits would do; only specific orbits would be allowed in the atom. After working for a year on this problem, he had a breakthrough when he came to realise that Rutherford's planetary model with discrete allowed orbits can be used to derive the emission/absorption spectrum of hydrogen. With that he laid down his atomic model with three postulates (fancy word for assumptions).

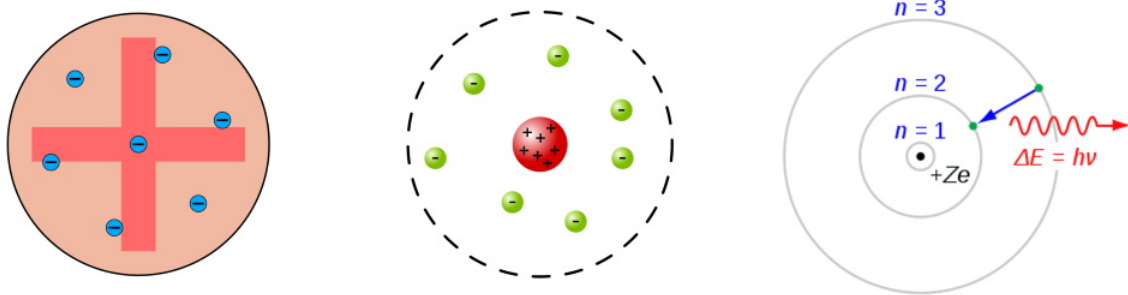


Figure 3.12: Atomic models. Left: Thompson's Plum pudding model. Center: Rutherford's model with a dense positively charged nucleus. Right: Bohr's model with electrons orbiting at specific energy levels. Image credits: (Left) Kurzon, CC BY-SA 4.0; (Center) Bensteele, CC BY-SA 3.0; (Right) JabberWok CC BY-SA 3.0.

### 3.4.1 The Bohr atomic model (1913)

The 3 postulate of Bohr's model of an atom are:

1. **Electrons** move in a **circular orbit** around the nucleus, much like how the earth orbits around the sun.
2. The **angular momentum** of the electron is **quantized**.
3. Any change in the electron's energy is caused by the emission or absorption of a **quantized packet of light known as a photon**.

Let us look into each of the postulate in detail.

#### Postulate 1

The electron orbits the nucleus in circular motion described by the following equation,

$$\mathbf{F} = -\frac{m_e v^2}{r} \hat{\mathbf{r}} \quad (3.10)$$

where  $F$  is the (resultant) centripetal force exerted on the object in motion,  $m_e$  is the mass of the electron,  $r$  is the radius of the circular motion, and  $v$  the speed of the electron in circular motion. We also know that the electric force exerted on the electron to be given by Eq.(3.9).

In the absence of all other forces, the electric force is the only force providing for the centripetal force. This gives us

$$m_e v^2 = \frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r} \quad (3.11)$$

#### Postulate 2

Much like how momentum is a measure of a body's tendency to remain in its linear motion, angular momentum is a measure of a body's tendency to remain in its rotary motion. For the electron in circular motion, the angular momentum  $L$  is given by

$$L = m_e v r \quad (3.12)$$

At this point, Bohr took a bold step and believed that angular momentum is quantized:

$$L = n \frac{h}{2\pi} = n\hbar \quad (3.13)$$



where  $n$  is a **positive integer** (i.e.  $n = 1, 2, 3, \dots$ ), and  $h$  is Planck's constant.  $\hbar = h/2\pi$  which is read as h bar, is a convenient shorthand notation. Putting Eq.(3.13) into Eq.(3.12), we have

$$m_e v = \frac{n\hbar}{r}$$

Putting this into Eq.(3.11), we have

$$\begin{aligned} \frac{n^2 \hbar^2}{r^2} &= m_e \frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r} \\ r &= \frac{4\pi\epsilon_0 n^2 \hbar^2}{m_e Ze^2}, \quad n = 1, 2, 3, \dots \end{aligned} \quad (3.14)$$

Note that now the radius of orbit is quantised, meaning that we can only find electrons at fixed radii from the proton; no closer or further. The speed of the electron is also fixed; it is neither too fast nor too slow!

You may have heard of “energy levels” of an atom. These refer to the possible discrete energies of an electron can have based on it's quantised radius of orbit. To work out the energy levels, we need to digress a little.

The potential energy of an electron experiencing Coulomb force Eq.(3.9) is given by<sup>3</sup>

$$V = -\frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r}$$

We write the potential energy with a negative sign because the electrons are bound to the nucleus: the electron would require extra energy to escape from the electric attraction from the positively charged nucleus.

Total energy of the system is given by

$$\begin{aligned} E &= \text{Kinetic energy} + \text{Potential Energy} \\ &= \frac{1}{2} m_e v^2 - k \frac{Ze^2}{r} \\ &= \frac{1}{2} \frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r} - \frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r} \quad (\text{see Eq.(3.11)}) \\ &= -\frac{1}{8\pi\epsilon_0} \frac{Ze^2}{r} \end{aligned}$$

Putting the quantised radius Eq.(3.14) into the above, we have

$$E = -\frac{Z^2 e^4 m_e}{32\pi^2 \epsilon_0^2 \hbar^2 n^2}, \quad n = 1, 2, 3, \dots \quad (3.15)$$

### Postulate 3

Eq.(3.15) gives discrete or quantised energies of an electron. The value of the energy depends on the integer value of  $n$ . The higher the  $n$ , the higher (less negative) the energy. The electron can transit from one energy level to another. But to do so, it must gain or lose the exact amount of energy difference by absorbing or emitting a photon with the specific energy.

$$hf = |E_{\text{final}} - E_{\text{initial}}| \quad (3.16)$$

For example, when an electron to fall from  $n = 3 \rightarrow 1$ , it will emit a photon of energy

$$E = hf = \frac{Z^2 e^4 m_e}{32\pi^2 \epsilon_0^2 \hbar^2} \left( \frac{1}{1^2} - \frac{1}{3^2} \right) = \frac{Z^2 e^4 m_e}{36\pi^2 \epsilon_0^2 \hbar^2}$$

The curious case of the Rydberg formula (Eq.(3.8)) was finally solved: the hydrogen spectra had puzzled scientists for many years until the day Bohr published his model. Bohr's model accurately predicted every single transition the Rydberg formula gave while giving meaning to the seemingly unknown coefficients present in it. The true success of the Bohr model comes from the results of the quantized energies and its ability to derive the Rydberg formula, which was first found empirically from experimental data. To this day, despite some shortcomings, the Bohr model remains an extremely important concept in modern physics.

<sup>3</sup>This “Coulomb potential” can be obtain from the Coulomb force given in Eq.(3.9) and the general force-potential relationship  $F = -\frac{dV}{dr}$

### 3.4.2 The Hydrogen Atom

Through Bohr's model, we found that energy transitions in the hydrogen atom between its different energy levels absorb or emit light. Furthermore, they should be extremely sharp and distinct: the energy levels are significantly far from each other. This means that every atom has a specific set of wavelengths that it would emit. The whole group of emissions could be further classified into the specific energy level that is involved in the transition; every transition between distinct energy levels can be uniquely identified by the light emitted or absorbed.

The energies of each level can be computed using equation 3.15, varying  $n$  for the different energy levels. Since energy cannot be created or destroyed, then we know that when a transition occurs from one state to another, the difference in energy levels must exactly correspond to the energy of the photon emitted or absorbed. Transitions that involve the innermost shell,  $n = 1$ , is eponymously known as the Lyman series and is predominantly ultraviolet. As such, we are unable to observe it with our eyes (we can most definitely detect it with sensors).

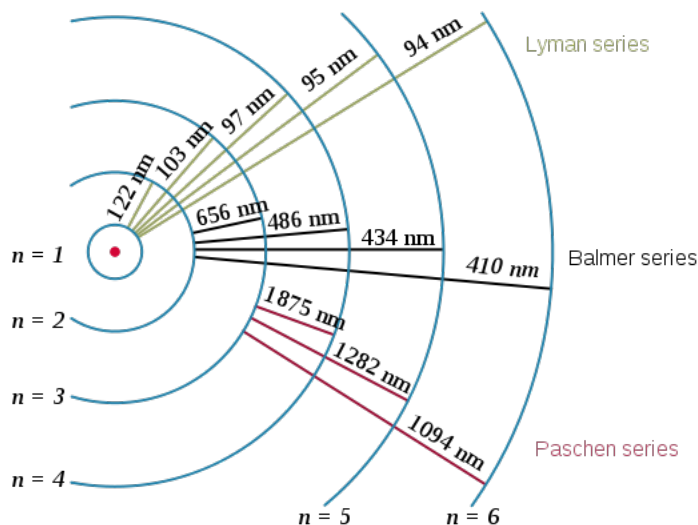


Figure 3.13: Electron transitions across states in Bohr's Hydrogen model. Credit: Szdori, OrangeDog, CC BY-2.5.

On the other hand, transitions to the second energy level  $n = 2$ , known as the Balmer series, lie predominantly in the visible light spectrum. In fact, the Balmer series is exactly the specific wavelengths of light observed in a Hydrogen lamp. The hydrogen emission spectrum is observed when hydrogen de-excites to the second energy level. The signature purple glow seen in a hydrogen lamp is a mixture of these colors, and can be observed clearly with a proper setup in the darkness. This is known as the emission spectra of the element. Since it is the transition that is quantized, we can just as equally try to measure the effects when hydrogen absorbs the energies needed to excite to higher energy levels. Since the other colors are not accepted by the hydrogen atom, we can shine a continuous spectrum of light onto Hydrogen and collect the light that passes through. The hydrogen would have absorbed the light that it can accept, and allow the rest through. The collected light is then analyzed, and we do indeed find the dark fringes where the emission spectra would have been. This equivalent method of finding the spectra is known as the absorption spectrum of the element.

At this point, we are able to mathematically predict the absorption and emission spectra of hydrogen and hydrogen-like atoms using Bohr's model. Any other system involving more than one electron is simply too difficult to calculate by hand (three body problem), and are usually approximated by other methods in quantum mechanics or computationally modelled with Schrodinger's model.

### 3.4.3 Wave Model

Despite its successes in recovering the empirical observation of the Hydrogen emission by a solely theoretical approach, Bohr's model suffered from several shortcomings. Most notably, it was only able to recover the emission spectrum of Hydrogen and other one-electron systems. It is unable to reproduce the results of atomic systems with two or more electrons.

In 1926, Erwin Schrödinger proposed a revolutionary new proposal of using wave mechanics as a way to approach the atomic model. His model builds upon Bohr's model in an attempt to further refine and overcome its shortcomings. It is also alongside this paper where he published the now eponymous Schrödinger equation which will be discussed in further detail later. The basis behind Schrödinger's modification hinges from work contributed by Louis de Broglie. In 1924, de Broglie proposed that our previous distinction between waves and particles, one that is well established at the height of classical mechanics, was to be blurred. He hypothesised that particles, when sufficiently small or fast, begin to exhibit wave-like properties; and when waves begin to carry enough momentum, they begin to obtain particle-like properties. The distinction that is broken is summarised in the following equation, known as the de Broglie relation:

$$\lambda = \frac{h}{p} \quad (3.17)$$

where  $p$  represents momentum, a fundamental property of particles, and  $\lambda$ , the wavelength, a fundamental property of waves. This was just like how light was originally thought of as waves, but eventually wave-particle duality became accepted. According to de Broglie, *everything exhibits wave-particle duality*. This property was eventually experimentally verified when electrons were found to behave like waves under specific conditions. This held enormous consequences; the de Broglie relation could be used to justify the quantization that Bohr proposed.

#### Go to Activity 7.

Applying the concept of matter waves into the Bohr model allows us to understand quantisation more intuitively. Waves exhibit interference. An electron-in-orbit behaving like a wave would loop back to itself and if a standing wave<sup>45</sup> is not formed, the “electron wave” would destructively interfere with itself. As a result, only specific setups that form standing waves were allowed to exist, creating these quantized orbits. These specific setups would eventually come to be known as *atomic or electron orbitals*.

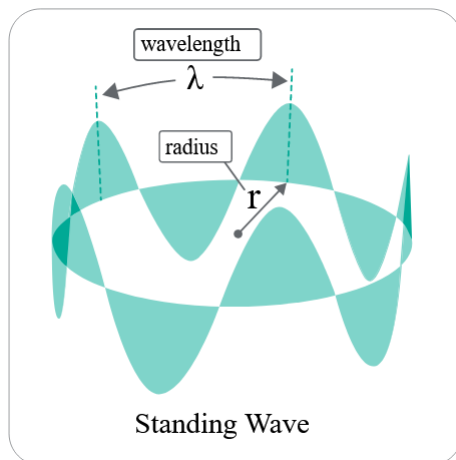


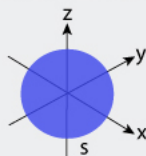
Figure 3.14: A standing wave that wraps around itself in 1D. Source: Khan Academy

<sup>4</sup>Excellent explanation of standing waves from Khan Academy

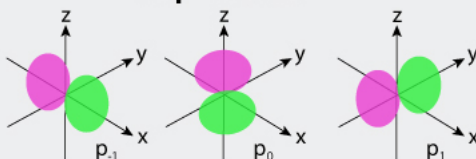
<sup>5</sup>Dr Chammika's awesome demonstration of standing waves :)

# Atomic Orbitals

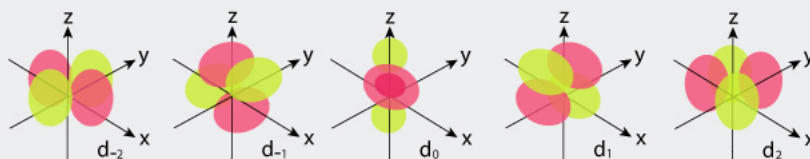
## 1. s-orbital



## 2. p-orbital



## 3. d-orbital



## 4. f-orbital

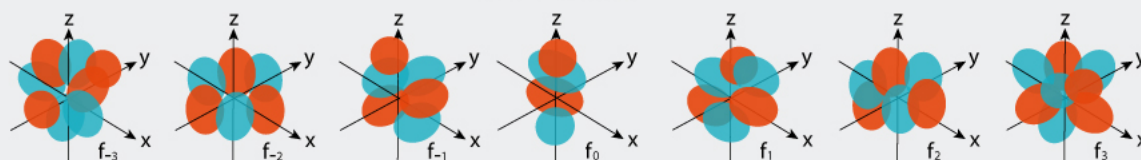


Figure 3.15: The first few atomic orbitals of the hydrogen atom. Credits: Sciencefacts

## 3.5 Quantum Mechanics

### 3.5.1 The Wavefunction and Schrödinger's equation

We shall now dive a little deeper into modern quantum mechanics<sup>6</sup>. From 1925-1927, three versions of quantum mechanics was independently developed by Erwin Schrödinger, Werner Heisenerg and Paul Dirac. They differed drastically from their initial formulism, but were later shown to be equivalent. Here we will adopt the Schrödinger “picture”, as out of the three, it is the least chim<sup>7</sup>.

Schrödinger postulated that a quantum system can be specified completely by a wavefunction:

$$\Psi$$

If one knows the wavefunction, then one will know all the mechanical information such as energy, position and momentum of the system. Schrödinger sought to find a differential equation that relates how the derivatives (change) of the wavefunction of a particle is affected by the energy and boundary conditions it is in.

He starts by assuming that the wavefunction can take on a simple but general wave-like expression:

$$\Psi(x, t) = \psi_0 e^{i(kx - \omega t)} \quad (3.18)$$

where  $\psi_0$  is the amplitude<sup>8</sup> of the wave,  $k = 2\pi/\lambda$  is the wavenumber and  $\omega = 2\pi f$  is the angular frequency (see Eq.(3.5) and (3.6)).

The derivatives of  $\Psi$  are

$$\begin{aligned} \frac{\partial \Psi}{\partial t} &= -i\omega \psi_0 e^{i(kx - \omega t)} = -i\omega \Psi \\ \frac{\partial^2 \Psi}{\partial t^2} &= -i\omega(-i\omega \Psi) = -\omega^2 \Psi \\ \frac{\partial \Psi}{\partial x} &= ik \psi_0 e^{i(kx - \omega t)} = ik \Psi \\ \frac{\partial^2 \Psi}{\partial x^2} &= -k^2 \Psi \end{aligned}$$

Borrowing de Broglie's idea of matter waves where we have

$$\begin{aligned} E &= hf = \hbar\omega \\ p &= \frac{h}{\lambda} = \hbar k \end{aligned}$$

The above derivatives can be rewritten as

$$\frac{\partial \Psi}{\partial t} = -i \frac{E}{\hbar} \Psi \quad (3.19)$$

$$\frac{\partial^2 \Psi}{\partial t^2} = -\frac{E^2}{\hbar^2} \Psi \quad (3.20)$$

$$\frac{\partial \Psi}{\partial x} = i \frac{p}{\hbar} \Psi \quad (3.21)$$

$$\frac{\partial^2 \Psi}{\partial x^2} = -\frac{p^2}{\hbar^2} \Psi \quad (3.22)$$

Using a total energy consideration

$$\text{Total energy} = \text{Kinetic energy} + \text{Potential energy}$$

$$E = \frac{p^2}{2m} + V(x)$$

---

<sup>6</sup>Bohr's version is known as the old quantum mechanics

<sup>7</sup>Singlish term for intellectually deep or astract.

<sup>8</sup>The amplitude can be a complex number, as opposed to real.

Multiply throughout by  $\Psi$  and using Eq.(3.19) and (3.22), we have

$$\begin{aligned} E\Psi &= \frac{p^2}{2m}\Psi + V(x)\Psi \\ i\hbar\frac{\partial\Psi}{\partial t} &= -\frac{\hbar^2}{2m}\frac{\partial^2\Psi}{\partial x^2} + V(x)\Psi \end{aligned} \quad (3.23)$$

The differential equation Eq.(3.23) is known as the Schrödinger's equation (SE). Different systems will have a different potential energy landscape  $V(x)$  and a different set of boundary conditions. By finding the solution of the SE, ie  $\Psi(x, t)$ , one will essentially be able to determine everything that can be known about the system.

The SE however is a difficult equation to solve as it has derivatives in both time  $t$  and position  $x$ . If one is interested to find the “stationary solutions” such as the standing waves mentioned in the previous section, then it is beneficial to remove time from the SE.

To do so, we go back to the assumed general wavefunction in Eq.(3.18) and rewrite it as

$$\begin{aligned} \Psi(x, t) &= \psi_0 e^{ikx} e^{-i\omega t} \\ &= \psi(x) e^{-i\omega t} \end{aligned}$$

Put this into the SE,

$$\begin{aligned} i\hbar\frac{\partial\psi(x)e^{-i\omega t}}{\partial t} &= -\frac{\hbar^2}{2m}\frac{\partial^2\psi(x)e^{-i\omega t}}{\partial x^2} + V(x)\psi(x)e^{-i\omega t} \\ i\hbar(-i\omega)e^{-i\omega t}\psi(x) &= -\frac{\hbar^2}{2m}\frac{\partial^2\psi(x)}{\partial x^2}e^{-i\omega t} + V(x)\psi(x)e^{-i\omega t} \\ E\psi(x) &= -\frac{\hbar^2}{2m}\frac{\partial^2\psi(x)}{\partial x^2} + V(x)\psi(x) \\ \left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)\right)\psi(x) &= E\psi(x) \end{aligned} \quad (3.24)$$

Eq.(3.24) is known as the time-independent Schrödinger equation. This equation is the one that will allow us to calculate the allowed discrete energy states of matter (such as electrons) in the atom or other systems.

For now, we understand a wavefunction as something that contains a particle's mechanical information, and the SE as the equation to solve to obtain the wavefunction as well as allowed energy states. But...

### 3.5.2 What are wavefunctions actually?

The wavefunction  $\Psi(x, t)$  is a complex (as oppose to real) function. Complex quantities cannot be measured in the real world. Is there actually a physical meaning associated with this all-important wavefunction?

No.

But Max Born offered a “working” statistical interpretation to the wavefunction:

$$|\Psi|^2 \equiv \Psi^*\Psi \text{ plays the role of a probability density function.}$$

This interpretation allows one to *use* the wavefunction to find physically relevant stuffs. For example:

$$\int_a^b |\Psi(x, t)|^2 dx = \text{probability of finding the particle between } a \text{ and } b \text{ at time } t$$

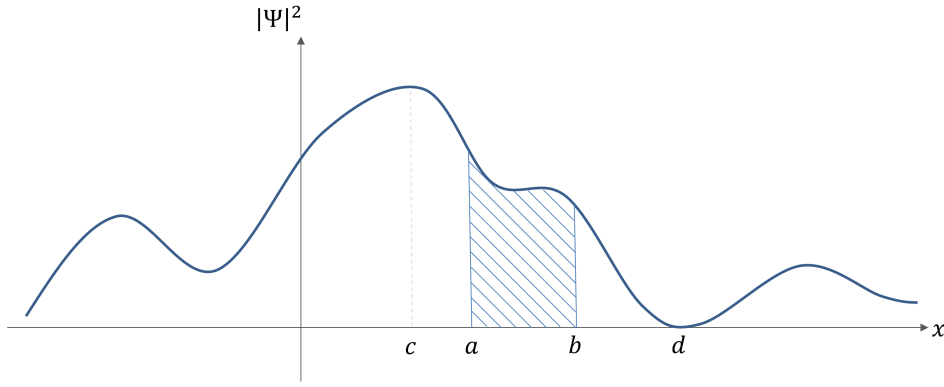


Figure 3.16: The Born interpretation of the wavefunction as a probability density function. The probability of finding the particle in the region  $a < x < b$  is equal to the area under the  $|\Psi|^2$  graph from  $a$  to  $b$ . The probability to find the particle around  $x = c$  is the highest while the probability to find the particle around  $x = d$  is near zero.

With the interpretation of  $|\Psi|^2$  as a probability density function, we have the property that

$$\int_{-\infty}^{\infty} |\Psi(x, t)|^2 dx = 1, \quad (3.25)$$

Eq.(3.25) is a statement that says that  $|\Psi|^2$  is normalised, which simply means that all probabilities add up to 1.

One can go further into the statistical interpretation by looking the expected values and variances of observable physical quantities, but it is out of the scope of the course and we will leave the interpretation and use of  $\Psi$  as is for now.

We can now try and explore how different systems give rise to different wavefunctions and allowed energy states..

### 3.5.3 Particle in a box

The particle in a box problem is a thought experiment made by Schrödinger to illustrate the basics of ‘motion’ in the quantum world. In this section, we will solve the time-independent SE for the particle in box problem<sup>9</sup>.

The formal way to state the problem is to ask what happens to the wavefunction of a single particle along a 1D line when subjected to the following boundary conditions:

$$V(x) = \begin{cases} 0 & \text{if } 0 < x < L, \\ \infty & \text{elsewhere} \end{cases}$$

where  $V(x)$  is the potential at any point in space. For simplicity, we shall assume that the particle’s wavefunction does not change with time.

We will first deal with the case of infinite potential as it is easier. Later we will see what happens when the barriers are finite.

Recall that Schrödinger’s equation states that

$$\left( -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x) \right) \psi(x) = E\psi(x)$$

Inside the box  $0 < x < L$  where  $V = 0$ , we have

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \psi(x)}{\partial x^2} = E\psi(x) \quad (3.26)$$

<sup>9</sup>What ‘solving’ means to physics is that we have to give a (as complete as possible) description of the physical system in question, which is usually aided using mathematical equations.

and the wavefunction outside the box must obey

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \psi(x)}{\partial x^2} + \infty \psi(x) = E \psi(x) \quad (3.27)$$

We can make an educated assumption that the wavefunction outside the box must be zero such that Schrodinger's equation still holds<sup>10</sup> (because  $0 = 0$ ). This also gives us the boundary conditions of the problem:

$$\psi(0) = 0 \quad (3.28)$$

$$\psi(L) = 0 \quad (3.29)$$

But now, what about the wavefunction inside the box?

We can guess the solution must resemble something of form (recall the restoring force case in Chapter 2 and see the similarity of the equations)

$$\psi(x) = ce^{\lambda x} \quad (3.30)$$

Putting the guess solution into the SE, we obtain the general solution to be

$$\psi(x) = c_1 e^{ikx} + c_2 e^{-ikx} \quad (3.31)$$

where

$$k = \sqrt{\frac{2mE}{\hbar^2}}$$

Applying the boundary conditions Eq.(3.28) and (3.29), we will find that

$$c_1 = -c_2$$

and

$$kL = n\pi$$

where  $n$  takes positive integer values. Consequently

$$\psi(x) = A \sin kx$$

and

$$E = \frac{\hbar^2 n^2 \pi^2}{2mL^2} \quad (3.32)$$

$A$  can be determined by normalising the wavefunction with Eq.(3.25). Finally the wavefunction of the particle in a box is

$$\psi(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi}{L}x\right) \quad (3.33)$$

and it's allowed energy levels are given by Eq.(3.32).

Also important is to recall that  $n$  takes only positive integer values, thus effectively quantising the energy states and wavefunction. For this reason,  $n$  is known as the quantum number for particle in a box.

### 3.5.4 Hydrogen atom and its wavefunction

Welcome back to the Hydrogen atom. The hydrogen atom consists of a proton and an electron separated by some distance  $r$ . The potential of the system is

$$V(r) = -\frac{1}{4\pi\epsilon_0} \frac{e^2}{r} = -\frac{1}{4\pi\epsilon_0} \frac{e^2}{(x^2 + y^2 + z^2)^{1/2}} \quad (3.34)$$

---

<sup>10</sup>As physicists we sometimes just take infinity times zero to be zero.



As the system is 3 dimensional, the time independent SE is

$$\left[ -\frac{\hbar^2}{2\mu} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) - \frac{1}{4\pi\epsilon_0} \frac{e^2}{(x^2 + y^2 + z^2)^{1/2}} \right] \psi = E \psi$$

where

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

is so called the reduced mass of the system. We will talk more about the reduced mass in the next chapter. Meanwhile, in here, since the mass of the proton  $m_p$  is much larger than the mass of the electron  $m_e$ , we have  $\mu \approx m_e$ . We can concise the notation and state that the SE of the hydrogen atom is

$$\left[ -\frac{\hbar^2}{2m_e} \nabla^2 - \frac{1}{4\pi\epsilon_0} \frac{e^2}{r} \right] \psi = E \psi \quad (3.35)$$

The boundary conditions are

$$\begin{aligned} \psi(0) &= 0 \\ \psi(\infty) &= 0 \end{aligned}$$

[Translates as: you will not find the electron at the nucleus ( $r = 0$ ) and at somewhere infinitely far away ( $r \rightarrow \infty$ )].

The procedure to solve the SE is same as that of particle in a box: Solve the SE with the above boundary conditions. The workings are much more complicated since the system is three dimensional. The higher dimensionality also means that more quantum numbers are required to describe the allowed states of the hydrogen atom. The quantum numbers are

1.  $n$ , the principal quantum number.  $n = 1, 2, 3, \dots$
2.  $l$ , orbital quantum number.  $l = 0, 1, 2, \dots, n-1$ .
3.  $m_l$ , magnetic quantum number.  $m_l = -l, \dots, -1, 0, 1, \dots, l$ .

The allowed energies of the system is given by

$$E = -\frac{e^4 m_e}{32\pi^2 \epsilon_0^2 \hbar^2 n^2}$$

The wavefunctions for the hydrogen atom are

$$\begin{aligned} \psi_{n=1, l=0, m_l=0} &= \frac{1}{\sqrt{\pi} a_0^{3/2}} e^{-r/a_0} \\ \psi_{n=2, l=0, m_l=0} &= \frac{1}{4\sqrt{2\pi} a_0^{3/2}} \left( 2 - \frac{r}{a_0} \right) e^{-r/2a_0} \\ \psi_{n=2, l=1, m_l=0} &= \frac{1}{4\sqrt{2\pi} a_0^{3/2}} \frac{r}{a_0} e^{-r/2a_0} \cos \theta \\ \psi_{n=2, l=1, m_l=+1} &= \frac{1}{8\sqrt{\pi} a_0^{3/2}} \frac{r}{a_0} e^{-r/2a_0} \sin \theta e^{i\phi} \\ \psi_{n=2, l=1, m_l=-1} &= \frac{1}{8\sqrt{\pi} a_0^{3/2}} \frac{r}{a_0} e^{-r/2a_0} \sin \theta e^{-i\phi} \end{aligned}$$

Here is 2D visualization of the probabilities of the electron's position around the nucleus.

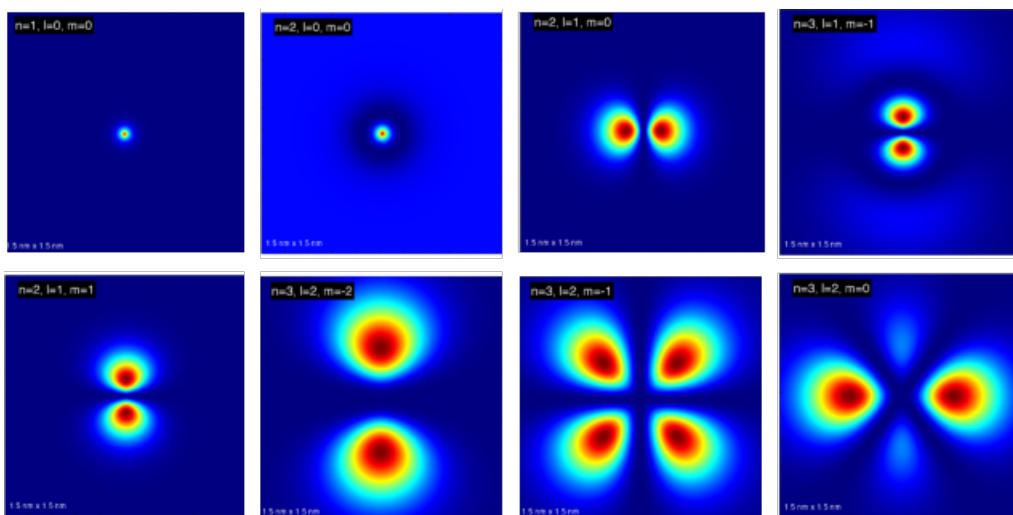


Figure 3.17: Projections of some wavefunctions of the hydrogen atom. Image credit: Chammika Udalagama

The solutions to the hydrogen atom not only opens a pathway to many new rich areas of physics such a molecular physics which is critical to the development of physical chemistry. Let us begin to dive into the how these orbitals play a role in composite systems such as molecules and their necessary rammifications.

### 3.6 Molecular Orbitals

Almost done! Up until now in this chapter, you have seen how we came from plum pudding models to atomic orbitals. At the end of this chapter, we will bring in one last concept called molecular orbitals.

As you have hopefully learned from previous sections, atomic orbitals are essentially functions that describe where electrons are the most likely to be found in an atom. However, what (most) scientists care about are not atoms, but rather molecules which are made up of a bunch of atoms. Thus, it is not surprising that the concept of “orbitals” needs to be extended to the context of a molecule.

But solving the Schrödinger equation to get the atomic orbital of a single H atom is already a non-trivial task, how are we supposed to do that to a molecule? Fortunately, scientists came up with an idea which allows us to obtain a decent guess of what molecular orbitals look like, but involving minimal effort. Motivated by the principle of superposition for waves, the molecular orbitals can be thought of as a superposition of atomic orbitals. This is known as the linear combination of atomic orbitals (LCAO).

Let’s start with something very simple: an  $H_2$  molecule. This molecule is obviously formed by two hydrogen atoms, which we name  $H_a$  and  $H_b$ . These two atoms each have their 1s orbitals, which are denoted as  $\chi_a$  and  $\chi_b$ . When these two atoms approach each other, the electron clouds surrounding them overlap and merge together, and thus the electron probability distribution needs to be described by new functions (molecular orbitals). The possible LCAOs are:

$$\psi_+ = N(\chi_a + \chi_b) \quad \psi_- = N(\chi_a - \chi_b) \quad (3.36)$$

where  $N$  is the normalisation factor. An intuitive way to understand this is to think of the wave functions as actual waves: if you recall from physics courses in the past, waves can interfere with each other either constructively or destructively. In this case, we can understand  $\psi_+$  as a result of constructive interference between  $\chi_a$  and  $\chi_b$ , and  $\psi_-$  as a result of destructive interference (see Fig. Formation of  $\psi_+$  and  $\psi_-$  (Image Credit: Seow Ryan) for visualization).

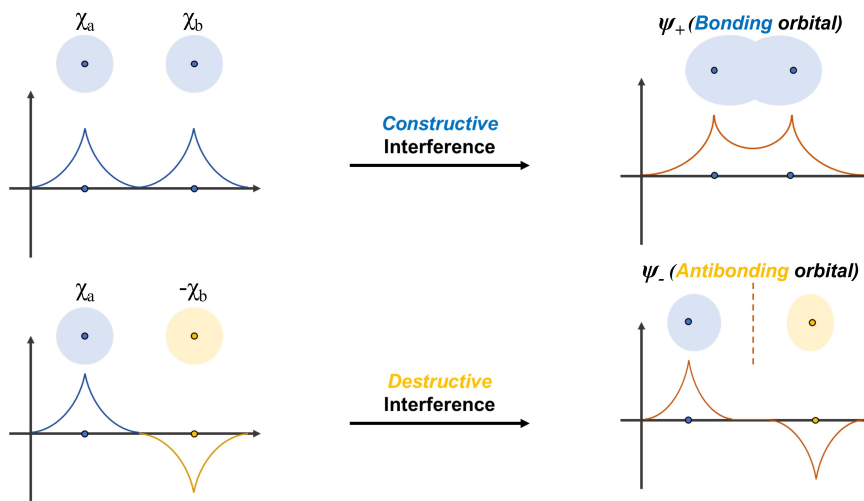


Figure 3.18: Formation of  $\psi_+$  and  $\psi_-$  (Image Credit: Seow Ryan)

Moreover, just like how each atomic orbital has its corresponding energy, here the two molecular orbitals we created also have specific energies. The molecular orbital that arises from constructive interference ( $\psi_+$ ) has the energy  $E_1$ , which is lower than the energies of the two atomic orbitals. On the other hand,  $\psi_-$ , which comes from destructive interference, has the energy  $E_2$ , which is higher than the energies of the two atomic orbitals. By filling both electrons into  $\psi_+$ , the total energy of the molecule is lowered compared to the two individual atoms. This is where bonding comes from! This is why we give  $\psi_+$  is called the bonding orbital, and  $\psi_-$  the antibonding orbital. In summary, this is all shown in the molecular orbital diagram below (Fig. (MO diagram of  $H_2$  molecule. (Image credit: Shriver & Atkins' *Inorganic Chemistry*, Fifth Edition.))).

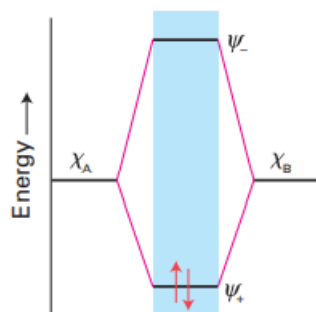
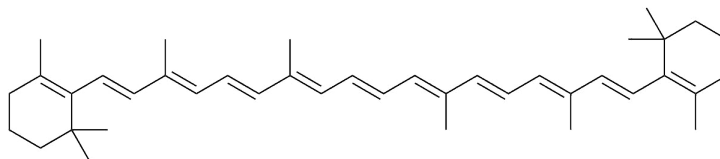


Figure 3.19: MO diagram of  $H_2$  molecule. (Image credit: Shriver & Atkins' *Inorganic Chemistry*, Fifth Edition.)

Just like how transitions between different energy levels in a hydrogen atom, transitions between molecular energy levels also correspond to absorbing and emitting light. A famous example is  $\beta$ -carotene, which is the pigment that gives carrots their orange colour. The most prominent energy transition of this molecule corresponds to the absorption of blue light, which is why this molecule is orange in colour!

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Ex.



Shown above is the molecular structure of  $\beta$ -carotene. Given that its most prominent energy transition corresponds to an energy gap of  $2.050 \times 10^{-19}$  J, verify that this corresponds to blue light. (hint: use  $E = \frac{hc}{\lambda}$ !)

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Let's make one final return to the  $H_2$  molecule. What do you expect its emission spectrum to look like? Following the logic shown above, you may expect to see one single emission line that corresponds to the energy  $E_2 - E_1$ . However, take a look at Table 1 of this paper: the actual emission spectrum of  $H_2$  observed by telescopes is actually much more complex!

Why? Chapter 4 awaits you!

## 3.7 Class Activities

### Activity 1

Watch the ripple tank demo in lecture. Play with it in if time allows. Note the interference pattern.

On Desmos and enter the following lines:

$$\begin{aligned}f &= \cos x \\g &= \cos(x + \phi) \\f + g\end{aligned}$$

Click to add slider for  $\phi$  the phase angle, and set it to go from 0 to  $2\pi$ . Slide to see how  $g$  changes for different values of  $\phi$ . Also observe how the superposition of the two waves  $f + g$  changes.

Relate the math (graphs on Desmos) and the phenomenon (waves in ripple tank).

### Activity 2

Form diffraction patterns using a thin wire, double slits, etc, and a laser.

### Activity 3

Watch the photoelectric effect demo in lecture and try it out during tutorial.

### Activity 4

Use a diffraction grating to look at various light sources: Gas discharge lamps, LEDS, incandescent light bulb, etc.

### Activity 5

Play with the PheT blackbody simulator. PhET.<sup>11</sup>

### Activity 6

Use a portable spectrometer (OceanOptics) to see the spectrum of sunlight. Think of what is inside a spectrometer.

### Activity 7

See electron diffraction demo. Explain the observations.

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<sup>11</sup>[https://phet.colorado.edu/sims/html/blackbody-spectrum/latest/blackbody-spectrum\\_en.html](https://phet.colorado.edu/sims/html/blackbody-spectrum/latest/blackbody-spectrum_en.html)

### 3.8 Discussion Questions

1. Waves exhibit superposition. What physical phenomena are a result of superposition of waves?
2. We saw how light passing through 2 slits exhibit a diffraction pattern and understood it from the principle of superposition. Light passing through a single slit also creates a diffraction pattern. Explain single slit diffraction qualitatively.
3. How did Einstein use the particle model of light to explain the findings of the photoelectric effect experiment?
4. How is spectroscopy used in other areas of science? Name some examples!
5. Derive the Rydberg formula Eq.(3.8) using the Bohr model. Evaluate the Rydberg constant  $R$ .
6. Plot the spectra of the Lyman and Balmer series computationally.

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7. Derive the allowed energy states and wavefunction for particle in a box given Eq.(3.32) and Eq.(3.33).

Guiding steps, if you need:

- Insert our guess solution Eq.(3.30) into Eq.(3.26) and to obtain the general solution Eq(3.31);
  - Apply the boundary conditions to the general solution. Using Eq.(3.28), you will find a sine function. Using Eq.(3.29) you will find that only integer values of  $\pi$  are allowed for the argument in the sine function.
  - Do a bit of algebra to get the allowed energy states.
  - Use the normalising condition given in Eq.(3.25) to find the coefficient  $A$ .
8. Graph the particle in a box wavefunction for  $n = 1, 2$  and  $3$ . Label each sketch with the value of energy associated with each  $n$ .