PHYS 271: Introduction to Quantum Physics

Guillaume Gervais

2010

Neils Bohr

Erwin Schrödinger

[1]Note: It is hoped that these are error free, however this not being the case, please let me know so that I can perform corrections. *joel.beaudry@mail.mcgill.ca*

Contents

1 Introduction

1.1 From Macroscopic to Microscopic Scale

The Macroscopic world, i.e. the world we live in, is composed of many particles packed together so as to give us the matter we know. You have learned in your previous chemistry courses that Avogadro's number, N_A, is $6.0 \cdot 10^{23}$, such that in a few grams of matter there are roughly 10^{23} particles (atoms). You have also learned that such matter, like "yourself" obeys Newton's laws, which is the theory that describes a falling apple from a tree, the motion of planets around the sun, the acceleration of a car due to a large force, the motion of a projectile, etc. But are those laws valid at a very small scale, say at the scale corresponding to that of a single atom? This is the purpose of this course, to explore how the laws of atoms are distinct from those of the planetary system.

How big is an atom? You know that 1 mole of H_2O weighs 18 grams for a volume of $18cm^3$. So,

$$V_{atom} \approx \frac{18 \times 10^{-6} m^3}{3N_A} \approx 10^{-29} m^3,$$

and the diameter of a single atom is therefore,

$$d_{atom} \approx V_{atom}^{1/3} = 10^{-29/3} m = 10^{1/3} \cdot 10^{-10} m = 0.2nm = 2\text{Å}$$

where we define the Angstrom, $1\text{Å} \equiv 10^{-10} m$. To compare, we know that the scale of very tiny organisms of biology is the micron, or $\mu m = 10^{-6} m$, whereas the size of the smallest transistor founds in chips at Intel is roughly $\approx 100nm$ or 1000 Å. We will explore how for the smallest devices made today (and tomorrow!) that this so-called quantum physics cannot be avoided.

1.2 Deterministic View of Our Classical World.

The Newton's Laws that describe our universe, i.e.

$$\vec{F} = \frac{d\vec{p}}{dt},$$

Newton's 2nd law, or their generalization as the Euler-Lagrange equation,

$$\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{q}}\right) - \frac{\partial L}{\partial q} = 0,$$

where $q(t)$ are the generalized coordinates and $\dot{q} \equiv \frac{dq}{dt}$ are velocities, are <u>deterministic</u>. That is, one can know completely the dynamics of a system for as long as the initial conditions $q(0)$ and $\dot{q}(0)$

are known and the Lagrange function (Lagrangian) $\mathcal{L}(q, \dot{q}, t)$ is determined.

We admit that this idea from so-called "classical physics" is to be correct in general. This classical and deterministic view of the world will differ at the scale of an atom. The Newtonian laws and their deterministic evolution will give way to another equation known as the Schrödinger Equation. Our view of the world will take a large blow allowing for new ideas to emerge in terms of "Probabilistic Evolution," "Uncertainty Principle," and "Wave-Particle Duality."

2 Particle-like Properties of Electromagnetism Radiation

2.1 The Photoelectric Effect

2.1.1 The Experimental Facts

We are considering the study of electromagnetic waves that in essence are the phenomena responsible for light, radio-frequency waves, etc. In particular, we are interested as to how light (electromagnetic waves) interacts with matter. We consider the following experiment:

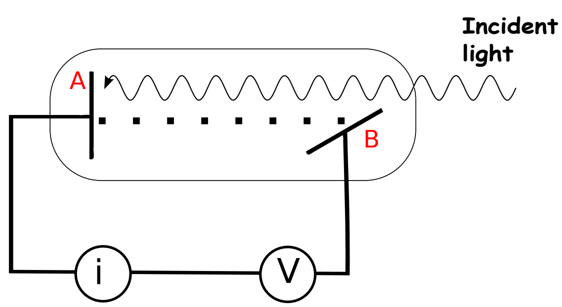


Figure 1: The Photoelectric Effect

Incident light is shining on a metallic plate (A), which frees up some electrons (e^-). These electrons can be detected as a current, i, created by the difference in potential $V \equiv V_B - V_A$. The results of such an experiment are as follows:

- There is saturation of the current i when $V \gg 0$. All electrons that are available participate to the current. If the light intensity is doubled, the saturation current is also doubled. This can be seen in Figure 2.
- A negative potential on B is required in order to completely stop the current flow. This V_0 is known as the stopping potential. The maximum kinetic energy of the electron is therefore $K_{MAX} = eV_0$, where eV_0 is the work done on the electron to stop them. It is found that V_0 is independent on the light intensity I.
- The potential V_0 depends linearly on the frequency of light, ν, as depicted in Figure 3.

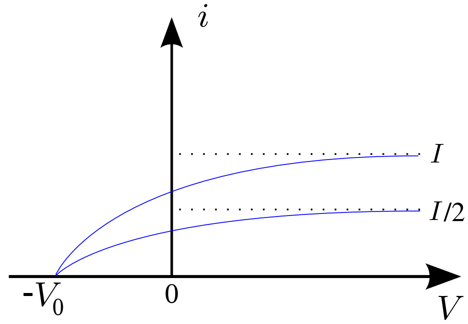


Figure 2: Saturation of current as seen in a typical photoelectric experiment. Note that for very large V, we find the current, i plateaus. I is the light intensity and $\frac{I}{2}$ is the half such a quantity.

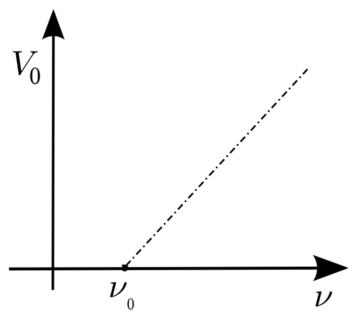


Figure 3: Linear Dependence of the potential, V_0, as a function of frequency, ν.

- There is a frequency threshold ν_0 so that for $\nu < \nu_0$ there is no electron emitted from the surface. This ν_0 is found to depend on the material of the surface.

2.1.2 Conflicts with the Classical Theory of Electromagnetism

The photoelectric effect is in conflict with the classical theory of electromagnetism, which had been developed in the 19^{th} century.

- Intensity: classical theory predicts that the intensity of incident light increases as the square of the electric field (i.e. $I \propto E^2$). If E increases, the work done on the electron should always increase so that its kinetic energy should increase. However, experimentally, we find K_{MAX} independent of the light intensity I.
- Frequency threshold: classical theory predicts that if the light intensity is sufficient to extract an electron, we should get a current i no matter what the frequency is. However, experimentally, one finds that $i = 0$ for $\nu < \nu_0$.

2.1.3 Einstein Quanta Hypothesis

In classical electromagnetism, light propagation is a wave phenomena where the amplitude of the wave is related to the electric field as

$$\vec{E} = \vec{E_0} sin(kx - \omega t),$$

where $k = 2\pi/\lambda$ is the wave number, λ the wavelength, and $\omega = 2\pi\nu$ is the angular frequency.

We have seen in the previous section that classical electromagnetism cannot explain the photoelectric effect. Einstein postulated an hypothesis which would explain the interaction between light and matter. In his theory, he states that:

> "Light, when interacting with matter, is formed of energy packets localized in space, where the energy of the packet is given by $E = h\nu$"

where h is the so-called Planck's constant and ν is the frequency. This wave-packet is called a "photon". When the electromagnetic wave is freely propagating in space (vacuum), it is formed from a very large number of wave packets and the resulting average can be described as a wave.

2.1.4 Explanation of the Photoelectric Effect by the Photon

Based on the photon theory, in the photoelectric effect a particle of light is absorbed by an electron as in an elastic collision between the particles. If after the process the electron is emitted by the surface, the kinetic energy of the electron, K, is given by

$$K = h\nu - W.$$

W is the work necessary to extract the electron, i.e. to extract an electron one needs to do work to compensate (at least in part) for the attractive forces not present at the interface. (See Figure 4)

So, inside the metal, the electron has a potential energy higher than outside. Let W_0 be the minimal work to extract an electron, so the maximum kinetic energy of the electron is

$$K_{max} = h\nu - W_0.$$

From this theory, the conclusions are:

- The characteristics of the photoelectric effect (V_0 and the frequency dependence) are <u>independent</u> of the light intensity, because the intensity determines only the number of photons.

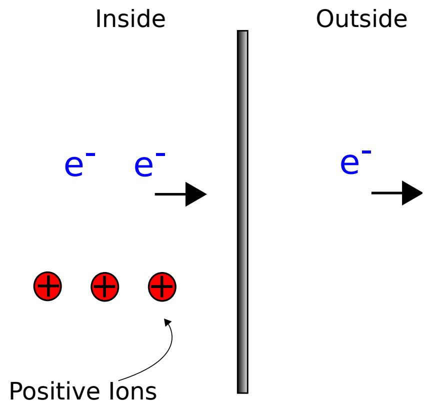
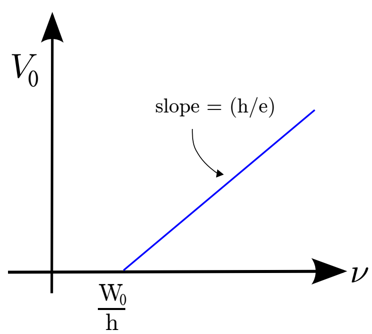


Figure 4: Attractive forces present at the interface of the metal.

- It explains the frequency threshold: let's define $h\nu_0 = W_0$, so for $\nu < \nu_0$, there is no electron emitted from the surface.
- The plot of the frequency dependence of V_0, i.e.



Where $eV_0 = K_{max} = h\nu - W_0$ yields a slope that is given by h/e. Since the charge of e is known, this means the slope is a measure of h, the Planck's constant. The value of h is extracted from the photoelectric experiment,

$$h = 6.626 \times 10^{-34} J \cdot s,$$

and is in agreement with the value of h extracted from black body experiments (see Section 2.3).

2.2 Generalization of the Photon Concept

2.2.1 Electromagnetic Spectrum

We can generalize the concept of photon where $E = h\nu$ to the entire electromagnetic spectrum. Let's take a wave with $\lambda = 10cm$ (a microwave), so in this case $E = h\nu = \frac{hc}{\lambda} = 1.2 \cdot 10^{-5} eV$, where we have used $c = \lambda\nu$, the relation linking the velocity c to the wavelength λ and frequency ν of the wave. This microwave with $E = 1.2 \cdot 10^{-5}eV$ cannot produce a photoelectric effect since experimentally $W_0 = h\nu_0 \approx 1eV$. However, the gamma-rays emitted from a radioactive nuclei with $E = 10^6 eV$ can easily produce the photoelectric effect.

2.2.2 Wave-Particle Duality of Electromagnetic Radiation

Light is thus a particle called the photon when interacting with matter with an energy $E = h\nu$. We can also define a momentum,

$$p = \frac{h}{\lambda}$$

that depends on the wavelength of the photon, λ. Compton, using photons with high energy, had shown in the early 20^{th} century that light can scatter off the nuclei inside matter, in a way very similar to billiard balls knocking each other around. This "momentum" of the photon shows that light has indeed a particle-like character.

2.2.3 Planck Postulate

> Any physical quantity with a degree of freedom corresponding to a coordinate that is a sinusoidal function of time (such as harmonic oscillation) can only possess as a total energy E the values
>
> $$E_n = nh\nu, \text{ where } n = 0, 1, 2, \ldots$$
>
> and ν is the classical frequency of the oscillation and h is the Planck's constant.

2.3 Blackbody Radiation

2.3.1 Classical Expectations

Historically, it's the interpretation of the so-called "Blackbody Radiation Problem" that had introduced the notion of quantized energy levels of the electromagnetic light. (Max Planck, 14, December 1900 at the German Physical Society). The blackbody radiation is however a complex phenomena for which a great number of electromagnetic radiation intervenes and so the knowledge of statistical mechanics and thermodynamics is required to fully understand it.

The blackbody radiation is the emission of light by a surface that absorbs all incident radiation (on that surface). A good experimental model system to study blackbody radiation consist of studying the light emitted by a small hole punched in a cavity with the inside walls being metallic.

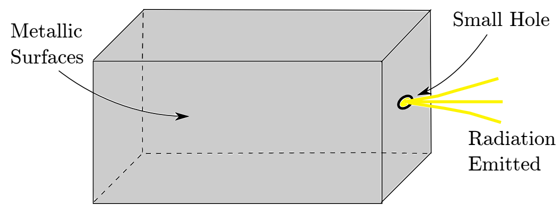


Figure 5: Light escaping from an interior lined metallic box by means of a small hole.

The experiment shows that the spectral radiance, i.e. the amount of energy emitted per unit time, per unit surface and per unit frequency in a frequency interval going from ν to $\nu + d\nu$ at a temperature T is

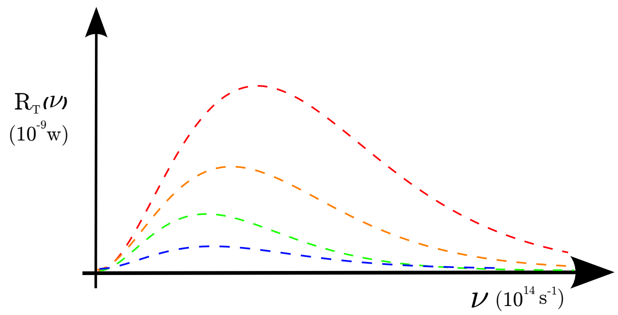


Figure 6: Spectral Radiance as a function of frequency. The different colors correspond to different temperatures, with red being the hottest and blue the coolest.

The spectral radiance $R_T(0)$ is simply related to the density of energy, $\rho_T(0)$ per unit volume in the cavity. This density is per unit frequency, for frequency between ν and $\nu + d\nu$. Classical Electromagnetism predicts the following "law" for $\rho_T(0)$,

$$\rho_T(0) = \frac{8\pi\nu^2 k_B T}{c^3}$$

where $k_B = 1.38 \cdot 10^{-23} J/K$ is the Boltzmann constant, and c is the speed of light. The Boltzmann constant appears here due to the large number of electromagnetic waves that are in thermodynamic equilibrium. The experimental data yields the plot shown in figure 7.

The classical prediction where $\rho_T(\nu) \propto \nu^2$ at high frequency leads to a conundrum known as the "Ultra-violet Catastrophe."

The energy contained in an electromagnetic wave hitting the walls is totally absorbed by the cavity and nearly instantaneously re-emitted as an electromagnetic wave. A priori, the re-emitted energy should be over all possible modes from $\nu = 0$ to $\nu \Rightarrow \infty$. Since classical theory predicts a number of modes increasing as ν^2, there should be more energy concentrated at high frequency. This is known as the UV catastrophe since the energy of the universe should be more concentrated at high frequency. In reality, this does not happen, as seen above, where the experimental data showed

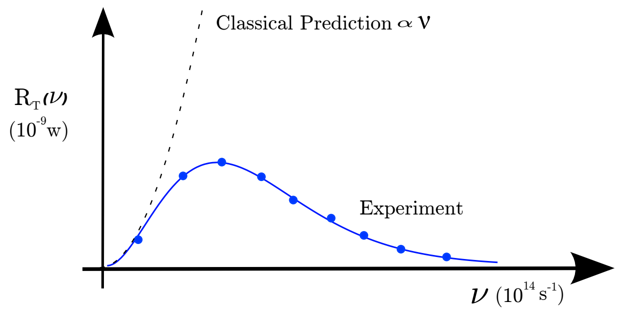


Figure 7: The ultraviolet catastrophe as shown by comparing the classical predictions with experimental data.

that $\rho_T(\nu)$ decreases with ν at high frequency.

2.3.2 Planck's Explanation

Planck proposed that the energy level of an electromagnetic wave has a discrete spectrum, rather than being continuous. He postulated that each wave of frequency ν had an energy equal to

$$E = nh\nu$$

where h is the Planck's constant. With this hypothesis, he obtained the following law for the energy density:

$$\rho_T(0) = \frac{8\pi\nu^2}{c^3}\frac{h\nu}{e^{\frac{h\nu}{k_B T}} - 1}$$

The data seen in Figure 8 correspond to this curve adjusting such that, $h = 6.57 \cdot 10^{-34} J \cdot s$, in agreement with the photoelectric effect.

3 Wave-like Properties of Particles (de Broglie)

3.1 Wavy Matter

3.1.1 de Broglie Wavelength

In 1924, de Broglie proposed that, as in the case for the photon, particles of matter (electrons, protons, etc...) also possess both properties that are particle-like and wave-like, a duality required to describe the dynamics of quantum particles. So de Broglie postulated that the energy and momentum is:

$$E = h\nu \text{ (generalization from photons)}$$

$$p = \frac{h}{\lambda}$$

where λ is the so-called de Broglie wavelength. For a particle of mass $m = 1$ kg and velocity $v = 10$ m/s, the de Broglie wavelength is $\lambda = h/p \approx 6.6 \cdot 10^{-35}$ Å. Whereas for an electron e with kinetic energy $K = 100eV$, one finds $\lambda = \frac{h}{\sqrt{2m_e K}} = 12$ Å or 1.2 nm, which is measurable, in principle.

3.1.2 Experimental Evidence for the de Broglie Wavelength (historical)

If we scatter an electron on an object that has a characteristic length on order of λ (e.g $\lambda \approx 12$Å), one could in principle put in evidence the wave-like nature of quantum particles. In a solid, the distance between the atoms is usually of this order. Davison and Germer proposed the following experiment on a nickel (Ni) target.

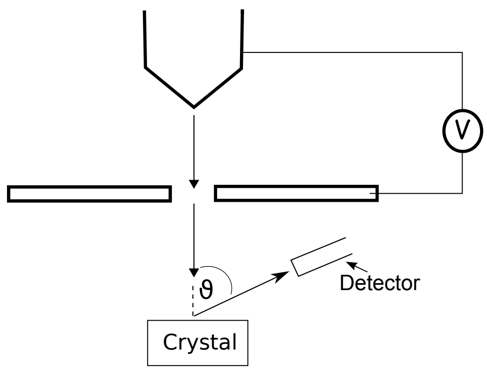


Figure 8: The Davison-Germer Experiment nicely depicts evidence for the wave-like nature of matter.

where V is the accelerating potential of the electrons and K is the kinetic energy of the electrons when they leave the slit, $K \approx eV$. The current i of scattered electrons is measured versus θ. The result is seen below, in which there is a peak at 50 deg for a nickel crystal. The interpretation of the experiment is as follows:

- the local maximum, or peak, at $\theta = 0$ is explained by inelastic collisions with the crystal (very heavy compared to electrons).
- the peak for $\theta \neq 0°$ is an interference phenomenon which qualitatively validates the de Broglie postulate.

Indeed, the interference between the wave-like nature of particles and a crystal leads to the Bragg condition

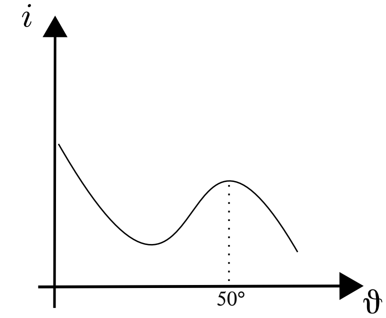


Figure 9: Experimental result of the Davison-Germer experiment, with the current i as a function of angle, θ.

$$n\lambda = 2d \sin\phi$$

where n is an integer number of wavelength and ϕ is the angle between the incident beam and the atomic plane, and d is the distance between the planes:

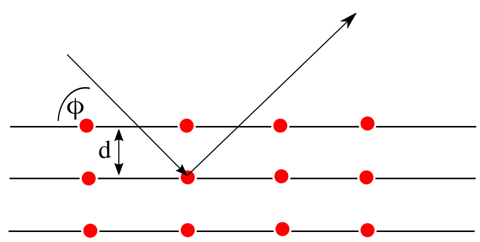


Figure 10: Schematic of Bragg Diffraction

For a crystal of Ni with $d = 0.91$ Å and $V = 54\ Volts$, to first order in interference, i.e $n = 1$, and since $\phi = 90° - \theta/2 = 65°$ for $\theta = 50°$, one finds $2d \sin 65° = 2(0.91) \sin 65°$ leading to $\lambda = 1.65$Å which is in agreement with $\lambda = \frac{h}{p} = \frac{h}{\sqrt{2m_e K}} \approx 1.65$Å. So the peak at 50° can be explained if electrons behave as a wave.

3.2 Dichotomy Between Wave-Like Properties of Matter and Determinism

3.2.1 Electrons in a Crossed Electric and Magnetic Field

When an electron is subjected to both an electric field $\vec{E}$ and magnetic field $\vec{B}$, it will obey to Newton's equation of motion $\vec{F} = m_e\vec{a} = m_e\frac{d^2\vec{r}}{dt^2}$, where the forces are given by

$$\vec{F}_{Tot} = \vec{F}_{electric} + \vec{F}_{magnetic} \quad (3.1)$$

$$= -e(\vec{E} + \frac{1}{c}\frac{d\vec{r}}{dt} \times \vec{B}) \quad (3.2)$$

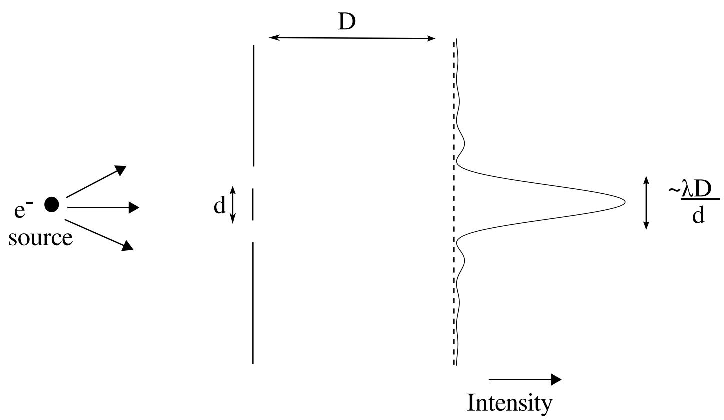
so that the electron obeys to

$$m_e \frac{d^2\vec{r}}{dt^2} = -e(\vec{E} + \frac{1}{c}\frac{d\vec{r}}{dt} \times \vec{B}).$$

Newton's laws are *determinstic*, i.e. it predicts that the trajectory of the particle is well determined and well characterized by the coordinate $\vec{r}(t)$ which depends on time only. But can this determinism hold for a particle that has a wave-like nature?

3.2.2 Determinism (lack of) and Interference

Consider an electron that would hit a screen with two slits. We expect to observe the following pattern on a detector screen located behind the two slits.



Assume the the electron current source is sufficiently weak so that only one electron travels through the apparatus at a time. From a classical point-of-view assuming the electron is just a hard particle, the trajectory of the electron must go through one slit or the other, but not both at the same time. If that were the case, we could close the other slit and the result should remain the same. If that is the case, the result should be the superposition of two experiments each which has only one slit open, and the other closed half of the time. The diffraction pattern for a single slit corresponds to a central peak of width $\approx \lambda D/a$, where a is the width of the slit. In this case we expect the result as shown below in figure 11.

So even if we attribute a wave-like property for the particles, one would never get an interference pattern, but rather two peaks separated by distance d. The classical notion of a well-defined trajectory is incompatible with experimental results shedding light on the wave-like nature of quantum particles. The notion of a trajectory $\vec{r}(t)$ must therefore be *abandoned*.

3.2.3 Quantum Interpretation of the two-slit experiment

Quantum mechanics will answer to that paradox in describing the electron properties with a single mathematical function $\Psi(\vec{r}, t)$ known as the "wavefunction." This function Ψ obeys to the

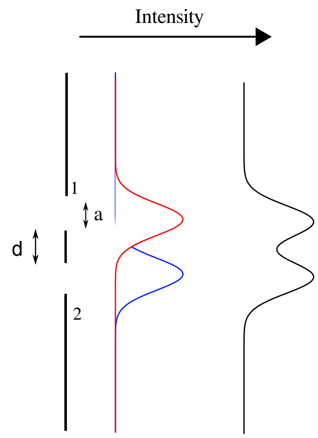


Figure 11: Expected classical result of the double slit experiment

Schrödinger Equation (to be discussed later)

$$i\hbar\frac{\partial\Psi(\vec{r},t)}{\partial t} = -\frac{h^2}{2m_e}(\frac{\partial^2\Psi}{\partial x^2} + \frac{\partial^2\Psi}{\partial y^2} + \frac{\partial^2\Psi}{\partial z^2}) + V(\vec{r})\Psi(\vec{r},t)$$

where $\hbar = \frac{h}{2\pi}$, m_e is the mass of the particle and $V(\vec{r})$ is the potential energy. This Schrödinger Equation *cannot* be derived from classical physics, and we shall see that the notion of classical trajectory will have to be abandoned. Rather, quantum physics will discuss the notion of "likelihood of presence," and so only a probabilistic view will become possible in the quantum world.

3.3 Wave Packet

3.3.1 Review of Classical Waves: The Wave Equation

A **wave** is simply a "disturbance of a continuous medium that propagates with a fixed shape and a constant velocity".

Let Ψ be a function, $\Psi = \Psi(x,t)$ which depends on position, x, and time, t. In general, one can show that Ψ will be a function which describes a wave propagation if it is a solution of the classical wave equation:

$$\frac{\partial^2\Psi}{\partial x^2} = \frac{1}{v^2}\frac{\partial^2\Psi}{\partial t^2}$$

where v is the velocity of propagation of the wave.

Lets introduce the variables, $u_1 = x - vt$ and $u_2 = x + vt$, then we have

$$\frac{\partial}{\partial u_1} = \left(\frac{\partial}{\partial x} - \frac{1}{v}\frac{\partial}{\partial t}\right)$$
$$\frac{\partial}{\partial u_2} = \left(\frac{\partial}{\partial x} + \frac{1}{v}\frac{\partial}{\partial t}\right)$$

and so we can write the wave equation as

$$\frac{\partial^2 \Psi}{\partial u_1 \partial u_2} = 0$$

which has solutions of the form

$$\Psi = \Psi_1(u_1) + \Psi_2(u_2)$$

or, writing in x, t coordinates

$$\Psi_{general} = \Psi_1(x - vt) + \Psi_1(x + vt)$$

This solution, known as the "D'Alambert Solution" is the sum of right traveling and left traveling waves, which is the most general solution of the wave equation.

3.3.2 Review of Classical Waves: Sinusoidal Waves in 1D

Assume a solution to the wave equation of the form

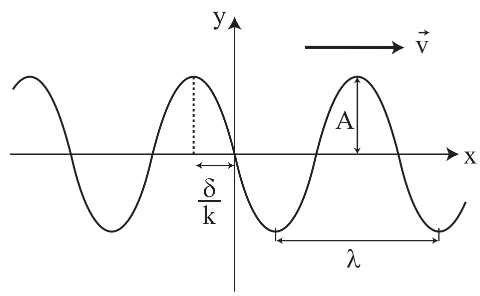
$$\Psi = Acos[k(x - vt) + \delta]$$

where:

$$\begin{aligned} k &\rightarrow \text{wave vector } = 2\pi\lambda \\ v &\rightarrow \text{propagating speed} \\ A &\rightarrow \text{amplitude} \\ \delta &\rightarrow \text{phase} \end{aligned}$$

First, verify this solution indeed satisfies the wave equation:

$$\frac{\partial^2 \Psi}{\partial x^2} = -Ak^2 cos[k(x - vt) + \delta] = -k^2 \Psi$$



Travelling Wave

and

$$\frac{\partial^2 \Psi}{\partial t^2} = -A(vk)^2 cos[k(x - vt) + \delta] = -(vk)^2 \Psi$$

Therefore we have

$$\frac{\partial^2 \Psi}{\partial x^2} = -k^2 \Psi$$

and

$$\frac{1}{v^2} \frac{\partial^2 \Psi}{\partial t^2} = -k^2 \Psi$$

and so

$$\frac{\partial^2 \Psi}{\partial x^2} = \frac{1}{v^2} \frac{\partial^2 \Psi}{\partial t^2}$$

which is the wave equation.

We call k the **wave number** (in 1D), or $\vec{k}$ the **wave vector** (in 2D), and we have

$$k = \frac{2\pi}{\lambda}$$

since, when $x \to x + 2\pi/k$, the cosine has executed a complete cycle, ie.

$$\Psi\left(x + \frac{2\pi}{k}, vt\right) = Acos\left[k\left(x + \frac{2\pi}{k} - vt\right) + \delta\right] = \Psi(x, vt)$$

Similarly, for a full cycle, we define the **period** as

$$T = \frac{2\pi}{kv}$$

So that

$$\Psi(x, v(t+T)) = \Psi(x, vt)$$

The frequency of the wave is simply the inverse of the period, $\nu = 1/T$, and so we have the relations

$$\nu = \frac{1}{T} = \frac{kv}{2\pi} = \frac{v}{\lambda}$$

Recall that for circular motion, we define the **angular frequency**, ω, as

$$\omega = 2\pi\nu = kv$$

We can therefore rewrite the wave equation in terms of wave vector, k, and angular frequency, ω, as

$$\Psi(x,t) = Acos(kx - \omega t + \delta)$$

Note that for a **right travelling wave**:

$$\begin{aligned}\Psi_R(x,t) &= Acos[k(x - vt) + \delta] \\ &= Acos[kx - \omega t + \delta]\end{aligned}$$

for a **left travelling wave**:

$$\begin{aligned}\Psi_L(x,t) &= Acos[k(x + vt) - \delta] \\ &= Acos[kx + \omega t - \delta]\end{aligned}$$

where the sign convention for the δ term is for a delay. But, the cosine function is an even function, ie. $cos(\theta) = cos(-\theta)$, and so we can rewrite Ψ_L as

$$\Psi_L(x,t) = Acos[kx + \omega t - \delta] = Acos[-kx - \omega t + \delta]$$

or, in other words

$$\Psi_L(x,t) = [\Psi_R(x,t)]_{k\rightarrow -k}$$

The inversion of $k \rightarrow -k$ transforms the wave from a right travelling to a left travelling wave and vice-versa.

Complex Notation:

Euler's Formula states

$$e^{i\theta} = cos\theta + isin\theta$$

and so we can write the sinusoidal solution as

$$\Psi(x,t) = Acos(kx - \omega t + \delta) = \Re\{Ae^{i(kx-\omega t+\delta)}\} \equiv \Re\{\tilde{\Psi}\}$$

Where $\Re\{\tilde{\Psi}\}$ is the real part of the complex solution

$$\tilde{\Psi} \equiv \tilde{A}e^{i(kx-\omega t)}$$

with complex amplitude defined by

$$\tilde{A} = Ae^{i\delta}$$

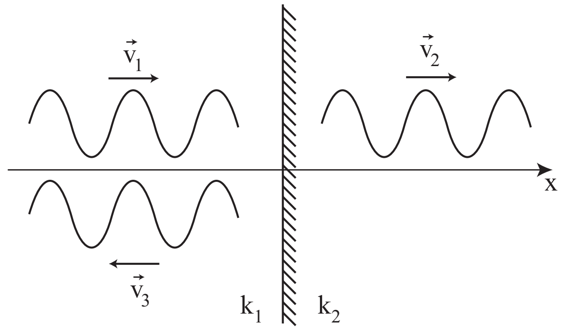
where the phase, δ, is now absorbed in the $\tilde{A}$. Note that we use complex notation because the $e^{i\theta}$ are easier to manipulate mathematically than sin and cos.

3.3.3 Review of Classical Waves: Boundary Conditions and Interfaces

$$\begin{aligned}
\tilde{\Psi}_I(x,t) &= \tilde{A}_I e^{i(k_1 x-\omega t)}, && x < 0 \rightarrow \text{incident wave} \\
\tilde{\Psi}_R(x,t) &= \tilde{A}_R e^{i(-k_1 x-\omega t)}, && x < 0 \rightarrow \text{reflected wave} \\
\tilde{\Psi}_T(x,t) &= \tilde{A}_T e^{i(k_2 x-\omega t)}, && x < 0 \rightarrow \text{transmitted wave}
\end{aligned}$$

Note that the frequency, ω, will be the same for all the waves. Therefore, since $\omega = kv$, kv must be constant and so

$$k_1 v_1 = k_2 v_2$$



Wave Boundaries/Interfaces

giving the result

$$\frac{k_2}{k_1} = \frac{v_1}{v_2}$$

Boundary Conditions (at x=0):

$$\Psi(0^-, t) = \Psi(0^+, t) \tag{1}$$

ie., wave must be **continuous across interface**.

In general, for a string for example, the 1st derivative of Ψ must also be continuous across an interface for, if the slope wasn't equal, it would give rise to a net force on the string. Therefore we also have

$$\left.\frac{\partial \Psi}{\partial x}\right|_{o^+} = \left.\frac{\partial \Psi}{\partial x}\right|_{o^-} \tag{2}$$

Applying boundary condition (1) to the wavefunctions yield (at x=0)

$$\tilde{A}_I + \tilde{A}_R = \tilde{A}_T \tag{i}$$

and boundary condition (2) yields

$$k_1(\tilde{A}_I - \tilde{A}_R) = k_2 \tilde{A}_T$$

or

$$(\tilde{A}_I - \tilde{A}_R) = \frac{k_2}{k_1}\tilde{A}_r \tag{ii}$$

Subtracting (i)-(ii) gives

$$2\tilde{A}_R = \tilde{A}_T\left(1 - \frac{k_2}{k_1}\right)$$

and adding (i)+(ii) gives

$$2\tilde{A}_I = \tilde{A}_T\left(1 + \frac{k_2}{k_1}\right)$$

giving

$$\tilde{A}_T = \frac{2k_1}{k_1 + k_2}\tilde{A}_I$$

and

$$2\tilde{A}_R = \frac{2k_1}{(k_1 + k_2)}\left(\frac{k_1 - k_2}{k_1}\right)\tilde{A}_I$$

$$\tilde{A}_R = \left(\frac{k_1 - k_2}{k_1 + k_2}\right)\tilde{A}_I$$

or, in terms of $v_{1,2}$ we have

$$\begin{aligned}\tilde{A}_R &= \left(\frac{v_2 - v_1}{v_2 + v_1}\right)\tilde{A}_I \\ \tilde{A}_T &= \left(\frac{2v_2}{v_2 + v_1}\right)\tilde{A}_I\end{aligned}$$

Which gives the amplitudes of the reflected and transmitted waves as a function of the time incident wave front.

3.3.4 Review of Classical Waves: Linear Combination and Power Transform

The sinusoidal solution of the wave equation can be written using complex notation as

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

In fact, any wave can be decomposed into a linear combination of sinusoidal waves:

$$\tilde{\Psi}(x,t) = \int_{-\infty}^{\infty} \tilde{A}(k)e^{i(kz-\omega t)}dk \quad \text{with } \omega = \omega(k)$$

The coefficient $\tilde{A}(k)$ can be obtained from the Fourier transform.

3.3.5 Wave Packet and Uncertainty Relation

We have seen in the previous section that the notion of a well-defined trajectory must be abandoned due to the wave-like nature of particles. This is based on double-slit experiments that have shown the interference of quantum particles that cannot be decomposed as a single superposition of two independent slits. We consider now mathematically a function for the particle that has a wave-like nature.

We consider the adding of many waves at $t = 0$ with a wave number $k = 2\pi/\lambda$ with different amplitudes $A(k)$ as a function of k. Summing for all wave vector k from $-\infty$ to ∞, we form the following function:

$$\Psi(x) = \int_{-\infty}^{\infty} A(k)\cos(kx)dk$$

We further consider a Gaussian distribution $A(k) = exp(-\alpha k^2)$ centered at $k = 0$. The larger α is, the more squeezed is the distribution at $k = 0$. So

$$\Psi(x) = \int_{-\infty}^{\infty} e^{-\alpha k^2}\cos(kx)dk = \sqrt{\frac{\pi}{\alpha}}\; e^{-\frac{x^2}{4\alpha}}$$

(See Mathematical Table), where $\Psi(x)$ is localized around $x = 0$ and symmetric with respect to $x = 0$. The smaller α is, the more the wave-packet is at $x = 0$, such distributions are shown in Figure 12.

We now define the width of $A(k)$ as the length for which $A(k)$ has fallen to its half-value at $k = 0$. So $e^{-\alpha k_0^2} = 1/2$ and thus $k_0 = \sqrt{\frac{\ln 2}{\alpha}}$, and

$$2k_0 = \text{width} = \sqrt{\frac{4\ln 2}{\alpha}} = \Delta k.$$

With the same definition, we can define the width of $\Psi(x)$ as $e^{\frac{-x^2}{4\alpha}} = 1/2$, so $\Delta x = \sqrt{4\ln 2 \cdot 4\alpha}$. We now consider the product,

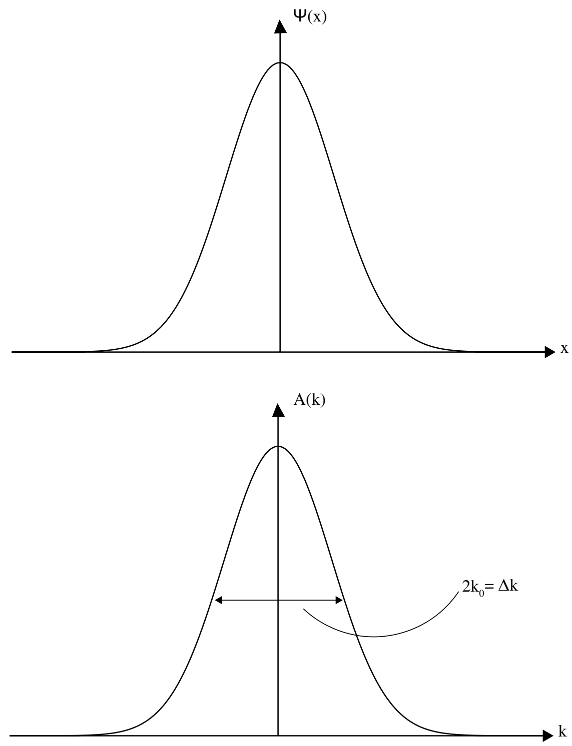


Figure 12: Gaussian functions depicting $\Psi(x)$ and $A(k)$. Note: The Gaussians should, of course, differ more.

$$\Delta x \Delta k = 4 \ln 2 \times 2 \approx 5.42$$

independent of α. Therefore, for a wave packet, there exist a reciprocity relation between the spatial width Δx and the frequency bandwidth Δk for which the wave packet is made out of. This means that the smaller that Δx is, the larger will be the uncertainty in wave vector Δk. We shall see later that this relation is intimately related to "Heisenberg Uncertainty Principle."

3.3.6 Motion of the Wave Packet

Our goal is to describe a particle in motion with a wave packet. To achieve this we need to know $\Psi(x,t)$ as a function of time. The harmonic waves forming the packet can be treated as traveling waves, as if they were traveling electromagnetic waves, i.e. having a dependence given by $\cos(kx - \omega t)$ where $\omega = 2\pi\nu = 2\pi c/\lambda = kc$. So let's write the wave packet as,

$$\Psi(x,t) = \int_{-\infty}^{\infty} A(k) \cos(kx - \omega t) dk \quad (3.3)$$

$$= \int_{-\infty}^{\infty} A(k) \cos k(x - ct) = \Psi(x - ct) \quad (3.4)$$

The wave packet written in this form is like an electromagnetic wave traveling at speed c. This holds true in vacuum, but in a real medium we shall take into account the index of refraction n so that now the traveling wave packet is, (since in a medium $\omega = kc/n$)

$$\Psi(x,t) = \Psi(x - \frac{c}{n}t)$$

where the velocity $v_p = c/n$ is called the phase velocity. Note that if n is a function of k, i.e. $n = n(k)$, the phase velocity v_p of different harmonics $v_p = c/n(k)$ is not the same anymore. This means that while the wavepacket travels, it will get deformed since each k component travels at different velocities.

For electrons propagating, the situation will be very similar to that of electromagnetic waves.

- For a particle, the relation between momentum p and wavelength is by the de Broglie relation

  $$k = \frac{2\pi}{\lambda} = \frac{2\pi p}{h} = \frac{p}{\hbar}$$

- According to Planck, the relation between energy and frequency is given by

  $$\omega = 2\pi\nu = 2\pi\frac{E}{h} = \frac{E}{\hbar} = \frac{p^2}{2m\hbar}$$

  Since $E = p^2/2m = E(p)$, the kinetic energy, this gives the following relation between ω and $\hbar$

  $$\omega = \frac{\hbar k^2}{2m}$$

  And the phase velocity is $v_p(k) = \frac{\omega}{k} = \frac{\hbar k}{2m}$. The wave packet for the particle can then be written as

  $$\Psi(x,t) = \int_{-\infty}^{\infty} \phi(p) \cos(\frac{px - E(p)t}{\hbar}) dp$$

  where we have replaced the integration on k by an integration on p. Here, $\phi(p)$ is the amplitude of each momentum components

- We can also show that $\Psi(x,t)$ moves as a particle, at least under some approximations. For this we consider a Gaussian packet centered at momentum $p = p_0$,

  $$\phi(p) = e^{-\frac{\alpha}{\hbar^2}(p-p_0)^2}.$$

  Expanding the energy $E(p)$ so that it is given by

  $$E(p) = E(p_0) + (p - p_0)(\frac{\partial E}{\partial p})_{p_0} + (1/2)(p - p_0)^2(\frac{\partial^2 E}{\partial p^2})_{p_0} + \dots$$

  we can show (to be done in the homework) that the wavefunction can be written as

$$\Psi(x,t) \approx \cos\left[\frac{1}{\hbar}(p_0 x - E(p_0)t)\right]\left(\frac{\pi}{\alpha}\right)^{1/2} e^{\frac{-\left(x-(\frac{\partial E}{\partial p})_{p_0} t\right)^2}{4\alpha}}$$

which means that with respect to the the time t=0, the wave packet has moved at $x = \left(\frac{\partial E}{\partial p}\right)_{p_0} t$, i.e. it is moving with a group velocity $v_g = \left(\frac{\partial E}{\partial p}\right)_{p_0}$.

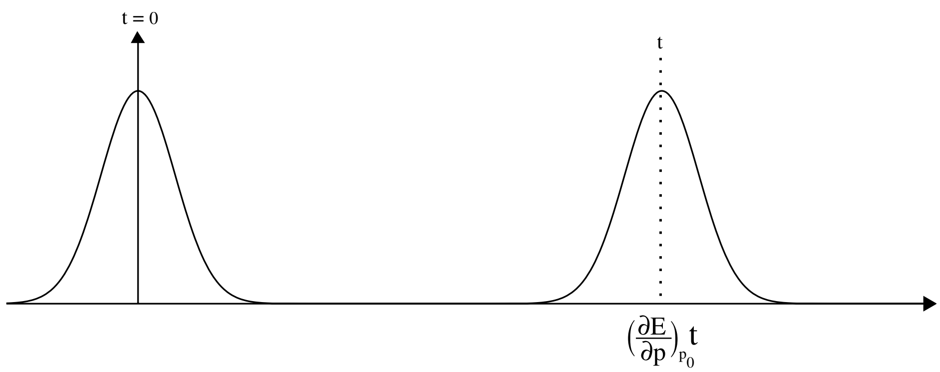


Figure 13: Movement of the wave packet from initial time, 0, to some later time, t.

The group velocity is given by $v_g = \left(\frac{\partial E}{\partial p}\right)_{p_0} = \frac{\partial}{\partial p}\left(\frac{p^2}{2m}\right) = \frac{p_0}{m} = v_0$, so the group velocity of the wave packet is simply the velocity of the particle.

3.3.7 Localization and Uncertainty Principle (Heisenberg)

We have seen previously that for a wave packet the following relation holds true between the spatial coordinate x and wave vector k:

$$\Delta x \Delta k \approx 1$$

From de Broglie, we also know that $p = \frac{h}{\lambda} = \hbar\frac{2\pi}{\lambda} = \hbar k$ and therefore

$$\Delta x \Delta p \approx \hbar$$

This relation is known as the "Heisenberg Uncertainty Principle." It states that the coordinate x and momentum p cannot be determined with an infinite precision. If there is no uncertainty in $\Delta x = \hbar/\Delta p$ then the uncertainty in the momentum $\Delta p = \hbar/\Delta x$ must be infinite, and vice-versa. For a particle moving with $v = c/100$, one finds $p_0 = mc/100$ so that for an uncertainty at the level of 10^{-3}, or in other words $\Delta p = 10^{-3}p_0 = 10^{-5}mc$, this corresponds to an uncertainty in x of $\Delta x \approx \hbar/10^{-5}mc \approx 4$ Å, which is the extent of the wave packet. We shall discuss later on more about the implications of the Heisenberg Uncertainty Principle.

3.3.8 Bohr's Complementarity Principle

We have seen earlier that particles manifest themselves with properties that are both wave-like and particle-like. Bohr enunciated the following principle regarding the two facets of quantum matter:

> The wave-like and particle-like aspects of quantum particles are complementary from one another; both are necessary, and each property cannot be observed individually. This aspect is put in evidence by "observations depends on the experiment."

4 Probabilistic View of the Wave Function

4.1 Wave Equation for the Wave Packet

4.1.1 Construction of the Schrödinger Equation

We are now interested in finding which wave equation can give rise to a solution of the form

$$\Psi(x,t) = \int_{-\infty}^{\infty} \phi(p) \cos(\frac{px - E(p)t}{\hbar}) dp$$

In order to identify such an equation, we first calculate a variety of partial derivatives with respect to x and t.

$$\begin{aligned}
\hbar \frac{\partial \Psi}{\partial x} &= -\int_{-\infty}^{\infty} dp\phi(p)p \sin(\frac{px - Et}{\hbar}) \\
\hbar^2 \frac{\partial^2 \Psi}{\partial^2 x} &= -\int_{-\infty}^{\infty} dp\phi(p)p^2 \cos(\frac{px - Et}{\hbar}) \\
\hbar^3 \frac{\partial^3 \Psi}{\partial^3 x} &= \int_{-\infty}^{\infty} dp\phi(p)p^3 \sin(\frac{px - Et}{\hbar}) \\
\hbar^4 \frac{\partial^4 \Psi}{\partial^4 x} &= \int_{-\infty}^{\infty} dp\phi(p)p^4 \cos(\frac{px - Et}{\hbar}) \\
\hbar \frac{\partial \Psi}{\partial t} &= \int_{-\infty}^{\infty} dpE\phi(p) \sin(\frac{px - Et}{\hbar}) \\
\hbar^2 \frac{\partial^2 \Psi}{\partial t^2} &= -\int_{-\infty}^{\infty} dpE^2\phi(p) \cos(\frac{px - Et}{\hbar})
\end{aligned}$$

From $E = p^2/2m$, we can deduce the the following partial derivatives satisfy

$$\frac{\hbar^4}{4m^2} \frac{\partial^4 \Psi(x,t)}{\partial x^4} = -h^2 \frac{\partial^2 \Psi(x,t)}{\partial t^2}$$

Unfortunately, this equation corresponds to the equation $E^2 = \left(\frac{p^2}{2m}\right)^2$ which admits two solutions, $E = \frac{p^2}{2m}$ and $E = -\frac{p^2}{2m}$. The negative solution is not physical, and so the above equation cannot be the correct one. This is because in order for E to not be squared, we need to use the first derivative with respect to time. To do this, we will need to use the complex relation $\cos\theta + i\sin\theta = e^{i\theta}$ such that we can use

$$\cos\left(\frac{px - Et}{\hbar}\right) + i\sin\left(\frac{px - Et}{\hbar}\right) = e^{i\left(\frac{px-Et}{\hbar}\right)}$$

and

$$\Psi(x,t) = \int_{-\infty}^{\infty} \phi(p) e^{i\left(\frac{px-E(p)t}{\hbar}\right)} dp.$$

It is now easy to verify that to get $E = p^2/2m$, we need the following equation

$$i\hbar\frac{\partial\Psi(x,t)}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2\Psi(x,t)}{\partial x^2}.$$

A linear equation with one pure imaginary coefficient and where $\Psi(x,t)$ is now complex. This equation is a version of the Schrödinger equation. (When the potential energy is zero, $V = 0$).

4.2 Probabilistic Interpretation of the Wave Function

4.2.1 Complex Wavefunction

As we have seen, for a particle with energy $E = p^2/2m$, the representation of its complex wavefunction is

$$\Psi(x,t) = \int_{\infty}^{\infty} \phi(p) e^{\frac{i}{\hbar}(px-Et)} dp$$

Which satisfies the Schrödinger equation

$$i\hbar\frac{\partial\Psi(x,t)}{\partial t} = \frac{-h^2}{2m}\nabla^2\Psi(x,t)$$

and "flow" at a group velocity $v_g = \frac{\partial E}{\partial p}\Big|_0$. This wavefunction is thus a complex function, which can be decomposed as

$$\Psi(x,t) = Re\Psi(x,t) + iIm\Psi(x,t).$$

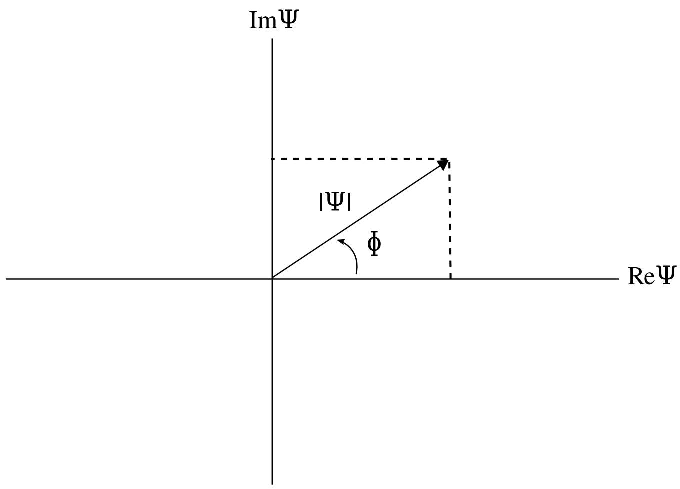
The complex wave function also implies that there is a phase $\phi(x,t)$ so that

$$\Psi(x,t) = \big|\Psi(x,t)\big|e^{i\phi(x,t)} = \big|\Psi(x,t)\big|(\cos\phi(x,t) + i\sin\phi(x,t))$$

so

$$Re\Psi(x,t) = |\Psi|\cos\phi(x,t) \tag{4.1}$$
$$Im\Psi(x,t) = |\Psi|\sin\phi(x,t). \tag{4.2}$$

The complex function is a vector in a two-dimensional space where the axes are ReΨ and ImΨ.



The magnitude of Ψ, i.e. $|\Psi|$ determines the length of the vector and $\phi(x,t)$ is the angle with respect to axis ReΨ. The absolute value is given by $|\Psi(x,t)|^2 = \Psi^*\Psi = (|\Psi|e^{-i\phi})(|\Psi|e^{i\phi}) = |\Psi|^2$. In analogy to the intensity of electromagnetic radiation where $I \propto |\vec{E}|^2$, we associate to $|\Psi|^2$ a large probability to find the particle in this region.

4.2.2 Principle of Superposition

The Schrödinger equation is linear, granting the following property for the wave function $\Psi(x,t)$.

> Let Ψ_1 and Ψ_2, each of which is a solution of the Schrödinger equation. Then the sum $\Psi_3 = \Psi_1 + \Psi_2$ is also a solution of the Schrödinger equation.

4.2.3 Interpretation of the Two-Slit Experiment

We shall now explore how the complex wave function introduced in the previous section can be applied to the two-slit experiment.

- let $\Psi_1(\vec{r},t)$ be the solution of the Schrödinger equation when only slit 1 is open.
- let $\Psi_2(\vec{r},t)$ be the solution of the Schrödinger equation when only slit 2 is open.

In both cases, $\Psi(\vec{r},t)$ is a 3D wavefunction. The intensity on the screen is

- For slit 1 open (2 closed) $\Rightarrow |\Psi_1(\vec{r},t)|^2$ where $\vec{r}$ is a point on the screen
- For slit 2 open (1 closed) $\Rightarrow |\Psi_2(\vec{r},t)|^2$ where $\vec{r}$ is a point on the screen

If both slits are open then the wave-function must be $\Psi(\vec{r},t) = \Psi_1(\vec{r},t) + \Psi_2(\vec{r},t)$, i.e. superposition of the solution for slit 1 and slit 2. Then the intensity on the screen will be:

$$|\Psi_1(\vec{r},t) + \Psi_2(\vec{r},t)|^2$$

But $\Psi_1 = |\Psi_1|e^{i\phi_1}$ and $\Psi_2 = |\Psi_2|e^{i\phi_2}$, and so

$$\begin{aligned}
|\Psi_1(\vec{r},t) + \Psi_2(\vec{r},t)|^2 &= \left||\Psi_1|e^{i\phi_1} + |\Psi_2|e^{i\phi_2}\right|^2 && (4.3)\\
&= \left(|\Psi_1|e^{-i\phi_1} + |\Psi_2|e^{-i\phi_2}\right)\left(|\Psi_1|e^{i\phi_1} + |\Psi_2|e^{i\phi_2}\right) && (4.4)\\
&= |\Psi_1|^2 + |\Psi_2|^2 + |\Psi_1||\Psi_2|\left(e^{i(\phi_1-\phi_2)} + e^{-i(\phi_1-\phi_2)}\right) && (4.5)\\
&= |\Psi_1|^2 + |\Psi_2|^2 + 2|\Psi_1||\Psi_2|\cos\left(\phi_1(\vec{r},t) - \phi_2(\vec{r},t)\right). && (4.6)
\end{aligned}$$

The first two terms are contributions from the slits as if they were individual, and the last term is the interference between the two slits. On the screen, there is a a spatially dependent phase difference $\phi_1(\vec{r},t) - \phi_2(\vec{r},t)$ which modulates the intensity even though $|\Psi_1|$ and $|\Psi_2|$ are constant.

4.2.4 Meaning of the wavefunction

The linearity of the Schrödinger equation is responsible for the wave-like properties of particles. However, we have seen in the two-slit experiment that the electron current could be reduced so that only one electron was crossing the apparatus. Even in this case, interference occurred meaning that each electron was described by a wavefunction, $\Psi = \Psi_1 + \Psi_2$. If only one electron was present, how did the interference occur? In other words, what is the meaning of the wavefunction Ψ?

The answer to this question was provided by Max Born. If a system is described by a wavefunction $\Psi(x,t)$, then $|\Psi(x,t)|^2$ is the probability to find the system at a point x and a time t with the following meaning:

$$\begin{aligned}
P(x,t)dx &= \text{Probability to find the system in the interval between } x \text{ and } x+dx \text{ at time t}\\
&= |\Psi(x,t)|^2 dx
\end{aligned}$$

Since the system must be "somewhere", then we must have

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

which will be only possible if we normalize the wavefunction. To do this we write

$$\Psi'(x,t) = \frac{1}{\sqrt{N}}\Psi(x,t)$$

and

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

and so now

$$\int_{-\infty}^{\infty} |\Psi'(x,t)|^2 dx = 1$$

With this normalization procedure $|\Psi(x,t)|^2$ can now be interpreted as a probability density. We note, however, that it is the spatial integral $\int_{-\infty}^{\infty} |\Psi(x,t)|^2 dx$ that yields the probability. For this probability interpretation to be correct, the "un-normalized" quantity $\int_{-\infty}^{\infty} |\Psi(x,t)|^2 dx = N$ must be time-independent. It is easy to show, from the Schrödinger equation, that the probability density $P(x,t) = |\Psi(x,t)|^2$ obeys to a continuity equation (to be done as Homework) of the form:

$$\frac{\partial P(x,t)}{\partial t} + \frac{\partial J(x,t)}{\partial x} = 0$$

where $P(x,t) = |\Psi(x,t)|^2$ and $J(x,t) = \frac{\hbar}{i2m}(\Psi^* \frac{\partial \Psi}{\partial x} - \Psi \frac{\partial \Psi^*}{\partial x})$. This conservation law for the probability $|\Psi(x,t)|^2$ is the equivalent to the conservation of electromagnetic charge in electromagnetism, $\frac{\partial \rho}{\partial t} - \frac{\partial J}{\partial x} = 0$, where ρ is the charge density and J is the current density.

4.3 Uncertainty Principle and Classical Description

The relation between the probability distribution Δx and the width Δp of the momentum distribution is given by the Heisenberg Uncertainty Principle

$$\Delta x \Delta p \geq \hbar$$

This uncertainty relation assesses that in quantum mechanics, it is no longer possible to determine the position or momentum with an arbitrary precision. If Δx is small, Δp will be large and vice versa.

The uncertainty does not come from an uncertainty in the Schrödinger equation. The latter is well-defined and starting with an initial wavefunction at time $t = 0$, $\Psi(x, 0)$, the Schrödinger equation can determine $\Psi(x, t)$ with the desired precision. Rather the uncertainty comes from our attempt to use classical concepts (such as the notion of a well-defined trajectory $\vec{r}(t)$) to characterize a quantum phenomenon. Since $\hbar$ is very small, the uncertainty principle has no impact at the macroscopic level, whereas at the microscopic level, it is playing an important role.

The representation of the particle as a wavefunction imposes the uncertainty principle. It is the need to reconcile the wave-like and particle-like nature of matter that forces the uncertainty relation to exist.

In analogy with $\Delta x \Delta k \geq 1$, we can also show that a similar relation exist in the time-frequency domain, where $\Delta\omega\Delta t \geq 1$. From $E = \hbar\omega$, we deduce that

$$\Delta E \Delta t \geq \hbar$$

which states that within a finite time Δt, there will be an uncertainty in the energy at the level of $\Delta E \geq \hbar/\Delta t$.

5 The Bohr Model

5.1 Atomic Models of Thomson and Rutherford

5.1.1 Thomson Model of the Atom

In the late 19^{th} century, Thomson proposed a model for the atom. It was already known that the atom must contain electrons (put in evidence in the photoelectric effect and other experiments). The atom is also electrically neutral, and so this implied the existence of positive charges called protons, also responsible for the mass of the atom. The electric charge e had also been measured by Millikan, and the ratio e/m_e been measured by Thomson.

Thomson proposed the following model:

> The electric charges (+) and (−) are uniformly distributed in a sphere of radius $\approx 10^{-10} m \equiv 1$Å

5.1.2 Experiments by Rutherford

In 1911, Rutherford made an experiment in which he sends α-particles onto a sheet of gold foil. The α-particles are nuclei of helium, i.e. two protons and two neutrons, that had been discovered by Becquerel and Pierre and Marie Curie. Since the mass of α-particles is much greater than the

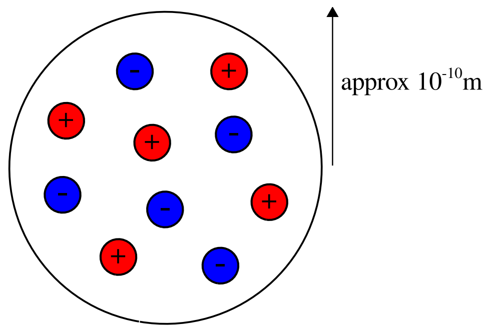


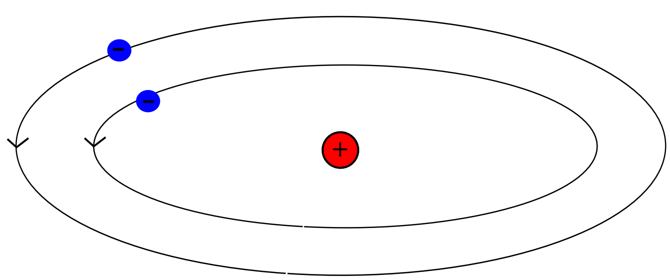
Figure 14: Thomson's plum pudding model of the atom

electron mass, these electrons cannot produce a large effect on the α trajectories. Also, the mass of positively charged particles, according to Thomson, is distributed uniformly in a sphere of radius $\approx 10^{-10}$ m.

The results of Rutherford's experiment were as followed. Most of the α-particles suffer only a very weak deviation when traveling across the golf foil. However, a small number of them (measurable) had suffered a very strong deviation, up to $180\,°$! This experimental fact entirely contradicted the Thomson Model, and ultimately lead to its abandonment by the scientific community.

5.1.3 The Rutherford Model and Stability Issues

In the Rutherford Model, the positive charges (and therefore nearly all of the mass) is concentrated in a very small region of space: in the nucleus. When the α-particles travel near the nucleus, they are strongly scattered by this "massive" region of positive charge. This model explains at least qualitatively the experimental results.



The Rutherford model is nevertheless not perfect. At the center of the atom the massive nucleus does have all of the positive charge (Ze), whereas much lighter electrons are located at distances much larger than the nucleus. The problems are

- If the electron are not moving, they should fall into the nucleus.
- If the electrons are orbiting around the nucleus they should emit electromagnetic radiation. The loss of energy during this process should lead to the electron crashing into the nucleus.

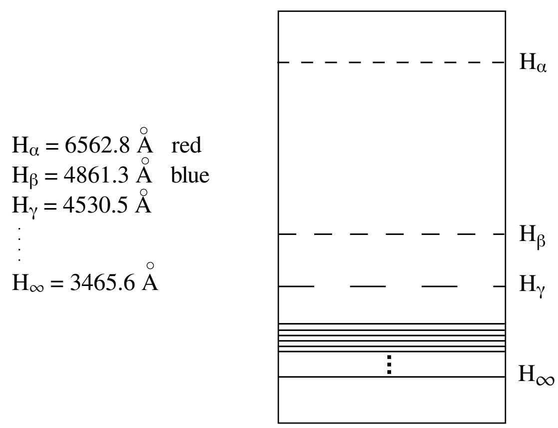
Therefore, a better atomic model needs to be found in order to explain the structure of an atom.

5.2 Atomic Spectroscopy

5.2.1 Atomic Spectroscopy by emission

Let's consider a volume of gas for which the atoms are excited via an electric discharge. We observe the emission of electromagnetic radiation by the excited gas. This radiation can be separated, or filtered, by a prism. On a photographic plate, we observe a discrete spectrum for which each line is well separated by one another.

Each element of the periodic table possess its own characteristic emission line. For example, for a gas of atomic hydrogen, we observe the following spectrum:



This series, for Hydrogen, converges towards $H_\infty = 3645.6$ Å. Note that we provided the spectrum in terms of wavelength λ, which is equivalent to the energy since $E = h\nu = hc/\lambda$.

In 1885, Balmer provided an empirical formula for this series,

$$\lambda(/AA) = 3645.6 \cdot \frac{n^2}{n^2 - 4}$$

where $n = 3$ for H_α, $n = 4$ for H_β, $n = 5$ for H_γ, and so forth.

Rydberg in 1890 wrote it under the form

$$\kappa = \frac{1}{\lambda} = R_H \left(\frac{1}{2^2} - \frac{1}{n^2} \right) \quad n = 3, 4, 5, \ldots$$

and R_H is the Rydberg constant for Hydrogen and $R_H = 10967757.6 \pm 1.2 m^{-1}$. This experimental fact shows de facto the existence of discrete energy levels in the spectrum of Hydrogen.

There exist several other series for the hydrogen atom:

Lyman (ultraviolet)	$\kappa = R_H \left(\frac{1}{1^2} - \frac{1}{n^2}\right)$	$n = 2, 3, 4, \ldots$
Balmer (visible)	$\kappa = R_H \left(\frac{1}{2^2} - \frac{1}{n^2}\right)$	$n = 3, 4, 5, \ldots$
Paschen (infrared)	$\kappa = R_H \left(\frac{1}{3^2} - \frac{1}{n^2}\right)$	$n = 4, 5, 6, \ldots$
Brackett (infrared)	$\kappa = R_H \left(\frac{1}{4^2} - \frac{1}{n^2}\right)$	$n = 5, 6, 7, \ldots$
Pfund (infrared)	$\kappa = R_H \left(\frac{1}{5^2} - \frac{1}{n^2}\right)$	$n = 6, 7, 8, \ldots$

Clearly, we need to develop a model for the atom that will account for these important experimental findings.

5.2.2 Atomic Spectroscopy by Absorption

In this kind of spectroscopy, electromagnetic radiation (white) is shone on a monoatomic gas and the light leaving the gas is analyzed. On the photographic screen, there will be lines (at some well-defined wavelength) that will be missing. For each line of the absorption spectrum, there will be one line on the emission spectrum. In absorption, at room temperature for the hydrogen atom, we only observe the Lyman series. For a very hot gas, we can also observe the Balmer series.

5.3 The Bohr Model

5.3.1 Bohr Postulates

1. An electron in an atom is moving on a circular orbit around the nucleus under the coulomb forces between the e^- and the nucleus. It obeys to the law of classical physics.

2. However, rather than the continuum of orbits allowed by classical physics, the electron can only be on orbits for which the orbital angular momentum L is an integer number of $\hbar$. So $L = n\hbar$ with $n = 1, 2, \ldots$ (Quantization condition).

3. While the electron is constantly accelerating, there is no radiation emitted on the quantized orbit.

4. Electromagnetic radiation is emitted by the electron if initially on an orbit of energy E_i, it moves to an orbit with energy E_f. The frequency of the electromagnetic radiation emitted is given by $h\nu = E_i - E_f$.

5.3.2 Contrast Between Bohr and Planck Quantization

We have seen earlier that in the case of photons, the Planck Quantization was given by $E = h\nu$. This was simply due to the wave-like nature of photons and matter. Bohr now proposes that for an electron moving in a Coulombian potential, it is angular momentum L that is quantized, i.e. $L = n\hbar$. This in essence leads to a different law than Planck for the quantization of energy levels.

We shall show below how the quantization condition provided by Bohr will lead to the explanation of the energy level for Hydrogen.

5.3.3 Bohr Model for an Atom with one Electron

We consider an atom with a charge Ze, a mass m and the unphysical assumption that there is only one electron. For Hydrogen, $Z = 1$, for ionized Helium $Z = 2$, ionized Lithium $Z = 3$ and so on. The electron is on a circular orbit around the nucleus with a radius r, and it is under the effect of a Coulomb potential $V \approx 1/r$. We know from classical mechanics that there must be, at equilibrium, compensation between Coulomb and centripetal forces,

$$\frac{1}{4\pi\epsilon_0}\frac{Ze^2}{r^2} = \frac{mv^2}{r} \tag{5.1}$$

where v is the tangential speed of the electron.

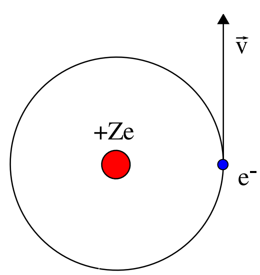


Figure 15: A single electron in orbit about a positively charged nucleus.

In classical mechanics, the angular momentum $L = mvr$ and is a constant of motion, i.e. a conserved quantity, if there is no net torque on the system. The Bohr quantization implies that

$$L = mvr = n\hbar.$$

This is equivalent to imposing that the circumference of the orbit ($= 2\pi r$) be given by an <u>integer</u> number of the de Broglie wavelength,

$$2\pi r = n\lambda = \frac{nh}{p} = \frac{nh}{mv}$$

and so $mvr = n\hbar$.

From Eq. 5.1 we obtain $Ze^2 = 4\pi\epsilon_0 mv^2 r = 4\pi\epsilon_0 mr\left(\frac{n\hbar}{mr}\right)^2$, since $v = n\hbar/mr$. Therefore

$$Ze^2 = 4\pi\epsilon_0\frac{n^2\hbar^2}{mr}$$

and we can now define a quantized radius,

$$r_n = 4\pi\epsilon_0 \frac{n^2\hbar^2}{mZe^2} \quad n = 1, 2, 3, \ldots$$

which increases with n increasing. On the other hand, the tangential velocity on the orbit is

$$v_n = \frac{n\hbar}{mr_n} = \frac{1}{4\pi\epsilon_0}\frac{Ze^2}{n\hbar}$$

which decreases with n increasing. For the Hydrogen atom where $Z = 1$ and its fundamental state with $n = 1$, we obtain

$$r_1 = 0.58\text{Å}$$

$$v_1 = 2.2 \times 10^6 m/s$$

The total energy for the electron in the orbit n is given by the sum of the kinetic and Coulomb potential energy:

$$E_n = \frac{1}{2}mv_n^2 - \frac{Ze^2}{4\pi\epsilon_0 r_n} \equiv K_n + V_n.$$

From Eq. 5.1, we deduce that

$$K_n = \frac{1}{2}\left(\frac{1}{4\pi\epsilon_0}\right)\left(\frac{Ze^2}{r_n}\right) = -\frac{1}{2}V_n.$$

Therefore, the total energy is simply

$$\begin{aligned} E_n &= -\frac{1}{2}V_n + V_n = \frac{1}{2}V_n & (5.2) \\ &= -\frac{1}{2}\frac{Ze^2}{4\pi\epsilon_0}\frac{mZe^2}{(4\pi\epsilon_0)n^2\hbar^2} & (5.3) \end{aligned}$$

And we finally obtain:

$$\boxed{E_n = -\frac{mZ^2e^4}{(4\pi\epsilon_0)^2\, 2\hbar^2}\left(\frac{1}{n^2}\right)} \tag{5.4}$$

and so the quantization of L leads to the quantization of the energy E_n. For $Z = 1$ (hydrogen), we calculate $E_\infty = 0, E_4 = -0.85eV, E_3 = -1.51eV, \text{and} E_2 = -3.39eV$. Note that

1. $n = 1$ is the lowest energy since $E < 0$. It is called the ground state.
2. $n = \infty,\ E_\infty = 0$ is an *unbounded* state.
3. $n > 1$ are excited states. During an electric discharge, the atom gets the energy necessary to transmit from the ground state to the excited state with $n > 1$.

5.3.4 Transition Energy in the Bohr Model

The atom emits electromagnetic radiation when transiting from an excited state to a state of lower energy, until the ground state is reached.

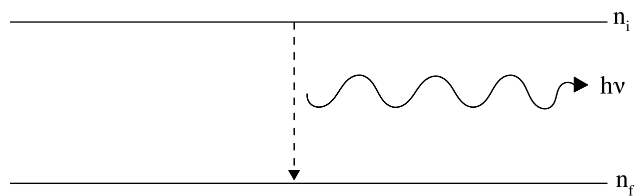


Figure 16: Emission of a photon with frequency ν, as the atom transists from an excited state to a lower one.

The energy of the photon emitted is given by

$$h\nu = E_i - E_f = -\frac{1}{(4\pi\epsilon_0)^2}\frac{mZ^2e^4}{2\hbar^2}\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right)$$

Since $r_n = (4\pi\epsilon_0)\frac{n^2\hbar^2}{mZe^2}$, we define $k \equiv \frac{1}{(4\pi\epsilon_0)}$ and for $n = 1$ we define the Bohr radius $a_0 \equiv \frac{\hbar^2}{kmZe^2}$. With these notations, we can rewrite

$$h\nu = \frac{kZe^2}{2a_0}\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right).$$

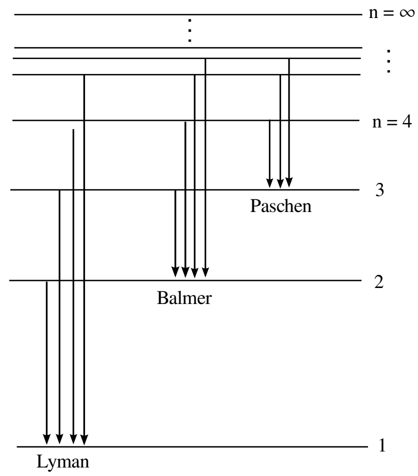
Defining K, such that

$$K = \frac{1}{\lambda} = \frac{\nu}{c} = \frac{kZe^2}{2a_0ch}\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) \equiv R_\infty\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$$

and where we note that we swept n_i and n_f so that the wavelength is positive. The constant R_∞ is called the Rydberg constant, and here the ∞ denotes that we have considered a nucleus with an infinite mass. So

$$R_\infty \equiv \frac{kZe^2}{2a_0hc}$$

and assume the numerical value $R_\infty = 1.0973732 \times 10^7 m^{-1}$. Please note that the Bohr radius is $a_0 = \frac{\hbar^2}{Zmke^2} = 0.529$ Å for $Z = 1$, which is in agreement with the experimental size of the hydrogen atom, where $n_F = 1$ (Lyman), $n_F = 2$ (Balmer), $n_F = 3$ (Paschen), $n_F = 4$ (Brackett) and $n_F = 5$ (Pfund).



Finally we note that the energy of the electron in the hydrogen atom ($Z = 1$) is

$$E_n = \frac{-me^4}{(4\pi\epsilon_0)^2 2\hbar^2}\frac{1}{n^2} = \frac{-ke^2}{2a_0}\left(\frac{1}{n^2}\right) = \frac{-13.6eV}{n^2}.$$

The integer n which can only assume discrete values is referred to as a quantum number. In the ground state, $E_1 = -13.6eV$ for the hydrogen atom, which is the ionization energy of the electron. That is, one needs to supply $13.6eV$ to strip the electron from the hydrogen atom. This ionization energy had been experimentally determined prior to Bohr's model. This, and the agreement with the atom radius, constitute two major triumphs for the Bohr model of the atom.

5.3.5 Experimental Verification of Discrete Atomic States: Franck-Hertz (1914)

In 1914, Franck and Hertz devised an experiment which would confirm the Bohr model, i.e. the occurrence of discrete atomic energy levels. In this experiment, a vapor of Mercury (Hg) was bombarded with electrons with known kinetic energy K. If this energy K is less than the first excited state of the atom, (measured with respect to the ground state), the electron energy loss is weak, and only due to scattering with the heavy ion. When the energy K was greater than the $1st$ excited state, the electrons were found to lose nearly all of their kinetic energy.

The difference between the ground state and first excited state was found to be 4.9eV in Hg. This experiment demonstrated the existence of discrete energy levels in atoms.

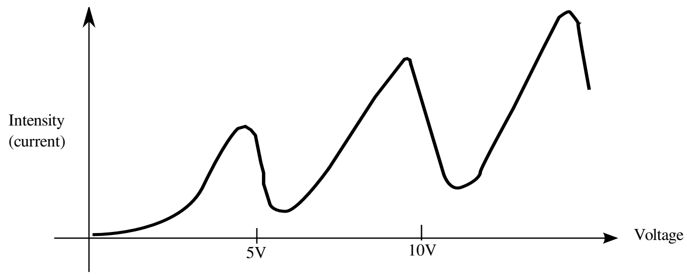


Figure 17: Distinct intensity (current) drops seen as a direct confirmation of Bohr's model. The current is measured by the number of electrons that make it across to the other voltage plate, however once their kinetic energy (applied from a voltage) matches to the energy levels of the Mercury atoms, the electrons lose energy as they transfer it to the Mercury atoms. The electrons can no longer make it to the other plate, and thus the current drops sharply and is easily measurable.

5.4 Interpretation of the Quantization Rules

5.4.1 Bohr-Sommerfeld Rule

We have seen earlier that in the Bohr model, the angular momentum is quantized, whereas in the case of Planck, it is the total energy that is quantized. But what is the connection between the two? Assume that the coordinate is a cyclic function of time, such as for the motion of a planet around the sun or the motion of a simple pendulum. In 1916, Wilson and Sommerfeld enunciate some quantization rules for all physical systems where the coordinates are cyclic function of time. It states that:

> For all system where the coordinates are periodic function of time, there exist a quantization rule for each coordinate. This rule is given by
>
> $$\oint P_q dq = n_q h$$
>
> where $q =$ coordinate, p_q is the momentum associated with q, n_q is a quantum number that must be an integer, and $\oint$ is the integral over one period of the coordinate q.

5.5 Example: the Bohr Atom

In the Bohr atom, the electron is on circular orbits of radius r and possess an angular momentum $L = mvr =$ constant (central force). This angular coordinate θ, is cyclic in time:

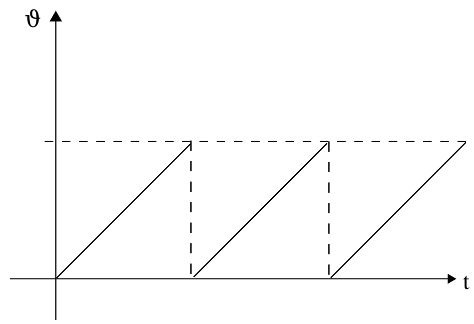


Figure 18: θ as a cyclic function of time, t

The Sommerfeld quantization condition is therefore:

$$\oint p_q dq = \oint L d\theta = 2\pi L = nh, \text{So } L = n\hbar$$

and we recover the Bohr quantization.

5.6 Quantum Particles with a "Spin"

5.6.1 Stern and Gerlach Experiment (1922)

In classical electrodynamics, a current loop is required in order to gain a magnetic moment $\vec{\mu}$. This magnetic moment is essentially given by

$$|\vec{\mu}| = \frac{I}{c} \times (\text{Area of loop}).$$

We also know that this current loop will interact with a magnetic field, with a potential energy equal to $U = -\vec{\mu} \cdot \vec{B}$. Quantum particles may have an electric charge, but as of now, no particle has been found that had a "magnetic charge." But can quantum particles such as an electron or an atom interact with a magnetic field?

In 1922, Stern & Gerlach devised an experiment to determine whether an atom has a magnetic moment. This experiment puts in evidence a new property that can be described as the quantization of space. In this experiment, Stern & Gerlach have measured the deviation of a beam of atoms (silver) when travelling across a region of space with a non-homogeneous magnetic field. The experimental scheme was as following:

The field between the north and south pole is inhomogeneous vertically, but there is azimuthal symmetry, i.e. the field is homogeneous under rotation around the axis z. For such a field, there will be a component of $\vec{B}$ along z that will be a function of z, i.e. $B_z = B_z(z)$. This magnetic field $\vec{B}$ adds a term to the potential energy of the atom in the field:

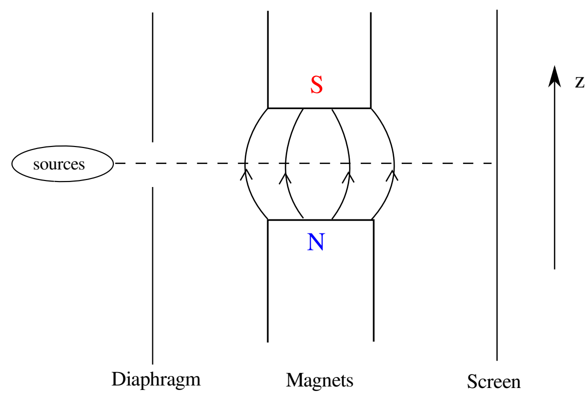


Figure 19: Schematic of the Stern-Gerlach experiment

$$U = -\vec{\mu} \cdot \vec{B}$$

where $\vec{\mu}$ is the magnetic moment of the atom (no matter where it is coming from). In the Bohr model, we could imagine that the magnetic moment will be perpendicular to the orbital plane of the electron. The force on the atom is given by:

$$\vec{F} = -\vec{\nabla} U$$

and so if $\vec{B}$ is homogeneous, there will be no net force and the beam should travel straight across the magnet. If the field is inhomogeneous along z, then the force is

$$F_z = -\frac{\partial U}{\partial z} = \mu_z \frac{\partial B_z(z)}{\partial z}.$$

Assuming the field gradient $\frac{\partial B_z}{\partial z}$ to be constant, then the force F_z is proportional to the z-component of the magnetic moment, μ_z.

Classically, we expect that the magnetic moments of the atoms in the beam be uniformly distributed in any direction. We expect that on the screen, there should be an elongated spot that is continuous. The experimental result is however very difficult from the expectations of classical physics.

What is seen in the experiment is the following. For a beam of silver atoms, the beam is split in two and gives rise to the distinct spots on the screen. The intensity of each spot is identical and located symmetrically with respect to 0 (no deflection). From the vertical displacement and $\frac{\partial B_z}{\partial z}$, the value of $\vec{\mu}$ along z can be calculated, i.e. $\mu_z^{\pm} = \pm\mu_0$ and experimentally, it is found to be very close to $\frac{e\hbar}{2m_e}$, where m_e is the electron mass. We shall come back to the interpretation of this experiment.

5.6.2 Orbital Magnetic Moment in the Bohr Model

Let's assume that the motion of an electron on a circular orbit creates a current loop I defining a surface with area A. Then,

$$\mu = I \cdot A$$

with

$$A = \pi r^2 \quad \text{and} \quad I = \frac{e}{(2\pi r/v)}$$

which is the number of charge e per unit time. The angular momentum L is given by $L = mvr$ and so

$$|\vec{\mu}| = \frac{ev\pi r^2}{2\pi r} = \frac{evr}{2} = \frac{e}{2m_e} m_e vr = \frac{e}{2m_e}|\vec{L}|.$$

However, the charge of electron is negative, and so $\vec{\mu}$ and $\vec{L}$ must be anti-parallel. We can therefore write

$$\vec{\mu} = -\frac{eg}{2m_e}\vec{L}$$

where g is defined as "the gyromagnetic factor" and $g = 1$ for the orbital magnetic moment of a single H-atom.

5.6.3 Interpretation of the Stern-Gerlach Experiment

If the formula above was correctly describing the Stern-Gerlach experiment then from $\vec{\mu} = -g\frac{e}{2m_e}\vec{L}$ we deduce that $g = 1$ and $L_z = \hbar$ in the experiment since μ_z was found to be close to $\mu_z = e\hbar/2m_e$. But what if the atom had an <u>intrinsic</u> angular momentum, one that would be the equivalent to the "spin" of a top. In this case, we could write

$$\vec{\mu}_i = -g\frac{e}{2m_e}|\vec{S}|$$

where $\vec{S}$ is the spin of the atom. For it to agree with the experiment we would need $g = 2$ and $S_z = \hbar/2$. We now need to look closely at the Stern Gerlach results in order to differentiate if it is $\vec{L}$ or $\vec{S}$ that is giving rise to the observed beam deflection and μ_z.

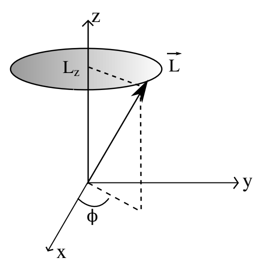
First, we realize that the axis $0z$ does not play any particular role. If we rotate the magnet by an axis θ, there are still two spots on the screen located symmetrically with respect to 0, but on an axis making an angle θ with the vertical axis.

First Conclusion: At the exact time where the magnetic field is applied on the atoms, the atoms have only two components of magnetic moment on the axis z.

But the question is, why do we observe two spots and not more?

First, Let's consider the classical case. Since in this case the force is a central force, then from a classical point-of-view the torque is given by $\vec{r}$ and $\vec{F} \equiv \vec{0}$ and so $\frac{d\vec{L}}{dt} = \vec{0}$. In the classical case, all components of angular momentum are conserved. This is a well-known case in classical physics: All central forces leads to conservation of angular momentum.

Now we consider the quantum case. Let's consider the following cartoon:



In quantum physics, only L^2 and the z-component of L, i.e. L_z, have well-defined quantum values at any given time. This can be understood from the uncertainty principle, which we have seen that $\Delta x \Delta p \geq \hbar$, and $\Delta E \Delta t \geq \hbar$.

The same is true for the projection of the angular momentum L_z along the axis z, where we can write $\Delta L_z \Delta \phi \geq \hbar$. However, in the Stern & Gerlach Experiment, the value of L_z is precisely determined, which means that the angle it makes in the $x - y$ plane is entirely unknown, i.e. the angle ϕ. If $\Delta \phi = \infty$, then L_x and L_y are entirely undetermined, and so $\vec{L}$ must precess on a cone with an opening θ. This is what is observed by Stern-Gerlach which can be interpreted as the quantization of space.

The quantum mechanics of Schrödinger for an hydrogen atom will produce the following rule for the possible value of L_z. These are:

$$L_z = m_l \hbar$$

where m_l is an integer so that $-l \leq m_l \leq$ and$l = 0, 1, 2, \ldots$. The simplest orbital case is $l = 1$, and so there are three possible values for m_l, i.e. $m_l = -1, 0$ and 1. We therefore expect three spots on the screen for μ_z. This is not observed in the Stern-Gerlach Experiment.

The fact that only two spots were observed led to the following hypothesis: the magnetic moment that was observed was not due to orbital, but was rather an "intrinsic" moment similar to the spin of a top. We have seen earlier that for it to work with the experiment, the intrinsic spin must be $S_z = \hbar/2$ with $g = 2$. With this, we now have the rule $-l \leq m_l \leq l$ that will become $-s \leq m_s \leq s$ and so $m_s = 1/2$ and $-1/2$. Therefore, $s_z = \hbar/2$ and $-\hbar/2$ and with $g = 2$, we obtain $\mu_z^{\pm} = \pm\mu_0 \approx \frac{e\hbar}{2m_e}$ and two spots on the screen with $\pm\mu_0$, as observed in the experiment.

6 Quantum Mechanics of Schrödinger Equation for a Free Particle

6.1 One-Dimensional Schrödinger Equation

6.1.1 Recall on the Schrödinger Equation

We have seen in the previous chapters that there is a wave equation for the wavefunction $\Psi(x,t)$ that describes a free particle in one dimension

$$i\hbar\frac{\partial\Psi(x,t)}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2\Psi(x,t)}{\partial x^2}.$$

The interpretation of the wave function $\Psi(x,t)$ is that it gives "the probability to find the particle described by $\Psi(x,t)$ between x and $x+dx$", or mathematically

$$P(x,t)dx \;=\; \Psi^*(x,t)\Psi(x,t)dx = |\Psi(x,t)|^2 dx,$$

where $P(x,t)$ is the probability. Since the Schrödinger equation is linear, we can construct a wave packet by adding the solutions of the Schrödinger equation.

6.2 Probabilistic Interpretation

Since the normalized wavefunction is such that $\int_{-\infty}^{\infty}\Psi^*(x,t)\Psi(x,t)dx = 1$ we can define a probability current

$$J(x,t) = \frac{\hbar}{2mi}\left(\Psi^*\frac{\partial\Psi}{\partial x} - \frac{\partial\Psi^*}{\partial x}\Psi\right)$$

so that we have an equation of conservation

$$\frac{\partial P(x,t)}{\partial t} + \frac{\partial}{\partial x}J(x,t) = 0.$$

This equation means that the "flux of probability" must be conserved. It is a continuity equation.

6.2.1 Average Value (or Expectation Value)

Since $P(x,t)$ is a probability, we can define the average or expectation value of a function $f(x)$ as

$$< f(x) > = \int_{-\infty}^{\infty} P(x,t) f(x) dx = \int_{-\infty}^{\infty} \Psi^*(x,t) f(x) \Psi(x,t) dx.$$

As an example, the expectation value of $< x^2 >$ is

$$< x^2 > = \int_{-\infty}^{\infty} \Psi^*(x,t) x^2 \Psi(x,t) dx.$$

The meaning of the expectation value is the following:

if we take an ensemble of identical systems, all described by the same wavefunction $\Psi(x,t)$, then $< f(x) >$ is the average value made on $f(x)$ for many measurements, while each measurement may give different values of $f(x)$.

6.2.2 Expectation Value of the Momentum p

We are now interested in calculating the expectation value of the momentum p or of a function of p, $f(p)$. Since $p = m\frac{dx}{dt}$, we begin by considering

$$\begin{aligned} \frac{d < x >}{dt} &= \frac{d}{dt} \int_{-\infty}^{\infty} dx \Psi^*(x,t) x \Psi(x,t) \\ &= \int_{-\infty}^{\infty} dx \left(\frac{\partial \Psi^*}{\partial t}(x,t) x \Psi(x,t) + \Psi^*(x,t) x \frac{\partial \Psi}{\partial t}(x,t) \right). \end{aligned}$$

From the Schrödiner equation, then $i\hbar\frac{\partial \Psi}{\partial t}(x,t) = -\frac{\hbar^2}{2m}\frac{\partial^2 \Psi(x,t)}{\partial x^2}$, then

$$\begin{aligned} \frac{\partial \Psi^*(x,t)}{\partial t} &= \frac{\hbar}{2mi} \frac{\partial^2 \Psi^*}{\partial x^2}(x,t) \\ \frac{\partial \Psi(x,t)}{\partial t} &= -\frac{\hbar}{2mi} \frac{\partial^2 \Psi}{\partial x^2}(x,t) \end{aligned}$$

and so

$$\begin{aligned} \frac{d}{dt} < x > &= \int_{-\infty}^{\infty} dx \frac{\hbar}{2mi} \left(\frac{\partial^2 \Psi^*}{\partial x^2}(x,t) x \Psi(x,t) - \Psi^*(x,t) x \frac{\partial^2 \Psi}{\partial x^2}(x,t) \right) \\ &= \int_{-\infty}^{\infty} dx \left[\frac{\hbar}{2mi} \frac{\partial}{\partial x} \left(\frac{\partial \Psi^*}{\partial x} x \Psi - \Psi^* x \frac{\partial \Psi}{\partial x} - \Psi^* \Psi \right) + \frac{\hbar}{im} \Psi^* \frac{\partial \Psi}{\partial x} \right] \end{aligned}$$

the first term in $\frac{\partial}{\partial x}$ must be zero since $\Psi(x,t)$ vanish to zero if x is at infinity. Therefore

$$m\frac{d<x>}{dt} = \int_{-\infty}^{\infty} dx \Psi^*(x,t)\frac{\hbar}{i}\frac{\partial}{\partial x}\Psi(x,t)$$

and a new rule imposes itself: if we want to take the expectation value of the momentum p, we calculate the expectation value of the differential operator $\frac{\hbar}{i}\frac{\partial}{\partial x}$ in between $\Psi^*(x,t)$ and $\Psi(x,t)$. So

$$<p>= \int_{-\infty}^{\infty} dx \Psi^*(x,t) p_{op} \Psi(x,t) = \int_{-\infty}^{\infty} dx \Psi^*(x,t)\left(\frac{\hbar}{i}\frac{\partial}{\partial x}\right)\Psi(x,t)$$

where $p_{op} \equiv \frac{\hbar}{i}\frac{\partial}{\partial x}$. Similarly, the expectation value of $<p^2>$ will be given by

$$\begin{aligned} <p^2> &= \int_{-\infty}^{\infty} dx \Psi^*(x,t) p_{op}^2 \Psi(x,t) \\ &= \int_{-\infty}^{\infty} dx \Psi^*(x,t)\left(-\hbar^2\frac{\partial^2}{\partial x^2}\Psi(x,t)\right). \end{aligned}$$

6.3 Schrödinger Equation for a Particle in a Potential

6.3.1 Generalization in a Potential $V = V(x)$

The Schrödinger equation for a free particle (i.e. $V = 0$) can be written as

$$i\hbar\frac{\partial\Psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2\Psi}{\partial x^2} = \frac{1}{2m}\left(-\hbar^2\frac{\partial^2}{\partial x^2}\right)\Psi.$$

However, we have seen that $p_{op}^2 = -\hbar^2\frac{\partial^2}{\partial x^2}$, that is the differential operator can replace the square of the momentum. Therefore

$$i\hbar\frac{\partial\Psi}{\partial t} = \frac{1}{2m}p_{op}^2\Psi.$$

For a free particle, we know that the energy is given by

$$E = \frac{p^2}{2m}$$

and so we can define an operator, called the Hamiltonian, that is given by

$$H = \frac{1}{2m} p_{op}^2.$$

Hence the Schrödinger equation for a free particle is given by

$$i\hbar \frac{\partial \Psi(x,t)}{\partial t} = H\Psi(x,t).$$

This suggest that we can generalize the Schrödinger for the case where the particle moves in a potential $V = V(x)$, simply by considering the total energy

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

and defining the Hamiltonian as

$$H = \frac{p_{op}^2}{2m} + V(x) = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x).$$

The Schrödinger equation then becomes

$$\boxed{i\hbar \frac{\partial \Psi(x,t)}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2 \Psi(x,t)}{\partial x^2} + V(x)\Psi(x,t).}$$

6.3.2 Continuity Equation for a Particle in a Potential V(x).

Recall that we have defined the density of Probability as $P(x,t) \equiv \Psi^*(x,t)\Psi(x,t)$. Let's consider $\frac{\partial P(x,t)}{\partial t}$:

$$\frac{\partial P(x,t)}{\partial t} = \frac{\partial}{\partial t}(\Psi^*\Psi) = \Psi^* \frac{\partial \Psi}{\partial t} + \frac{\partial \Psi^*}{\partial t}\Psi$$

but we know from the Schrödinger equation

$$\frac{\partial \Psi}{\partial t} = -\frac{\hbar}{2mi}\frac{\partial^2 \Psi}{\partial x^2} + \frac{V}{i\hbar}\Psi$$

and

$$\frac{\partial \Psi^*}{\partial t} = \frac{\hbar}{2mi}\frac{\partial^2 \Psi^*}{\partial x^2} - \frac{V}{i\hbar}\Psi^*$$

and so

$$\begin{aligned}\frac{\partial P}{\partial t} &= -\frac{\hbar}{2mi}\left[\Psi^*\frac{\partial^2\Psi}{\partial x^2} - \frac{\partial^2\Psi^*}{\partial x^2}\Psi\right] + \frac{V}{i\hbar}\Psi^*\Psi - \frac{V}{i\hbar}\Psi^*\Psi \\ &= -\frac{\partial}{\partial x}\left[\frac{\hbar}{2mi}\left(\Psi^*\frac{\partial \Psi}{\partial x} - \Psi\frac{\partial \Psi^*}{\partial x}\right)\right].\end{aligned}$$

And so since we have defined the probability current as

$$J(x,t) = \frac{\hbar}{2mi}\left(\Psi^*\frac{\partial \Psi}{\partial x} - \Psi\frac{\partial \Psi^*}{\partial x}\right)$$

and therefore we have verified that

$$\frac{\partial P(x,t)}{\partial t} + \frac{\partial J(x,t)}{\partial x} = 0.$$

6.3.3 Schrödinger Equation for a Time-Independent Potential

When the potential energy V does not depend on time, then we can use the method of separation of variables.We write a solution of the form

$$\Psi(x,t) = T(t)U(x).$$

Replacing this solution in the Schrödinger equation, we obtain

$$i\hbar U(x)\frac{dT(t)}{dt} = T(t)\left(-\frac{\hbar^2}{2m}\frac{d^2U(x)}{dx^2} + V(x)U(x)\right)$$

which we can rewrite as

$$i\hbar\frac{dT/dt}{T(t)} = \frac{\frac{-\hbar^2}{2m}\frac{d^2U(x)}{dx^2} + V(x)U(x)}{U(x)}.$$

The left hand side only depends on time, whereas the right hand side only depends on x. The only way for this equation to be satisfied is if each side is equal to a constant. This constant must have units of $\hbar/time$ which is energy. This constant is the total energy of the system. We now have the two following equations to solve:

$$i\hbar\frac{dT(t)}{dt} = ET(t)$$
$$-\frac{\hbar^2}{2m}\frac{d^2U(x)}{dx^2} + V(x)U(x) = EU(x).$$

Thus, the Schrödinger equation (with partial derivatives) comes from two equations with total derivatives. The solution to the first equation (for $T(t)$) is easy to integrate. The solution is

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

The second equation (spatial) can be rewritten as

$$\left[\frac{p_{op}^2}{2m} + V(x)\right]U(x) = EU(x)$$

i.e.

$$HU(x) = EU(x)$$

where $p_{op} \equiv i\hbar\frac{d}{dx}$ and where the Schrödinger equation is now defined by an operator H, called the Hamiltonian of the system, so that $H \equiv \frac{p_{op}^2}{2m} + V(x)$.

This equation, $HU(x) = EU(x)$, reduces to an eigenvalue problem. The function $U(x)$ for which $HU(x) = EU(x)$ is satisfied, are eigenfunctions, and the energies are the eigenvalues.

6.3.4 Energy Quantization in the Schrödinger Theory

Our goal is now to find the qualitative solutions of the Schrödinger equation for a time-independent potential $V = V(x)$. The equation to solve is

$$\frac{d^2\Psi}{dx^2} = \frac{2m}{\hbar^2}\left[V(x) - E\right]\Psi(x).$$

The solution will depend on the shape of V(x). For the sake of the discussion, we consider the potential energy for an atom bounded to another atom such that it forms a diatomic molecule. Here, x is the separation between the atoms.

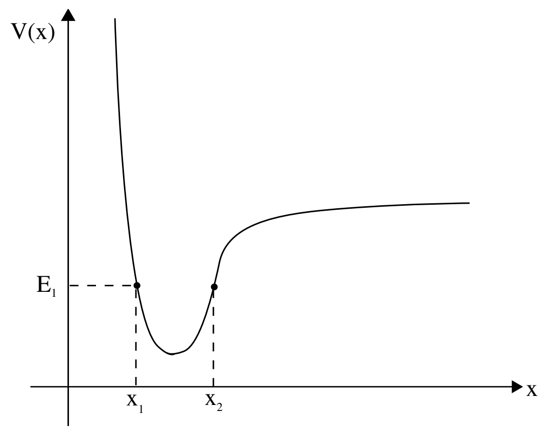


Figure 20: Potential Energy as a Function of x.

In order to examine the type of solution, we shall examine different values of the total energy E.

We first consider $E = E_1$ and $\Psi(x) > 0$:

In this case, if we examine $\frac{d^2}{dx^2} = \frac{2m}{\hbar^2}\left[V(x) - E_1\right]\Psi(x)$ we will have for $x_1 < x < x_2$, $\frac{d^2\Psi}{dx^2} < 0$, i.e. a downward concave shape, and for $x > x_2$, $x < x_1$, $\frac{d^2\Psi}{dx^2} > 0$, i.e. an upward concave shape. For $\Psi(x) < 0$, this situation is reversed.

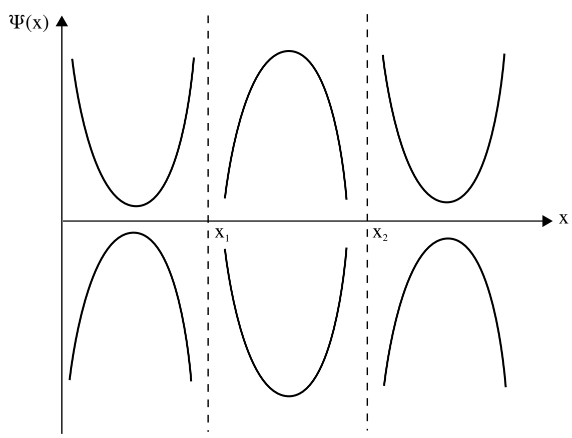


Figure 21: Different concave shapes will be present in different regions of x depending on our particular scenario.

So there are two possibilities, depending on the sign of $\Psi(x)$. The Schrödinger equation determines the general behavior of $\Psi(x)$. Given the conditions $\Psi(x)$ and $\frac{d\Psi}{dx}|_{x_0}$, we can obtain the specific behavior of $\Psi(x)$ and $\frac{d\Psi}{dx}|_{x_0}$ where $x_1 < x_0 < x_2$ and $\Psi(x_0) > 0$. We plot below the possibilities for $\Psi(x)$.

Starting from $\Psi(x_0)$ and $\frac{d\Psi}{dx}|_{x_0}$, $\Psi(x)$ must be downward concave in the region $x_1 < x < x_2$. At the crossing $x > x_2$, the shape may now be upward concave since $\left[V(x) - E\right]_{x_0}$ changes sign. With

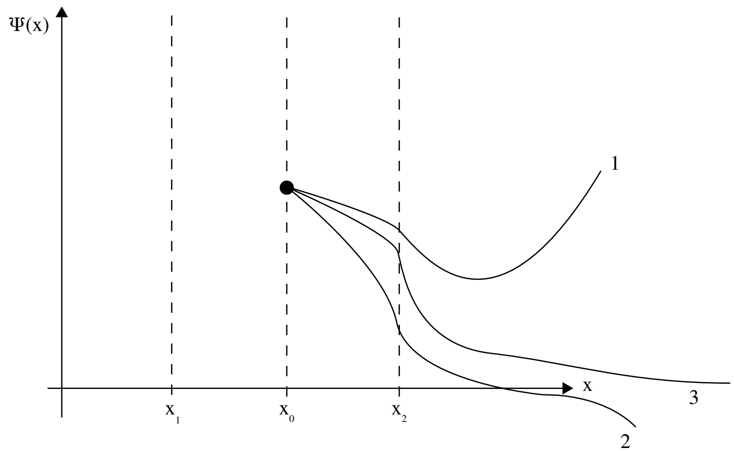


Figure 22: Possible wavefunctions depending on our particular scenario. Note that only line 3 is of physical importance as we need our wavefunction to be finite.

this choice of $\frac{d\Psi}{dx}|_{x_0}$, we obtain the line 1 on the plot above. This solution is not correct since $\Psi(x)$ goes to infinity with $x \to \infty$. For a different choice (smaller) of $\frac{d\Psi}{dx}|_{x_0}$ where $\Psi(x)$ changes sign at $x = x_2$, we can also obtain the shape 2 where it becomes downward concave and goes to $-\infty$ with $x \to \infty$. This solution is certainly not correct since the wavefunction must be finite, or localized. There exist, however, a choice of $\frac{d\Psi}{dx}|_{x_0}$ for which we can obtain the line 3, a reasonable solution at large x and for which $\Psi(x) \to 0$ with $x \to \infty$.

While this may seem as if we have solved the problem, the situation is still complex since the same $\Psi(x_0)$ and $\frac{d\Psi}{dx}|_{x_0}$ must be used for finding the solution in the $x < x_1$ region. In general, for an arbitrary choice of E, there is no value of $\Psi(x_0)$ and $\frac{d\Psi}{dx}|_{x_0}$ that will satisfy the condition $\Psi(x) \to 0$ with $\to \pm\infty$. However, there is certainly a discrete set of energy E_i. For which there can be convergence at $x \to \pm\infty$. This set of discrete $\{E_i\}$ for a discrete spectrum of energies which are associated with a discrete set of wavefunction $\{\Psi_i\}$.

Let E_1, E_2, $E_3 \ldots$ be the total energy associated with convergent solutions Ψ_1, Ψ_2, $\Psi_3 \ldots$ of the Schrödinger equation. We depict below these energy levels:

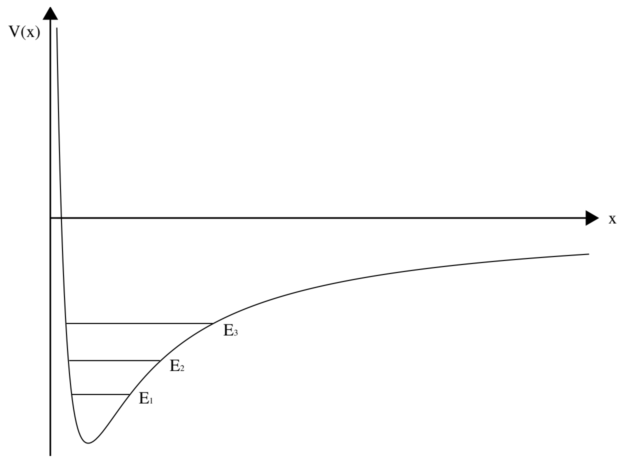


Figure 23: Energy levels associated with solutions of the Schrödinger equation with potential $V(x)$

Let E_1 be the ground state energy. For this ground state, the wave function Ψ, will have the following shape

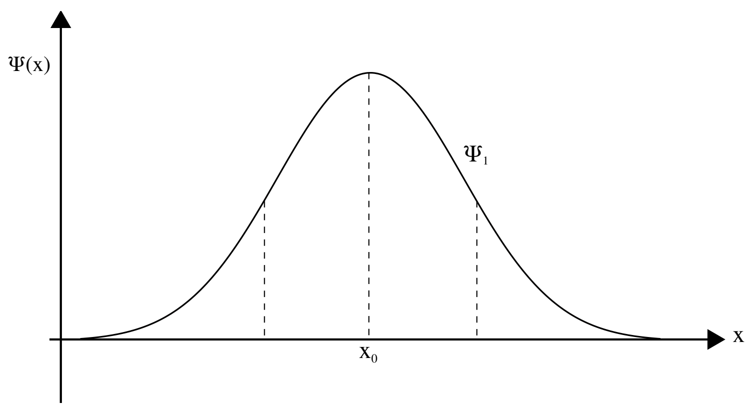


Figure 24: Ground state wavefunction

For Ψ_1, there is no sign change. The wavefunction will either be all positive or all negative. However, only one of them will by physical and so there is only one way we can plot Ψ_1. In this case, since for E_1 there is only one possible Ψ_1, we say the E_1 is not degenerate. Being degenerate means there are several physical states Ψ_i associated with a same energy E.

For $E > E_1$, the next physical solution will be for the following situation

and corresponds to $E = E_2$. However, $|\frac{d^2\Psi_2}{dx^2}|_{x_0} > |\frac{d^2\Psi_1}{dx^2}|_{x_0}$ and the difference is finite at $x = x_0$. So the Schrödinger equation $|V(x_0) - E_2| > |V(x_0) - E_1|$ has a finite difference and therefore we must have $E_2 > E_1$.

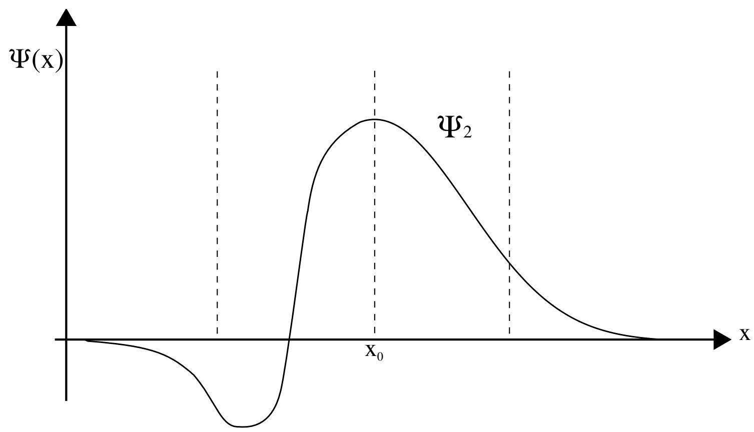
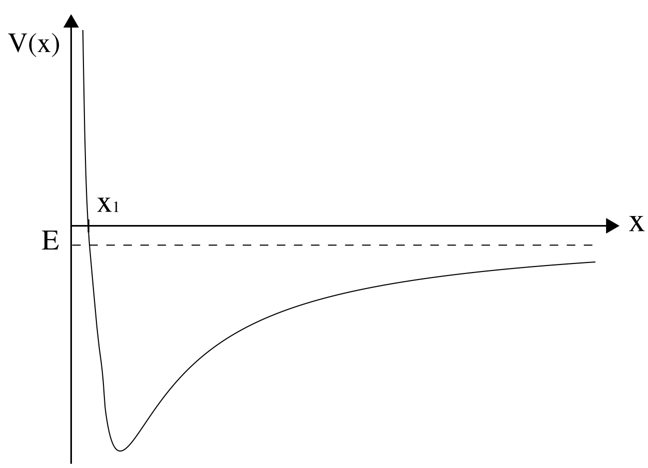


Figure 25: First excited state wavefunction

6.3.5 Case Where the Energy $E > V$.

We are now interested in the following situation



where we now have only two region, $x > x_1$ and $x < x_1$. The Schrödinger equation is

$$\frac{d^2\Psi}{dx^2} = \frac{2m}{\hbar^2}\left[V(x) - E\right]\Psi(x).$$

For $x > x_1$, then $V(x) - E < 0$ if $\Psi(x) > 0$. Therefore $\frac{d^2\Psi}{dx^2} < 0$ and the solution is downward concave. For this case, $\Psi(x)$ will converge. If $\Psi(x) < 0$, then $\frac{d^2\Psi}{dx^2} > 0$, which means it will be upward concave, and thus will reach the axis such that $\Psi(x) \to 0$ with $x \to \pm\infty$. There are solutions that are oscillatory at large $x\,(x > x_1)$ around the axis $\Psi(x) \equiv 0$.

6.4 Conclusion

1. If, with respect to $V(x)$, E is such that classically the particle would be bounded, then we obtain quantized energy levels (discrete spectrum).

2. If, classically, E is such that the particle would be unbounded, then quantum physics predicts that all values of E are possible. We obtain a continuum of solutions.

7 Solution to the Schrödinger Equation For Simple Potentials

7.1 Particle in a Square Box

7.1.1 Statement of the Problem

We consider a particle confined in a "box". By that we mean that the particle is confined by a potential of the following form:

$$\begin{aligned} V(x) &= 0 \quad \text{for} \quad -a \le x \le a \\ &= \infty \quad \text{elsewhere} \end{aligned}$$

From a classical standpoint, the particle would simply bounce between the walls at $x = \pm a$ with a constant but arbitrary energy value. The momentum would not be conserved since the walls would not be necessarily perfectly rigid. The energy in the ground state would be zero.

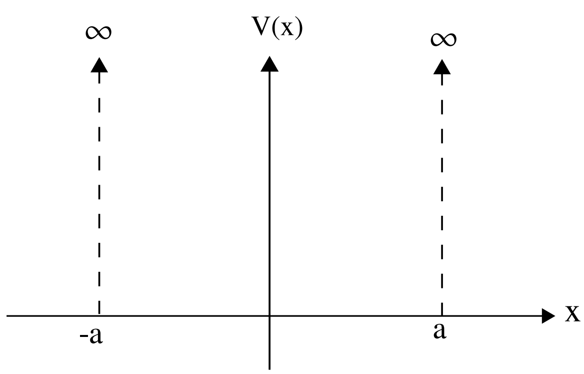


Figure 26: Potential Square Well

Quantum physics will offer a different view from the Schrödinger equation. In order to do this, we need to solve the Schrödinger equation, for the spatial function U(x)

$$\frac{d^2U}{dx^2} = \frac{2m}{\hbar^2}EU(x) = \frac{2m}{\hbar^2}V(x)U(x)$$

where we have posed $\Psi(x,t) = U(x)e^{-\frac{iEt}{\hbar}}$. Our goal is to solve the equation for the infinite potential (walls).

7.1.2 Solution for the Particle in a Box: Energy Valves

Let's consider first $-a \leq x \leq a$. In this region, $V \equiv 0$, so we have

$$\frac{d^2U}{dx^2} + \frac{2mE}{\hbar^2}U(x) = 0$$

which we rewrite as

$$\frac{d^2U}{dx^2} + k^2U(x) = 0; \qquad k^2 \equiv \frac{2mE}{\hbar^2} > 0. \tag{7.1}$$

For $x > a$ or $x < -a$, we have $V(x) = \infty$, so we must have that $U(x) = 0$ otherwise E would not be finite. We also have that $U(x)$ must be continuous across the potential at $x = \pm a$, and so $U(\pm a) = 0$. There is no constraint on $\frac{dU}{dx}|_{x=\pm a}$ since $V(x) = \infty$ at this point.

The general solution of (7.1) is therefore

$$\begin{aligned} U(x) &= A\cos kx + B\sin kx, \quad \text{or} \\ U(x) &= Ce^{ikx} + De^{-ikx}. \end{aligned}$$

Let's use the *sin* and *cos* solutions. Using the boundary conditions $U(\pm a) = 0$, we get

$$A\cos ka \pm B\sin ka = 0$$

There are therefore two different type of solution: Either $B = 0$ and the solution is $A\cos ka = 0$, or the solution is $A = 0$ with $B\sin ka = 0$.

Let's choose $\cos ka = 0$. Then we must have that $\cos ka = 0$, implies that $k_n a = n\frac{\pi}{2}$, where $n = 1, 3, 5, \ldots$ Since the energy is given by $E = \frac{\hbar^2 k_n^2}{2m}$, the energy is therefore discretized in energy levels E_n given by

$$E_n = \frac{\hbar^2 k_n^2}{2m} = \frac{\hbar^2}{2m}\frac{n^2\pi^2}{4a^2}.$$

We call these energy levels the "eigen-energies" or "eigenvalues". Simiarly, for the solution with $A = 0$ and $B\sin ka = 0$, we must have that $k_n a = \frac{n\pi}{2}$, where $n = 2, 4, 6, \ldots$ and similarly the energy levels are given by $\frac{\hbar^2 n^2 \pi^2}{2m4a^2}$.

Therefore, we have that in general:

$$\boxed{E_n = \frac{\hbar^2 n^2 \pi^2}{8ma^2} \qquad n = 1, 2, 3, \ldots}$$

Note that the lowest energy value is given by $n = 1$ where $E_1 = \hbar^2\pi^2/8ma^2$. This is called the ground state energy. Note that classically the lowest energy the particle could have was $E = 0$. For this reason, E_1 is often referred to as the zero-point energy.

7.1.3 The Wavefunction For the Particle in a Box

Let's consider the solution where $A = \ldots$ and the time-independent spatial function is given by $U(x) = B \sin ka$. We have seen previously that the wavefunction gives a measure of the probability to find the system, and so must be properly normalized. Therefore $\int_{-\infty}^{\infty} |\Psi(x)|^2 dx = 1 = \int_{-\infty}^{\infty} \Psi(x)\Psi^*(x)dx$. We now must normalize the wave function. Since $\Psi(x,t) = U(x)e^{-\frac{iEt}{\hbar}}$, it implies that the time-dependent part plays no role in the normalization since $e^{-\frac{iEt}{\hbar}} e^{\frac{iEt}{\hbar}} = 1$. Therefore, $\int_{-\infty}^{\infty} \Psi(x)\Psi^*(x)dx$ reduces to $\int_{-\infty}^{\infty} U(x)U^*(x)dx = 1$. This gives us the condition

$$\int_{-\infty}^{\infty} U(x)U^*(x)dx = |B|^2 \int_{-a}^{a} sin^2\left(\frac{n\pi x}{2a}\right) dx = 1.$$

But

$$\int_{-a}^{a} sin^2\left(\frac{n\pi x}{2a}\right) dx = \frac{1}{2}\int_{-a}^{a} \left[1 - \cos\left(\frac{2n\pi x}{2a}\right)\right] dx$$

and only the first term contributes since the integral of a cosine gives us a sine and $\sin(\pm n\pi) = 0$. Therefore, $|B|^2 \int_{-a}^{a} \sin^2\left(\frac{n\pi x}{2a}\right) dx = \frac{1}{2}\left[a - (-a)\right] = a$ and so $B = 1/\sqrt{a}$. We can therefore write the wave-function for the particle in a box as

$$\Psi^n_{even}(x,t) = \frac{1}{\sqrt{a}} \sin\left(\frac{n\pi x}{2a}\right) e^{-\frac{iE_n t}{\hbar}}, \qquad \text{for} \quad n = 2, 4, 6, \ldots$$

Similarly, we can show that for the cos solution with $n = 1, 3, 5, \ldots$ the solution is given by

$$\Psi^n_{odd}(x,t) = \frac{1}{\sqrt{a}} \cos\left(\frac{n\pi x}{2a}\right) e^{-\frac{iE_n t}{n}}.$$

For the first three solutions that are lowest in energy, i.e. Ψ^1, Ψ^2, and Ψ^3, we can plot the time-independent wavefunction u^1, u^2, u^3:

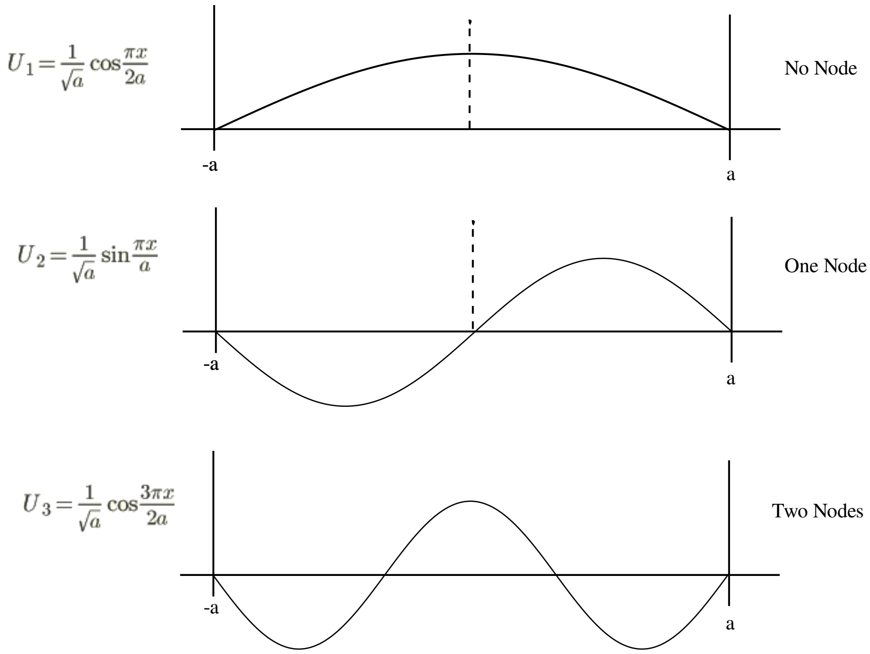


Figure 27: The first three wavefunctions for our square well potential.

Thus, the more the energy E_n increases, the more nodes there will be (distinct from those at $x = \pm a$). The more nodes there will be, the average curvature will increase. The energy is therefore related to the average curvature of $\Psi(x,t)$. We can write for the average energy

$$
\begin{aligned}
< p^2/2m > &= \frac{1}{2m}\int_{-\infty}^{\infty} \Psi^*(x,t)\left(-\hbar^2\frac{\partial^2}{\partial x^2}\right)\Psi(x,t)dx \\
&= \frac{-\hbar}{2m}\int_{-a}^{a} U^*(x)\frac{d^2}{dx^2}U(x)dx \\
&= \frac{-\hbar^2}{2m}\int_{-a}^{a} dx\left[\frac{d}{dx}(U^*\frac{dU}{dx}) - \frac{dU^*}{dx}\frac{dU}{dx}\right] \quad (byparts) \\
&= \frac{-\hbar^2}{2m}U^*\frac{dU}{dx}|_{-a}^{a} + \frac{\hbar^2}{2m}\int_{-a}^{a}|\frac{dU}{dx}|^2 dx.
\end{aligned}
$$

Since $U^*(\pm a) = 0$, we have shown that

$$< \frac{p^2}{2m} >= \frac{\hbar^2}{2m}\int_{-a}^{a}|\frac{dU}{dx}|^2 dx$$

i.e. the average curvature of $U(x)$.

Finally, the most general solution for $\Psi(x,t)$ will be a linear combination of all U^n, so that we write

$$\Psi(x,t) = \Sigma_{n=1}^{\infty} A_n U^n(x) e^{\frac{-E_n t}{\hbar}}$$

where the ground state is given by n=1 and the n=0 does not exist since otherwise $U_0(x) = 0$ everywhere, which is not physical.

7.2 The Entirely Free Particle

7.2.1 Solutions for the Free Particle

In the previous section, we have seen that the presence of boundary conditions, i.e. in particular infinite potentials or wells in a box defined by $x = \pm a$, led to a "quantized energy spectrum" for the particle. But what if we set $V \equiv 0$ in the Schroödinger equation, i.e. if the particle was entirely free, then would it have quantized energy levels?

Setting $V \equiv 0$ in the Schrödinger equation lends to the time-independent equation

$$\frac{d^2U}{dx^2} + k^2 U = 0 \quad \text{with} \quad k^2 = \frac{2mE}{\hbar^2}.$$

The solution for this equation is given by

$$U(x) \propto e^{\pm ikx}$$

and the complete solution is given by

$$\Psi(x,t) = Ce^{\pm ikx} e^{\frac{-iEt}{\hbar}}$$

and the energy is given by $E = \frac{\hbar^2 k^2}{2m}$ and is <u>not</u> quantized anymore since there is no boundary conditions in this case. The energy spectrum is continuous, and can assume any values of k.

7.2.2 Normalization Issues For the Free Particle

The normalization of the free particle is unlike the particle in the box since the wavefunction is considered from $-\infty$ to ∞. Consider, for the discussion, an extent ranging from $-a$ to $+a$. Then $U(x) = \frac{1}{\sqrt{a}} e^{ikx}$ or $U(x) = \frac{1}{\sqrt{a}} e^{-ikx}$. Taking the limit $a \to \infty$, $U(x)$ becomes in this limit neglectable. The probability density, $|U(x)|^2$ is simply $|U(x)|^2 = 1/a$, so it is uniform. Since the momentum for these states is perfectly known, i.e. $p = \pm\hbar k$, according to the uncertainty principle we can find the particle <u>anywhere</u>. It is therefore normal that $|U(x)|^2$ be uniform and that the density of probability goes to zero with $a \to \infty$.

7.3 The Finite Square Well

7.3.1 The Quantum Box

Imagine now that the infinite square well is replaced by a finite square well of the form:

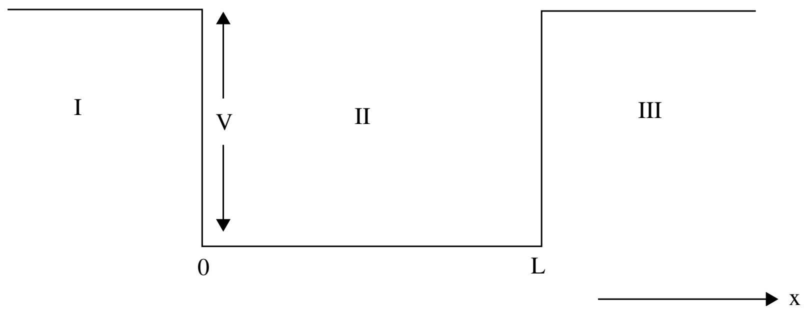


Figure 28: The different regions of our now finite square well.

i.e. with a height V and extending from 0 to L in a direction given by $\hat{x}$. Classically, if a particle has an energy $E < V$ it would be confined to the box (II). However quantum physics asserts that the particle can penetrate region I and III that are forbidden classically. To show this, we must study the Schrödinger equation in all regions I, II, III, and in particular the boundary conditions.

7.3.2 Solution for the Finite Box

Let's consider the region I and III, i.e $x < 0$ and $x > L$. For this case, the Schrödinger equation for the time dependent wavefunction $U(x)$, where $\Psi(x,t) = U(x)e^{\frac{iEt}{\hbar}}$, will be given

$$\frac{d^2U}{dx^2} - k^2U(x) = 0$$

where $k^2 = \frac{2m(V-E)}{\hbar^2}$ is constant. Note that $k^2 > 0$ for $E < V$, but $k^2 < 0$ for $E > V$. For this latter case, it means that k is a complex number, i.e $k = i\kappa$, where κ(kappa)$\in R$. The solutions for the equation above for $E < V$ are real exponentials given by $e^{\pm kx}$. The positive solution must be rejected since in region III where $x > L$ we must have Ψ to remain finite in the limit $x \to \infty$. Likewise, in region I, the negative solution must be thrown out. The solution is therefore

$$U(x) = Ae^{kx} \quad \text{for} \quad x < 0$$
$$U(x) = Be^{-kx} \quad \text{for} \quad x > L.$$

The coefficients A and B are found by matching this wave smoothly with the wavefunction inside the well. This means that $U(x)$ and $\frac{dU}{dx}$ must match at the boundary given by $x = 0$ and $x = L$. This will lead, once again, at the generation of quantized energy levels. In region I and III, the wavefunction given by e^{-kx} (or e^{kx} for $x < 0$) means that the particle penetrates these classically forbidden regions over a distance given by $\delta \equiv \frac{1}{k} = \frac{\hbar}{\sqrt{2m(V-E)}}$. At a distance δ beyond the wall edge, the wave amplitude has decayed by an amount of $1/e$. The figure below shows a cartoon of the wavefunction $U_n(x)$ and the probability density $|U(x)|^2$ for the lowest three energy levels, $n = 1, 2, \text{and } 3$.

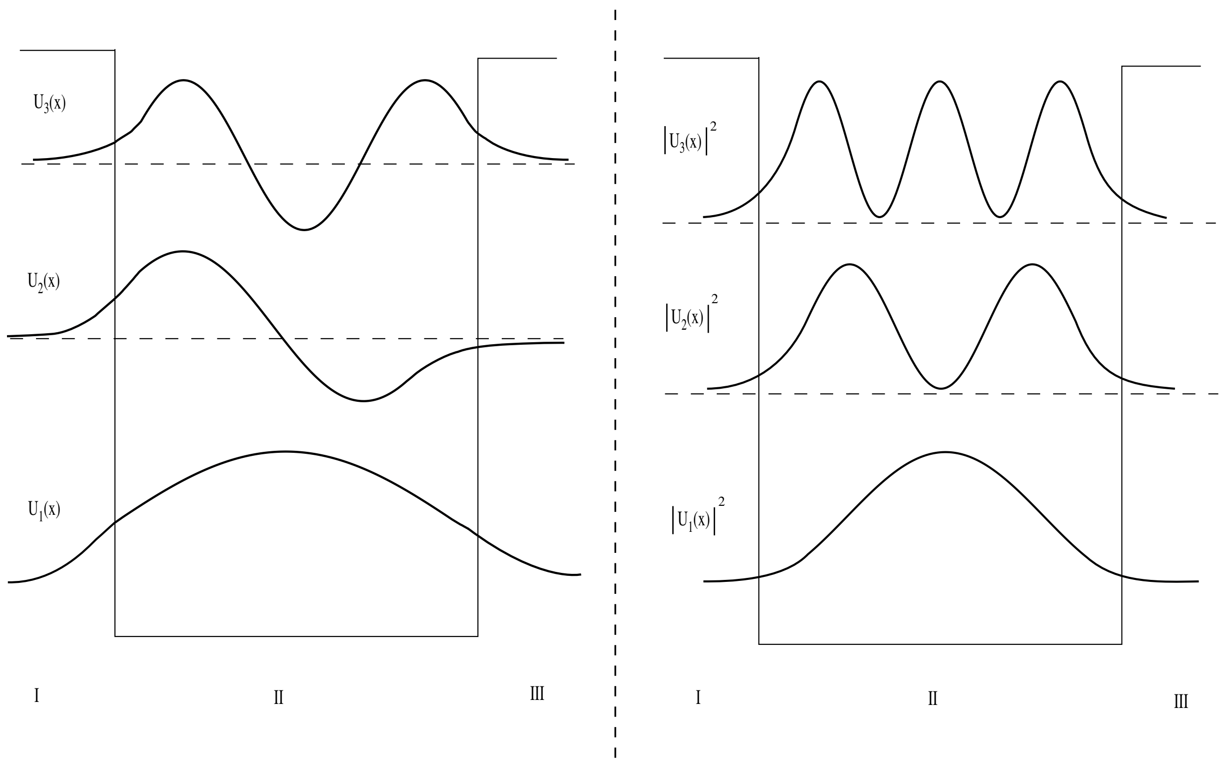


Figure 29: The first three wavefunctions for our finite square well potential.

We can therefore see that the probability to find the particle, i.e. given by $|\Psi|^2 = |U(x)|^2$, is not zero in region I and III. Lastly, it can be shown to be approximately, when $\delta << L$, given by

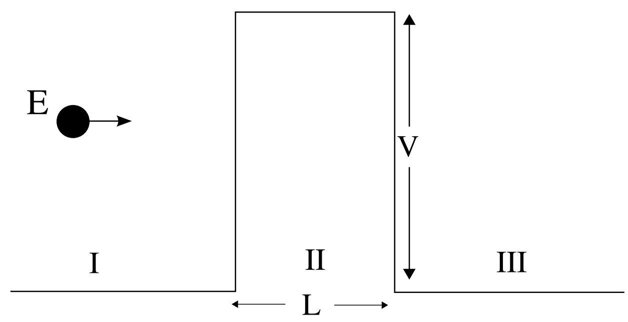
$$E_n = \frac{\hbar^2 \pi^2 n^2}{2m(L + 2\delta)^2} \; ; E << V$$

However, when the energy of the particle E approaches V, this formula above breaks down. In the limit $E << V$, this energy quantization of the finite square well is similar to the infinite well but with an effective well size given by $L + 2\delta$.

7.4 The Square Barrier: Quantum Tunneling

7.4.1 Statement of the Problem

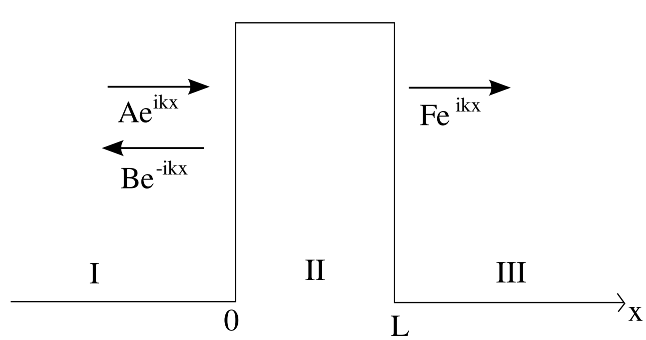
We are now interested in the problem of a particle with an energy E hitting a potential barrier of height V, and width L, see picture below.



We can already expect the following situation: the incident wave will be reflected in region I and a transmitted wave will be transmitted in III. This means that quantum-mechanically we can have the particle tunneling through region II despite the energy $E < V$, which cannot happen classically. Assuming a time-independent wavefunction $\Psi(x,t) = U(x)e^{\frac{-iEt}{\hbar}} \equiv U(x)e^{-i\omega t}$, we write for region I:

$$\begin{aligned} \Psi_I(x,t) &= Ae^{i(kx-\omega t)} + Be^{i(-kx-\omega t)} \\ &\equiv \Psi_{inc} + \Psi_{ref} \end{aligned}$$

which is the sum of the two plane waves, one incident and one reflected, each of which have an energy $E = \hbar\omega = \hbar^2 k^2 2m$. The first term is the incident wave and the second the reflected one propagating with a wave vector $-k$ to the left. The problem is to calculate these coefficients, A, B, and the transmitted part, $\Psi_{trans} = Fe^{i(kx-\omega t)}$.



7.4.2 Coefficient of reflection, transmission, and tunneling

We shall define the coefficient of reflection R for the barrier as the ratio of the probability density to the incident probability density

$$R = \frac{(\Psi^*\Psi)_{ref}}{(\Psi^*\Psi)_{inc}} = \frac{B^*B}{A^*A} = \frac{|B|^2}{|A|^2}.$$

R is therefore the wave intensity in the reflected beam, or in particle language, the probability that the particle be reflected by the barrier. Similar arguments apply for the transmitted part and we can define a transmission coefficient T as:

$$T = \frac{(\Psi^*\Psi)_{trans}}{(\Psi^*\Psi)_{inc}} = \frac{F^*F}{A^*A} = \frac{|F|^2}{|A|^2}.$$

The transmission coefficient thus is a measure of the probability that a particle emerge through the barrier. Since the sum of the all probabilities must be 1, this implies that

$$R + T = 1.$$

Inside the barrier, similarly we must write the solution as

$$\Psi_{II} = Ce^{i(kx-\omega t)} + De^{i(-kx-\omega t)}.$$

However, inside the barrier, if $E < V$, we have that $k = \sqrt{\frac{2m(E-V)}{\hbar^2}} \in C$; i.e. $k \equiv i\alpha$, a pure imaginary number. Thus the wavefunctions in this region are given by

$$\Psi_{II} = Ce^{-\alpha x - i\omega t} + De^{\alpha x - i\omega t}.$$

This means that, in the barrier, the waves spatially decay exponentially by a factor $e^{\pm\alpha x}$. We define the penetration depth $\delta = 1/\alpha$, so that after a distance δ into the barrier, the wave amplitude has decayed by an amount of $1/e$.

To find the coefficients C, D, F, and B, so that we can calculate R and T, we must apply some boundary conditions at the beginning and end of the barrier. In particular, we must have that Ψ and $\frac{\partial\Psi}{\partial x}$ be continuous at $x = 0$, L. This leads to the following 4 continuity equations:

$$
\begin{aligned}
A + B &= C + D & \text{(continuity of } \Psi \text{ at } x = 0) \\
ikA - ikB &= \alpha D - \alpha C & \text{(continuity of } \frac{\partial \Psi}{\partial x} \text{ at } x = 0) \\
Ce^{-\alpha L} + De^{\alpha L} &= Fe^{ikL} & \text{(continuity of } \Psi \text{ at } x = L) \\
\alpha De^{\alpha L} - \alpha Ce^{-\alpha L} &= ikFe^{ikL} & \text{(continuity of } \frac{\partial \Psi}{\partial x} \text{ at } x = 0)
\end{aligned}
$$

Dividing these Four equations by the incident amplitude A provides four equations for the ratios $\frac{B}{A}$, $\frac{C}{A}$, $\frac{D}{A}$, $\frac{F}{A}$. These equations can be solved to find $\frac{B}{A}$ and $\frac{F}{A}$ and so on. For the transmission coefficient $T \equiv \frac{|F|^2}{|A|^2}$ it can be shown that

$$
T(E) = \left\{ 1 + \frac{1}{4} \left[\frac{V^2}{E(V-E)} \right] \sinh^2 \alpha L \right\}^{-1} .
$$

This holds for $E < V$ only. When $E < V$, then α is imaginary and $sinh(\alpha L)$ becomes oscillatory.

8 Many-particle Systems

8.1 Schrödinger Equation for Many-Particle Systems

8.1.1 One-dimensional Case with N-particle

We want to generalize the Schrödinger equation for N particles, all of which are in 1 dimension. We shall consider:

$$
\Psi(x,t) = \Psi(x_1, x_2, x_3, \ldots, x_N, t)
$$

as the wavefunction for the N-particles. Therefore, the Schrödinger equation becomes:

$$
i\hbar \frac{\partial}{\partial t} \Psi(x_1, x_2, \ldots, x_N, t) = H\Psi(x_1, x_2, \ldots, t)
$$

where H is the Hamiltonian for the N-particles, i.e. the total energy for the N-particles. Such Hamiltonian is given by

$$
H = \frac{p_1^2}{2m} + \frac{p_2^2}{2m} + \cdots + \frac{p_N^2}{2m} + V(x_1, x_2, \ldots, x_N)
$$

where p_i^2 is the momentum squared for the i^{th} particle and where $p_i \equiv \frac{\hbar}{i}\frac{\partial}{\partial x_i}$. If the potential $V(x_1, x_2, \ldots, x_N)$ is not dependent on time, then we can write the wavefunction as:

$$\Psi(x_1, x_2, \ldots, x_N, t) = U(x_1, \ldots, x_N) e^{\frac{-iEt}{\hbar}}$$

and the Schrödinger equation in this case can be written, for the time-independent part $U(x)$ as,

$$\left[\frac{-\hbar^2}{2m_1}\frac{\partial^2}{\partial x_1^2} + \cdots + \frac{-\hbar^2}{2m_N}\frac{\partial^2}{\partial x_N^2} + V(x_1, x_2, \ldots, x_N)\right] U(x_1, \ldots, x_N) = E\, U(x_1, x_2, \ldots, x_N).$$

In general, this equation is notoriously difficult to solve. We must therefore look at special cases, or make approximations. For instance, we could consider particles that do not interact, so that $V(x_1, x_2) = V(x_1) + V(x_2)$, a sum of independent potentials. In this case, we can use the method of separation of variables.

8.1.2 Case Where Parameters Do Not Interact

We now consider potentials such that $V(x_1, x_2) = V(x_1) + V(x_2)$. So we pose $U(x_1, x_2) = U(x_1)\, U(x_2)$ and the time-independent Schrödinger equation becomes

$$\frac{-\hbar^2 U(x_2)}{2m_1}\frac{d^2U(x_1)}{dx_1^2} - \frac{\hbar^2 U(x_1)}{2m_2}\frac{d^2U(x_2)}{dx_2^2} + V(x_1)U(x_1)U(x_2) + V(x_2)U(x_1)U(x_2) = E\, U(x_1)U(x_2)$$

Dividing by $U(x_1)U(x_2)$, we obtain

$$\frac{\frac{-\hbar^2}{2m_1}\frac{d^2U(x_1)}{dx_1^2} + V(x_1)U(x_1)}{U(x_1)} = \frac{\frac{-\hbar^2}{2m_2}\frac{d^2U(x_2)}{dx_2^2} + V(x_2)U(x_2)}{U(x_2)} = \text{constant} = E.$$

Therefore,

$$\frac{-\hbar^2}{2m_1}\frac{d^2U(x_1)}{dx_1^2} + V(x_1)U(x_1) = E_1\, U(x_1)$$

$$\frac{-\hbar^2}{2m_2}\frac{d^2U(x_2)}{dx_2^2} + V(x_2)U(x_2) = E_2\, U(x_2)$$

and $E = E_1 + E_2$. So the problem reduces to independent Schrödinger equation for each particle i^{th}.

8.1.3 Translation invariant Potentials

There exist a very interesting class of potentials for the two-particle problem that we have seen above. It is the case when

$$V(x_1, x_2) = V(x_1 - x_2)$$

i.e. the potential is only a function of the distance between the two particles. A translation for the whole system does not modify the potential interaction energy between the particles. In this case, we can separate the motion of the centre-of-mass, with that of the relative coordinates of the two particles, as in classical mechanics.

Let X be the coordinate of centre-of-mass and $X = \frac{m_1 x_1 + m_2 x_2}{m_1 + m_2}$. Let $x = x_1 - x_2$ be the relative coordinate between the particles. We have that

$$\begin{aligned} \frac{\partial}{\partial x_1} &= \frac{\partial X}{\partial x_1}\frac{\partial}{\partial X} + \frac{\partial x}{\partial x_1}\frac{\partial}{\partial x} \\ &= \frac{m_1}{M}\frac{\partial}{\partial X} + \frac{\partial}{\partial x} \end{aligned}$$

and

$$\frac{\partial}{\partial x_2} = \frac{m_2}{M}\frac{\partial}{\partial X} - \frac{\partial}{\partial x}$$

and we can show that

$$\frac{-\hbar^2}{2m_1^2}\frac{\partial^2}{\partial x_1^2} - \frac{\hbar^2}{2m_2^2}\frac{\partial^2}{\partial x_2^2} = \frac{-\hbar^2}{2M}\frac{\partial^2}{\partial X^2} - \frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial x^2}$$

where $\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2}$ is the reduced mass.

In the equation above, the first term is the kinetic energy of the centre-of-mass, and the second is the kinetic energy of relative motion. The Schrödinger equation becomes:

$$\left[-\frac{\hbar^2}{2M}\frac{\partial^2}{\partial X^2} - \frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial x^2} + V(x)\right] U(x, X) = E\, U(x, X).$$

Using the method of separation of variables, we can write the function $U(x, X)$ as being

$$U(x, X) = \phi(x) e^{\frac{ipx}{\hbar}}$$

where p is the momentum of centre-of-mass, and where $\phi(x)$ is given by solving

$$\left[\frac{-\hbar^2}{2\mu}\frac{d^2}{dx^2} + V(x)\right]\phi(x) = \left[E - \frac{p^2}{2M}\right]\phi(x) = E\,\phi(x).$$

8.2 Identical Particles and Pauli Exclusion Principle

8.2.1 Statement of the Problem

Because of the uncertainty principle and the absence of precise trajectories, in quantum physics we cannot distinguish between the identical properties. For example:

1. Two e^-'s in an atom
2. Two protons in a nucleus
3. Two photons in a free space
4. etc.

The Hamiltonian for the identical particles becomes:

$$\left[\frac{-\hbar^2}{2\mu}\frac{d^2}{dx_1^2} - \frac{\hbar^2}{2m}\frac{\partial^2}{\partial x_2^2} + V(x_1, x_2)\right]U(x_1, x_2) = E\,U(x_1, x_2)$$

where $V(x_1, x_2) = V(x_2, x_1)$ since the particles must be indistinguishable, and so $U(x_1, x_2)$ and $U(x_2, x_1)$ must satisfy the same equation. Thus we can only have:

$$U(x_1, x_2) = \pm U(x_2, x_1)$$

either symmetric or antisymmetric with respect to the exchange of two particles.

8.2.2 Pauli Exclusion Principle

Pauli has proposed that for two identical particles particles, the change in the wavefunction for the particles upon an adiabatic exchange is not arbitrary, or fixed by the initial conditions. Rather, according to him there are only two types of particles:

1. Fermions: where $U(x_1, x_2) = -U(x_2, x_1)$

   Example: electron, proton, neutron, etc.

2. Bosons: where $U(x_1, x_2) = +U(x_2, x_1)$

   Example: Photons, 4He, deutron, etc.

Pauli Principle:

> the wave function of a system with many identical particles is anti-symmetric with respect to the adiabatic exchange of two fermions:
>
> $$\Psi_F(x_1, x_2, \ldots, x_N) = -\Psi_F(x_2.x_1, \ldots, x_N)$$
>
> and the wave function for a system with many bosons is symmetric with respect to the adiabatic exchange of two bosons:
>
> $$\Psi_B(x_1, x_2, \ldots, x_N) = \Psi_B(x_2, x_1, \ldots, x_N)$$

This principle has severe consequences and will be the defining factor for many issues related to the behaviour of matter.

8.2.3 Example: Two non-interacting electrons

We consider two electrons, non-interacting, that are subjected to the same external potential $V(x)$ such that the total potential energy is

$$V_T(x_1, x_2) = V(x_1) + V(x_2)$$

The wavefunction of the two electron system can therefore be written as:

$$U(x_1, x_2) = U_{E_1}(x_1)\, U_{E_2}(x_2)$$

where

$$\left[\frac{-\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)\right] U_{E_n}(x) = E_n\, M_{E_n}(x)$$

and $E = E_1 + E_2$ is the total energy of the two electron system. If the potential $V(x) = V(x_1) + V(x_2)$ is an infinite square well potential, of width ranging from $x = 0$ to $x = b$, the wavefunction of the two-particle system, without any constraint from symmetry, is given by

$$U(x_1, x_2) = \frac{2}{b}\sin\frac{n_1\pi x_1}{2b}\sin\frac{n_2\pi x_2}{2b}.$$

The sinusoidal solution arises from the fact that there are infinite walls at $x = 0$. This wavefunction, however, is not antisymmetric with respect to the exchange of particles. To render it anti-symmetric, we must take the following combination

$$U_A(x_1, x_2) = \frac{1}{\sqrt{2}} \frac{2}{p} \left(\sin \frac{n_1 \pi x_1}{2b} \sin \frac{n_2 \pi x_2}{2b} - \sin \frac{n_1 \pi x_2}{2b} \sin \frac{n_2 \pi x_1}{2b} \right).$$

So, in general, we shall have for the wavefunction of two non-interacting electrons (fermions)

$$U_A(x_1, x_2) = \frac{1}{\sqrt{2}} \left(U_{E1}(x_1) U_{E_2}(x_2) - U_{E1}(x_2) U_{E_2}(x_1) \right).$$

In the case where $E_1 = E_2$, i.e. when the two electrons are in the same quantum state, then $U(x_1, x_2) \equiv 0$.

Pauli Exclusion Principle:

> "no more than one fermion can be in the same quantum state"

8.2.4 Quantum Number for the Spin of the Electron

As we have seen before, electrons do not only possess a charge, but they also have a "spin". This spin of the electron is purely quantum mechanical in nature, and does not have a true classical equivalent. For the electron, the spin can only take two values: spin $= 1/2$ or spin $= -1/2$. With the spin included, the Pauli Exclusion principle states that

> "No more than one electron can be in the same quantum state. Two electrons can be in the same state characterized by the quantum number n, but only if they have different spin."