

PHY 115A
Lecture Notes

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Chapter 1

The Wave Function

1.1 The Experimental Foundation of Quantum Mechanics

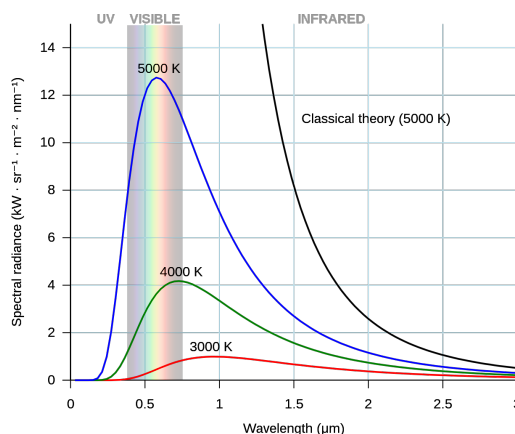


Figure 1.1: The ultraviolet catastrophe.

By the start of the 1900's classical physics had achieved a series of remarkable experimental and theoretical breakthroughs.

- Young's Double Slit experiment (1801) showed that when monochromatic light passes through a single slit followed by two double slits, the intensity of the light reaching a distant plane exhibits an interference pattern:

$$I(\theta) = I_0 \cos^2 \left(\frac{\pi d}{\lambda} \sin \theta \right)$$

where λ is the wavelength of the light, d the distance between the slit, θ the angle relative to the center of the slits, and I_0 the intensity at $\theta = 0$.

- The Maxwell Equations (1861) unified the magnetic and electrical forces within a theory that accurately describes an array of phenomenon that is breathtaking in scope. It predicted radio waves and how to produce and detect them. It alluded to special relativity. The theory showed that light was a propagating disturbance in the electromagnetic field: an EM wave.
- JJ Thomson discovered the electron (1897) using cathode ray tubes and determined its charge to mass ratio. The Millikan oil drop experiment (1909) determined the electron charge e .

Despite these impressive achievements, there were also shortcomings in the classical theory:

- The prediction of the classical theory for the spectral radiance of black body radiation failed spectacularly at low wavelength.
- In the photoelectric effect, light shining on a material causes the emission of electrons. The classical theory predicts that the kinetic energy of the photoelectrons emitted depends on the intensity of the light, but experiments showed it depended on the wavelength. Below a certain wavelength for each material, there was no emission at all.
- Atomic spectroscopy: hydrogen (and other atoms) were shown to emit electromagnetic radiation at specific wavelengths. For the hydrogen atom, the quantized wavelengths are described by the empirically-determined Rydberg formula:

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

where $1/R_H = 91 \text{ nm}$ and $n_1 < n_2$ are both quantum numbers.

The explanation for these phenomenon relied upon quantization:

- Planck's Law: the observed spectral radiance from black body radiation can be accurately predicted if light consists of discrete quanta, called photons, with energy

$$E = h\nu.$$

The ultra-violet catastrophe is avoided because it requires a great deal of energy to produce each ultra-violet photon.

- The surprising features of the photoelectric effect can also be understood as due to photons. Individual photons below a certain wavelength do not have enough energy to liberate an electron, and the kinetic energy of the electrons depends on the energy of the photon, which depends on the wavelength of light, not the intensity.
- The Bohr model of the atom constrained electrons to orbits at discrete energy levels with angular momentum that is an integer ratio of Planck's constant. This model perfectly predicted the Rydberg formula.

The quantization of photons inspired Louis de Broglie to the hypothesis that matter behaves like a wave with wavelength

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

This hypothesis was the beginning of our modern formulation of quantum mechanics. Modern demonstrations of electron interference, as shown in Fig. ??, clearly reveal the wave nature of matter.

The fascinating conversation between theory and experiment that led to the formulation of quantum mechanics is worthy of studying. However, it isn't the easiest way to come to terms with the shocking theory. Instead of developing the theory piece by piece, we'll jump right to the Schrödinger Equation as our starting assumption, and work through the consequences.

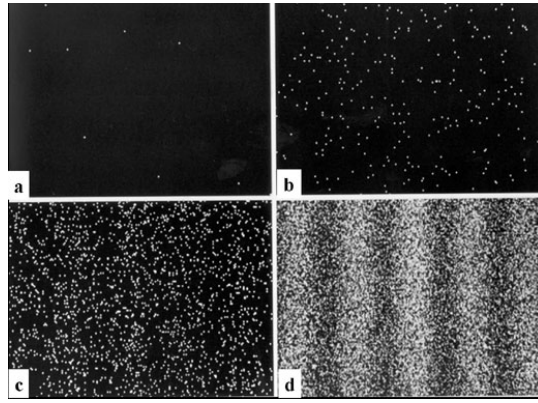


Figure 1.2: After passing through a double slit apparatus, the location of individual electrons are observed as dots of light. When enough electrons are observed an interference pattern emerges.

1.2 An Experimental Perspective

- Never forget that physics is an **experimental discipline**: the most compelling mathematical argument you can imagine could be rendered invalid by a single well-executed experiment.
- **You cannot derive Quantum Mechanics.** Quantum Mechanics is a set of assumptions that are mathematically consistent with experimental results. It offers no explanation for those assumptions.
- **Derivations are useful for predicting the outcomes of future experiments** based on the results from our previous experiments, within the context of a theory. The more successful we are at playing this little game, the more confidence we have in the theory.
- By this metric, **Quantum Mechanics is an exceptionally successful theory!**
- **The starting assumptions are not unique.** You can learn a lot by seeing how different assumptions lead to the same physical theory. We'll do some of this.

1.3 The Schrödinger Equation

Here's a summary of Griffiths sections 1.1-1.2.

- A state of a particle is described by its wave function $\Psi(x, t)$.
- The wave function $\Psi(x, t)$ is a solution to the Schrödinger Equation (SE):

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} + V\Psi \quad (1.1)$$

where m is the mass of the particle, V the potential energy function or just “potential”, and:

- The reduced plank's constant $i\hbar = \frac{h}{2\pi} = 1.054573 \times 10^{-34}$ Js.
- The physical interpretation of the wave function is statistical. The probability $P_{ab}(t)$ that the particle will be found between points a and b at time t is:

$$P_{ab}(t) = \int_a^b |\Psi(x, t)|^2 dx \quad (1.2)$$

Suppose we divide the x -axis into six regions A, B, C, D, E, F and the particle is in a state where it has equal probability to be found in any region at $t = 0$. At $t = 0$ we observe the particle in region C . Where was the particle before this measurement? There are several schools of thought:

- realist: The particle was already in region C and we just didn't know that yet.
- orthodox: The particle wasn't in any one region, it was the measurement itself that caused one of several possible outcomes.
- agnostic: I don't know. It doesn't matter where the particle was before a measurement, because physics is about predicting the outcome of measurements.

As we'll see later, John Bell showed that this seemingly philosophical question could be explored experimentally. Of these three possibilities, the orthodox interpretation is the most supported by the experimental evidence.

1.4 Review of Statistics and Probability

Given that the physical interpretation of Quantum Mechanics is statistical, we'll review the relevant concepts from statistics. This is also covered in Griffiths sections 1.3. In the language of statistics, at the time t that we make a measurement of the particles position, the measured value x is a random variable of the probability distribution function $P(x) = |\Psi(x, t)|$.

More generally, probability distribution functions can describe a discrete random variable m that takes on a countable number of distinct values like $m = 0, 1, 2, 3, \dots$. Or they can describe a continuous random variable x . We will encounter both cases in this course.

The value of the probability distribution function for a discrete random variable is simply a probability. To determine the probability that an outcome is within a range of integers, say m_1 to m_2 the probability distribution function is simply added:

$$P = \sum_{m=m_1}^{m_2} P(m).$$

Because the probability that the outcome m is some value must be 1, the normalization is:

$$\sum_{m=0}^{\infty} P(m) = 1$$

A probability distribution function can also describe a continuous random variable x . In this case, the probability of any particular outcome, say $x = 1.24323$, is vanishing small. But the probability that the value lies within a range of values is non-zero, and is determined by integrating:

$$P = \int_{x_{\min}}^{x_{\max}} P(x) dx$$

As the outcome must be some value of x between $-\infty$ and $+\infty$ the normalization is:

$$\int_{-\infty}^{+\infty} P(x) dx = 1$$

The probability distribution function of a continuous random variable is called a probability density function (PDF). A discrete probability distribution is sometimes referred to as probability mass

function (PMF), to draw upon an analogy with physical mass and density: a PDF is probability per unit volume while a PMF is simply a probability.

Given a probability distribution describing the outcomes of an experiment, our most urgent questions are generally “what is a typical outcome?” and “how widely will outcomes typically vary from one another?”.

There are a number of ways to quantify the answer to first question, but generally the most useful answer is the mean value of the distribution, μ , which we calculate as a weighted average across all possible outcomes. For the Binomial distribution, which describes probabilities for outcomes which are natural numbers up to n , we calculate the sum:

$$\mu = \sum_{m=0}^n m P(m) \quad (1.3)$$

For a continuous probability distribution, where outcomes can be any real value, we integrate instead:

$$\mu = \int_{-\infty}^{+\infty} x P(x) dx \quad (1.4)$$

across a range appropriate to the situation, typically $[-\infty, \infty]$.

The mean is an example of an expectation value. In general, the expectation value of a function $f(x)$ of a random variable x drawn from a probability distribution function $P(x)$ is:

$$\langle f(x) \rangle \equiv \int_{-\infty}^{+\infty} f(x) P(x) dx.$$

For a discrete random variable, the integral becomes a sum:

$$\langle f(m) \rangle \equiv \sum_m f(m) P(m)$$

Using this notation, we can define the mean as the expectation value of the random variable:

$$\mu \equiv \langle x \rangle$$

To answer the second question, we define an expectation value which characterizes the variation of outcomes from the mean value, which we call the variance (σ^2) of the distribution:

$$\sigma^2 \equiv \langle (x - \mu)^2 \rangle.$$

The square root of the variance is referred to as the standard deviation (σ).

There are other ways to quantify the variation from outcome to outcome, but they are generally inferior to the variance in some way. For example $\langle x - \mu \rangle$ can be zero, even for wide distributions, as long as $P(x)$ is symmetric. The quantity $\langle |x - \mu| \rangle$ (called the average deviation) avoids this pitfall but is generally much harder to calculate, due to the absolute value.

The variance, on the other hand, is quite convenient to calculate. For example, you can show that:

$$\langle (x - \mu)^2 \rangle = \langle x^2 \rangle - \langle x \rangle^2. \quad (1.5)$$

We need only calculate $\langle x \rangle$ and $\langle x^2 \rangle$ in order to determine both the mean and variance of a distribution.

1.5 Normalization of the Wave Function

This material is covered in Griffiths section 1.4.

- If $\Psi(x, t)$ is a solution to the SE, then so is $k \cdot \Psi(x, t)$ for any value k (check!) So it would seem we could make the probability density $|\Psi(x, t)|^2$ any value that we like and still satisfy the SE!
- In fact, we are constrained in our choice by the realization that the probability of finding the particle *somewhere* must be 1, and so we must choose the value k such that:

$$\int_{-\infty}^{+\infty} |\Psi(x, t)|^2 dx = 1 \quad (1.6)$$

- If $\Psi(x, t) = 0$ for all x then we cannot find such a k .
- If the integral:

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

diverges then we cannot find such a k

- Being good physicists, we simply throw away useless unphysical solutions that cannot be normalized, and we are never troubled by them again!

But now here's a troubling thought. Suppose at $t = 0$, we have normalized $\Psi(x, t)$ such that

$$\int_{-\infty}^{+\infty} |\Psi(x, 0)|^2 dx = 1$$

. From this point on, the time dependence of $\Psi(x, t)$ is given by the SE, outside of our control. What if changes in such a way that:

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

at later times? Might we have to renormalize $\Psi(x, t)$ again at each t ?

Fortunately, solutions to the SE preserve their normalization. We can show this using the SE and integration by parts (reviewed above). We note that:

$$\frac{d}{dt} \int_{-\infty}^{+\infty} |\Psi(x, t)|^2 dx = \int_{-\infty}^{+\infty} \frac{\partial}{\partial t} |\Psi(x, t)|^2 dx.$$

Working on the integral:

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

Reworking SE:

$$\begin{aligned} i\hbar \frac{\partial \Psi}{\partial t} &= -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} + V\Psi \\ \frac{\partial \Psi}{\partial t} &= \frac{i\hbar}{2m} \frac{\partial^2 \Psi}{\partial x^2} - \frac{iV}{\hbar} \Psi \\ \frac{\partial \Psi^*}{\partial t} &= -\frac{i\hbar}{2m} \frac{\partial^2 \Psi^*}{\partial x^2} + \frac{iV}{\hbar} \Psi^* \end{aligned}$$

where in the last step we've taken the complex conjugate of the preceding equation. Substituting these results we have:

$$\begin{aligned} \frac{\partial}{\partial t} |\Psi(x, t)|^2 &= \frac{i\hbar}{2m} \left(\Psi^* \frac{\partial^2 \Psi}{\partial x^2} - \frac{\partial^2 \Psi^*}{\partial x^2} \Psi \right) \\ &= \frac{i\hbar}{2m} \frac{\partial}{\partial x} \left(\Psi^* \frac{\partial \Psi}{\partial x} - \frac{\partial \Psi^*}{\partial x} \Psi \right) \end{aligned} \quad (1.7)$$

So now:

$$\begin{aligned} \frac{d}{dt} \int_{-\infty}^{+\infty} |\Psi(x, t)|^2 dx &= \frac{i\hbar}{2m} \int_{-\infty}^{+\infty} \frac{\partial}{\partial x} \left(\Psi^* \frac{\partial \Psi}{\partial x} - \frac{\partial \Psi^*}{\partial x} \Psi \right) dx \\ &= \frac{i\hbar}{2m} \left(\Psi^* \frac{\partial \Psi}{\partial x} - \frac{\partial \Psi^*}{\partial x} \Psi \right) \Big|_{-\infty}^{+\infty} \\ &= 0 \end{aligned}$$

where in the last step we've used the fact that the wave function and it's derivative must go to zero at infinity to be physical.

1.6 Review of Integration by Parts

We'll make use of integration by parts in the following sections, so let's review the idea. We apply the chain rule to the functions $u(x)$ and $v(x)$:

$$\frac{d(uv)}{dx} = u \frac{dv}{dx} + v \frac{du}{dx}$$

and then integrate both sides:

$$\int_a^b \frac{d(uv)}{dx} dx = \int_a^b u \frac{dv}{dx} dx + \int_a^b v \frac{du}{dx} dx$$

By the fundamental theorem of calculus:

$$\int_a^b \frac{d(uv)}{dx} dx = uv \Big|_a^b$$

If the product $u(x)v(x)$ vanishes at $x = a$ and $x = b$ then

$$uv \Big|_a^b = 0$$

and so:

$$\int_a^b u \frac{dv}{dx} dx = - \int_a^b v \frac{du}{dx} dx \quad (1.8)$$

Suppose a definite integral consists of two parts, one of which (dv/dx here) is a derivative with respect to the integration variable (x here). Further suppose that the integrand with the derivative removed (uv here) vanishes at the limits of the integration. In this case, we can move the differentiation between parts of the integrand (from v to u here) by adding a negative sign.

1.7 Position and Momentum Operators

- From the probability interpretation of the wavefunction $P(x) = |\Psi|^2$, we define the expectation value of the x position as:

$$\langle x \rangle \equiv \int_{-\infty}^{+\infty} x P(x) dx = \int_{-\infty}^{+\infty} x |\Psi|^2 dx$$

- There is some subtlety here: the expectation value for the observable x is the mean value of the results of many repeated measurements of the x position of a particle *always starting* in the same state Ψ .
- Due to the collapse of the wave function, repeated measurements of the x position of the same particle *after* it was already observed at some position $x = a$ would reproduce the same result (to within the experiments ability to do so before the particles state changes).

In classical physics, the state of a particle is completely determined from it's position and momentum. So it is natural to consider the expectation value for the momentum:

$$\begin{aligned} \langle p \rangle &= m \frac{d}{dt} \langle x \rangle \\ &= m \int_{-\infty}^{+\infty} x \frac{\partial}{\partial t} |\Psi|^2 dx \end{aligned}$$

We already worked out the time derivative in the integrand before (Equation ??) so we have:

$$\langle p \rangle = \frac{i\hbar}{2} \int_{-\infty}^{+\infty} x \frac{\partial}{\partial x} \left(\Psi^* \frac{\partial \Psi}{\partial x} - \frac{\partial \Psi^*}{\partial x} \Psi \right) dx$$

We can use integration by parts to move the outer partial derivative onto the x :

$$\begin{aligned} \langle p \rangle &= -\frac{i\hbar}{2} \int_{-\infty}^{+\infty} \frac{\partial x}{\partial x} \left(\Psi^* \frac{\partial \Psi}{\partial x} - \frac{\partial \Psi^*}{\partial x} \Psi \right) dx \\ &= -\frac{i\hbar}{2} \int_{-\infty}^{+\infty} \left(\Psi^* \frac{\partial \Psi}{\partial x} - \frac{\partial \Psi^*}{\partial x} \Psi \right) dx \end{aligned}$$

And one more application of integration by parts to second term in the parenthesis:

$$\begin{aligned}\langle p \rangle &= -i\hbar \int_{-\infty}^{+\infty} \left(\Psi^* \frac{\partial \Psi}{\partial x} \right) dx \\ &= \int_{-\infty}^{+\infty} \Psi^* \left[-i\hbar \frac{\partial}{\partial x} \right] \Psi dx\end{aligned}\tag{1.9}$$

Compare to the expectation value for the position:

$$\langle x \rangle = \int_{-\infty}^{+\infty} \Psi^* [x] \Psi dx\tag{1.10}$$

- In general, we calculate expectation values using the *operator*:

$$\langle o \rangle = \int_{-\infty}^{+\infty} \Psi^* [\hat{o}] \Psi dx\tag{1.11}$$

- For the position observable with have the position operator

$$\hat{x} = x.\tag{1.12}$$

- For the momentum observable with have the momentum operator

$$\hat{p} = -i\hbar \frac{\partial}{\partial x}.\tag{1.13}$$

- We can construct the operator \hat{f} for any classical function of position and momentum $f(x, p)$ by substituting \hat{p} and \hat{x} for p and x .
- Have a close look at Equation ???. Had we applied integration by parts to the first term instead of the section, we would have instead concluded:

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

evidently, there is also a momentum operator that operates on the Ψ^* . We'll return to this later.

1.8 Ehrenfest's Theorem

$$\begin{aligned}\frac{d\langle p \rangle}{dt} &= \frac{d}{dt} \int_{-\infty}^{+\infty} \Psi^* \hat{p} \Psi dx \\ &= -i\hbar \int_{-\infty}^{+\infty} \frac{\partial}{\partial t} \left(\Psi^* \frac{\partial \Psi}{\partial x} \right) dx \\ &= -i\hbar \int_{-\infty}^{+\infty} \left(\frac{\partial \Psi^*}{\partial t} \frac{\partial \Psi}{\partial x} + \Psi^* \frac{\partial}{\partial x} \frac{\partial \Psi}{\partial t} \right) dx\end{aligned}$$

where in the last part we have used:

$$\frac{\partial}{\partial t} \frac{\partial \Psi}{\partial x} = \frac{\partial}{\partial x} \frac{\partial \Psi}{\partial t}$$

now using integration by parts on the second term:

$$\begin{aligned} \frac{d \langle p \rangle}{dt} &= -i\hbar \int_{-\infty}^{+\infty} \left(\frac{\partial \Psi^*}{\partial t} \frac{\partial \Psi}{\partial x} - \frac{\partial \Psi^*}{\partial x} \frac{\partial \Psi}{\partial t} \right) dx \\ &= -i\hbar \int_{-\infty}^{+\infty} \left(\left[-\frac{i\hbar}{2m} \frac{\partial^2 \Psi^*}{\partial x^2} + \frac{iV}{\hbar} \Psi^* \right] \frac{\partial \Psi}{\partial x} - \frac{\partial \Psi^*}{\partial x} \left[\frac{i\hbar}{2m} \frac{\partial^2 \Psi}{\partial x^2} - \frac{iV}{\hbar} \Psi \right] \right) dx \\ &= -\frac{\hbar^2}{2m} \int_{-\infty}^{+\infty} \left(\frac{\partial^2 \Psi^*}{\partial x^2} \frac{\partial \Psi}{\partial x} + \frac{\partial \Psi^*}{\partial x} \frac{\partial^2 \Psi}{\partial x^2} \right) + \int_{-\infty}^{+\infty} V \left(\Psi^* \frac{\partial \Psi}{\partial x} + \frac{\partial \Psi^*}{\partial x} \Psi \right) dx \\ &= -\frac{\hbar^2}{2m} \int_{-\infty}^{+\infty} \frac{\partial}{\partial x} \left(\frac{\partial \Psi^*}{\partial x} \frac{\partial \Psi}{\partial x} + \frac{\partial \Psi^*}{\partial x} \frac{\partial \Psi}{\partial x} \right) dx + \int_{-\infty}^{+\infty} V \frac{\partial}{\partial x} (\Psi^* \Psi) dx \end{aligned}$$

The first integral vanishes¹ and using integration by parts on the second integrand:

$$\frac{d \langle p \rangle}{dt} = - \int_{-\infty}^{+\infty} \frac{\partial V}{\partial x} \Psi^* \Psi dx$$

so now:

$$\frac{d \langle p \rangle}{dt} = - \langle \frac{\partial V}{\partial x} \rangle \quad (1.14)$$

which is known as Ehrenfest's Theorem.

Newton's Law in one dimension in classical physics can be written as:

$$\frac{dp}{dt} = - \frac{dV}{dx} \quad (1.15)$$

which remains true in Quantum Mechanics in an average sense.

1.9 Chapter Review

We are considering a particle of mass m , in one dimension x , in a potential V .

- The state of a particle is described by its wave function $\Psi(x, t)$.
- The wave function $\Psi(x, t)$ is a solution to the Schrödinger Equation (SE):

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} + V\Psi \quad (1.16)$$

¹If you want to go for the hat trick (three scores in one game) on using integration by parts, you can do it here, noting that $d1/dx = 0$.

- The physical interpretation of the wave function is statistical. The probability $P_{ab}(t)$ that the particle will be found between points a and b at time t is:

$$P_{ab}(t) = \int_a^b |\Psi(x, t)|^2 dx \quad (1.17)$$

- The wave functions are normalized such that

$$\int_{-\infty}^{+\infty} |\Psi(x, t)|^2 dx = 1 \quad (1.18)$$

- Once a wave function is normalized, it will remain normalized for all time as a consequence of the Schrödinger equation.
- Measurements of observable quantities are associated with operators. Given an operator \hat{o} we can calculate the expectation value for the observable o as:

$$\langle o \rangle = \int_{-\infty}^{+\infty} \Psi^* [\hat{o}] \Psi dx \quad (1.19)$$

The operator acts toward its right.

- For the position observable with have the position operator

$$\hat{x} = x. \quad (1.20)$$

- For the momentum observable with have the momentum operator

$$\hat{p} = -i\hbar \frac{\partial}{\partial x}. \quad (1.21)$$

- Newton's law is still true, but only in an average sense, by Ehrenfest's Theorem:

$$\frac{d \langle p \rangle}{dt} = - \left\langle \frac{\partial V}{\partial x} \right\rangle \quad (1.22)$$