



## van Quantum tot Molecuul

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### 1 HC1+HC2: Introduction to Quantum Theory

General introduction to quantum theory

Based on Atkins and de Paula, *Physical Chemistry* 10th edition.

In this lecture we present the mathematical framework of quantum theory. We introduce the main postulates of quantum mechanics and study the main physical consequences. We introduce the quantum wave-function and study the equation that determine its behaviour: the Schroedinger equation. We also introduce a number of mathematical tools which are required to compute phenomena in the quantum formalism. We also discuss Heisenberg's uncertainty principle, and show that it entails a fundamental limitation about the physical knowledge that we can have about quantum systems.

**Learning goals** of these two lectures:

- Understanding that the state of a quantum system is fully described by the quantum wave-function, which is a solution of the time-independent Schroedinger equation.
- Becoming familiar with the mathematical formalism of quantum physics, including Hermitian operators, eigenvalue equations, and orthogonality.
- Determining how experimental observables can be calculated from the wave-function, and perform sample calculations in specific systems.
- Understanding the probabilistic interpretation associated to the quantum wave-function.
- Computing the expectation values of physical quantities in selected quantum states.

**Introduction.** In this first two lectures of the course (HC1 and HC2), we will present a concise overview of the basic principles of quantum theory, the mathematical language relevant for the description of small objects such as atoms, molecules, and electrons.

We will state these central principles of quantum theory as established facts, avoiding (due to lack of time) the historical discussion of how these principles were developed or what is the experimental evidence

that validates them. The interested student can find a brief introduction to the historical developments that lead to the formation of quantum theory on the slides that I have posted in Canvas:

<https://canvas.vu.nl/courses/35399/files/folder/Historical%20Introduction%20to%20Quantum%20Theory>

In the following, we present the central concepts of quantum theory, focusing on those which are of special relevance for this course. When required, we will also briefly review the corresponding mathematical methods that are needed to deal with the idea of quantum theory.

## 1.1 Wave-particle duality

Every object, from a plane to a proton or an electron, will under specific conditions behave as a *wave*: this concept is known as *wave-particle duality*. Therefore, this object will experience a behaviour usually associated with waves, such as diffraction when crossing a narrow slit and the formation of interference patterns.

This of course sounds quite anti-intuitive: we don't see every day cars interfering between them or diffracting as they cross a tunnel. The reason that the wave-like character of everyday objects is that quantum theory tells us that it should become apparent only when the length scales involved (say the width of an aperture) are of the same order or smaller than their so-called *De Broglie wavelength*, defined as

$$\lambda \equiv \frac{h}{p} = \frac{h}{mv}, \quad (1.1)$$

where  $h = 6.26 \times 10^{-36} \text{ m}^2\text{kg/s}$  is a numerical constant known as *Planck's constant*, ubiquitous in the quantum theory, and  $p = mv$  is the linear momentum of the object with  $m$  being its mass and  $v$  its velocity. Planck's constant is one of the defining features of quantum theory, and in particular it determines when genuinely quantum effects will be important.

Let us illustrate under which conditions the wave-like nature of two very different objects will become relevant: an electron and a car:

First of all let us consider an electron that travels at 1% of the speed of light. This electron will have associated a linear momentum of  $p = m \cdot v = 2.73 \times 10^{-24} \text{ kg m/s}$ , and therefore its De Broglie wavelength, that is, the distance scale for which an electron should exhibit a wave-like character, is

$$\lambda = \frac{h}{p} \simeq 0.5 \times 10^{-10} \text{ m}, \quad (1.2)$$

which is the typical separation between atoms in a crystal. Therefore one expects to observe the wave character of electrons when crossing a crystalline lattice.

On the other hand, for a car of mass  $m = 1000 \text{ kg}$  moving at a velocity of  $v = 100 \text{ km/h}$ , such that its momentum is  $p = 2.8 \times 10^4 \text{ kg m/s}$ , we can associate a De Broglie wavelength of

$$\lambda = \frac{h}{p} \simeq 2 \times 10^{-38} \text{ m}, \quad (1.3)$$

implying that the wave character of a car is unobservable: a car would diffract only when crossing a tunnel of width  $\sim \lambda$ , much smaller than an atom itself.

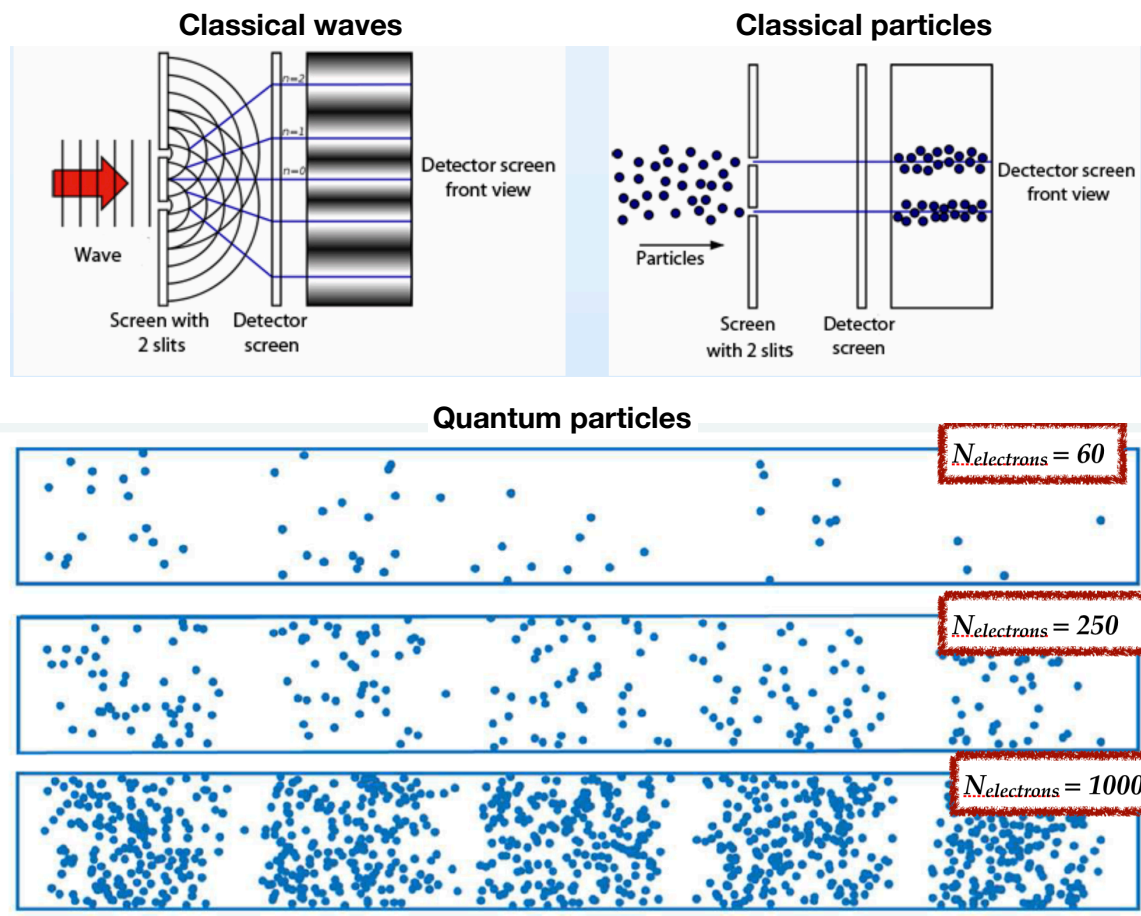


Figure 1.1: In classical theory, the behaviour of waves and particles in the double slit experiment is very different: waves lead to an interference pattern, while particles lead to just two blobs in the detector screen (upper diagrams). In quantum particle, the situation is very different (lower diagrams): if the number of incident particles is large enough, a clear interference pattrer also appears, just as if the particles behaved as waves.

Therefore, in quantum theory, when particles interact with objects of length similar or smaller than their de Broglie wavelength, their wave-like character will become apparent. In general particles such as protons and electrons will exhibit phenomena that we classically associate with either particles or waves depending on the specific circumstances.

The remarkable wave-particle behaviour of quantum theory is illustrated nicely by the famous double slit experiment, schematically represented in Fig. 1.1. In this experiment, electrons are beamed through a wall that has only two narrow slits, and then the position of the electrons is recorded in a detector screen. In classical theory, the behaviour of waves and particles in the double slit experiment is very different: waves lead to an interference pattern, while particles lead to just two blobs in the detector screen (upper diagrams). In quantum particle, the situation is very different (lower diagrams): if the number of incident particles is large enough, a clear interference pattrer also appears, just as if the particles behaved as waves. On the other hand, each particle leads to a single dot in the detector screen, so its wave-like character becomes clear only when the number of incident electrons is very large.

Interestingly, if one of the slits depicted in Fig. 1.1 is covered, then the wave-like interference pattrer formed in the detector screen disappears and the pattern of impacts is the same as for classical particles. The double slit experiment is perhaps the most iconic of those foundational experiments that highlight how

the quantum world is radically different from our everyday experience.

## 1.2 The quantum wave-function

In classical mechanics, one can obtain all the possible information about a system composed by  $N$  particles by specifying their positions  $\vec{x}_i(t)$  and linear momenta  $\vec{p}_i(t)$  at any given time  $t$ . One can in principle measure positions and velocities to any given precision, and therefore the state of the system can be completely determined.

The picture is quite different in quantum theory. There, all the *information* that can be obtained about a given quantum system is encoded in its so-called *wave-function*  $\Psi(\vec{x})$ . What is the physical interpretation of this wave function? Quantum theory tells us that the *probability* of finding the particle in a small region  $d\vec{x}$  around the position  $\vec{x}$  is given by the square of the wave function:

$$P(\vec{x}) = |\Psi(\vec{x})|^2 d\vec{x}. \quad (1.4)$$

In other words, the square of the wave function  $|\Psi(\vec{x})|^2$  represents the *probability density* of finding the particle in a specific region of space and at given time upon its measurement. Knowledge of the wave-function specifies *all* the physical information that we can access for an specific quantum system: there is no additional “hidden” information on the system that is not already present in its wave function.

Since the wave function squared,  $|\Psi(x)|^2$ , represents the probability density in the coordinate  $x$  for this particle, we have that regions in  $x$  where  $|\Psi(x)|^2$  is higher correspond to those regions where the particle has a higher likelihood to be found when a measurement is performed. This interpretation is known as the Born interpretation of the wave-function, and is further illustrated in Fig. 1.2. Those values of  $x$  where  $|\Psi(x)|^2$  is maximal (minimal) have the highest (lowest) likelihood of being those where the particle is found upon a measurement.

Note that in general the quantum wave function is a complex function, so that the square is computed as

$$|\Psi(\vec{x})|^2 = \Psi^*(\vec{x})\Psi(\vec{x}), \quad (1.5)$$

where the \* sign indicates the *complex conjugate*. To be more precise, we have that

$$|\Psi|^2 = \Psi^*\Psi = [\text{Re}(\Psi) - i\text{Im}(\Psi)][\text{Re}(\Psi) + i\text{Im}(\Psi)], \quad (1.6)$$

in terms of the real and of the imaginary components of the wave function.

Let me give an specific example of a quantum wave function that arises in a relatively simple system - we will explain later how it has been computed. As we will see in HC3, for a particle that is confined in a one-dimensional box of dimensions  $0 \leq x \leq L$  from an infinite potential of the form

$$\begin{aligned} V(x) &= 0, & 0 \leq x \leq L, \\ V(x) &= \infty, & x \leq 0 \text{ or } x \geq L, \end{aligned} \quad (1.7)$$

one possible wave function allowed is:

$$\begin{aligned} \Psi(x) &= \sqrt{\frac{2}{L}} \sin\left(\frac{\pi x}{L}\right), & 0 \leq x \leq L, \\ \Psi(x) &= 0, & x \leq 0 \text{ or } x \geq L, \end{aligned} \quad (1.8)$$

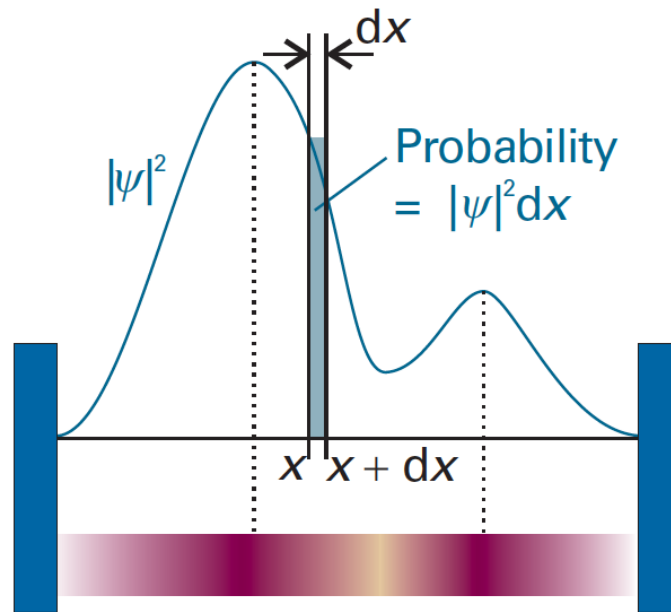


Figure 1.2: The physical interpretation of the quantum wave-function  $\Psi(x)$  is that its square  $|\Psi(x)|^2$  is the probability density associated to measuring the particle in a position  $x$  in space. Therefore, the probability to find the particle at position  $x$  in the range  $dx$  will be given by  $|\Psi(x)|^2 dx$ .

We can use this wave function to illustrate some important properties of the quantum wave function:

- The wave function is *normalised* to ensure that the probability of finding the particle *anywhere* in space is unity:

$$\int_{-\infty}^{\infty} dx P(x) = \int_{-\infty}^{\infty} dx |\Psi(x)|^2 = 1, \quad (1.9)$$

as we can check with our specific example:

$$\int_0^L dx \frac{2}{L} \sin^2\left(\frac{\pi x}{L}\right) = \frac{2}{L} \frac{L}{\pi} \left[ \frac{x}{2} - \frac{1}{4} \sin(2x) \right]_0^\pi = 1 \quad (1.10)$$

which is appropriately normalised as expected. In computing this integral, we have used the indefinite integral Eq. (A.1) from the appendix, which reads

$$\int \sin^2 x dx = \frac{x}{2} - \frac{\sin(2x)}{4}. \quad (1.11)$$

This normalisation condition ensures the conservation of probability in quantum systems.

If a given wave function  $\tilde{\Psi}(x)$  is not normalised, one can easily construct a normalised version as  $\Psi(x) = N\tilde{\Psi}(x)$ , where the normalisation factor  $N$  is constructed as

$$N = \left( \int dx |\tilde{\Psi}(x)|^2 \right)^{-1/2}, \quad (1.12)$$

Note that here we assume that the wave function is always *square-integrable*, namely that integrals of the form Eq. (1.12) are always well defined (else the probabilistic interpretation would be impossible).

- The wave function is always *continuous*, specifically across boundaries. In the example we are considering one has two boundaries, at  $x = 0$  and  $x = L$ . At these points the wave function is clearly continuous, since

$$\sin\left(\frac{\pi x}{L}\right)\Big|_{x=0,L} = 0. \quad (1.13)$$

Note that this continuity condition does not necessarily extend to derivatives of the wave function, for example the derivative of the wave function Eq. (1.8) is

$$\begin{aligned} \Psi'(x) &= \sqrt{\frac{2\pi}{L^2}} \cos\left(\frac{\pi x}{L}\right), \quad 0 \leq x \leq L, \\ \Psi'(x) &= 0, \quad x \leq 0 \quad \text{or} \quad x \geq L, \end{aligned} \quad (1.14)$$

which is not continuous at  $x = 0$  or  $x = L$ , as you can easily check.

The condition that the first derivative of the quantum wave function can be discontinuous applies only to boundaries where the potential  $V(x)$  that a particle experiences becomes infinite (as is the case here, since the particle is confined in a box). In more realistic cases, where the potential  $V(x)$  is finite, one can show that also the *first derivative of the quantum wave function is also continuous* and single-valued everywhere in space.

So for quantum systems where  $V(x)$  is finite everywhere, then both the quantum wave function  $\Psi(x)$  and its derivative  $d\Psi(x)/dx$  should be continuous for all values of  $x$ .

- In general there is not a unique answer to the question of where exactly a quantum particle is at a given time: all we know is what is the probability density of all possible positions  $x$ . However we can compute what is the *most likely value* of a given property to find upon measurement. For example, if we want to compute the expectation value (the mean) of an observable  $f(x)$  that depends on the particle position  $x$ , we can use the following expression:

$$\langle f(x) \rangle \equiv \int_{-\infty}^{+\infty} dx f(x) P(x) = \int_{-\infty}^{+\infty} dx \Psi^*(x) f(x) \Psi(x). \quad (1.15)$$

In the case of our example wave function Eq. (1.8), we can compute the most likely value of the position  $x$  of our particle as follows:

$$\langle x \rangle = \int_0^L dx x \frac{2}{L} \sin^2\left(\frac{\pi x}{L}\right) = \frac{2L}{\pi^2} \int_0^\pi dy y \sin^2(y) = \frac{2L}{\pi^2} \frac{\pi^2}{4} = \frac{L}{2}, \quad (1.16)$$

where we have used the integral in Eq. (A.2). This result implies that if we measure the position of the particle characterised by this wave function, the most likely result is that we find it in the middle of the box where is it confined, at  $x = L/2$ .

Later in this lecture we will present the general formalism that allows the calculation of expectation values of arbitrary physical observables in quantum theory.

- In addition to studying the mathematical properties of the quantum wave function, it is often useful to draw it to gain some intuition of these properties. For instance, the graphical representation of the wave function  $\Psi(x)$  in Eq. (1.8) and its corresponding probability density  $|\Psi(x)|^2$  are shown in Fig. 1.3, assuming that  $L = 1$ . From there we can see how both  $\Psi(x)$  and  $|\Psi|^2(x)$  peak at  $x = 1/2$ , the midpoint of the box, consistent with the result above indicating that the most likely value for the position of the particle is  $\langle x \rangle = L/2$ .

As an example, the Python code used to produce Fig. 1.3 is the following:

```
npts=100
for i in range(0,npts+1):
    x[i] = i/npts
    phi[i] = (2)**1/2 * math.sin(math.pi*x[i])
    phi2[i] = phi[i]**2
import matplotlib.pyplot as plt
plt.plot(x,phi,color="blue",label=r"$\phi(x)$")
plt.plot(x,phi2,color="red",label=r"$\phi^2(x)$")
plt.xlabel(r"$x$")
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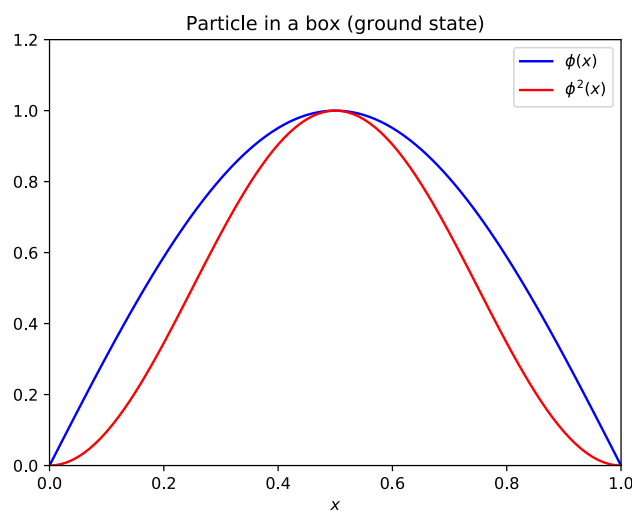


Figure 1.3: Graphical representation of the wave function  $\Psi(x)$  in Eq. (1.8) for the ground state of a particle in a box and its corresponding probability density  $|\Psi(x)|^2$ . Here we assume that  $L = 1$ .

**The Hilbert space.** To be more accurate, the wave function in quantum theory is an element of an abstract vector space called the *Hilbert space*. We can project elements of this vector space into specific bases to construct different representations of the wave function. In particular, the notation  $\Psi(x)$  that we have used so far is associated to the wave function of an specific *representation*, namely the *position representation*.

Since the wave function is an abstract quantity living in the *Hilbert* vector space, we can denote it using the so-called *braket* notation:  $|\Psi\rangle$  (introduced by Paul Dirac). Its complex conjugate is denoted by  $(|\Psi\rangle)^* = \langle\Psi|$ , and their inner (scalar) product is written as  $\langle\Psi|\Psi\rangle$ . As we have discussed before, the wave function is normalised so that the probability of finding a particle *somewhere* must be one, and in this abstract notation this condition reads  $\langle\Psi|\Psi\rangle = 1$ . In order to express the wave function in specific representation, we need to project the Hilbert space elements into an specific basis. For example we can construct the position-space wave function as

$$\Psi(x) = \langle x|\Psi\rangle, \quad (1.17)$$

and similar for other presentations, such as the *momentum representation*.

Another important property of the quantum wave function, that we can express in this abstract Hilbert space notation, is known as the *superposition principle*. This means that a given quantum system can

exist in  $n$  different states, which we label as

$$|k\rangle, \quad k = 1, \dots, n, \quad (1.18)$$

which  $k$  being the *quantum number* that classifies the elements of this vector space, then *any linear superposition* of the possible states of a quantum system is also a well-defined quantum state itself. In the above case, this means that a general quantum state of this system will be given by

$$|\Psi\rangle = \sum_{k=1}^n a_k |k\rangle, \quad (1.19)$$

with  $\{a_k\}$  arbitrary numerical coefficients. As we will see in this course, this is a very important principle that in particular allows to construct approximate solutions for complex quantum systems where finding the exact solution is very challenging.

### 1.3 The Schroedinger equation

In classical physics, the motion of a free particle is described by the second Newton equations, which in one dimension reads

$$ma = m \frac{d^2 x(t)}{dt} = F_{\text{tot}}, \quad (1.20)$$

with  $a$  being the particle acceleration,  $x(t)$  its position at time  $t$ , and  $F_{\text{tot}}$  is the total force acting on the particle. For a *free particle*  $F_{\text{tot}} = 0$  and the solution is simply

$$x(t) = x_0 + v(t - t_0), \quad (1.21)$$

where  $x_0$  and  $v_0$  are the initial conditions for the position and velocity of the particle at  $t = 0$ .

As we discussed above, for a quantum system all information is provided by its wave function  $\Psi(x)$  (now back to the position representation). So we need a different equation that determines the time evolution of the wave function, namely the analog of Newton's Eq. (1.20) for the quantum case. The corresponding dynamical equation in quantum theory is known as the *Schroedinger equation*. Here we will restrict ourselves to the time-independent Schroedinger equation, which determines the wave function of a quantum system in terms of its properties such as the local potential energy. In the simplest case of motion in one dimension, the time-independent Schroedinger equation read

$$-\frac{\hbar^2}{2m} \frac{d^2 \Psi(x)}{dx^2} + V(x)\Psi(x) = E\Psi(x), \quad (1.22)$$

where  $V(x)$  is the potential experienced by the particle when at position  $x$  and  $E$  is its total energy (the sum of kinetic plus potential energy). In this equation we find  $\hbar \equiv h/2\pi = 1.054 \times 10^{-34}$ , which is known as the *reduced Planck's constant*. In the case of a particle moving in three dimensions, the corresponding form of the time-independent Schroedinger equation reads as follows:

$$-\frac{\hbar^2}{2m} \left( \frac{d^2}{dx^2} + \frac{d^2}{dy^2} + \frac{d^2}{dz^2} \right) \Psi(\vec{x}) + V(x, y, z)\Psi(\vec{x}) = E\Psi(\vec{x}). \quad (1.23)$$

A general quantum system will be defined by the masses  $m_i$  of the particles that compose it and the potential  $V(x_1, x_2, \dots)$  that these particles experience, as well as by suitable boundary conditions. By *boundary conditions* we mean requirements that the wave function must obey in some regions of space, for



example, that the wave function should be zero in regions where the potential is infinite,  $V(x) = \infty$ . Solving a quantum system then means finding the wave functions that satisfy the Schrodinger equation subject to these conditions.

**The free particle.** The simplest quantum system is a free particle moving in one dimension. For such free particle the potential vanishes,  $V(x) = 0$ , and therefore the equation that we need to solve is:

$$-\frac{\hbar^2}{2m} \frac{d^2\Psi(x)}{dx^2} = E\Psi(x). \quad (1.24)$$

This equation is a second-order ordinary differential equation (ODE). To solve it, one can try a test solution of the form

$$\Psi(x) = \sin(Bx), \quad (1.25)$$

which is a solution of Eq. (1.24) provided that

$$\begin{aligned} \frac{d}{dx}\Psi(x) &= B \cos(Bx), \\ -\frac{\hbar^2}{2m} \frac{d^2}{dx^2}\Psi(x) &= -\frac{\hbar^2}{2m} (-B^2 \sin(Bx)) = \frac{\hbar^2 B^2}{2m} \sin(Bx), \\ E &= \frac{\hbar^2 B^2}{2m} \rightarrow B = \pm \sqrt{\frac{2mE}{\hbar^2}}. \end{aligned} \quad (1.26)$$

The more general solution is therefore of the plane-wave form:

$$\Psi(x) = A \cos\left(\sqrt{\frac{2mE}{\hbar}}x\right) + B \sin\left(\sqrt{\frac{2mE}{\hbar}}x\right). \quad (1.27)$$

The coefficients  $A$  and  $B$  in Eq. (1.27) are free parameters to be fixed by the specific boundary conditions of the problem. This result shows that under exactly the same conditions, a particle propagates rather differently in classical theory, Eq. (1.20) as compared to quantum theory, Eq. (1.27).

In Fig. 1.4 we show the same graphical representation as in Fig. 1.3 now for the wave function of the free particle, Eq. (1.27), for  $A = 0$  and  $B = 1$ , with an energy chosen so that  $2mE/\hbar^2 = 1$ . We can see clearly the periodic nature of the wave function, with the probability of finding the particle at the position  $x$ ,  $P(x) = |\Psi(x)|^2$ , peaking at fixed separations. You might have noticed that the free-particle wave function Eq. (1.27) cannot be normalised: the integral of  $|\Psi(x)|^2$  between  $-\infty$  and  $\infty$  is clearly infinite. This means that a free particle is not really a physical state. This fact is related to the Heisenberg uncertainty principle, which we discuss next.

## 1.4 Heisenberg's uncertainty principle

In quantum theory, certain pairs of physical variables, named *conjugated variables*, cannot be measured simultaneously with arbitrarily good precision. This limitation is not a matter of using measurement apparatus that have a finite resolution. It is actually a matter of principle: this statement holds true even for an ideal measurement apparatus without any experimental uncertainty associated. This condition restricts the amount of information that we can access for a specific quantum system, and is known as the *Heisenberg's uncertainty principle*. This principle is one of the building blocks of quantum mechanics.

Perhaps the most important incarnation of the Heisenberg's uncertainty principle is the one that relates the position and the linear momentum of a particle. If we denote by  $\Delta x$  the uncertainty associated to

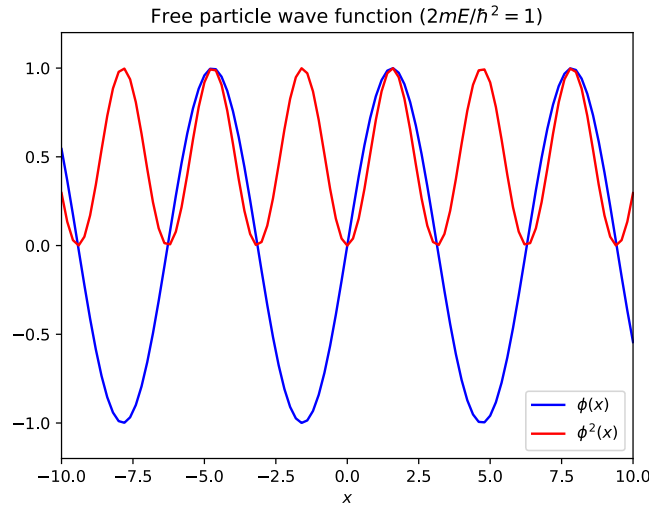


Figure 1.4: Same as Fig. 1.3 for the wave function of the free particle, Eq. (1.27), for  $A = 0$  and  $B = 1$ , with an energy chosen so that  $2mE/\hbar^2 = 1$ . Note that this wave function cannot be normalised, highlighting that these solutions do not correspond to physical systems.

the position of a given particle, and  $\Delta p_x$  the uncertainty associated to its linear momentum (in the same direction), quantum theory tells us that both  $\Delta x$  and  $\Delta p_x$  cannot be arbitrarily small at the same time. Instead, they need to satisfy the following inequality:

$$\Delta x \cdot \Delta p_x \geq \hbar, \quad (1.28)$$

in terms of the reduced Planck's constant. This means, for example, that if we aim to measure the momentum of a particle with resolution  $\Delta p$ , then we will not be able to determine its position with a resolution better than

$$\Delta x \geq \frac{\hbar}{2\pi} \frac{1}{\Delta p_x}. \quad (1.29)$$

We emphasize again that Eq. (1.28) is not merely a restriction due to the imprecision of our experimental measurement apparatus: this is a fundamental limitation about the information that can be extracted from a quantum system even with a perfect measurement. The same principle holds for other variables, such as energy and time, where we have that

$$\Delta E \cdot \Delta t \geq \hbar. \quad (1.30)$$

This inequality implies that in order to measure the energy of a particle with perfect precision, the measurement would take infinite time, since  $\Delta t \geq (\hbar/\Delta E)$ .

It is important to emphasize at this point that not all physical variables are conjugate among them: for example, while there is a limitation in how well we can measure simultaneously the position and momentum of a given particle in the same direction,

$$\Delta y \cdot \Delta p_y \geq \hbar, \quad \Delta z \cdot \Delta p_z \geq \hbar, \quad (1.31)$$

this restriction is not present to measure the position in a given direction and its linear momentum in an

orthogonal direction, for example we can have that

$$\Delta y \cdot \Delta p_x \geq 0, \quad \Delta x \cdot \Delta p_z \geq 0. \quad (1.32)$$

meaning that we can measure the position of a particle in one direction at the same time that its linear momentum in an orthogonal direction with arbitrarily good precision.

Heisenberg's principle is a radical departure from the classical picture, where the limits in which how well we can measure arbitrary physical quantities are only determined by the resolution of our measurement apparatus. How come then that classically we can measure the properties of any given object to any precision?

Because the restriction imposed by Heisenberg's uncertainty principle is only relevant when either distances or momenta are *very small*, else it is inconsequential. For example, let's consider the same car as in the previous example, with  $m = 1000$  kg and  $v = 100$  km/h, so that  $p = 27.8 \times 10^3$  kg · m/s. So if one measures this momentum with precision better than *one part in a billion*, with  $\Delta p = 10^{-12} \times p$ , then Heisenberg's uncertainty principle implies that the uncertainty in the knowledge of the position of the car will be

$$\Delta x = \hbar/\Delta p = (1.05 \times 10^{-34} \text{ m}^2\text{kg/s}) / (27.8 \times 10^{-8} \text{ kg} \cdot \text{m/s}) = 3.8 \times 10^{-28} \text{ m}, \quad (1.33)$$

which certainly is irrelevant from the practical point of view.

On the other hand, for the electron with momentum  $p = m \cdot v = 2.73 \times 10^{-24}$  kg m/s, if we measure its momentum with a 10% uncertainty, then the position of the electron will have an uncertainty of

$$\Delta x = \hbar/\Delta p = (1.05 \times 10^{-34} \text{ m}^2\text{kg/s}) / (2.73 \times 10^{-25}) = 3.8 \times 3.8^{-10} \text{ m}, \quad (1.34)$$

which is of the same order of the size of an atom, thus certainly relevant in practice.

Heisenberg's uncertainty principle is also useful to understand what happens with the free-particle wave function. We saw that this wave function, Eq. (1.27), could not be normalised. The reason is that this wave function corresponds to a particle with well defined kinetic energy  $E$  and thus well-defined linear momentum  $p_x = \sqrt{2mE}$  (since for a free particle  $E = mv^2/2 = (mv)^2/2m = p^2/2m$ ). Therefore, the free-particle wave function corresponds to a quantum state with a well-definite momentum, and therefore characterised by  $\Delta p_x = 0$ . However, in this case Heisenberg's uncertainty principle implies that the uncertainty in the position of the particle will be

$$\Delta x \geq \hbar/\Delta p_x \geq \infty \quad (1.35)$$

so the particle is maximally delocalised: this is why it is not possible to normalise its wave function.

**Commutation relations.** Heisenberg's uncertainty principle illustrates an important concept of quantum theory: the *complementarity between physical observables*. We define two observables  $\Omega_1$  and  $\Omega_2$  to be *complementary* if the sequential application of the corresponding operators  $\hat{\Omega}_1$  and  $\hat{\Omega}_2$  onto a generic wave function  $\Psi$  does not *commute*, that is,

$$\hat{\Omega}_1 (\hat{\Omega}_2 \Psi) \neq \hat{\Omega}_2 (\hat{\Omega}_1 \Psi), \quad (1.36)$$

or in other words, the results of applying the two operators  $\hat{\Omega}_1$  and  $\hat{\Omega}_2$  to a generic wave-function depends on the *order in which they have been applied*. It can be demonstrated that for each pair of complementary observables there will be a relation of the form of the Heisenberg uncertainty principle, Eq. (1.28), implying that a simultaneous measurement of the physical quantities  $\Omega_1$  and  $\Omega_2$  with arbitrary precision is not possible. As mentioned above, two examples of complementary variables are position and momentum in the same direction,  $\Omega_1 = x$  and  $\Omega_2 = p_x$ , as well as time and total energy,  $\Omega_1 = t$  and  $\Omega_2 = E$ .

The result that in quantum theory the subsequent application of operators associated to physical observables to a quantum wave function does not necessarily commute can be represented introducing another useful mathematical concept, the *commutator* between two operators. This commutation operator is defined as

$$[\hat{\Omega}_1, \hat{\Omega}_2] \equiv \hat{\Omega}_1 \hat{\Omega}_2 - \hat{\Omega}_2 \hat{\Omega}_1, \quad (1.37)$$

where note that the commutator of two operators *is another operator*, that is, it should be understood as being applied to a wave-function. With this definition, for the position and momentum operators we find that their commutator is given by

$$[\hat{x}, \hat{p}_x] = i\hbar, \quad (1.38)$$

as is easy to verify explicitly. Indeed, since

$$\hat{x} \hat{p}_x \Psi = x \left( \frac{\hbar}{i} \frac{d}{dx} \right) \Psi = \frac{\hbar}{i} x \frac{d\Psi}{dx}, \quad (1.39)$$

$$\hat{p}_x \hat{x} \Psi = \left( \frac{\hbar}{i} \frac{d}{dx} \right) (x\Psi) = \frac{\hbar}{i} \Psi + \frac{\hbar}{i} x \frac{d\Psi}{dx}, \quad (1.40)$$

then their commutator gives

$$[\hat{x}, \hat{p}_x] \Psi = -\frac{\hbar}{i} \Psi = i\hbar \Psi, \quad (1.41)$$

which is the sought-for result Eq. (1.38). Therefore,  $x$  and  $p$  are *complementary observables* (their operators do not commute) and thus they cannot be measured simultaneously with arbitrary precision. This is another way of representing Heisenberg's uncertainty principle.

In general, for any two operators representing physical quantities, if one finds that

$$[\hat{\Omega}_1, \hat{\Omega}_2] \neq 0, \quad (1.42)$$

that is, that the two operators do not commute, then the physical observables to which these two operators are associated are complementary and have associated a Heisenberg uncertainty relation.

## 1.5 Quantum entanglement

A remarkable consequence of the basic principles of quantum theory, particularly at odds with our intuition that any system composed by many particles can be understood from the sum of the properties of individual particles, is that there exists many-particle systems of many particles which *cannot be expressed as a combination of single-particle states*. This is the opposite as with the classical view of the world, where any system, no matter how complex it is, can always be decomposed in all of its components, each one obeying well-defined dynamical equations. In quantum theory this is not necessarily true, and some states (actually the wide majority) do not admit a description in terms of quantum states of individual particles. Those states are said to be *entangled*.

Let us consider the case in which a particle can occupy only two states, so our basis vectors will be

labelled as  $|0\rangle$  and  $|1\rangle$ . It does not really matter what  $|0\rangle$  and  $|1\rangle$  stand for: could be two different values of the energy, or two different orientations of the internal angular momentum of a particle, the following argument does not depend on which physical system we consider. We will write the state composed by two of such particles as follows

$$|ab\rangle \equiv |a\rangle_1 |b\rangle_2, \quad (1.43)$$

so the state  $|ab\rangle$  is such particle 1 one is in the state  $|a\rangle$  and particle 2 in the state  $|b\rangle$ . Is clear that some of the possible states admit a description in terms of single-particle states, for example, one can construct

$$|\Psi\rangle = |01\rangle = |0\rangle_1 |1\rangle_2, \quad (1.44)$$

but however other states do not admit such description, for example, the so-called *Bell state*:

$$|\Psi\rangle_B = \frac{1}{\sqrt{2}} (|00\rangle + |11\rangle). \quad (1.45)$$

This state cannot be decomposed into something like “state of particle 1” combined with “state of particle 2”: it has no classical analog.

To demonstrate this interesting property, note that if the quantum state  $|\Psi\rangle_B$  could be decomposed in terms of single particle states, one should be able to write it (using the superposition principle) as a linear combination of quantum states with well-defined values for  $|a\rangle_1$  and  $|b\rangle_2$ , namely

$$|\Psi\rangle = (a|0\rangle_1 + b|1\rangle_1)(c|0\rangle_2 + d|1\rangle_2) = ac|00\rangle + ad|01\rangle + bc|10\rangle + db|11\rangle, \quad (1.46)$$

but you can easily convince yourself that Eq. (1.45) does not admit a decomposition of the form of Eq. (1.46). For example, either  $a$  or  $d$  must be zero since the ket  $|01\rangle$  is absent, but this is inconsistent with the kets  $|00\rangle$  and  $|11\rangle$  being present. Therefore, in the quantum state Eq. (1.45) it is not possible to describe separately the individual particles: they are fundamentally *entangled* with each other.

There exist many ways of quantifying the *entanglement* that is present in a given quantum system. For example, our two-particle quantum state can be generically written as

$$|\Psi\rangle = \alpha|00\rangle + \beta|01\rangle + \gamma|10\rangle + \delta|11\rangle, \quad (1.47)$$

where  $|\alpha|^2 + |\beta|^2 + |\gamma|^2 + |\delta|^2 = 1$  due to normalization. Now, we can define a measure of entanglement in terms of its *concurrence* as follows

$$\Delta \equiv 2|\alpha\delta - \beta\gamma|, \quad (1.48)$$

By construction,  $0 \leq \Delta \leq 1$ , where the extreme cases  $\Delta = 0$  ( $1$ ) correspond to a product (maximally entangled) state. You can convince yourselves that Eq. (1.45) is not only an entangled state, but actually it corresponds to a *maximally entangled* state with  $\Delta = 1$ . Likewise, any state that can be decomposed into single particle states such as Eq. (1.46) has  $\Delta = 0$ , so exactly zero entanglement.

Entanglement is a very powerful feature of quantum theory. For instance, the exponential speed up in computational efficiency that *quantum computers* exhibit over the classical ones arises from the manipulation and exploitation of entanglement. Entanglement also plays a crucial role in many theories of elementary particle physics.

## 1.6 Observables and operators in quantum theory

As we have discussed, the wave-function  $\Psi$  of a quantum system contains the complete physical information on the system. In particular, the various properties of the system should be calculable only from the knowledge of the wave-function, without any additional inputs required. In quantum theory, we denote as an *observable* a given property of a quantum system (energy, momentum, angular momentum, electric charge, ...) that can be extracted from a *experimental measurement* of this system. Mathematically, the tools that we will use to compute the expected outcome of a measurement of a quantum system are known as *operators*, which can be expressed in the language of *eigenfunctions* and *eigenvectors*. So before discussing the role that operators have in quantum theory, let's briefly review the concept of an eigenvalue system with matrices.

**Eigenvalue equations with matrices.** As you have seen in linear algebra courses, an eigenvalue equation is a mathematical equation of the form

$$A\mathbf{v} = \lambda\mathbf{v}. \quad (1.49)$$

where  $A$  is a square matrix of dimensions  $n \times n$  and  $\mathbf{v}$  is a column vector with  $n$  dimensions. The scalar  $\lambda$  is known as the *eigenvalue* of the equation. So the key feature of Eq. (1.56) is that applying a matrix  $A$  to the vector  $\mathbf{v}$  returns the original vector with an overall rescaling,  $\lambda\mathbf{v}$ . In order to compute the eigenvalues of a matrix, we need to evaluate the solutions of the *characteristic equation* of the matrix  $A$ , given for

$$\det(A - \lambda \cdot I) = 0, \quad (1.50)$$

where  $I$  is the identity matrix of dimensions  $n \times n$ , and  $\det$  is the determinant.

To illustrate how to compute eigenvalues, let's consider the following matrix

$$A = \begin{pmatrix} 1 & -3 \\ 3 & -5 \end{pmatrix} \quad (1.51)$$

which has associated the following characteristic equation

$$\det(A - \lambda \cdot I) = \begin{vmatrix} 1 - \lambda & -3 \\ 3 & -5 - \lambda \end{vmatrix} = \lambda^2 + 4\lambda + 4 = 0. \quad (1.52)$$

We can easily solve this quadratic equation finding that the two eigenvalues associated to the matrix  $A$  are  $\lambda_1 = \lambda_2 = -2$ . So in this case the two eigenvalues are the same.

Once we know the eigenvalues  $\lambda_i$  associated to a given matrix  $A$ , we can compute the corresponding eigenvectors  $\mathbf{v}_i$ , defined as the vectors that satisfy

$$A\mathbf{v}_i = \lambda\mathbf{v}_i. \quad (1.53)$$

which is an  $n$ -dimensional system of linear equations. In our example case, the equation that needs to be solved is

$$\begin{pmatrix} 1 & -3 \\ 3 & -5 \end{pmatrix} \begin{pmatrix} v_{1,1} \\ v_{1,2} \end{pmatrix} = \lambda_1 \begin{pmatrix} v_{1,1} \\ v_{1,2} \end{pmatrix} \quad (1.54)$$

$$\begin{aligned}v_{1,1} - 3v_{1,2} &= -2v_{1,1} \\3v_{1,1} - 5v_{1,2} &= -2v_{1,1}\end{aligned}\tag{1.55}$$

which is solved to find  $\mathbf{v}_i = (1, 1)$ , as you can check. Note that the normalisation of the eigenvectors is arbitrary: if  $\mathbf{v}_i$  is an eigenvector of a given matrix  $A$ , then  $b\mathbf{v}_i$ , with  $b$  being an arbitrary complex number, is also an eigenvector.

You can also solve eigenvalue equations using numerical software. For instance, using `Python` you can easily find the eigenvalues and eigenvectors of an arbitrary matrix  $A$  using the following instructions:

---

```
from numpy import linalg as LA
A = [[1, -3],
     [3, -5]]
# Solve the eigensystem
w, v = LA.eig(A)
# Print the results
print("eigenvalues = ",w)
print("eigenvectors = ",v)
```

---

**Eigenvalue equations in quantum systems.** Formally, an *operator* is a way to represent the action of a specific mathematical function onto the wave-function  $\Psi$ . For instance, Schroedinger's equation Eq. (1.23) can be expressed in operator form as follows

$$\hat{H}\Psi(x) = E\Psi(x),\tag{1.56}$$

where the "hat" (^) symbol indicates an operator, in this case the *Hamiltonian operator*, defined as

$$\hat{H} \equiv -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x).\tag{1.57}$$

Operators in quantum theory act on wave function and return either numbers or functions. An operator equation of the form of Eq. (1.56) has the same form as the eigenvalue equations that we saw before in Eq. (1.56), replacing the matrix  $A$  by the Hamiltonian operator  $\hat{H}$  and the eigenvector  $\mathbf{v}$  by the quantum wave function  $\Psi(x)$ . Actually the analogy is more transparent for those quantum systems where the number of quantum states is finite, and where the Hamiltonian operator can be written as a square matrix as we will see.

In the case of Eq. 1.56, the application of the Hamiltonian operator  $\hat{H}$  to the wave-function returns the total energy  $E$  of the quantum state. This implies that  $\hat{H}$  is the operator that represents the total energy of a given quantum system. Therefore, we can determine the energy of a quantum system by applying the operator  $\hat{H}$  to its wave function. Note that not all wave functions are eigenvalues of  $\hat{H}$ , meaning that one can construct wave functions for which

$$\hat{H}\Psi(x) \neq E\Psi(x).\tag{1.58}$$

In general, solving a quantum system corresponds to determining the eigenvalues and eigenvectors of Eq. 1.56, which is the equivalent to solving the Schroedinger equation.

In general, an eigenvalue equation in quantum theory will take the general form

$$\hat{\Omega} \Psi_k = \omega_k \Psi_k, \quad k = 1, \dots, n\tag{1.59}$$

where we have:

- $\hat{\Omega}$  represents a generic operator associated to the observable property  $\Omega$  (such as the energy or momentum) of the quantum system,
- $\Psi_k$  is the  $k$ -th eigenfunction, corresponding to the  $k$ -th eigenvalue  $\omega_k$ .
- $n$  is the number of eigenvalues that this equation has.

Note that the eigenvalues  $\omega$  are in general complex and can be either constant or functions of other variables, such as the position  $x$ .

Let us provide two examples of eigenvalue equations in quantum theory.

- (a) Is  $\Psi(x) = e^{\alpha x}$  an eigenfunction of the operator  $\hat{\Omega} \equiv d/dx$ ? To verify if this is the case, we apply the operator to the wave-function to find

$$\hat{\Omega}\Psi = \frac{d}{dx}e^{\alpha x} = \alpha e^{\alpha x} = \alpha\Psi, \quad (1.60)$$

so indeed in this case  $\Psi(x)$  is an eigenfunction of  $\hat{\Omega}$ , with  $\alpha$  being the associated eigenvalue.

- (b) Is  $\Psi(x) = e^{\alpha x} + e^{\alpha x^2}$  an eigenfunction of the same operator? Let us check it in the same way as before:

$$\hat{\Omega}\Psi = \frac{d}{dx}(e^{\alpha x} + e^{\alpha x^2}) = \alpha e^{\alpha x} + 2\alpha x e^{\alpha x^2} \neq \omega\Psi, \quad (1.61)$$

thus now the wave function  $\Psi(x)$  is *not* an eigenfunction, since it cannot be written as the product of an eigenvalue and the same eigenfunction once the operator  $\hat{\Omega}$  acts upon it.

Now going back to the Schroedinger equation as an written eigenvalue equation, Eq. (1.56), we can write its solutions as

$$\hat{H}\Psi_k(x) = E_k\Psi_k. \quad (1.62)$$

Using the quantum superposition principle, we know that we have function

$$\varphi(x) = \sum_k c_k \Psi_k(x), \quad (1.63)$$

with  $c_k$  complex numbers, is also a possible valid quantum state for the system. However, crucially,  $\varphi(x)$  is not itself a solution of Schroedinger's equation. You can check this easily using the operator form of the equation

$$\hat{H}\varphi(x) = \sum_k c_k \hat{H}\Psi_k(x) = \sum_k c_k E_k \Psi_k(x) \neq \omega\varphi(x), \quad (1.64)$$

showing how there exist physically allowed quantum systems that are not solutions of Schroedinger's equations. The reason is that these quantum states do not have a definite energy.

**Observables and operators.** Therefore in quantum theory any observable property  $\Omega$  of a quantum system will be represented by an operator  $\hat{\Omega}$  built up. We can determine the value of this property associated to the specific quantum system  $\Psi$  by solving the corresponding eigenvalue equations  $\hat{\Omega}\Psi_k = \omega_k\Psi_k$ . We now list the most important cases for this correspondence between observables and operators (for simplicity in one dimension only).



Observable	Operator
Position: $x$	$\hat{x} = x$
Linear momentum: $p_x = mv_x$	$\hat{p}_x = \frac{\hbar}{i} \frac{d}{dx}$
Kinetic energy: $T = \frac{1}{2}mv_x^2 = p_x^2/2m$	$\hat{T} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2}$
Potential energy: $V = V(x)$	$\hat{V} = V(x)$
Total energy: $E = T + V = p_x^2/2m + V(x)$	$\hat{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x)$

Later in the course we will see how this correspondence between observables and operators in quantum theory can be extended to other cases, such as the angular momentum.

**The free particle revisited.** We can now revisit the free-particle solution of the Schrodinger's equation, Eq. (1.27). We want to compute which is the linear momentum associated to this quantum state. What we need to do is to apply the linear momentum operator to the corresponding wave function (for  $B = 0$ ):

$$\hat{p}_x \Psi(x) = \frac{\hbar}{i} \frac{d}{dx} \left[ A \cos \left( \sqrt{\frac{2mE}{\hbar^2}} x \right) \right] = -\frac{\hbar}{i} A \sqrt{\frac{2mE}{\hbar^2}} \sin \left( \sqrt{\frac{2mE}{\hbar^2}} x \right) \neq p_x \Psi(x), \quad (1.65)$$

so we find that a plane wave solution of the form of Eq. (1.27) with  $B = 0$  is not an eigenvector of the linear momentum operator: we cannot associate a well-defined value of  $p_x$  to this quantum state.

On the other hand, if we impose that  $B = iA$  we have that the wave function reads

$$\Psi(x) = A \cos \left( \sqrt{\frac{2mE}{\hbar^2}} x \right) + iA \sin \left( \sqrt{\frac{2mE}{\hbar^2}} x \right) = A \exp \left( i \sqrt{\frac{2mE}{\hbar^2}} x \right), \quad (1.66)$$

and if now we apply the momentum operator to this wave function we get

$$\hat{p}_x \Psi(x) = \frac{\hbar}{i} \frac{d}{dx} \left[ A \exp \left( i \sqrt{\frac{2mE}{\hbar^2}} x \right) \right] = \sqrt{2mE} \Psi(x) \quad (1.67)$$

so the momentum along the  $x$  direction  $p_x$  that can be associated to the free particle with wave function Eq. (1.66) is  $p_x = \sqrt{2mE}$ . One can easily show that the solution where  $B = -iA$  is also an eigenvalue of the linear momentum operator with eigenvector  $p_x = -\sqrt{2mE}$ . Therefore, the general solution of the Schrodinger equation for the free particle is a linear combination of plane waves moving in the positive direction with well defined momentum and the corresponding plane waves moving in the negative direction.

This calculation indicates that not all the solutions of the Schrodinger's equation for a free particle are eigenvectors of the linear momentum operator. In other words, one can have states that have well-defined energy  $E$  but not well-defined linear momentum  $p_x$ . This is a consequence of the fact that the linear momentum has sign and direction, while the kinetic energy depends only on its modulus,  $E \propto |\vec{p}|^2$ .

So does this mean that free particles always have well-defined values of their linear momentum  $p_x$ ? Does this imply that the position of a free particle is always maximally uncertain? No, if we take into account that physically, from Eq. (1.28), there should be an uncertainty associated also to the expectation value of  $\hat{p}$ , the momentum of the quantum state, if we want to have the particle localised in a finite region of space. A wave function for a free particle with a *finite momentum resolution* (and therefore a certain amount of spatial localisation) can be constructed by means of a *superposition* of free-particle solutions, each with *different*

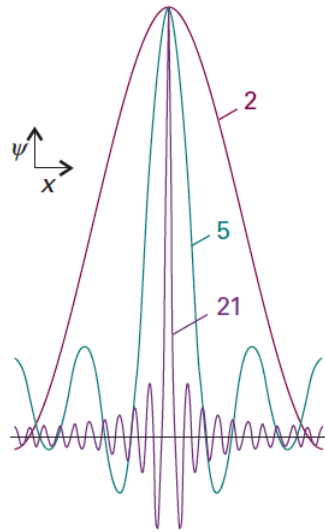


Figure 1.5: The wave function Eq. (1.69) corresponding to the superposition of  $N$  plane-wave free particle solutions, each with a different value of  $k = n\pi$ . We show the results from the addition of  $N = 2, 5, 21$  terms in Eq. (1.69), showing that the more terms we include, the better the localization of the free particle (since the higher is the indetermination of its momentum  $p_x$ ).

wave numbers  $k$ , namely

$$\Psi(x) = \sum_k^N c_k e^{ikx}. \quad (1.68)$$

The more the number of contributions  $N$  to the above sum, the higher the uncertainty on the momentum of the particle, and thus we obtain an increased localization of the particle in  $x$ . This can be seen by plotting the free-particle wave-function superposition:

$$\Psi(x) = \sum_{n=1}^N \cos(n\pi x), \quad (1.69)$$

which is shown in Fig. 1.5: the more terms we add in the sum, the more values the momentum  $\hbar k$  of the particle can take, hence  $\Delta p$  is higher (more uncertain) and  $\Delta x$  smaller (increased localization in space).

**Hermiticity and orthogonality.** In quantum mechanics, observable properties of a system have associated operators, whose eigenvalues correspond to the values than these observables can take when the measurement is performed in a quantum state described by an eigenfunction of this operator. However, not all operators will lead to physically sensible observables. In particular, only operators which are *Hermitian* are physically allowed. Hermitian operators have important properties, in particular in this course we will exploit the fact that:

- Hermitian operators have always associated *real eigenvalues* as opposed to complex ones.
- The eigenfunctions of Hermitian operators are always *orthogonal* among them: the overlap integral between two of such eigenfunctions vanishes.

What is the defining characteristic of an Hermitian operator? We say that an operator  $\hat{\Omega}$  is Hermitian

provided that, given two arbitrary wave-functions  $\Psi_i$  and  $\Psi_j$ , it satisfies the following property:

$$\int dx \Psi_i^* \hat{\Omega} \Psi_j = \left( \int dx \Psi_j^* \hat{\Omega} \Psi_i \right)^\dagger, \quad (1.70)$$

where the “dagger” symbol  $\dagger$  indicates to interchange  $i$  and  $j$  (that is, taking the transpose matrix), and then taking the complex conjugate, that is

$$\left( \int dx \Psi_i^* \hat{\Omega} \Psi_j \right)^\dagger = \int dx \left( \Psi_j^* \hat{\Omega} \Psi_i \right)^*. \quad (1.71)$$

One can verify that all the operators that we have introduced so far, such as the position  $\hat{x}$  and the linear momentum  $\hat{p}_x$  operators are Hermitian. For example, in the latter case we have

$$\int dx \Psi_i^* \hat{p} \Psi_j = \int dx \Psi_i^* \left( \frac{\hbar}{i} \frac{d}{dx} \right) \Psi_j = \frac{\hbar}{i} \left( \Psi_i^* \Psi_j \Big|_{-\infty}^{+\infty} - \int dx \Psi_j \frac{d}{dx} \Psi_i^* \right) = \int dx \Psi_j \left( -\frac{\hbar}{i} \right) \frac{d}{dx} \Psi_i^* \quad (1.72)$$

where we have used integration by parts, and exploited the facts that wave-functions must vanish at infinity (since they must be square-integrable). Therefore we have demonstrated that

$$\int dx \Psi_i^* \hat{p} \Psi_j = \int dx \Psi_j \left( -\frac{\hbar}{i} \right) \frac{d}{dx} \Psi_i^* = \left( \int dx \Psi_i^* \hat{p} \Psi_j \right)^\dagger. \quad (1.73)$$

and thus the linear momentum operator  $\hat{p}$  is Hermitian.

In quantum theory, all physical observables (associated to quantities that can be accessed experimentally) are represented by Hermitian operators. This ensures that the expectation values of these observables in physical systems (as well as the outcome of any individual measurement) are real instead of complex (which could not be otherwise, since *i.e.* a physical system cannot have a complex energy or a complex position).

The key property that the eigenvalues of an Hermitian operator  $\hat{\Omega}$  are real can be demonstrated from its definition Eq. (1.70) as follows. Let us assume that  $\Psi_i = \Psi_j = \psi$  is an eigenfunction of this operator with eigenvalue  $\omega$ , that is, the relation  $\hat{\Omega}\psi = \omega\psi$  holds. Then we have that

$$\int dx \psi^* \hat{\Omega} \psi = \int dx \psi^* \omega \psi = \omega \int dx \psi^* \psi = \omega, \quad (1.74)$$

since the wave-function is normalized to one, and that also we have that the “dagger” version of the above expression gives

$$\left( \int dx \psi^* \hat{\Omega} \psi \right)^\dagger = \left( \omega \int dx (\psi^* \psi)^* \right) = \omega^* \quad (1.75)$$

and since  $\hat{\Omega}$  is Hermitian, then it follows that  $\omega^* = \omega$ . In other words,  $\omega$  is a real number irrespective of the specific operator that we use provided that it is Hermitian.

It is also possible to show that, for an Hermitian operator, its eigenfunctions are *orthogonal* among them. In other words, they constitute a *set of linearly independent basis functions* in the sense of a vector space in linear algebra. Mathematically, the orthogonality property implies that if  $\Psi_i(x)$  and  $\Psi_j(x)$  are two

eigenfunctions of the operator  $\hat{\Omega}$ , then the following relation holds:

$$\int dx \Psi_i^*(x) \Psi_j(x) = \delta_{ij}, \quad (1.76)$$

that is, the integral vanishes unless the eigenfunctions are the same,  $i = j$ , in which case the integral equals one because of the normalization condition (the eigenvectors can always be normalised to ensure that Eq. (1.76) is satisfied). This important property allows to project a general quantum state as a *linear superposition* of the eigenfunctions of an Hermitian operator, which form a complete basis of the corresponding vector space.

## 1.7 Expectation values of physical quantities

The wave-function  $\Psi$  can be used to determine the *expectation value* of physical observables of a given quantum system, that is, the expected average over many measurements of this quantity. This is a familiar concept from probability theory: if we measure a given quantity  $b$   $n$  times, say  $b_i$ , then the mean value over the measurements is

$$\langle b_i \rangle = \frac{1}{n} \sum_{i=1}^n b_i, \quad (1.77)$$

and represents our best estimate of the *true value* of the observable  $b$ . In quantum theory, we cannot predict in general the outcome of individual measurements, but we can predict what will be the average over a large number of measurements.

In quantum theory, if we have an observable  $\Omega$  associated to an operator  $\hat{\Omega}$ , we can compute its expectation value in a quantum state characterised by the wave function  $\Psi(x)$  as follows

$$\langle \Omega \rangle = \int dx \Psi^* \hat{\Omega} \Psi, \quad (1.78)$$

Here we can have two possible situations:

- The first one is that the wave function  $\Psi$  is already an eigenvector of the operator  $\hat{\Omega}$ , namely  $\hat{\Omega}\Psi = \omega\Psi$ . In that case we have that the expectation value is given by

$$\langle \Omega \rangle = \int dx \Psi^* \hat{\Omega} \Psi = \int dx \Psi^* \omega \Psi = \omega \int dx \Psi^* \Psi = \omega, \quad (1.79)$$

so it coincides with the corresponding eigenvalue. This is the simplest possible situation: if we measure the observable  $\Omega$  in the system characterised by this wave function, then the outcome of the measurement will always be the same:  $\omega$ .

- In general however the wave function  $\Psi(x)$  will not be an eigenvector of the operator  $\hat{\Omega}$ . In this case, we can use the fact that the eigenvectors of  $\hat{\Omega}$ , defined by the condition

$$\hat{\Omega}\Psi_k = \omega_k\Psi_k, \quad k = 1, \dots, n \quad (1.80)$$

form a complete basis in the Hilbert vector space. This means that I can always expand the original wave function  $\Psi(x)$  as a linear combination of the eigenvectors  $\Psi_k$ , in the same way that if I have a basis in a vector space I can always expand a general vector in terms of a linear combination of the

elements of the basis. In other words, I can always construct an expansion of the form

$$\Psi(x) = \sum_{k=1}^n c_k \Psi_k(x). \quad (1.81)$$

with  $c_k$  being complex numerical coefficients. The coefficients  $c_k$  can be determined by exploiting the condition that the eigenvectors of an Hermitian operator form a complete basis:

$$\int dx \Psi^*(x) \Psi_j(x) = \int dx \left( \sum_{k=1}^n c_k \Psi_k(x) \right)^* \Psi_j(x) = \sum_{k=1}^n c_k^* \int dx \Psi_k^*(x) \Psi_j(x) = c_j^*, \quad (1.82)$$

since the  $\{\Psi_k\}$  eigenvectors are orthonormal among them.

Therefore, in full generality, we can always expand a quantum wave function as in Eq. (1.81) in terms of the eigenvectors of the operator associated to the physical observable that we want to measure. In this case, the expectation value  $\langle \Omega \rangle$  will be given by the weighted sum of eigenvalues, with weight  $|c_k|^2$ :

$$\langle \Omega \rangle = \int dx \left( \sum_k c_k \Psi_k \right)^* \hat{\Omega} \left( \sum_j c_j \Psi_j \right) = \sum_{k,j} c_k^* c_j \omega_j \int dx \Psi_k^* \Psi_j = \sum_{k,j} c_k^* c_j \omega_j \delta_{ij} = \sum_k |c_k|^2 \omega_k, \quad (1.83)$$

where we have used the orthogonality property of the eigenfunctions of an Hermitian operator Eq. (1.76). Note that in this derivation we assume that the coefficients of the linear superposition Eq. (1.81) are canonically normalized, that is, they satisfy

$$\sum_k |c_k|^2 = 1, \quad (1.84)$$

as implied by the condition that the original wave function  $\Psi(x)$  is appropriately normalised.

Therefore, if we know the expansion of a given wave function in terms of the eigenvectors of an Hermitian operator, Eq. (1.81), we can readily compute the expectation value of this operator as a weighted sum of its eigenvalues as indicated by Eq. (1.83).

## 1.8 Radioactivity

The concepts of *radioactivity* and *radiation* are intrinsically linked to quantum theory, and will appear frequently along the various topics covered in this course. By radioactivity we understand the spontaneous emission of energetic particles from unstable atoms. This phenomenon is a direct consequence of quantum theory. Radioactivity is a very important phenomenon in nuclear and particle physics, which has led to many applications such as nuclear energy as well as to important medical imaging applications.

There are three main types of radioactive processes:

- *$\alpha$  radiation*: the emission of a He nucleus (a bound state of two protons and two neutrons).

This radioactive decay process is mediated by the strong nuclear force. If the initial unstable element is  ${}^A_Z X$ , where  $Z$  is the *atomic number* (number of protons) and  $A$  is the *mass number* (numbers of protons plus neutrons), then the daughter element will be  ${}^{A-4}_{Z-2} Y$ , given the proton and neutron content of an  $\alpha$  particle

- *$\beta$  radiation*: the emission of an electron (or its anti-particle, the positron), together with a neutrino.

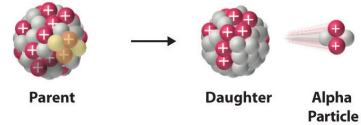
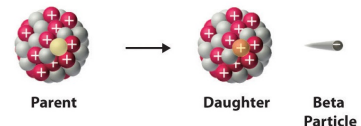

Decay Type	Radiation Emitted	Generic Equation	Model
Alpha decay	${}^4_2\alpha$	${}^A_ZX \longrightarrow {}^{A-4}_{Z-2}X' + {}^4_2\alpha$	 <p>Parent → Daughter + Alpha Particle</p>
Beta decay	${}^0_{-1}\beta$	${}^A_ZX \longrightarrow {}^A_{Z+1}X' + {}^0_{-1}\beta$	 <p>Parent → Daughter + Beta Particle</p>
Gamma emission	${}^0_0\gamma$	${}^A_ZX^* \xrightarrow{\text{Relaxation}} {}^A_ZX' + {}^0_0\gamma$	 <p>Parent (excited nuclear state) → Daughter + Gamma ray</p>

Figure 1.6: The three main types of radioactive decay processes. In alphas decay, mediated by the strong interaction, a He nucleus (2 protons and 2 neutrons) is emitted. In beta decay, mediated by the weak interaction, either an electron or a positron are emitted (together with a neutrino). In gamma decay, mediated by electromagnetism, a high energy photon is emitted.

This radioactive decay process is mediated by the weak interaction. If the initial unstable element is  ${}^A_ZX$ , for this process the final element will be  ${}^A_{Z\pm 1}Y$ , depending on whether an electron or a positron has been emitted.

- $\gamma$  radiation: the emission of a high energy photon  $\gamma$ .

This radioactive decay process is mediated by the *electromagnetic interaction*. In this case, the values of the atomic  $Z$  and mass  $A$  numbers will be the same for the initial and final element: actually this transition consist of the relaxation of an excited atomic state to a state with less energy.

Therefore each of these three radioactive processes is mediated by a different fundamental interaction. The mean features of these three kinds of radioactive processes are summarized in Fig. 1.6.

You might ask yourselves: what causes a specific atom to decay? And how does exactly the atom know at which time it has to decay? Since radioactive decays are determined by quantum theory, at this point you might have already figured out that they are intrinsically probabilistic in nature. In other words, quantum theory allows us to predict when average a large collection of atoms will decay, but we cannot know when a given specific atom will decay. That is, in quantum theory we can compute the expectation value of the time it takes for a given type of atoms to decay radioactively.

If the number of atoms in a given radioactive sample is  $N(t)$ , and we have  $N_0 = N(t = 0)$  atoms to begin with, the infinitesimal variation  $dN$  in a time interval  $dt$  will be proportional to the number of atoms themselves, so it will be given by  $-\lambda N(t)dt$ , with  $\lambda$  known as the *decay constant* of this specific radioactive process. Solving the associated differential equation we see that the number  $N(t)$  of radioactive atoms at any given time will be

$$dN = -\lambda N(t)dt \quad \rightarrow \quad N(t) = N_0 e^{-t/\tau}, \quad (1.85)$$

with  $\tau = 1/\lambda$  representing the *average lifetime* of the atoms, that is, the average time they take to decay. To validate this interpretation, note that the average of a stochastic variable  $t$  with probability density  $N(t)$

is given by

$$\langle t \rangle = \frac{\int_0^\infty dt t N(t)}{\int_0^\infty dt N(t)} = \tau. \quad (1.86)$$

Therefore, we see from Eq. (1.85) that the number of nuclei of a given sample that undergo radioactive decays decreases exponentially with time. One sometimes also defines the activity of a radioactive sample, defined as (minus) the rate of change of  $N(t)$  per unit time,

$$A(t) \equiv -\frac{dN(t)}{dt} = \frac{N_0}{\tau} \exp\left(-\frac{t}{\tau}\right). \quad (1.87)$$

The higher the value of the activity  $A(t)$ , the faster the radioactive decay process takes place.

The value of the decay constant  $\lambda$  is different for each atomic element and isotope. This provides among other things a rather useful method to determine the age of objects, the so-called *radiocarbon dating method*. This method is based on the fact that one of the isotopes of carbon,  $^{14}\text{C}$ , has a decay constant of a few thousand years, while the more frequent isotope  $^{12}\text{C}$  is stable. This means that if we know somehow the initial abundance of  $^{14}\text{C}$  in a given sample, and measure the current abundance, since we know  $\tau$  we can determine  $t$  from Eq. (1.85). In other words, we can determine in a rather reliable way the age of this specific sample. The original abundance of  $^{14}\text{C}$  can be determined for instance by comparing with the current one of  $^{12}\text{C}$ , since the ratio between the abundances of the two isotopes in various systems is rather well understood.

Let us illustrate the radiocarbon dating method with an example. The mean-life of the unstable isotope of Carbon,  $^{14}\text{C}$ , is  $\tau = 8267$  years. If we assume that a given sample had the same ratio  $^{14}\text{C}/^{12}\text{C}$  as the one we have now in the atmosphere, we can compute the value  $N_0$  of  $^{14}\text{C}$  atoms in the original sample. By comparing with the current value of  $^{14}\text{C}$  atoms in the sample,  $N(t)$ , we can then determine  $t$ .

For instance, assume that we find that a sample with only 10% of  $^{14}\text{C}$  atoms as compared to its original abundance. By applying Eq. (1.85), we have that

$$0.1 N_0 = N_0 e^{-t/(8267 \text{ yr})} \quad \rightarrow \quad t = 19000 \text{ yr}, \quad (1.88)$$

illustrating how radioactive dating can be used to determine the age of a given object.

## 1.9 Summary

We can now recapitulate what we have learned in these two lectures about the basic postulates and concepts of quantum mechanics. These postulates will be extensively used in the rest of the course, and applied to a wide variety of different quantum systems.

- I/ All the physical information about a quantum system is contained in its wave-function  $|\Psi\rangle$ , which lives in an abstract vector space called the Hilbert space.
- II/ In this course we will work mostly with the position representation of the wave function,  $\Psi(x) = \langle x|\Psi\rangle$ .
- III/ The square of the wave-function  $|\Psi(x)|^2$  represents the probability density for finding the particle at the position  $x$  upon a measurement.

- IV/** The wave-function  $\Psi(x)$  must be continuous, have a continuous first derivative (unless the potential is infinite at the boundary), be single valued, and be squared-integrable.
- V/** Physical observables  $\Omega$  are represented by Hermitian operators  $\hat{\Omega}$  built upon the position  $\hat{x}$  and momentum  $\hat{p}$  operators, that act on the wave function of a quantum system. Examples of this are the total energy  $\hat{H}$  and the linear momentum  $\hat{p}_x$ .
- VI/** For time-independent systems with defined energy  $E_k$ , the wave function is the solution of Schroedinger's equation, which in operator form reads  $\hat{H}|\Psi_k\rangle = E_k|\Psi_k\rangle$ .
- VII/** By means of the superposition principle, we can always express a general wave function as a combination of eigenvectors of Schroedinger's equation,

$$|\Psi\rangle = \sum_n c_n |\Psi_n\rangle. \quad (1.89)$$

The same type of expansion holds for the eigenvectors of any other Hermitian operator.

- VIII/** Some physical observables are complementary, that is, they can not be measured simultaneously with arbitrary precision (even for a perfect measurement apparatus). Mathematically, their associated observables do not commute. Complementary observables obey relations of the form of Heisenberg's uncertainty principle.
- IX/** The knowledge of the wave function of a system allows us to evaluate the expectation value  $\langle\Omega\rangle$  of any observable quantity  $\Omega$  by computing matrix elements of its associated operator  $\hat{\Omega}$ .