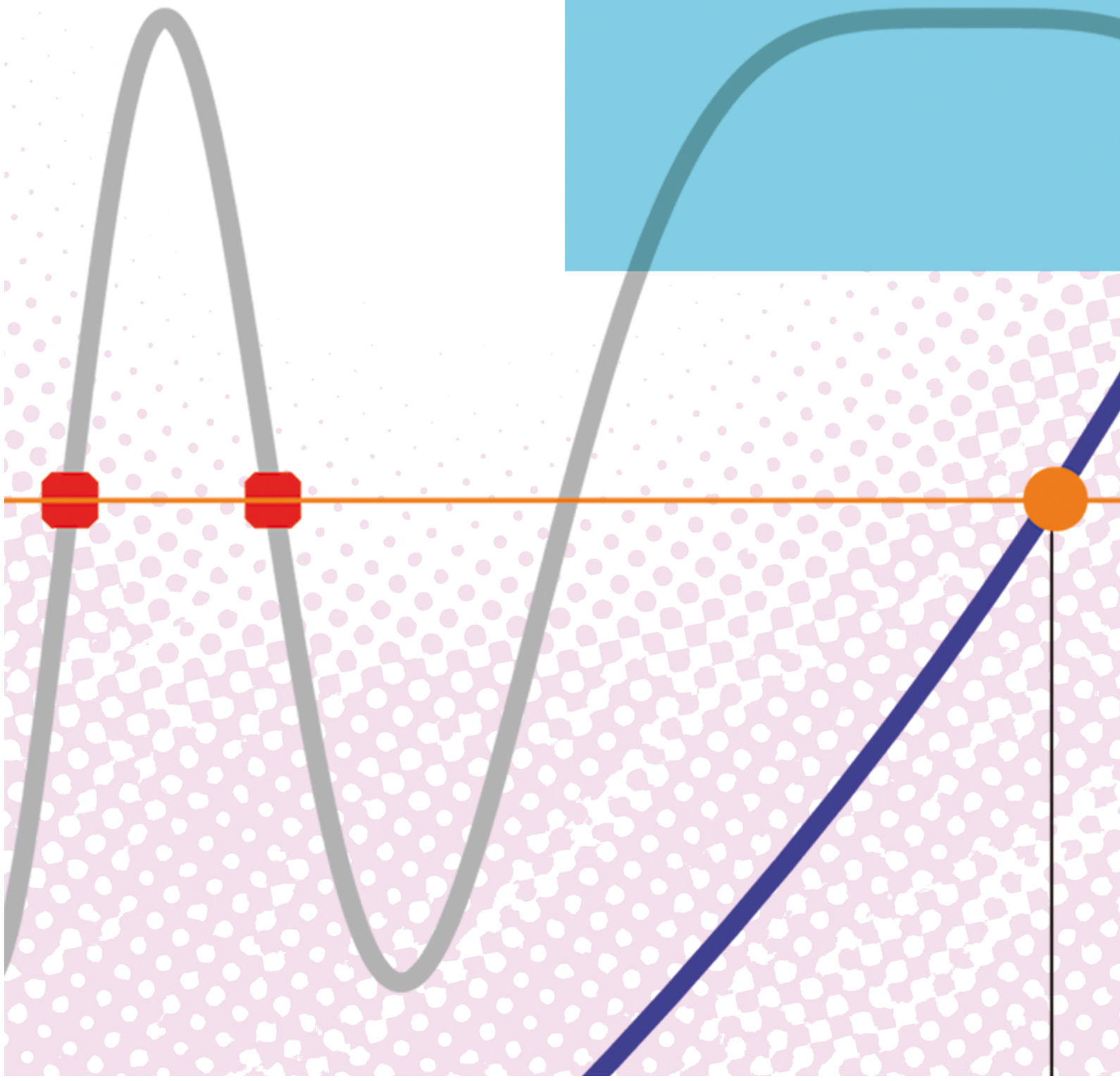


Bernardo Adeva Andany
University of Santiago de Compostela

CONCEPTUAL INTRODUCTION TO QUANTUM MECHANICS

Some key ideas



CONCEPTUAL INTRODUCTION TO QUANTUM MECHANICS

Some key ideas

Bernardo Adeva Andany *
Departamento de Física de Partículas
University of Santiago de Compostela

bernardo.adeva@usc.es

12 May 2016



This work is licensed under a Creative Commons Attribution 4.0 International ShareAlike License CC BY-SA. Title: Conceptual Introduction to Quantum Mechanics, some key ideas. Author: B. Adeva from University of Santiago de Compostela. To view a copy of this license visit <http://creativecommons.org/licenses/by/4.0/>

*I thank Dolores Cortina Gil and Marcos Seco Miguélez for their invaluable help in the preparation of these notes

Preface

The course material presented here is a brief and mathematically precise introduction to the conceptual body, and calculation tools, of Quantum Mechanics and Quantum Physics. It is addressed to those that, having a mathematical background in differential and integral calculus, and being familiar with Classical Mechanics and waves, would like to be given an insight into the foundations of the quantum theory. In particular, to undergraduate students following a course of Quantum Physics, in any Science or Engineering program. It allows the reader to acquire in a short period of time the calculation skills necessary to resolve physical problems in this field.

The introduction to Quantum Mechanics is performed using the semiclassical framework, where Newton's Classical Mechanics and Relativity are the reference points, both for its conceptual value and for its technical advantage. Not only the radical conceptual differences that the latter have with respect to Quantum Mechanics are underlined, but also the smooth transition which is observed between them. We have tried to avoid a double exposition of Quantum Mechanics by which the Planck constant phenomenology would be exposed first, following the "old theory of quanta", to proceed later to a different, more rigorous, theory. We think such an artifice can be avoided today, and the conceptual exposé is made consistently in one go, without recourse to independent phenomenological layers.

Feynman's propagation is used as an axiomatic basis for Quantum Mechanics, completed with the generally admitted ideas about the measurement problem. A simple notion is provided of the immersion that Quantum Mechanics undergoes in Quantum Field Theory, illustrated with photon emission.

This course has been conducted at the University of Santiago de Compostela in recent years, as part of the graduate program in Physics. It is continued with the analytic resolution of a number of normalized cases of the Schrödinger equation, within the subject of Quantum Physics I.

Contents

1	The principle of Least Action	3
2	The Planck constant	5
2.1	The observation through very short time intervals	7
2.2	The periodic motion	8
2.3	Atom sizes and the Bohr radius	9
2.4	The harmonic oscillator	11
2.5	Density of energy levels	12
2.6	The wave motion	14
3	The Feynman propagation	16
3.1	Exact propagation over a finite time	20
4	The instantaneous velocity	21
5	The Schrödinger equation	23
6	The wave function	24
7	Plane waves and Fourier transform	26
8	Mean values and uncertainty	28
9	The Uncertainty Principle	31
10	Extension to three dimensions	33
11	Eigenstates and measurable values	34
12	The stationary states	36
13	The Bohr formula	40
14	Quantum Mechanics in the relativistic framework	42

1 The principle of Least Action

Let us consider a moving body in one dimension, subject to a given potential energy $U(x, t)$. For instance an apple of mass m falling down from a tree branch to the ground, with uniformly accelerated motion. Denoting by $x(t)$ its height from the ground, its kinetic energy equals $T = \frac{1}{2}m\dot{x}^2$, and its potential energy $U(x) = mgx$. The Lagrangian equals $L = T - U$. Starting from rest at an initial height x_1 , the motion can be represented by a trajectory in the (x, t) plane, that, in this case, is the parabola $x = x_1 - \frac{1}{2}gt^2$.

Under the specified initial conditions, the above trajectory is the *only* one that fulfils Newton's second law

$$-\frac{\partial U}{\partial x} = m\ddot{x} , \quad (1)$$

or equivalently, it is the only solution to Lagrange's equation $\frac{d}{dt}(\frac{\partial L}{\partial \dot{x}}) - \frac{\partial L}{\partial x} = 0$.

The **action integral** of the motion is defined for any trajectory $x(t)$ as

$$S = \int_{t_1}^{t_2} L(x(t), \dot{x}(t), t)dt = \int_{t_1}^{t_2} (\frac{1}{2}m\dot{x}^2(t) - mgx(t))dt , \quad (2)$$

where (t_1, t_2) represents any desired time interval to calculate the action (e.g. from the instant the apple leaves the branch until it hits the ground). It is clear that the action integral has dimensions of energy \times time, for $L = T - U$ is an energy difference, which is multiplied by a time interval. In the International System of Units (SI) it is measured in $J \cdot s$ (Joule \times second).

It is known from the 18th century that Newton's second law is derived from a variational principle, the **principle of least action**, stating that the action integral between the initial (x_1, t_1) and final (x_2, t_2) space-time points is an extremum ¹ over the real trajectory $x(t)$ ².

As a matter of fact, any differentiable function $x(t)$ other than $x(t) = x_1 - \frac{1}{2}gt^2$ will render a value of the integral (2) larger than

$$S = \Delta t (-mgx_1 + \frac{1}{3}mg^2(\Delta t)^2) ,$$

and we suggest the student to verify that this expression is indeed the action integral over the above parabola, for the time interval $\Delta t = t_2 - t_1$.

The general procedure to derive Newton's second law from the least action principle, by performing the variation of a finite trajectory, and requiring it to be zero, is well known in Mechanics ³ and leads to the Euler-Lagrange equations as a previous step.

Let us see how the same derivation can be attained more directly by analysing the motion at a given point in the trajectory, through an infinitesimal time interval $\Delta t = t_2 - t_1$. Just assume that the body of mass m is moving from (x_1, t_1) to (x_2, t_2) in a very short time Δt , subject to the potential $U(x, t)$, and consider the position x occupied at the central time $t = (t_1 + t_2)/2$ as represented in Figure 1.

¹it can be shown that, for any potential, the action integral is a minimum for sufficiently short trajectories. In the most general case, it is either a minimum or a saddle point. The action can never be a maximum over the real trajectory.

²we take here Hamilton's formulation of the least action principle.

³see, for instance "Mechanics" Landau-Lifshitz, Vol.1, pag.2.

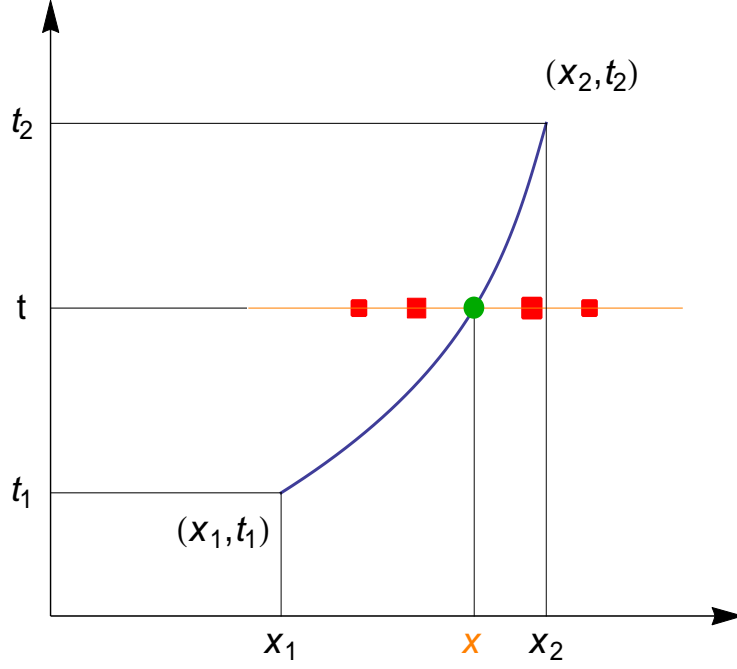


Figure 1: *Motion in the plane (x, t) according to different trajectories: that of minimal action (green) and others beyond Classical Mechanics (red)*

The only intermediate point x allowed by the least action principle is precisely the one that fulfils Newton's second law $-\frac{\partial U}{\partial x} = m\ddot{x}$. Indeed, we can separately calculate the average velocities v_1 and v_2 in the first half (t_1, t) and in the second half (t, t_2) of the time interval, respectively. The acceleration at time t is then given by

$$\ddot{x} = \frac{v_2 - v_1}{\Delta t/2},$$

so Newton's second law can be expressed as

$$\frac{m}{(\Delta t/2)} \left[\frac{x_2 - x}{(\Delta t/2)} - \frac{x - x_1}{(\Delta t/2)} \right] + \frac{\partial U}{\partial x} = 0. \quad (3)$$

Furthermore we can calculate the action S over the interval Δt as a sum of two terms

$$\begin{aligned} S &= \int_{t_1}^{t_2} L dt = \int_{t_1}^{t_2} (T - U) dt = \bar{L}_1 \frac{\Delta t}{2} + \bar{L}_2 \frac{\Delta t}{2} \\ &= \frac{\Delta t}{2} \left[m \frac{(x - x_1)^2}{2(\Delta t/2)^2} - U\left(\frac{x_1 + x}{2}\right) \right] + \frac{\Delta t}{2} \left[m \frac{(x_2 - x)^2}{2(\Delta t/2)^2} - U\left(\frac{x + x_2}{2}\right) \right], \end{aligned} \quad (4)$$

where $U((x_1 + x)/2)$ represents the average potential over the first half interval (similarly $U((x + x_2)/2)$). Obviously, the action will take different values for each intermediate point x that the particle may occupy at time $t = (t_1 + t_2)/2$.

Yet the least action principle states that the only reachable point x is the one making the value of S *extremal* (minimum), therefore satisfying $\frac{\partial S}{\partial x} = 0$. It is easy to show, by deriving expression (4) with respect to x , that formula (3) is readily obtained, which is equivalent to (1).

It should be made clear that, during the variational process considered above, the trajectory end-points (x_1, t_1) and (x_2, t_2) are to be held fixed. In a time independent field ($\frac{\partial U}{\partial t} = \frac{\partial L}{\partial t} = 0$), the total energy $E = T + U$ becomes a constant of the motion. It is noteworthy that, in several space dimensions, a given point (x_2, t_2) may be reached from the initial point (x_1, t_1) through more than one real trajectories (with extremal S).

It is of interest to calculate the action integral over the points of a classical trajectory $(x(t), t)$ that, starting from point (x_1, t_1) , keeps a constant energy E ⁴

$$S(t_2 - t_1) = \int_{t_1}^{t_2} L(t)dt = \int \left(\frac{\partial S}{\partial t} dt + \frac{\partial S}{\partial x} dx \right) = -E \cdot (t_2 - t_1) + \int_{x_1}^{x_2} p(x)dx . \quad (5)$$

The quantity

$$S_0 = \int_{x_1}^{x_2} p(x)dx = S + E \cdot (t_2 - t_1) \quad (6)$$

is known in the literature as **reduced action integral**, or characteristic action integral. It has the property of being invariant under any redefinition of the zero of the potential energy $U(x) \rightarrow U(x) + C$, due to the presence of an opposite sign term in $L = T - U$, thus being a measurable quantity in the laboratory. It plays an important role in the motion of particles and waves, and it has in Nature an *intrinsically oscillatory* character which we shall study next.

2 The Planck constant

The reduced action S_0 being a measurable quantity, in the sense indicated above, it is conceivable to perform measurements of it, in units $J \cdot s$. This would require to determine the position and the kinetic energy of the moving body at multiple successive time slices, seeking to cause minimal disturbance to the trajectory. According to the laws of conventional Mechanics, nothing prevents us to proceed in that way, and achieve a measurement of S_0 as accurate as we want, only limited by the precision of our experimental apparatus.

Still the physics reality provides us a surprise. It is known from over a century ago that the reduced action is a *discrete* quantity, that appears to be *nonzero* and take values which are integer multiples of a universal constant, the Planck constant, known today with 9 digits of precision. Its numerical value is close to $h = 6.626 \times 10^{-34} Js$, and it appears to be exactly the same, no matter the kind of energy which is represented by the potential $U(x, t)$, should it be electromagnetic, nuclear, electroweak or gravitational. Furthermore, it equally affects the motion of bodies of given mass m , and waves.

The true continuity of space and time at very short scales is an open question in Physics, to which no established answer is available today. It is unknown whether they are continuous or not. However a discontinuity is well established in the small-scale observational process, that refers unequivocally to the reduced action. Its impact in all branches of Physics, and of general knowledge, is huge, and we are going to perform a first discussion of the most important cases in what follows.

⁴ $S(x, t)$ builds a function in the plane (x, t) which is called Hamilton's principal function, that fulfils the equations $\frac{\partial S}{\partial t} = -E$ and $\frac{\partial S}{\partial x} = p$, with p being the momentum at the point (x, t) .

Taking the discontinuity of the reduced action as an additional postulate in Physics, without any new ideas, would not be sufficient to create a new Mechanics of consistent and predictive nature. It would simply reflect reality. As we shall see next, such hypothesis is incompatible with the existence of differentiable trajectories, whereupon the laws of conventional Mechanics lose their meaning. The problem of creating a new consistent and predictive Mechanics will be solved in Section 3. A *phenomenological statement* of the above fact, formulated under the limited terms of Classical Mechanics, goes as follows:

Principle of quantization of the classical action

For every physical observation of a moving body or ensemble of them, subject to a force field, or of a wave, both realized during a time interval Δt , the reduced action S_0 extended over Δt , appears to take values that are essentially integer multiples of the Planck constant. The quantization occurs in the form $S_0 = (n + \alpha)h$, where $n = 1, 2, \dots \infty$, and $\alpha > -1$ is a constant, specific to each problem.

The above principle is universally applied to systems with an arbitrary number of degrees of freedom N , whether they be relativistic or non relativistic. It holds for integrable systems, where $N - 1$ constants of motion exist other than the total energy, as well as for fully chaotic systems where only energy is conserved. A modern view reveals it is an excellent approximation, even if not completely exact. As we shall see in Feynman's theory, its lack of complete accuracy is a consequence of the fact that not only classical trajectories contribute to the motion, but all possible trajectories. Of course, a challenge for any new Mechanics is to be able to predict the exact value of α in each case where the principle appears to hold. The constant α is related to focusing properties of the classical trajectories, and it can actually be interpreted precisely in Classical Mechanics. We shall not elaborate on this here ⁵, but rather focus on the development of the new Mechanics.

Some comments are still in order, about the action quantization principle:

- given the fact that differentiable trajectories do not actually represent the real motion, it is difficult to verify its validity in a *direct* way. If we try to perform a measurement of S_0 , it is found that the precision required to test the hypothesis (better than $\pm h$) can never be attained in practice, as we shall see in Section 9, since the system will necessarily get perturbed.
- one way to test the principle, regarding periodic motion, is to measure the *energies* belonging to the sequence $n = 1, 2, \dots \infty$, giving up any attempt to observe the trajectory at the same time. It turns out that these can indeed be measured with unlimited precision, in the above conditions. Alternatively, for any kind of motion, it is possible to measure the energy and the time elapsed during the measurement, by processing signals from the moving body with clocks of given precision.
- the trajectories where the S_0 quantization rule is accomplished, in periodic motion, are assumed to be differentiable, and should be understood as the closest approach to the real motion that can be formulated under the terms of Classical Mechanics.

⁵ α is meaningful for integrable systems in periodic motion, and it is additive for each irreducible closed circuit around the *invariant tori* which characterize this kind of systems. For each degree of freedom i , and assuming n runs from zero $n = 0, 1, \dots \infty$, it takes the value $\alpha_i = \beta_i/4$ with β_i being an integer, called the Maslov index.

Given the small value in $J \cdot s$ that the Planck constant takes in Nature ⁶, it is clear that the domain of Physics splits up into two sectors, with a continuous transition between them: either its nonzero value is imperceptible, or its effects produce a noticeable difference. The former case happens when, after evaluation of the reduced action S_0 in a given problem, it appears to be $S_0 \gg h$. We shall call it the **classical limit**, where we would expect full validity of the conventional laws of Mechanics. The latter occurs quite the opposite, when $S_0 \simeq h$, and it is known as the **quantum limit**, which we shall deal with in the following.

2.1 The observation through very short time intervals

Let us assume we want to observe a moving body of mass m during a very short time interval Δt . The reduced action then takes the value $S_0 = S + E\Delta t = 2T\Delta t$, where T is its kinetic energy $\frac{1}{2}mv^2$. It is obvious that the quantum limit is reached when Δt is of the order of the ratio h/T , or shorter

$$\Delta t \lesssim \frac{h}{T}. \quad (7)$$

If we admit S_0 must remain finite ($\gtrsim h$), then no observation will be possible during a time less than indicated (or of the same order) without an increase of the body's kinetic energy, which is called *quantum fluctuation*, so as to verify $T \gtrsim h/\Delta t$.

Note that if the time interval is really small, the potential energy can be considered a constant over the trajectory and we can identify the kinetic energy with the total energy E , such that the critical time for fluctuations to become important is simply $\Delta t \sim h/E$.

We suggest the student to check that the critical observation time for a tennis ball of 100g moving at 50 Km/h would be $\Delta t \sim 1 \times 10^{-35}s$, which is less by many orders of magnitude than the exposure time of any photographic camera ($\Delta t \geq 1ms$), or than the light collection time for any electronic device based on photo-sensitive cells ($\Delta t \geq 1ns$).

Nonetheless if we were able to “take a photo” of the moving body during a time interval of $10^{-35}s$, we would undoubtedly observe fluctuations, and we could see that the motion actually takes place in a zigzag manner, on that scale.

That is to say, the time location Δt of a moving body in the laboratory entails an energy increase by $h/\Delta t$. This energy can be regarded as a necessary expenditure to achieve that location, or as a manifestation of it. In either case it is clear that we cannot maintain the existence of an instantaneous velocity, to be determined through the observational process of taking the limit

$$v = \lim_{\Delta t \rightarrow 0} \frac{\Delta x}{\Delta t},$$

and that such limit does not actually exist, but it is infinite. Therefore moving bodies do not follow differentiable trajectories. It appears to us that they do so, due to the fact that our senses or measurement apparatuses are not able to verify sufficiently short time intervals.

However, the periodic motion of electrons inside atoms and molecules, as well as that of protons and neutrons inside nuclei, entails a significant time location related to their revolution period, and are therefore entirely governed by quantum fluctuations.

⁶both the Joule and the second are units bound to our evolutionary observational scale.

Relativistic consideration

In order to rebut the existence of differentiable trajectories, we have restricted ourselves to the consideration of the non relativistic kinetic energy. However it is clear that for sufficiently short observation times, the increase of the kinetic energy necessarily takes every moving body to the relativistic limit, and its velocity will approach the light velocity c . An instructive exercise for the interested student is to take the relativistic action S for the free motion ⁷ and find out what time location Δt would be required for the reduced action $S_0 = S + mc^2\gamma\Delta t$ to be of order h (γ is the relativistic factor).

The result is $\Delta t \sim h/mc^2$, with m being its rest mass. If we were to apply it to atoms, molecules, or nuclei, it would mean an extremely short time, in which those systems would lose their integrity, and would be of no relevance to their study. If we apply it to an electron, the above location time is also too short as to be relevant for the study of ordinary matter, despite having the interesting implication of producing electron-positron pairs, wherever that location would be realized.

2.2 The periodic motion

Given the fact that a great deal of motions observed in Nature are of periodic type (particularly in the microscopic domain) let us see what the condition is for such a motion to be in the *quantum* limit. We assume for instance a closed orbit ($E < 0$) in three dimensions, with a central potential of the type $U(r) = \beta r^d$. According to the virial theorem, the mean values of the kinetic (\bar{T}) and potential (\bar{U}) energy, extended over one period ⁸ Δt , are exactly related by the expression $\bar{T} = \frac{d}{2}\bar{U}$. This theorem allows to perform the exact calculation of the action integral over one cycle

$$S = \int_0^{\Delta t} L dt = \bar{L} \Delta t = (\bar{T} - \bar{U}) \Delta t = \left(\frac{d-2}{d+2} \right) E \Delta t, \quad (8)$$

and the reduced action is therefore: $S_0 = S + E\Delta t = [2d/(d+2)]E\Delta t$. The quantum limit is then reached when $S_0 \sim h$. In this kind of periodic motion, in one or more dimensions, there exists a 1–1 relationship between the period Δt (or the quasiperiod) and the energy E of the orbits, the only exception being the harmonic oscillator, where the period turns out to be independent of the energy.

So once the energy E and the period Δt are known, we know precisely whether the motion is in the quantum limit or not, by simply evaluating their product. It is clear that in the above limit it will not be possible to talk about trajectories, and the motion will take place erratically, with quantum fluctuations acting strongly over each cycle.

⁷the relativistic action for the free motion is $S = - \int_0^{\Delta t} mc^2 \sqrt{1 - v^2/c^2} dt$.

⁸for central potentials of the type indicated above, only the cases $d = -1$ and $d = 2$ give rise to trajectories which are always periodic. In all other cases it would make perfect sense to replace the period with the time interval Δt over which r completes a cycle between (r_{min}, r_{max}) , called quasiperiod.

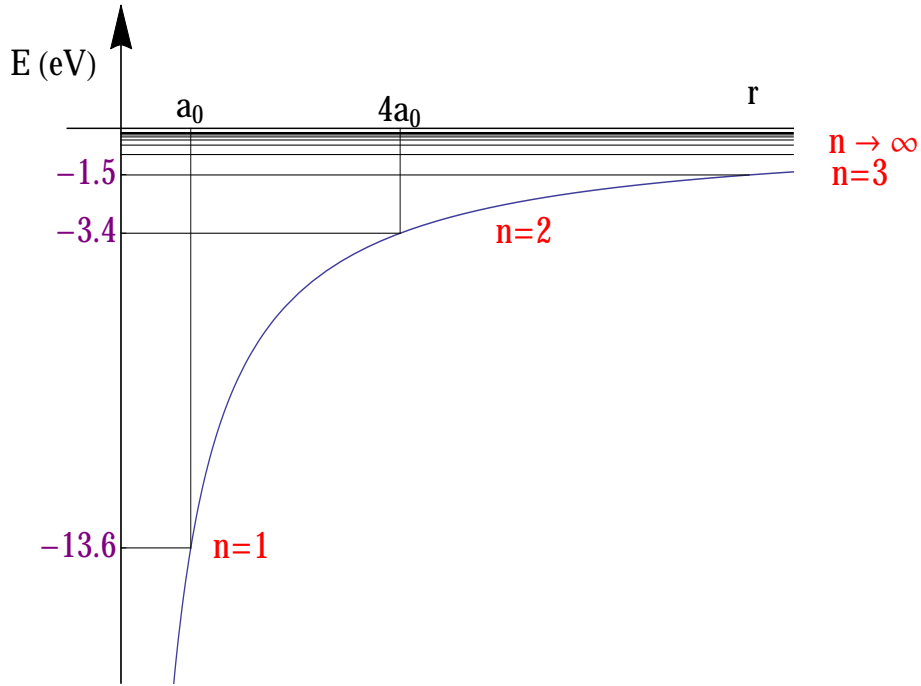


Figure 2: *Coulomb potential in the Hydrogen atom showing the discrete energy states that correspond to integer multiples of h for the classical reduced action S_0 . The lowest level corresponds to the Bohr radius a_0 . For $n \rightarrow \infty$ the energies approach continuous values.*

2.3 Atom sizes and the Bohr radius

In order to understand the finite size of atoms, let us begin with the simpler case of Hydrogen. We consider the problem of an electron moving under the electrical attraction of a proton (Z protons in general). The interaction potential is given by Coulomb's law $U(r) = -\beta/r$, with $\beta = \frac{Ze^2}{4\pi\epsilon_0}$, where e is the magnitude of the electron charge and ϵ_0 the vacuum electrical permittivity ⁹.

According to Newton's laws, the motion takes place in a plane, and for energies $E < 0$ the solution takes the form of elliptic orbits in which one of the particles moves around the center of mass, located at one of the foci. Furthermore, Kepler's third law

$$\Delta t = \frac{\pi}{\sqrt{2}} \frac{\beta m^{1/2}}{|E|^{3/2}} = \frac{2\pi}{\omega} \quad (9)$$

establishes a precise relationship between the orbit energy and its period Δt , related to the angular frequency through the expression $\Delta t = 2\pi/\omega$. Note that m represents here the reduced mass of the two-body system (electron and nucleus) $m = m_1 m_2 / (m_1 + m_2)$, which is quite close to the electron mass m_e .

As we have seen, according to the virial theorem ($d = -1$ in this case), the action takes the value $S = -3E\Delta t$ and the reduced action $S_0 = -2E\Delta t$. From Kepler's third law, we know that the quantum limit will occur when the action S_0 comes down to the level of h . And this happens when the orbits acquire very small radii, high frequencies, and negative energies with high absolute value.

⁹this potential also describes the gravitational attraction between two masses m_1 y m_2 , with $\beta = G_N m_1 m_2$, and the physics analysis entirely applies to this case as well.

The action quantization principle is then applied: $S_0 = nh$ with $n = 1, 2, \dots \infty$, with a constant α which is effectively zero in this case ¹⁰.

This allows us to establish a filter on the allowed electron energies, which become quantized in the form

$$-E_n = \frac{1}{2} \frac{m\beta^2}{\hbar^2} \frac{1}{n^2} = \frac{1}{2} \frac{mZ^2e^4}{(4\pi\epsilon_0)^2 \hbar^2} \frac{1}{n^2}. \quad (10)$$

Their value for $n = 1$ and $Z = 1$ ($\hbar \equiv h/2\pi$) corresponds to the minimum energy of an electron in the electrical field of a proton, and the progression of the energies towards zero for $n \rightarrow \infty$ is depicted in Figure 2.

The electron binding energy in a Hydrogen atom is known with great precision (better than one part in 10^8), from the wavelengths of its emission lines (Balmer series), and it is called in the literature **Rydberg energy** E_y . The value we obtain from (10), when using precision values of the fundamental constants involved, is

$$-E_1 = \frac{1}{2} \frac{m\beta^2}{\hbar^2} = 2.180 \times 10^{-18} J, \quad (11)$$

which is in excellent agreement with the tabulated value of E_y , from which it differs by a relative amount of the order 10^{-3} , attributed to having ignored the electron magnetic moment, to the lack of precision of the non relativistic calculation, to the finite proton mass, to the proton magnetic moment, and to the vacuum polarization.

Such state of minimum energy, which arises from quantum fluctuations in binding potentials, is generically called **ground state**. Although small in Joules, for Hydrogen E_1 is exactly equivalent to the energy acquired by an electron through a potential drop of 13.6 Volts (13.6 eV).

As we have shown, E_1 is proportional to the coupling constant squared β^2 (the “intensity” of the interaction), to the mass m of the fluctuating particle, the electron, and inversely proportional to the square of the Planck constant. Should \hbar be zero, the electron energies would become infinitely negative ($E \rightarrow -\infty$), and in fact no other principle of Mechanics would prevent this to happen, no matter the initial conditions ¹¹.

If we think in terms of the classical trajectory, the electron returns to the same position after completing one cycle, which implies a time location for the extent of the period ($\sim 10^{-16}s$). Since this time is close to the ratio \hbar/T , T being the kinetic energy, quantum fluctuations become important. They are actually responsible for the kinetic energy itself, causing the motion around the proton to be erratic. At the ground state, the motion does not resemble any kind of elliptical trajectory, neither does it take place on a plane. Yet the average distance between the electron and the proton is well defined, and univocally determined by its energy E , according to the expression $a = \beta/(-2E)$ that gives the major axis in Kepler’s motion.

¹⁰to be precise, the quantization condition in this case is: $S_0 = (n + \beta/4)\hbar$, with the Maslov index $\beta = 4$. In 2D we have $\beta = 2$, meaning two conjugate points on the ellipse sitting on a straight line through the secondary focus. But this ellipse must be embedded in 3D, and two more conjugate points appear, sitting on the straight line through the main focus (one of them is repeated). The general rule, with several degrees of freedom, is that at least one of them has $\beta \neq 0$ and n actually runs from zero $n = 0, 1, \dots \infty$.

¹¹according to Maxwell’s equations of Electromagnetism, every charge e subject to an acceleration a radiates energy with power P in watts given by Larmor’s radiation law: $P = \frac{e^2 a^2}{6\pi\epsilon_0 c^3}$. The electron energy loss would cause a very rapid fall onto the proton ($\sim 0.1 ns$ time scale). We suggest to assess and solve the related differential equation, assuming circular orbits.

The experimental data indicate that the angular momentum is zero at the ground state, so that the ellipse would degenerate into a straight line, and the radial distance is oriented at random in 3D. The atom acquires a spherical shape, and the average electron-proton distance is known in the literature as the **Bohr radius** a_0 , which value can then be predicted to be

$$a_0 = \frac{\beta}{-2E_1} = \left(\frac{Ze^2}{4\pi\epsilon_0} \right) \frac{1}{-2E_1} = \frac{\hbar^2 4\pi\epsilon_0}{Z me^2} ,$$

and numerically evaluated for known values of m_e , ϵ_0 , and e , for $Z = 1$, to yield

$$a_0 = 0.529 \times 10^{-10} m = 0.529 \text{ \AA} = 0.0529 \text{ nm} = 52.9 \text{ pm} ,$$

where the Armstrong (\AA) is an ad hoc unit $1 \text{ \AA} = 10^{-10} m$ sometimes used in atomic physics. Although too small to be observed with an optical microscope, due to light diffraction, it can nonetheless be observed with more powerful experimental techniques.

The existence of discrete energy levels in Hydrogen according to (10), in correspondence with the squares of the natural numbers $n = 1, 2, \dots \infty$, is well established experimentally through the wavelengths of the light emitted by the electron, when the atoms are subject to thermal collisions at several thousand degrees of temperature.

Note how in the limit $n \rightarrow \infty$ the allowed energies seem to recover continuous values, for the differences $|E_{n+1} - E_n|$ become very small with respect to $|E_n|$, as it can be appreciated in Figure 2. This is to be expected in the classical limit.

The state of minimum energy that arises in the atom can be understood as a balance between two opposite forces: the kinetic energy due to quantum fluctuations, which becomes very large at small distances, that tends to separate the electron from the nucleus, and the energy loss due to Larmor's radiation law, that tends to bring it closer. The latter arises in turn from the electron acceleration in the Coulomb field. Equilibrium is reached at an average distance which is the Bohr radius.

One would think of an analogy with classical Kepler's motion, where such a balance also occurs between the centrifugal force and the attraction force. However, it is to be taken into account that the ground state energy of the Hydrogen atom *does not originate* from the centrifugal barrier, as the orbital angular momentum of the electron is known to be precisely zero.

So we see that the size of the Hydrogen atom (and similarly of all other atoms) is actually determined by the Plank constant: **if it were zero, all atoms would be infinitely small**. The atomic structure of matter originates from quantum fluctuations.

2.4 The harmonic oscillator

Every potential well in one dimension $U(x)$ generates, for a particle of mass m , a periodic motion between its two turning points. When it is parabolic $U(x) = (1/2)kx^2$ we talk about a harmonic oscillator, which has the remarkable property that the period (or frequency) of the oscillations $\Delta t = 2\pi/\omega$ becomes independent of the total energy E . The latter is only determined by the amplitude A , $E = (1/2)kA^2$.

All branches of Physics profusely refer to harmonic oscillators. We might think that the energy (amplitude) of an oscillator would be as small as we want, but nothing further from the truth. The quantization principle of the classical action radically impedes that.

Given the general solution for the trajectory $x(t) = A\cos(\omega t - \phi)$, we suggest to verify that a null value is obtained for the action integral ($S = 0$) when extended over the period Δt . Nonetheless the reduced action is $S_0 = S + E\Delta t = 2\pi E/\omega$, and the action quantization principle implies in this case $S_0 = (n + \beta/4)h$ with $\beta = 2$ ¹² and $n = 0, 1, \dots \infty$.

The above renders the energy levels of the harmonic oscillator

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega \quad n = 0, 1, 2, \dots \infty, \quad (12)$$

which is one of the most far-reaching and best-tested results in Physics. It means that no oscillator can gain or transfer energy by an amount smaller than $\hbar\omega$. This quantity is called in the literature **quantum** of energy, and grows linearly with frequency, as we see. It was originally conjectured by the German physicist Max Planck in 1900, as referring to the atomic oscillators that belong to the walls of a cavity in equilibrium with its radiation. The result is also telling us that no oscillator can vibrate with energy less than 1/2 the quantum. This is the so-called **zero-point energy** which completely revolutionized the low-temperature Thermodynamics a century ago.

2.5 Density of energy levels

We have seen, in two simple and most characteristic Hamiltonian systems, how action quantization generates discrete energy levels. A crucial feature arises at this point, which is independent of the nature of the system, namely that the phase-space is itself quantized.

Consider a general Hamiltonian $H(\mathbf{q}, \mathbf{p})$ with N degrees of freedom, having generalized coordinates \mathbf{q} and momenta \mathbf{p} in a $2N$ -dimensional phase-space. The action quantization over periodic trajectories of the system is expressed by the closed line integral

$$S_0 = \oint \mathbf{p}d\mathbf{q} = \sum_{i=1}^N \oint p_i dq_i = \sum_{i=1}^N S_0^i = \sum_{i=1}^N (n_i + \alpha_i)h,$$

and if we take the limit of high quantum numbers $n_i \gg 1$ in every coordinate, it is clear from Green's theorem¹³ that $\oint p_i dq_i = \iint dq_i dp_i = n_i h$, so that the area enclosed by the trajectory in (q_i, p_i) space is a multiple n_i of an elementary tile $\delta q_i \delta p_i$ of area h , as illustrated in Figure 3. Therefore every volume in (\mathbf{q}, \mathbf{p}) space will be an integer multiple of the elementary $2N$ -cube of size $(\delta q_1 \delta p_1)(\delta q_2 \delta p_2) \cdots (\delta q_N \delta p_N) = h^N$. This means that the phase-space becomes partitioned in **elementary cells of volume h^N** .

In Classical Mechanics, the total volume of the phase-space of trajectories with energy below a given value E , is defined by the following multiple integral

$$\Omega(E) = \int d^N q \int d^N p \theta(E - H(\mathbf{q}, \mathbf{p})),$$

where H is the Hamiltonian and $\theta(x)$ is the unit step function¹⁴. Having the above partitioning in mind, we define the average *number of energy levels* as $\langle \mathcal{N}(E) \rangle \equiv \Omega(E)/h^N$ and the average *density* of levels per unit energy as $\langle d\mathcal{N}/dE \rangle \equiv (d\Omega(E)/dE)/h^N$.

¹²in every potential well in 1D, β equals the number of turning points, namely two.

¹³ the line integral should be taken *clockwise*, since $p_i dq_i$ is always nonnegative.

¹⁴ we propose as an exercise to show that for a 1D oscillator $\Omega(E) = 2\pi E/\omega$, and for an ensemble of N independent oscillators with Hamiltonian $H = \sum_i^N p_i^2/2m + (1/2)m\omega^2 q_i^2$, $\Omega(E) = (2\pi E/\omega)^N (1/N\Gamma(N))$, Γ being Euler's function.

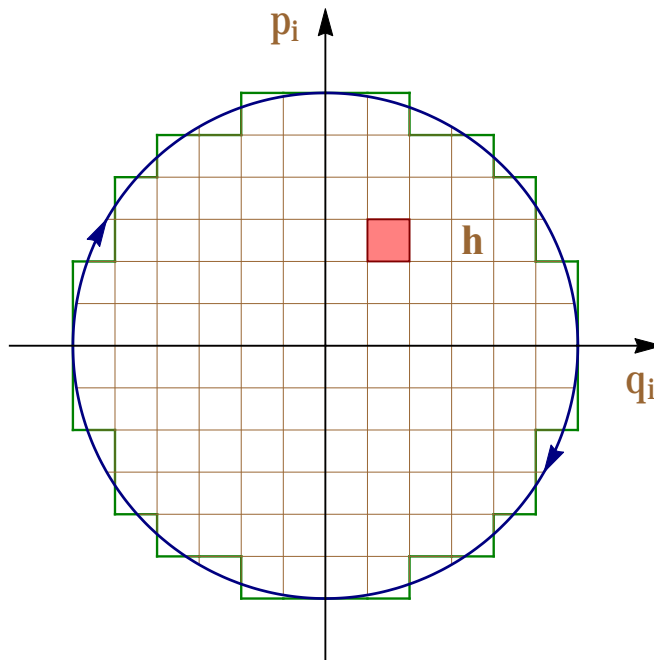


Figure 3: *Periodic trajectory of one degree of freedom i , having coordinate q_i and generalized momentum p_i . The phase-space volume is quantized in multiples of h .*

The above average quantities $\langle \mathcal{N}(E) \rangle$ and $\langle d\mathcal{N}/dE \rangle$ illustrate the fact that, for every physical system, the action quantization creates in general a *finite* number of discrete energy levels¹⁵, that can be calculated just from the knowledge of Planck's constant, and of the classical phase-space volume $\Omega(E)$. This calculation is actually quite accurate, if we apply it to energy intervals $(E, E + \Delta E)$, with ΔE small in comparison with E , but large enough as compared with the mean energy spacing $\langle d\mathcal{N}/dE \rangle^{-1}$.

Thus we see how every physical system, that we have assumed to be confined in periodic motion, is subject to the presence of discrete energy levels, which is in sharp contrast with Classical Mechanics, where the energy is allowed to take continuous values. It is revealing that discretization holds in the case we previously defined as the *classical limit*, showing how Classical Mechanics is *never actually retrieved*, even in that limit.

Let us finally mention an interesting curiosity for the keen student, whose details would take us far from the scope of this course. For classically chaotic systems, where no constants of motion exist other than the total energy E , the quantized level spacings appear to be remarkably regular. In fact, the number of levels $\mathcal{N}(E_q)$ below the energy E_q , as a function of $E_q \in (E, E + \Delta E)$, fits well to a straight line, and the mean square deviation of the fit turns out to be much smaller for chaotic systems than it is for integrable systems. In the latter case, where $N - 1$ constants of motion exist, the level positioning surprisingly occurs at random in general, with respect to the mean energy spacing. Both phenomena are understood¹⁶, and the former is known in the literature as *quantum level repulsion*. It has been extensively observed in classically chaotic systems with a large number of freedoms N , including nuclear resonances, heavy atoms and molecules.

¹⁵for particular choices of the energy E , the number of discrete levels may become infinite, but that is not the general rule.

¹⁶see M. V. Berry, "Semiclassical Mechanics of regular and irregular motion", Les Houches Lecture, 1983, and M. Gutzwiller, "Chaos in Classical and Quantum Mechanics", Springer 1990.

2.6 The wave motion

The realm of Physics primarily consists of two kinds of objects: moving bodies of given mass m , and waves. Yet the discontinuous nature of the reduced action affects both of them equally.

Waves are objects that describe the propagation of physical magnitudes in a continuous manner across space and time. For the sake of simplicity, we restrict ourselves to one dimension, even if their natural domain are the three space dimensions. Their most general mathematical definition is a propagation amplitude in the form $Ae^{i(kx-\omega t)}$, where A is the physical magnitude that propagates, measured in appropriate SI units, ω is the time periodicity, or angular frequency (units s^{-1}) and k is the spatial periodicity or number of waves per unit length (m^{-1}). Both periodicities are always related by a function $\omega = \omega(k)$, called *dispersion relation*. There exists in Physics a great diversity of waves, either propagating in a material medium or in vacuum, where nearly all conceivable functions are realized as $\omega(k)$. This function must in general be determined experimentally. The utilization of complex numbers to describe waves is convenient, but not essential (waves could equally well be defined with the cosine function).

When $\omega(k)$ is the linear function $\omega = vk$ we talk about a non dispersive wave, with v being its propagation velocity. In general the group velocity $v = d\omega/dk$ defines the propagation of wave pulses.

Waves carry energy (and thereby information) across the space. At each space point they have an energy density \mathcal{E} per unit volume. They also have a Lagrangian density \mathcal{L} (per unit volumen) ¹⁷, that governs, through the least action principle, the partial differential equations to be fulfilled by the magnitude A . When the waves propagate in a material medium made of atoms or molecules, these act as carriers just because they vibrate harmonically around their equilibrium positions. For that reason the wave inherits from the harmonic oscillator most of its properties.

Let us consider a wave with frequency ω , enclosed in a rectangular box of volume V , whose dimensions are integer multiples of half the wavelength. The reduced action, extended over one cycle $t_2 - t_1 = 2\pi/\omega$, takes the value

$$S_0 = \int_{t_1}^{t_2} \left(\int_V \mathcal{L}(\mathbf{x}, \dot{\mathbf{x}}, t) d^3\mathbf{x} \right) dt + E(t_2 - t_1) ,$$

where E is the integral of the energy density \mathcal{E} over the volume V . Both in the case of a continuous distribution of oscillators and of an electromagnetic wave, the first term comes to be zero ¹⁸. The principle of action quantization, using the same results as for the harmonic oscillator, leads to the conclusion that the energy in the box is quantized in the same way as it is for the oscillator

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega \quad n = 0, 1, 2, \dots \infty . \quad (13)$$

¹⁷for instance, the Lagrangian density for the electromagnetic field, in absence of currents and charges, is given by $\mathcal{L} = \frac{1}{2}(\epsilon_0\mathbf{E}^2 - \frac{1}{\mu_0}\mathbf{B}^2)$.

¹⁸this is simple to work out, and in both cases it is related to the integral of a cosine function over an integer number of cycles.

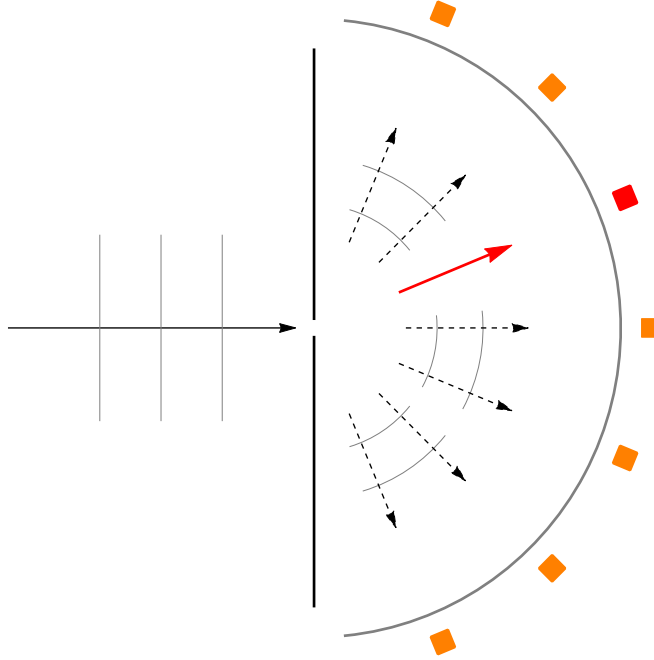


Figure 4: When a low intensity wave is diffracted, only one of the detectors will register the quantum, the rest will not fire. We cannot predict which one will fire.

If we open a hole at an outer surface of the box, the wave will propagate out with a certain velocity, and the energy transferred towards a given detector will be quantized in full units of the quantum $\hbar\omega$, which is directly proportional to the frequency. This happens irrespective of whether the wave propagates in a medium or in vacuum, as well as of the physical nature of the propagating magnitude A . The existence of a well defined frequency is what matters. Therefore the *transferable* energy of any wave is an integer number of quanta $E = n\hbar\omega$ con $n = 1, 2, \dots \infty$.

However, the wave enclosed in the box of volume V has a **non transferable energy** $\frac{1}{2}\hbar\omega$ which is stored inside and not carried away with the wave. If the wave propagates in vacuum, this energy becomes infinite when summing over all possible frequencies in the box, which is not regarded in general as contradictory ¹⁹. But if the wave propagates through atoms or molecules, an upper limit to its possible frequency arises, from the minimum wavelength equal to the atom sizes, and no infinities can possibly arise.

Let us consider a wave that carries a certain power per unit area through its wave front (in Wm^{-2}), and impinges on a normal surface of area A_S . For example, an electromagnetic wave. We shall underline four essential aspects related to the detection of quanta in the laboratory, in the limit where the wave power is very weak, and the individual signals from quanta are detectable:

- The transfer of the quantum is **instantaneous**, sudden, and not gradual. The time at which the transfer takes place, counted from the instant the wavefront arrives to the surface, is unpredictable, within the interval $\Delta t = \hbar\omega/(WA_S)$ associated with the average time distance between the arrival of quanta.

¹⁹this energy has been indirectly observed in precision experiments, in the case of the electromagnetic field. The field fluctuations in vacuum generate an attractive force between two very close parallel metallic plates, which is known in the literature as *Casimir force*.

- To all effects, the wave behaves as a collection of **particles** which travel with it, although they are *not synchronized* with it.
- The random character of the quantum is extensive to the spatial direction of the energy transfer. Take the example of a wave which is diffracted through a small hole, and set an ensemble of detectors uniformly distributed over a spherical surface centered in it. It is **unpredictable** which detector will fire and which will not. This is illustrated in Figure 4. A relevant example is the direction in which a photon is emitted from an atom, or from a nucleus, within the 4π solid angle.
- The idea of **instantaneous power** (in Wm^{-2}) becomes meaningless in the limit of very low intensity waves. Obviously, the instantaneous power for the absorption of a quantum is infinite, if we divide a finite energy over *zero* time. The wave power must then be understood as an *average* power. What happens here is *not dissimilar* to the failure we encountered of the instantaneous velocity of a particle of mass m .

All of the above properties have been confirmed in the laboratory with high accuracy, particularly in the case of photons. It is clear that the existence of quanta introduces a random element in the energy transmission by waves. In the limit of very small intensity waves, also the information transmission will be affected by inevitable noise.

A surprising consequence of the presence of the Planck constant in Physics is, as we have just seen, that both moving bodies of mass m and waves acquire similar properties, for they share a **common random nature**, which in neither case was expected.

3 The Feynman propagation

As has been seen, the discrete and *nonzero* character of the action ($S_0 \gtrsim h$) requires that any measurement attempted on a particle during a time $\Delta t \lesssim h/E$ will generate an increase of its kinetic energy that is not reconcilable with a differentiable trajectory.

If we try to imagine the motion as a succession of small time intervals, we should not be surprised that accepting the discrete character of the reduced action (as originally encountered by Planck) entails a great *conceptual transformation* in Physics, which can be summarized as follows: the motion for $\Delta t \lesssim h/E$ takes place in a **nondeterministic** way, such that the observed position of a particle at a given time, cannot be inferred with certainty from its position and velocity at an earlier time.

Such statement may seem astonishing, and indeed it is against what the theory of differential equations tells us, where the specification of the initial conditions (position and velocity) suffices to determine the unique solution for the motion at any later time t . However, the above theory is based upon differentiability.

We therefore understand why a suitable description of Physics which includes the motion of atoms, molecules and elementary particles, compels us to abandon its deterministic character. On the other hand, it is clear that any formulation given along these lines must also recover the laws of classical motion, of deterministic nature, which we know describe with great precision the motion for large observation time intervals $\Delta t \gg \frac{h}{E}$.

Let us see how such formulation can be achieved in a rigorous manner. For this purpose, we focus on the one dimensional motion, and come back to the discussion of Section 1, for a particle moving in a short time interval $\Delta t \rightarrow 0$, subject to a potential $U(x, t)$. The real motion “chooses”, among the infinite intermediate positions x between x_1 and x_2 , the one satisfying second Newton’s law $-\frac{\partial U}{\partial x} = m\ddot{x}$ which, as has been seen, is the one where the action S is minimal (see Figure 1), such that any other position x must be rejected. Hence, the new nondeterministic formulation of Mechanics consists in admitting that ALL intermediate positions of the particle are in principle **possible**.

This admitted, it stands to reason that if the particle occupies position x_1 at time t_1 , after a short time $\Delta t = t - t_1$ it has virtually occupied all space. In order to be more precise about this virtuality, we define the **propagation amplitude** $K(x, t) \equiv \langle x \ t \mid x_1 \ t_1 \rangle$ as a COMPLEX number, that characterizes the motion from x_1 to x . Its *phase* makes possible the *interference* between propagation amplitudes through different intermediate positions x in the transition from x_1 to x_2 . The *modulus* of this complex number only depends on the time interval $t - t_1$. The propagation amplitude for the transition from $(x_1 \ t_1)$ to $(x_2 \ t_2)$ satisfies the following **postulate of propagation**:

$$\langle x_2 \ t_2 \mid x_1 \ t_1 \rangle = \int_{-\infty}^{+\infty} \langle x_2 \ t_2 \mid x \ t \rangle \langle x \ t \mid x_1 \ t_1 \rangle dx , \quad (14)$$

where t is an intermediate time $t \in (t_1, t_2)$. The integration of this product of complex numbers is done over all the virtual space of intermediate positions x (real, of course). This expression defines the fundamental property that propagation amplitudes must fulfill²⁰. It can be thought up as follows: “in order to move from one point to another, objects must probe all positions in space”.

In the deterministic (Classical) Mechanics, such amplitude would be restricted to the values of one (the motion from (x_1, t_1) to (x_2, t_2) is possible), or zero otherwise. In other words, the only intermediate point x that could contribute to the integral (14) at time t , would be the one fulfilling Newton’s law. By contrast, in Quantum Mechanics the zero amplitude never happens, and it is possible to go from $+1$ to -1 through a continuum of values on the unit circle of the complex plane, making *interference* possible.

A proper definition of the propagation amplitude, in a new formulation of Physics, must achieve that, in the case of macroscopic motion (for long time intervals $\Delta t \gg \frac{h}{E}$), the mechanism of interference between different “jumps” x far away from the classical trajectory, is strongly **destructive**, in order to verify Newton’s law with sufficient precision.

Postulate (14) is calling for the utilization of the exponential function, with its defining property $\exp(a + b) = \exp(a) \exp(b)$. Moreover, we are compelled to use an oscillatory function in order to achieve interference. Therefore, the use of **complex numbers** for the description of the laws of motion becomes *unavoidable*, under the form $e^{if(x)}$ ²¹. Interestingly, these are not needed in the formulation of Classical Mechanics.

Such definition of the propagation amplitude for $\Delta t \rightarrow 0$, which we take here as a postulate, was given in 1948 by Richard P. Feynman. This postulate is a realization of equation (14), and should be adopted together with it.

²⁰the amplitude (14) arises from a sum (integral) over many different amplitudes (paths), which simultaneously contribute to the motion. This is often referred to in the literature as **superposition principle**. We shall see in Section 6 how this principle immediately extends to the state of motion itself.

²¹it can be explicitly checked that the cosine function, real part of the above, fails to fulfill the integral equation (14).

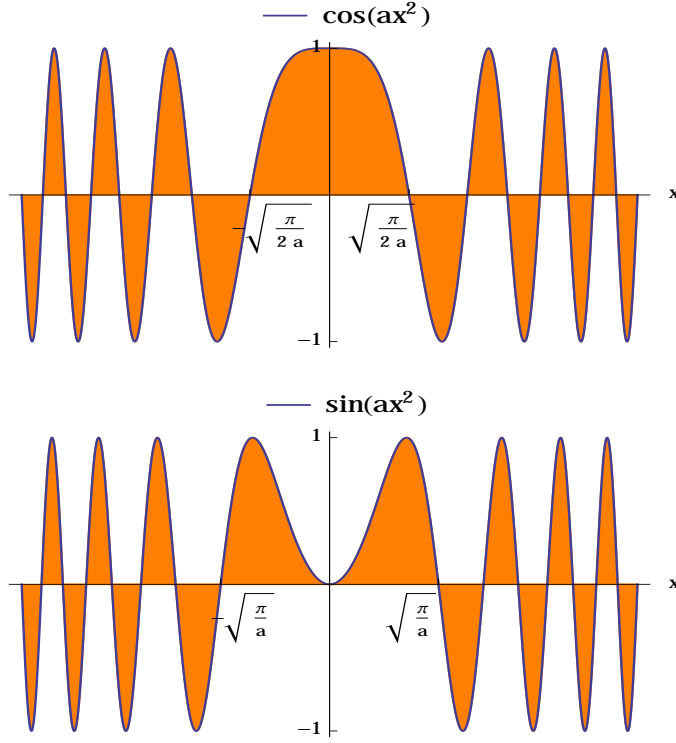


Figure 5: Graphical representation of the Fresnel functions, which are the real (top) and imaginary (bottom) part of the function e^{iax^2} .

Feynman's propagation principle: The propagation amplitude for the motion of a particle of mass m , subject to a potential $U(x,t)$, from point x_1 at time t_1 to point x at time t , in the limit $\Delta t = t - t_1 \rightarrow 0$, is given by:

$$\begin{aligned} \langle x t | x_1 t_1 \rangle &= A e^{\frac{iS}{\hbar}} = A e^{\frac{i}{\hbar} L \Delta t} \\ &= \sqrt{\frac{m}{i2\pi\hbar\Delta t}} \exp \left[\frac{i}{\hbar} \left(\frac{m(x-x_1)^2}{2\Delta t} - U\left(\frac{x+x_1}{2}, t\right) \Delta t \right) \right], \end{aligned} \quad (15)$$

where $S = L\Delta t = (T - U)\Delta t$ is the classical action that corresponds to the motion in the space-time interval from (x_1, t_1) to (x, t) .

In order to deduce the value of the coefficient $A = \sqrt{m/(i2\pi\hbar\Delta t)}$, one should first realize that in the limit $\Delta t \rightarrow 0$ the potential energy has no influence on this factor, by simply comparing the opposite asymptotic behaviour of the two terms in the exponent, so that the exact value of A actually corresponds to the free motion case ($U(x, t) = 0$)²². The coefficient A is obtained from postulate (14) after dividing the interval Δt into two halves $\Delta t/2$, and adding the exponents of the respective propagators. This is left as an exercise to the student, using for that purpose the value of the integral

$$\int_{-\infty}^{+\infty} e^{ax^2+bx} dx = \sqrt{\frac{\pi}{-a}} e^{-b^2/4a} \quad a, b \in \mathbb{C} \quad \text{Re}(a) \leq 0. \quad (16)$$

²²this is only valid for potentials having an asymptotic increase for $x \rightarrow \pm\infty$ at most quadratic, i.e. if $|U(x, t)| \leq C(x - x_1)^2 \forall x$, for some constant C .

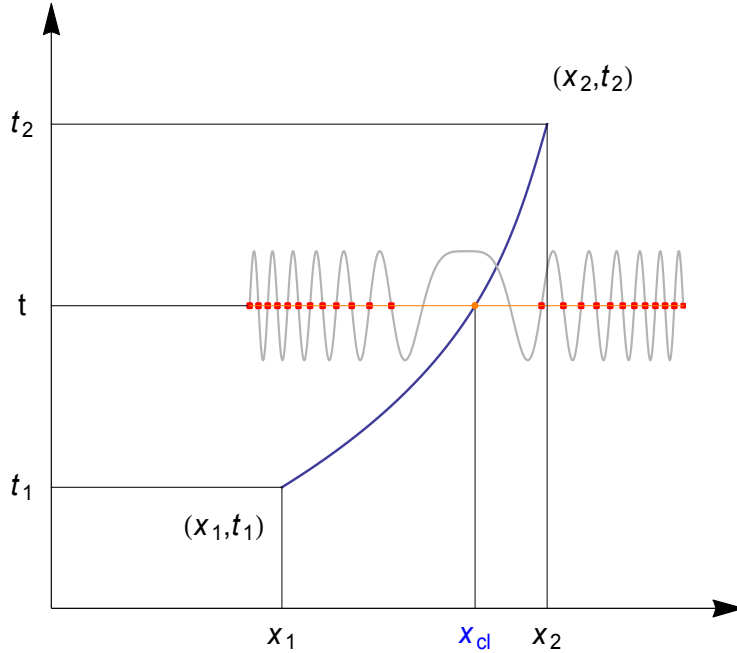


Figure 6: Positions occupied by a moving body (red) at an intermediate time t when moving from x_1 to x_2 in a short time interval, far away from the classical trajectory (blue), and the real part of the amplitude assigned to them by the Feynman propagator (grey).

When making the above calculation with equation (14), note that the left-hand side is proportional to $A(\Delta t)$, whereas the right-hand side is proportional to $A^2(\Delta t/2)\sqrt{\Delta t}$. The solution is $A \propto 1/\sqrt{\Delta t}$ and therefore we have $A(\Delta t/2) = \sqrt{2}A(\Delta t)$, so that the desired result follows immediately.

If we consider, for the sake of simplicity, the case of free motion, the real and imaginary parts of the propagator are then the well known Fresnel functions, which integral is obtained by setting $b = 0$ in equation (16)

$$\int_{-\infty}^{+\infty} \cos(ax^2)dx = \int_{-\infty}^{+\infty} \sin(ax^2)dx = \sqrt{\frac{\pi}{2a}}.$$

A graphical representation of these functions is shown in Figure 5. Detailed observation of the curve reveals the reason why these integrals are convergent: due to the rapid oscillation of the phase for values $x \rightarrow \pm\infty$, the positive and negative contributions cancel out more precisely the larger the $|x|$ values are, so that the main contribution to the integral comes from x in the neighbourhood of the first zeros²³ ($|x| \lesssim \sqrt{\frac{\pi}{a}}$).

Coming back to Feynman's principle, we grasp the physical importance of the above, since according to (14), all contributions from the intermediate points x , shown in Figure 6, must be summed up. The highest contribution comes from the interval $(x_{cl} - \Delta x, x_{cl} + \Delta x)$ around the point x_{cl} of the classical trajectory, with

$$\Delta x \lesssim \sqrt{\frac{\pi\hbar\Delta t}{m}}, \quad (17)$$

²³the zeros are located at $x_n = \pm\sqrt{(2n-1)\pi/2a}$ for the cosine function and $x_n = \pm\sqrt{n\pi/2a}$ for the sine, with $n = 1, 2, \dots \infty$.

so that fluctuations of larger extent are unlikely, and contribute very little to the motion, due to the aforementioned cancellations. We shall see in Section 4 more details about the significance of Figure 6, and its consequences. Section 3.1 next is not indispensable to comprehend the rest of this course, and may be skipped.

3.1 Exact propagation over a finite time

Expression (15) is valid for an infinitesimal time interval Δt . If a finite time interval is required, then it is necessary to apply (15) repeatedly, at successive time steps dt , taking into account that, at each step, the particle may move from any previous point to any other in space.

Only for the student specifically interested, we indicate below the detailed way in which such integration is performed. The interval $\Delta t = t_b - t_a$ is divided into small steps $\epsilon = t_{i+1} - t_i$ with $\Delta t = N\epsilon$, so that at each time t_i we select some arbitrary point x_i and construct a path by connecting all points so selected (x_i, t_i) , for $i = 0, \dots, N$, with $t_N = t_b$. We evaluate the Lagrangian $L(x, \dot{x}, t)$ at each point (x_i, t_i) and then apply the propagator (15) at each step

$$K(i+1, i) = \frac{1}{A} \exp \left[\frac{i\epsilon}{\hbar} L \left(\frac{x_{i+1} + x_i}{2}, \frac{x_{i+1} - x_i}{\epsilon}, \frac{t_{i+1} + t_i}{2} \right) \right],$$

then the propagator over the finite interval is just the product of all of them

$$K(x_b, t_b; x_a, t_a) = \lim_{\epsilon \rightarrow 0} \prod_{i=0}^{N-1} K(i+1, i), \quad (18)$$

which corresponds to the detailed expression

$$K(x_b, t_b; x_a, t_a) = \lim_{\epsilon \rightarrow 0} \frac{1}{A} \int \int \dots \int e^{\frac{i}{\hbar} S[b,a]} \frac{dx_1}{A} \frac{dx_2}{A} \dots \frac{dx_{N-1}}{A}, \quad (19)$$

where $S[b, a] = \int_{t_a}^{t_b} L(x, \dot{x}, t) dt$ is the line integral obtained from the path of straight-line steps (x_i, t_i) mentioned above, and A is the factor calculated in the previous Section. The integration over the space coordinates is performed at each time t_i in the same way as before, which gives rise to a $(N-1)$ -dimensional multiple integral. Finally the limit $N \rightarrow \infty$ is taken (which is equivalent to $\epsilon \rightarrow 0$).

Expression (19) is known in the literature as Feynman's **path integral**. As said above, it is a $(N-1)$ -dimensional integral over the space coordinates, where the time sum comes to complete the action integral in the exponent, in the limit $\epsilon \rightarrow 0$. It is customary to use the succinct notation

$$K(b, a) = \int_a^b e^{\frac{i}{\hbar} S[b,a]} \mathcal{D}x(t), \quad (20)$$

where the symbol $\mathcal{D}x(t)$ reminds us that the multiple spatial integration (19) is equivalent in fact to a sum over *all possible trajectories* $x(t)$ between the points x_a and x_b . In the discussion that follows, particularly the derivation of Schrödinger's equation in Section 5, the consideration of the infinitesimal interval (15) will suffice.

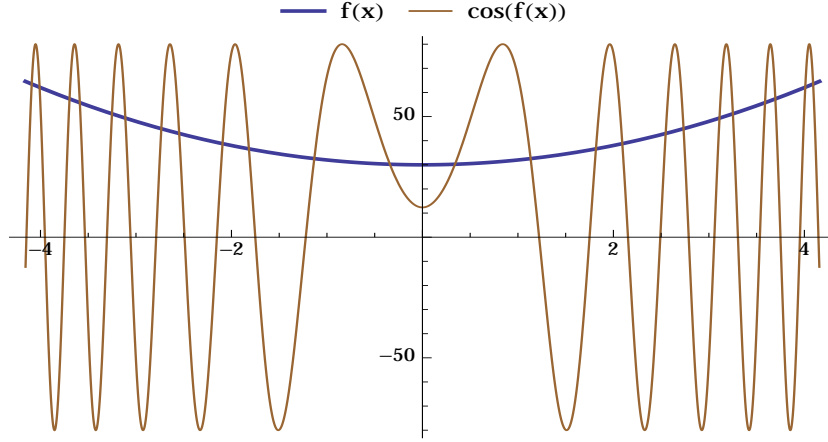


Figure 7: The function $\cos(f(x))$ shows a smaller number of oscillations near the minimum of $f(x)$.

4 The instantaneous velocity

Let us see below how the intermediate position $x_1 < x < x_2$ that verifies the second Newton's law is, according to Feynman's hypothesis, precisely the central value around which the particle's position fluctuates.

Consider again the sequence represented in Figure 6, where a particle of mass m moves from (x_1, t_1) to (x_2, t_2) through the intermediate position x (at time $t = (t_1 + t_2)/2$), with $\Delta t = t_2 - t_1$. Then the amplitude for the transition $1 \rightarrow 2$, according to (14) is given by:

$$\langle x_2 t_2 | x_1 t_1 \rangle = \int_{-\infty}^{+\infty} M(x) dx = \int_{-\infty}^{+\infty} \langle x_2 t_2 | x t \rangle \langle x t | x_1 t_1 \rangle dx ,$$

which, according to (15), can be expressed as:

$$\begin{aligned} & \int_{-\infty}^{+\infty} A^2 e^{\frac{i}{\hbar} \left[\left(\frac{m}{2} \frac{(x-x_1)^2}{(\Delta t/2)^2} - U\left(\frac{x_1+x}{2}\right) \right) \frac{\Delta t}{2} \right]} e^{\frac{i}{\hbar} \left[\left(\frac{m}{2} \frac{(x_2-x)^2}{(\Delta t/2)^2} - U\left(\frac{x+x_2}{2}\right) \right) \frac{\Delta t}{2} \right]} dx \\ & = \int_{-\infty}^{+\infty} A^2 e^{\frac{i}{\hbar} \frac{\Delta t}{2} \left[\frac{m}{2} \frac{(x-x_1)^2 + (x_2-x)^2}{(\Delta t/2)^2} - (U\left(\frac{x_1+x}{2}\right) + U\left(\frac{x+x_2}{2}\right)) \right]} dx . \end{aligned}$$

It is easy to check that the main contribution to the integral comes from the region where x is close to the value that makes the expression under the square brackets minimal. In general, for a function $f(x)$ having a minimum at $x = x_c$, the value of the integral $\int_{-\infty}^{+\infty} \cos(f(x)) dx$, which is the real part of the above expression, gets the largest contribution from those values $x \simeq x_c$ where the cosine has the least number of oscillations per unit length, as illustrated in Figure 7. Yet the value of x where the expression in square brackets is minimal is precisely that verifying second Newton's law ($-\frac{\partial U}{\partial x} = m\ddot{x}$), as was shown in Section 1, according to formula 4.

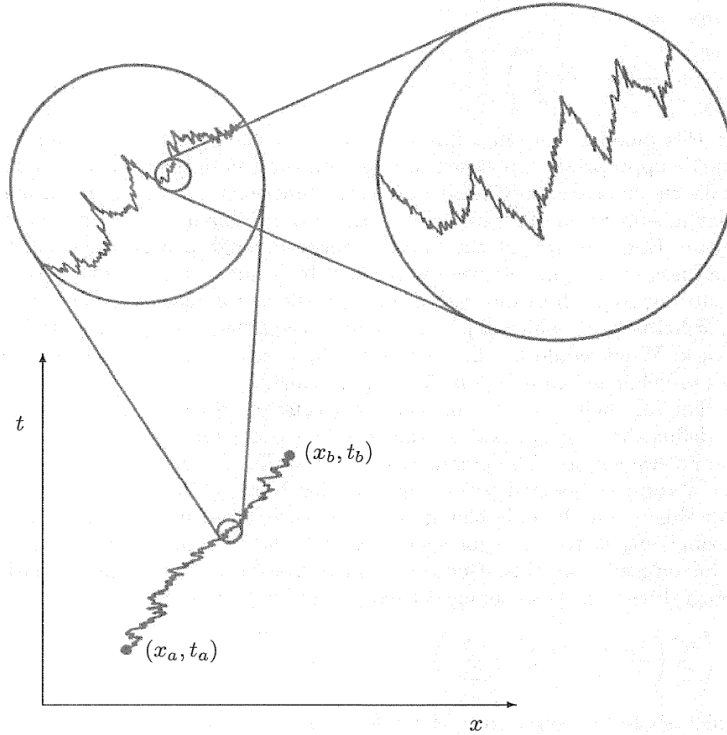


Figure 8: Irregular path followed by a particle when looked in detail in a space-time diagram: the trajectory is not differentiable. Original drawing by Richard Feynman in [Quantum Mechanics and Path Integrals](#), 1948.

Therefore, we see that the effect of destructive interference derived from expression (15) is essential to produce a probability suppression of far-away positions from the classical trajectory of the particle (fluctuations) during the observation time Δt . Let us recall that the region where these fluctuations become important is determined by expression (17), where we can see that, even if the spot Δx blurred by these fluctuations becomes infinitely small in the limit $\Delta t \rightarrow 0$, it does not do so linearly, but proportional to $\sqrt{\Delta t}$ (less rapidly). The ratio $\Delta x/\Delta t$ is **not finite** in the above limit, but diverges as $1/\sqrt{\Delta t}$, which tells us that the instantaneous velocity does not make sense. Its absolute value becomes infinite, if we take the non relativistic expression for the kinetic energy ²⁴.

This important conclusion, which is ultimately a consequence of the discrete (*nonzero*) character of the action, undoubtedly breaks up with preconceived ideas about the differentiability of trajectories. It is clear that particle observation during shorter and shorter time intervals will produce higher and higher velocities. On the other hand, if the observation time interval is sufficiently long, as for instance, when a photography is taken with exposure time some fraction of a second (10^{-2} – $10^{-3}s$), then the motion appears to be perfectly continuous, without fluctuations. This idea can be appreciated in Figure 8, taken from the book by Feynman and Hibbs *Quantum Mechanics and Path Integrals*, Dover (2010).

²⁴we recall here the relativistic consideration made in (2.1), which takes the velocity to c .

5 The Schrödinger equation

We have seen up to now how the particle's motion in the limit $\Delta t \rightarrow 0$ can be represented by means of a space-time propagation amplitude $\langle x \ t \mid x_1 \ t_1 \rangle$, which is actually a complex function of the real variables (x, t) . This idea has allowed us to reconcile the discontinuous character of the action at short time scales with a mathematical description that renders the use of differentiable functions possible, for the study of motion.

Despite its conceptual riches, the practical use of expression (20) to propagate the particle from (x_1, t_1) to (x_2, t_2) when $\Delta t = t_2 - t_1$ is *finite* (not infinitesimal), requires the introduction of new mathematical tools of integration, which we shall not develop here. Instead, we shall show an easier way to use expression (20), based upon partial differential equations. All it takes is to realize that the function $K(x, t) \equiv \langle x \ t \mid x_1 \ t_1 \rangle$ actually behaves as a strongly dispersive wave in the coordinates (x, t) .

Indeed, let us show that, according to expression (14), and to the form (15) of the propagation amplitude $K(x, t) \equiv \langle x \ t \mid x_1 \ t_1 \rangle$ for $\Delta t = t - t_1 \rightarrow 0$, the function $K(x, t)$ satisfies the following differential equation, called **Schrödinger's equation** :

$$i\hbar \frac{\partial K(x, t)}{\partial t} = \frac{-\hbar^2}{2m} \frac{\partial^2 K(x, t)}{\partial x^2} + U(x, t)K(x, t) . \quad (21)$$

For this purpose, let us take into account that the point $(x, t + \Delta t)$ is reached from all space points $x - \xi$ at an earlier time t , so the amplitude $K(x, t + \Delta t) \equiv \langle x \ t + \Delta t \mid x_1 \ t_1 \rangle$ can be written as an integral over all these points $x - \xi$, according to expression (14)

$$K(x, t + \Delta t) = \int_{-\infty}^{+\infty} K(x, t + \Delta t ; x - \xi, t) K(x - \xi, t) d\xi .$$

This first factor in the integrand $K(x, t + \Delta t ; x - \xi, t) \equiv \langle x, t + \Delta t \mid x - \xi, t \rangle$ can be expressed using the Feynman propagator, with the result

$$K(x, t + \Delta t) = \sqrt{\frac{m}{2\pi i \hbar \Delta t}} \int_{-\infty}^{+\infty} \exp\left(\frac{i m \xi^2}{\hbar 2 \Delta t}\right) \exp\left(\frac{i}{\hbar} [-U(x - \xi/2) \Delta t]\right) K(x - \xi, t) d\xi \quad (22)$$

Since the function $K(x, t)$ is infinitely differentiable for $t \neq t_1$, in order to relate its partial derivatives we write down its expansion in powers of Δt

$$K(x, t + \Delta t) = K(x, t) + \Delta t \frac{\partial}{\partial t} K(x, t) + \dots ,$$

and in powers of ξ

$$K(x - \xi, t) = K(x, t) - \xi \frac{\partial K(x, t)}{\partial x} + \frac{\xi^2}{2} \frac{\partial^2 K(x, t)}{\partial x^2} + \dots , \quad (23)$$

as well as the expansion of the exponential function

$$e^{-\frac{i}{\hbar} U(x - \xi/2) \Delta t} = 1 - \frac{i}{\hbar} U(x - \xi/2) \Delta t + \dots = 1 - \frac{i}{\hbar} U(x) \Delta t + \frac{i \xi}{\hbar 2} \frac{\partial U}{\partial x} \cdot \Delta t - \frac{i \xi^2}{\hbar 4} \frac{\partial^2 U}{\partial x^2} \cdot \Delta t + \dots \quad (24)$$

It is clear that when making the cross products between the expansions (23) and (24) in the right hand side of equation (22), 12 terms will appear, of which those with odd powers of ξ vanish out, after integration from $-\infty$ and $+\infty$. In order to evaluate the even powers, we use the following integrals ²⁵

$$\int_{-\infty}^{+\infty} e^{\frac{i}{\hbar} \frac{m\xi^2}{2\Delta t}} d\xi = \sqrt{\frac{2\pi i \hbar \Delta t}{m}} \quad \text{and}$$

$$\int_{-\infty}^{+\infty} \xi^2 e^{\frac{i}{\hbar} \frac{m\xi^2}{2\Delta t}} d\xi = \sqrt{2\pi} \left(\frac{i\hbar \Delta t}{m} \right)^{3/2},$$

so that the remaining terms in the right-hand side of (22) are proportional to powers of Δt , of which we neglect $(\Delta t)^2$, $(\Delta t)^3$, \dots in the limit $\Delta t \rightarrow 0$. The expression finally obtained is

$$\Delta t \frac{\partial K(x,t)}{\partial t} = \sqrt{\frac{m}{2\pi i \hbar \Delta t}} \sqrt{2\pi} \left(\frac{i\hbar \Delta t}{m} \right)^{3/2} \frac{1}{2} \frac{\partial^2 K(x,t)}{\partial x^2} - \frac{i}{\hbar} \Delta t U(x) K(x,t),$$

from which equation (21) follows after elimination of Δt from both sides. Note that terms containing $\frac{\partial^2 U}{\partial x^2} K$, $\frac{\partial U}{\partial x} \frac{\partial K}{\partial x}$, and $U \frac{\partial^2 K}{\partial x^2}$, come out proportional to $(\Delta t)^2$ and do not contribute in the limit $\Delta t \rightarrow 0$. The differential equation (21) is a fundamental tool for all applications of Quantum Mechanics. It was discovered in 1926 by the Austrian physicist Erwin Schrödinger.

6 The wave function

We have defined $K(x_2, t_2; x_1, t_1)$ as the propagation amplitude for a particle of mass m to move from (x_1, t_1) to (x_2, t_2) under a potential $U(x, t)$, and we have done it using the classical action. Contrary to what happens in Classical Mechanics, where the motion may or may not be possible under given conditions, in Quantum Mechanics the motion is always possible, since the exponential function is never zero. Therefore, the particle initially located at point x_1 , will have virtually propagated to all space points at a later time $t > t_1$, and each point is in turn subject to subsequent propagation. It becomes then necessary to define the state of occupation of space that a particle has at a given time.

It is of interest to consider the propagation amplitude for a particle to arrive at a given point, without any particular information about its previous motion. A complex function $\psi(x, t)$ can then be defined as the **total amplitude** to reach the point (x, t) . This amplitude is called the **wavefunction**. There is no conceptual difference with respect to the propagation amplitude we have seen. In fact, the propagator $K(x, t; x_1, t_1)$ is a wavefunction itself, since it represents a concrete amplitude to reach the space-time point (x, t) , specifically from (x_1, t_1) . When we use the notation of the wavefunction, it means we are not interested in the particle's prior motion.

²⁵the second is deduced from the first by derivation with respect to the coefficient multiplying ξ^2

As $\psi(x, t)$ is a propagation amplitude, it complies with the general postulate of propagation (14). Since that equation is valid for *all* points x_1 , then the wavefunction must satisfy the integral equation

$$\psi(x, t) = \int_{-\infty}^{+\infty} K(x, t; x_1, t_1) \psi(x_1, t_1) dx_1 . \quad (25)$$

This result can be stated in physical terms: the total amplitude to reach (x, t) is the sum (integral) over all possible values of x_1 , of the total amplitude to reach the point (x_1, t_1) ($\psi(x_1, t_1)$), times the amplitude to move from x_1 to x ($K(x, t; x_1, t_1)$). The effects of the past history of the particle can then be expressed in terms of a single function. Equation (25) holds with the exact form of the propagator given in Section 3.1, and its approximation by expression (15), for short time intervals, is particularly useful.

Just as the propagator satisfies the Schrödinger equation

$$i\hbar \frac{\partial K(x, t)}{\partial t} = \frac{-\hbar^2}{2m} \frac{\partial^2 K(x, t)}{\partial x^2} + U(x, t)K(x, t) ,$$

so does the wavefunction $\psi(x, t)$

$$i\hbar \frac{\partial \psi}{\partial t} = \left(\frac{-\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + U(x, t) \right) \psi , \quad (26)$$

as it is straightforward to show by partial derivation under the integral sign in (25), the details of which we leave as an exercise to the student. The full mathematical content of equation (25) can now be appreciated, since the function $\psi(x_1, t_1)$ plays the role of a single (arbitrary) initial condition for the time evolution of $\psi(x, t)$ ²⁶.

So the complex function $\psi(x, t)$ is taken as a definition of the *state of motion* of the particle at time t . Associated with it comes the **probabilistic interpretation**, introduced by the German physicist Max Born in 1926: the probability density to find the particle at $(x, x + dx)$, as a result of a measurement, is given by

$$\frac{dP(x, t)}{dx} = |\psi(x, t)|^2 ,$$

which implies the **normalization condition**²⁷ for the full probability

$$\int_{-\infty}^{+\infty} |\psi(x, t)|^2 dx = 1 , \quad (27)$$

so that a 1–1 correspondance can be established between the states of motion of a particle and the complex functions that verify equations (26) and (27).

An important property of the wavefunction is that multiplication by any **global phase** factor $e^{i\theta}$, with $\theta \in \mathbb{R}$ independent of space and time coordinates, cannot change any of its physical properties, and the state of motion it represents remains exactly the same. This is a consequence of the undefined zero level of the potential energy in Mechanics, and of the way it acts in Feynman's propagator (15). In fact, a redefinition $U(x, t) \rightarrow U(x, t) + C$ comes out to be indistinguishable from a change of the origin ($t = 0$) of time $t \rightarrow t + t_0$.

²⁶note that Schrödinger's equation is of first order in t , so its solutions depend on a single integration constant. Therefore it is not required to specify the function $\frac{\partial \psi}{\partial t}$ at $t = 0$, as initial condition. This is in contrast to Newton's equation, and to the wave equation, both of which are of second order in t , containing $\frac{\partial^2}{\partial t^2}$.

²⁷note the implicit requirement that $\psi(x)$ has to be **square-integrable** at all times.

7 Plane waves and Fourier transform

The Schrödinger equation (26) is a partial second order differential equation, belonging to the same family as the wave equation and the diffusion or heat propagation equation (which essentially results from replacing i by 1). Let us consider as a possible solution of (26) a monochromatic plane wave in 1D

$$\psi(x, t) = Ae^{i(kx - \omega t)} . \quad (28)$$

We know this expression represents a propagating wave along the positive X axis, with angular frequency ω , wave number k and velocity $v_p = \omega/k$, that fulfils the wave equation

$$\frac{\partial^2 \psi}{\partial x^2} - \frac{1}{v_p^2} \frac{\partial^2 \psi}{\partial t^2} = 0$$

and therefore it will not fulfill equation (26) with $U(x, t) = 0$, unless the dispersion relation $\omega = \omega(k)$ takes the form

$$\omega(k) = \frac{\hbar k^2}{2m} \quad (29)$$

as it is easy to show, by applying equation (26) to (28).

We shall associate the plane wave represented by the solution (28) of Schrödinger's equation with a particular state of the particle, following the historical path laid down by the French physicist Louis De Broglie²⁸, who conjectured in 1923 the following idea:

De Broglie's hypothesis

Every moving body with momentum p carries with it a wave, which is inseparable from its state of motion, with wavelength

$$\lambda = \frac{h}{p} , \quad (30)$$

where h is the Planck constant.

Indeed this wave, represented in Figure 9 for $t = 0$, with the dispersion relation (29), is nothing but the state $\psi(x, t)$ of a particle in free motion with momentum $p = \hbar k$, if we associate its velocity with the group velocity $v_g = \frac{d\omega}{dk}$ of the wave, since

$$p = mv_g = m \frac{d\omega}{dk} = m \frac{\hbar k}{m} = \hbar k = \frac{h}{\lambda} ,$$

the kinetic energy of the particle being associated with its frequency ω :

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

Formulae $p = \hbar k$ and $E = \hbar \omega$ are known in the literature as **De Broglie's relations**. When the dispersion relation $\omega = \sqrt{\hbar^2 c^2 k^2 + m^2 c^4} / \hbar$ is used, associated to the total energy $E = \sqrt{p^2 c^2 + m^2 c^4}$, the plane wave (28) retains the same physical meaning, and it becomes perfectly relativistic.

²⁸although he followed a relativistic approach quite different from the one outlined here.

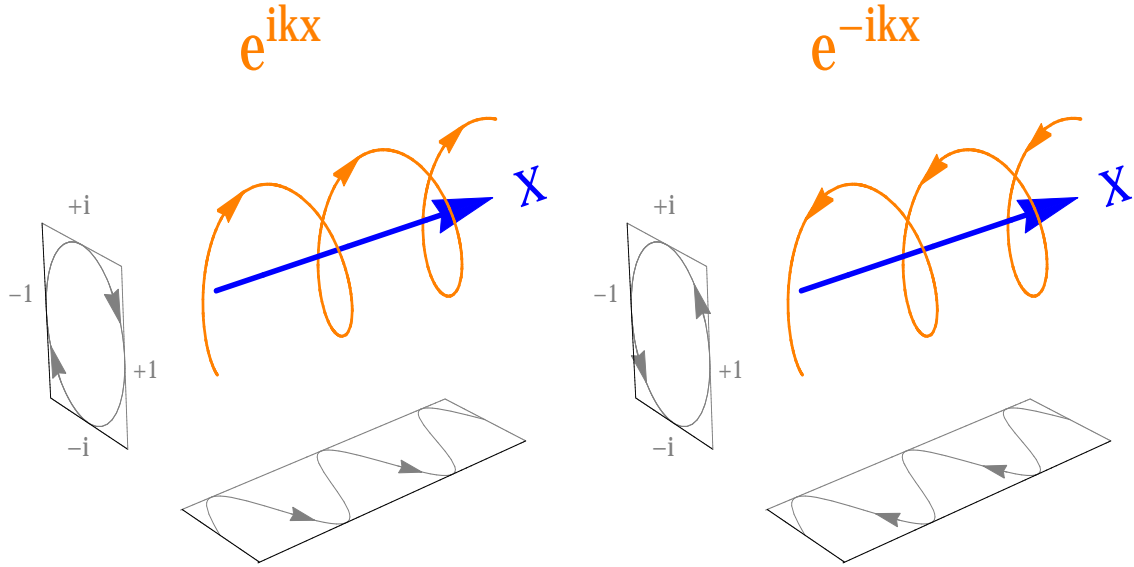


Figure 9: Plane wave representing a particle moving along the X axis, for both signs of the wave number $\pm k$. Note how the function is never zero, and shows a dextro/levo character associated with forward/backward motion.

The strongly dispersive character becomes evident when we overlap waves with different values of λ to form wave packets, since the propagation velocities of their phases are inversely proportional to their wavelengths ($v_p = \omega/k = h/2m\lambda$), which causes the wave packets lose their shape.

With this assignment of momentum and energy to the **plane wave** (28), its phase exactly coincides with the classical action S divided by \hbar , and therefore it also represents the propagation amplitude for a *free particle* moving with constant velocity across the space, according to Feynman's propagator. Indeed, $x = vt$ and we have

$$kx - \omega t = \frac{px}{\hbar} - \frac{Et}{\hbar} = \frac{1}{\hbar} \left(2 \frac{mv^2}{2} t - Et \right) = \frac{1}{\hbar} Lt = \frac{1}{\hbar} S ,$$

where, since $U = 0$, we have $L = E = T = mv^2/2$.

At all times t , the solution (28) shows a constant probability density across the space

$$|\psi(x, t)|^2 = |A|^2 = \text{constant} \quad \forall x \in \mathbb{R} . \quad (31)$$

It is clear that this means a *mathematical idealization*, since it is natural to think that wave packets prepared in the laboratory should not have wavelengths much larger than the laboratory size itself, however large we may consider it to be, and they should decay to zero outside. A consequence of the ideal character of the above states is that the correct value of the constant A in (28) cannot be simply determined from the normalization condition (27), since this integral will diverge. In other words, we are not talking about a square-integrable function.

At a given time we define the **Fourier transform** of the wavefunction $\psi(x)$ as

$$f(k) \equiv \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} \psi(x) e^{-ikx} dx . \quad (32)$$

The Fourier transformation is one of the most powerful mathematical tools ever invented, and consequently their properties and related theorems can be found in many textbooks ²⁹. The *inversion theorem* of the Fourier transformation states that the wavefunction can always be retrieved as

$$\psi(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} f(k) e^{ikx} dk , \quad (33)$$

with the additional property that $\int_{-\infty}^{+\infty} |f(k)|^2 dk = 1$. This actually means that we can use plane waves e^{ikx} with different wavelengths to build up any complex function defined on \mathbb{R} . Since $|\psi(x)|^2 dx$ represents the probability for a particle to be detected in $(x, x + dx)$, we should associate $|f(k)|^2 dk$ with the probability for the particle to have its momentum in $(p, p + dp) = \hbar(k, k + dk)$. Note that while x is measured in length units (m), k is measured in inverse length units (m^{-1}), or number of waves per unit length.

Just as the moving body simultaneously occupies a distributed region in the position space, we must admit its velocity is not unique, the velocity space being also occupied in a continuous manner, according to the Fourier transform. It should be emphasized that the complex functions $\psi(x)$ and $f(k)$ provide two equivalent descriptions of **the same state of motion**, since they contain exactly the same information. Such *correlation* between position and velocity of a moving body is an *unknown phenomenon* in Classical Mechanics.

8 Mean values and uncertainty

Since the particle's wavefunction stretches out over all space, it is of great interest to know precisely how to calculate the mean value $\langle x \rangle$ of the measurements one could get of its position. Also how to calculate the dispersion Δx of the measurements around the mean value, i.e. the spatial extent over which the particle fluctuates with highest probability.

The above quantities are calculated from the information encoded in the wavefunction $\psi(x)$ as follows:

$$\langle x \rangle = \int_{-\infty}^{+\infty} x |\psi(x)|^2 dx \quad \text{and} \quad (34)$$

$$(\Delta x)^2 = \langle x^2 \rangle - \langle x \rangle^2 ,$$

where $\langle x^2 \rangle$ is the mean value of x^2 , which is obviously calculated as

$$\langle x^2 \rangle = \int_{-\infty}^{+\infty} x^2 |\psi(x)|^2 dx .$$

Not being possible to define an instantaneous velocity, as has been described, it makes perfect sense after all to calculate the *mean velocity* $\langle v \rangle$, and the mean momentum $\langle p \rangle$ of the particle. The latter is determined, as discussed in the previous Section, from the mean value of k in the Fourier transform

$$\langle p \rangle = \hbar \langle k \rangle = \hbar \int_{-\infty}^{+\infty} k |f(k)|^2 dk = m \langle v \rangle .$$

²⁹see for instance "The Fourier Transform and its Applications", R. N. Bracewell (2000).

However, it is possible to perform a more direct calculation of the mean momentum, without prior calculation of the Fourier transform, just by performing a single integral. In order to achieve that, we must learn some properties of the Fourier transformation.

In the ensemble of wavefunctions (mathematically the Hilbert space $L^2(\mathbb{R})$), a **scalar product** can be defined as

$$\langle \psi_1 | \psi_2 \rangle \equiv \int_{-\infty}^{+\infty} \psi_1(x)^* \psi_2(x) dx ,$$

where $\langle \psi_1 | \psi_2 \rangle$ is a *complex* number. Note that $\langle \psi_2 | \psi_1 \rangle = \langle \psi_1 | \psi_2 \rangle^*$.

It can be easily shown that the existence of such scalar product grants the Hilbert space the structure of a vector space. It is useful to know that the Fourier transform then fulfils the following property, known in mathematics textbooks as *generalized Parseval's identity*:

$$\int_{-\infty}^{+\infty} \psi_1(x)^* \psi_2(x) dx = \int_{-\infty}^{+\infty} f_1(k)^* f_2(k) dk \quad \forall \psi_{1,2} \in L^2(\mathbb{R}) ,$$

that is, the scalar product remains invariant under the transformation of each factor: $\langle \psi_1 | \psi_2 \rangle = \langle f_1 | f_2 \rangle$. In other words, it truly represents the projection of a quantum state into another, and the result is the same, whether it is performed in the position representation, or in the momentum representation of the wavefunction.

The above result allows us to calculate $\langle p \rangle$ directly. Indeed, derivation with respect to x on both sides of equation (33) renders

$$\frac{\partial \psi}{\partial x} = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} ik f(k) e^{ikx} dk ,$$

which is telling us a general property, namely that the Fourier transform of the derivative $\frac{\partial \psi}{\partial x}$ is simply $ik f(k)$. Now, using the invariance of the scalar product, we get

$$\langle k \rangle = \int_{-\infty}^{+\infty} k |f(k)|^2 dk \equiv \int_{-\infty}^{+\infty} \frac{1}{i} f(k)^* (ik f(k)) dk = \int_{-\infty}^{+\infty} \frac{1}{i} \psi^*(x) \frac{\partial \psi}{\partial x} dx ,$$

that, according to De Broglie's relation, amounts to

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

which is the direct formula we were looking for. The attentive reader will note that this expression shows the same structure as that in (34), and both of them can be considered as particular cases of a more general definition of the mean value of an **operator** that represents any **measurable physical magnitude** A

$$\langle A \rangle = \int_{-\infty}^{+\infty} \psi^*(x) (A\psi) dx = \langle \psi | A\psi \rangle , \tag{35}$$

with $A = x$ (position) or p (momentum). In fact, a unique operator form for can be found for every measurable magnitude A , just from the above two.

These operators (that are intended essentially to calculate mean values), are *linear* mathematical applications mapping each element of the Hilbert space $L^2(\mathbb{R})$ into another element of the same space in a linear transformation ($\psi \rightarrow A\psi \in L^2(\mathbb{R})$). As we have just seen, the **momentum operator** is represented by a partial derivative with respect to the coordinate of motion

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

Of course, the mean values $\langle A \rangle$ must be *real* for every wavefunction, as are the laboratory measurements of any physical magnitude A . This forces all physical operators A to be **self-adjoint**, i.e. they must fulfill $\langle \psi | A\psi \rangle = \langle A\psi | \psi \rangle \equiv \langle \psi | A | \psi \rangle \forall \psi$, so that the above can be accomplished. The evaluation of $\langle A^2 \rangle$ also makes perfect sense. In this case, the action of A^2 should be understood as the repeated application $A(A\psi)$. Note the *profound analogy* of these operators with the complex Hermitian matrices, which are also linear self-adjoint operators on a vector space, of finite dimension. Similarly higher powers can be defined, power series, etc.

Individual laboratory measurements of the magnitude A , obtained from the same initial state ψ , will manifest the nondeterministic character of Quantum Mechanics by throwing random values. However, we can predict with certitude the dispersion of the measurements ΔA around their mean value, through the expression

$$(\Delta A)^2 = \langle A^2 \rangle - \langle A \rangle^2 . \tag{36}$$

If we want to calculate, for instance, the momentum dispersion Δp , the calculation of $\langle p^2 \rangle$ is achieved by means of the integral

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

that is always nonnegative for square-integrable functions, as can be shown using integration by parts. We see then that the operator $H = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + U(x, t)$, which appeared in Schrödinger's equation (26), represents the total energy, since the first term represents the kinetic energy.

As a consequence of all of the above, we now have a rule which allows us to evaluate, just from integration techniques, the mean value and the dispersion, not only of the position and the momentum of a particle, but of every magnitude A constructed from them. In other words, we have learned how to decode the information residing in the wavefunction $\psi(x)$, in order to make statistical predictions about the results of laboratory measurements performed on a particle.

Similarly to matrices, the action of the operators A is not in general commutative. It is a simple exercise, for instance, to show that, for every wavefunction ψ , the following equation is accomplished

$$xp - px = i\hbar ,$$

where it is to be warned about a customary habit in Quantum Mechanics: the same symbols are often used to designate the *values* of the physical magnitudes and the *operators* representing them. What is actually meant in the above equation is that: $(xp - px)\psi = i\hbar\psi \forall \psi$.

9 The Uncertainty Principle

One of the most distinctive properties of the Fourier transformation is that, if the original function is very narrow ($\Delta x \rightarrow 0$), its Fourier transform is very wide ($\Delta k \rightarrow \infty$). The mathematical idea behind this is quite intuitive: we cannot build a narrow function by only summing over wavelengths ($\lambda = 2\pi/k$) larger than the function's width. In other words, the product $\Delta x \Delta k$ is approximately unity. The precise statement of the mathematical theorem is: $\Delta x \Delta k \geq 1/2, \forall \psi$.

A formal proof of this general theorem of the Fourier transformation (independent of the Planck constant), can be attained by following the steps below:

a) Start from the obvious expression

$$\int_{-\infty}^{+\infty} \left[\left(x + \lambda \frac{\partial}{\partial x} \right) \psi \right]^* \left(x + \lambda \frac{\partial}{\partial x} \right) \psi dx \geq 0 \quad \forall \lambda \in \mathbb{R},$$

where $x + \lambda \frac{\partial}{\partial x} = x + i\lambda k$ is a *real* operator, with $k \equiv -i \frac{\partial}{\partial x}$.

b) Add and subtract $\psi \cdot (x - \lambda \frac{\partial}{\partial x})$ to the expression in square brackets, and show that

$$\int_{-\infty}^{+\infty} \left[\left(x + \lambda \frac{\partial}{\partial x} \right) \psi^* - \psi^* \cdot \left(x - \lambda \frac{\partial}{\partial x} \right) \right] \left(x + \lambda \frac{\partial}{\partial x} \right) \psi dx = 0,$$

because the integrand is actually a full derivative, and

$$\int_{-\infty}^{+\infty} \frac{\partial}{\partial x} \left[\psi^* \cdot \left(x + \lambda \frac{\partial}{\partial x} \right) \psi \right] dx = 0,$$

since every square-integrable function ψ must fulfill $\left. x|\psi|^2 + \lambda \psi^* \frac{\partial \psi}{\partial x} \right|_{-\infty}^{+\infty} = 0$.

c) Finally express the remainder of the original integral as

$$\langle x^2 \rangle + \lambda^2 \langle k^2 \rangle - \lambda \geq 0,$$

and notice that, without loss of generality, $\langle x^2 \rangle = (\Delta x)^2$ and $\langle k^2 \rangle = (\Delta k)^2$, just because these quantities are independent of the choice of the origin of coordinates. The theorem proof follows after examination of the discriminant of the above parabola in λ .

We leave as an exercise to the student to work out the details of each of the above steps, and just comment about the transcendental physical significance of this result, when we take into account that the partial derivation $\frac{\partial}{\partial x}$ actually represents the *momentum* of the particle, according to $p = -i\hbar \frac{\partial}{\partial x} = \hbar k$.

The result was first stated by the German physicist Werner Heisenberg in 1926, and it is known in Physics as position-momentum **uncertainty principle**: if we know with great precision (Δx) the position occupied by a moving body, then large fluctuations are inevitable on the value of its momentum (Δp), their respective wavefunction widths being related by the inequality

$$\Delta x \Delta p \geq \hbar/2, \tag{37}$$

which is accomplished by every wavefunction, at all times. The physics impact of the above is huge. It reveals the impossibility to know simultaneously with total precision the position of a moving body, and its momentum along the direction of motion.

It is clear that, at the limiting case of the plane wave (28), we have $\Delta x = \infty$ (particle totally delocalized) and $\Delta p = 0$ (strictly monochromatic). On the opposite extreme, the function $K(x, t) = \langle x | t | x_1 | t_1 \rangle$ represents the time evolution of a particle localized at the point x_1 at time t_1 ($\psi(x) = \delta(x - x_1)$) with $\Delta x = 0$, having in addition $\Delta p = \infty$. Indeed, according to expression (15) the particle originally located at x_1 (time t_1) can reach any space point x at a later time $t > t_1$ with equal probability, therefore its velocity spectrum at time t is really infinite, and so $\Delta p = m\Delta v = \infty$.

When the particle moves in the form of a dispersive pulse with group velocity v , it makes sense to define a **time uncertainty**, arising from its space uncertainty, as $\Delta t \equiv \Delta x/v$. The energy uncertainty can also be derived from Δp as

$$\Delta E = \Delta\left(\frac{p^2}{2m}\right) = \frac{p}{m}\Delta p = v\Delta p ,$$

where the velocity of the particle is also involved, and we have used the chain rule to relate the variations of energy and momentum. The same result is obtained by differentiating the relativistic expression for the energy $E = \sqrt{p^2c^2 + m^2c^4}$ (with m being the particle's rest mass), taking into account that $v = \beta c = pc^2/E$ in this case. It is clear that the product $\Delta E\Delta t$ does not depend on v anymore, and from expression (37) we get the **energy-time uncertainty principle**

$$\Delta E\Delta t \geq \hbar/2 . \tag{38}$$

An immediate consequence of expression (37) is that every moving body confined to a region of space of size $2\Delta x$ necessarily acquires a kinetic energy with mean value

$$\langle T \rangle = \frac{1}{2m}(\Delta p)^2 \geq \frac{1}{4} \frac{1}{2m} \frac{\hbar^2}{(\Delta x)^2} ,$$

as is evident, if we disregard the overall velocity of the system, with $\langle p \rangle = 0$. Because what we have calculated is the mean value of T , we are not talking about individual quantum fluctuations of a particular measurement of the kinetic energy, but of an offset of the majority of the measurements. For this reason, it is customary to use the uncertainty principle as an approximate equality, in the form $\Delta x\Delta p \sim \hbar$ ³⁰, and directly write $T \sim \frac{\hbar^2}{2m(\Delta x)^2}$ for the kinetic energy acquired by the particle.

In order to get a numerical idea of the amount of energy provided by quantum fluctuations, we may consider the lightest particle we have in ordinary matter, the electron. With mass $m_e = 9.109 \times 10^{-31}$ Kg, we evaluate its kinetic energy in eV for three reference sizes: $\Delta x = 1mm$, $1\mu m$, and 1\AA , and obtain respective values: 3.8×10^{-14} eV, 3.8×10^{-8} eV and 3.8 eV.

³⁰it is useful to know that for most potential wells on their ground state, the above-mentioned approximation is accomplished with higher precision than if $\Delta x\Delta p \sim \hbar/2$ was used.

While in the first two cases the energy is unobservable in the laboratory, in the third case it becomes quite significant. This is just the case we had in the Hydrogen atom, which we have rudely approximated here in one dimension. In this case we know the confinement potential, namely Coulomb's law. But the important thing is we have been able to reach rather precise conclusions on the energy of the system without knowing the potential, just from the object's size.

If in addition the confinement potential is known, then the uncertainty principle always allows us to estimate the energy of the ground state, at least in 1D, without having to solve Schrödinger's equation. This can be done easily by finding the minimum of the total energy. Expression (38) for the energy-time uncertainty can also be used as the approximate equality: $\Delta E \Delta t \sim \hbar$. It allows to estimate the kinetic energy ΔE acquired as a consequence of the time location. For instance, we see that if $\Delta t \sim \hbar/E$ then this energy becomes significant in relative terms, since $\Delta E/E \sim (\hbar/E)(1/\Delta t) \sim 1$.

10 Extension to three dimensions

All of the ideas developed above have been formulated assuming that the motion and the force field $U(x, t)$ occur in one dimension. However, the real motion takes place along the three space coordinates $\mathbf{r} = (x, y, z)$. The extension to three dimensions of all of the above can be achieved immediately, and we suggest the student to write down correctly, with vector notation $\mathbf{r}(t)$, the following expressions:

- Feynman's propagation amplitude
- Schrödinger's equation
- wavefunction
- plane wave, dispersion relation and group velocity
- mean value of a scalar A and of a vector magnitude $\mathbf{A} = (A_x, A_y, A_z)$
- Fourier transformation
- scalar product of wavefunctions
- \mathbf{p} operator
- $H = \mathbf{p}^2/2m + U$ operator
- uncertainty principle

The normalization factors in the Fourier transformation and in the Feynman propagator need to be changed from $(2\pi)^{1/2}$ to $(2\pi)^{3/2}$. We shall write below the result for Schrödinger's equation in 3D:

$$i\hbar \frac{\partial \psi}{\partial t} = \left(\frac{-\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) + U(\mathbf{r}, t) \right) \psi . \quad (39)$$

Using the Laplace operator $\Delta \equiv \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$, the equation is commonly written as

$$i\hbar \frac{\partial \psi}{\partial t} = \left(\frac{-\hbar^2}{2m} \Delta + U(\mathbf{r}, t) \right) \psi . \quad (40)$$

Or even simpler, using the Hamiltonian operator $H = \frac{\mathbf{p}^2}{2m} + U(\mathbf{r}, t)$

$$i\hbar \frac{\partial \psi}{\partial t} = H\psi . \quad (41)$$

When extending to 3D the uncertainty principle it should be kept in mind that position and momentum are only correlated along the same direction $\Delta x_i \Delta p_i \sim \hbar$ with $x_i = x, y, z$. The inverse Fourier transform in 3D is written as

$$\psi(\mathbf{r}) = \frac{1}{(2\pi)^{3/2}} \iiint f(\mathbf{k}) e^{i\mathbf{k}\mathbf{r}} d^3\mathbf{k} , \quad (42)$$

which implies that the energies generated independently by confinement on each coordinate x_i actually add up, according to $\langle T \rangle = [(\Delta p_x)^2 + (\Delta p_y)^2 + (\Delta p_z)^2] / 2m$.

There is a particular physical magnitude that makes no sense in 1D, namely the angular momentum, denoted by the vector \mathbf{L} . At all times t , it is calculated as the vector product of the position $\mathbf{r}(t)$ and the momentum $\mathbf{p}(t)$: $\mathbf{L} = \mathbf{r} \times \mathbf{p}$. The uncertainty principle prevents to know simultaneously its three components $\mathbf{L} = (L_x, L_y, L_z)$ with full precision. Nonetheless the mean values and dispersion of its components may be calculated, for a given wavefunction, according to formulae (35) and (36), although knowledge of the eigenstates will generally simplify the calculations.

11 Eigenstates and measurable values

Given a measurable magnitude A , we ask ourselves the question: are there wavefunctions ψ such that A is well defined on them, i.e. a repetition of the measurements on the state ψ will always throw the same real value $a \in \mathbb{R}$? In a more precise way: are there wavefunctions ψ , such that $\Delta A = 0$ on them? We are now ready to answer this question mathematically, according to the definition of ΔA we gave in (35). Let us assume we are able to solve the **eigenvalue problem** for the operator A : $A\psi = a\psi$. This means finding the possible eigenvalues a and eigenvectors ψ for the above equation³¹. Then expression (36) allows us to verify immediately that indeed $(\Delta A)^2 = a^2 \langle \psi | \psi \rangle - a^2 \langle \psi | \psi \rangle^2 = 0$ on the eigenvectors, since $\langle \psi | \psi \rangle = 1$ according to the normalization property.

So the problem has been formulated in mathematical terms: we have to solve the eigenvalue problem for the operator A . The states ψ looked for are then the corresponding eigenvectors, called in Quantum Mechanics **eigenstates**. We know the eigenvalues a are bound to be real, although in general they do not fill up the real line, but define a subset $\mathbb{A} \subset \mathbb{R}$ therein. In many cases this subset, which is called *spectrum* of the operator A , will be discrete. All real values $a \notin \mathbb{A}$ will be forbidden, and will never be measured in the laboratory. Furthermore, the measurements performed on the same eigenstate will always throw the same value, and be therefore reproducible. We remark that in order to determine the spectrum, it is essential to impose the condition that the wavefunction must be continuous in \mathbb{R}^3 , and square-integrable.

³¹which will be, in general, a partial differential equation.

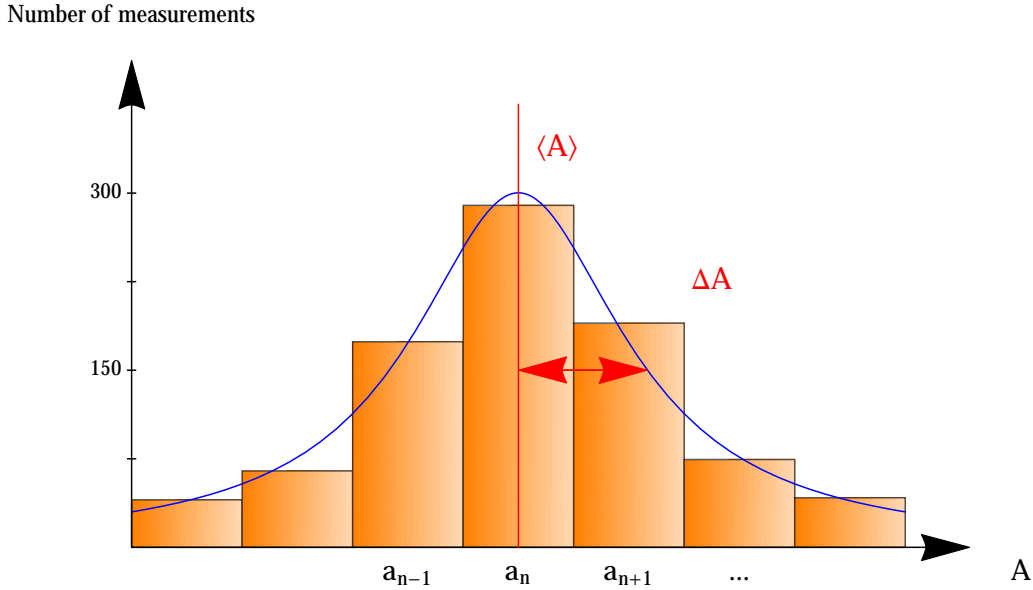


Figure 10: *Distribution of 1000 laboratory measurements of the magnitude A . The initial state ψ is not an eigenstate of the operator A , and it has been prepared to be the same everytime. The measurements are randomly distributed, according to a calculable probability density, and only the eigenvalues a_n of A are measurable.*

Just as eigenvectors of a matrix corresponding to different eigenvalues are orthogonal to each other, the same occurs with the eigenstates of an operator: they form an orthonormal set of functions (the **eigenfunctions**), according to our definition of the scalar product. Furthermore, the eigenstates corresponding to the same eigenvalue a_n form a subspace of dimension $N(a_n)$ within the Hilbert space, in which it is also possible to define an orthonormal basis $\{\psi_{n,k}, k = 1, N(a_n)\}$, where k is called degeneracy index.

Let us assume we perform a measurement of the magnitude A on an initial state ψ which is *not* an eigenstate, and obtain the value $a \in \mathbb{R}$. Then it is generally admitted that the wavefunction has changed after the measurement, and must now be an eigenstate ψ_a , corresponding to the measured value.

Since the measurement excludes alternative values $a_x \neq a$ ³² which have not been realized, these should no longer be considered as part of the particle's state of motion. This phenomenon by which the realization of a measurement randomly alters the state of the moving body is known in the literature as the **collapse of the wavefunction**. The idea was originally put forward in 1932 by the Hungarian mathematician John Von Neumann, and it is today generally accepted in Quantum Mechanics. The collapse of the wavefunction takes place in the laboratory in a sudden and unpredictable way, just as we described earlier in Section 2.6 for the detection of a photon. It is just the way quantum fluctuations manifest themselves, such that full knowledge of the wavefunction does not allow us to know a priori what the measured eigenvalue will be. An example of how these measurements can be distributed is illustrated in Figure 10.

It should be emphasized that the time evolution of the wavefunction $\psi \rightarrow \psi_a$ during the measurement **is not governed by the Schrödinger equation**, being unknown as of today what are the physical laws behind the collapse of the wavefunction. This is easily understood, since the resulting wavefunction using the Schrödinger equation would be uniquely determined from ψ by the Feynman propagator, according to (25).

³²we are not considering here the statistical fluctuations inherent to the experimental measurement, thus implicitly assume no statistical or systematic uncertainty.

As a general rule, we can say that the eigenfunctions of any Hermitian operator A form an orthonormal basis in the Hilbert space, and therefore every wavefunction, at a given time, can be expanded as

$$\psi(\mathbf{r}) = \sum_n \sum_k c_{n,k} \psi_{a_n,k}(\mathbf{r}) , \quad (43)$$

where $\{\psi_{a_n,k}(\mathbf{r}), k = 1, N(a_n)\}$ are the orthogonal eigenfunctions corresponding to each different real eigenvalue a_n , and the complex coefficients $c_{n,k}$ can be obtained as scalar products $c_{n,k} = \langle \psi_{a_n,k} | \psi \rangle$. The normalization property demands that $\sum_{n,k} |c_{n,k}|^2 = 1$, which implies that the values $\sum_k |c_{n,k}|^2$ are actually the probabilities that the measurement made on ψ throws the value a_n .

Note that the inverse Fourier transform we saw in equation (42) is in fact a particular case of (43), which corresponds to the eigenfunctions of the momentum (plane waves $e^{i\mathbf{k}\mathbf{r}}$), the degeneracy index k being absent, with $a_n = \mathbf{p}_n = \hbar\mathbf{k}_n$ and $c_n = f(\mathbf{k}_n)$. In the inverse Fourier transform, the sum (triple integral) actually extends over a continuous set, since the momentum spectrum \mathbf{p} is continuous.

12 The stationary states

Let us imagine a periodic classical trajectory of energy E ³³, starting from \mathbf{r}_0 with period Δt , such as the one represented in Figure 11. The particle goes over the points of this trajectory as a function of time, and we can associate to each point \mathbf{r} the value of the phase given by the Feynman propagator $K = Ae^{iS/\hbar} = Ae^{i(S_0 - Et)/\hbar} = e^{-iEt/\hbar} Ae^{iS_0/\hbar}$, where S is the classical action $S = \int_{t_0}^t L dt$. If we want the motion to retain the periodic character it has in Classical Mechanics, this phase must return, at every point \mathbf{r} , to its original value after a closed orbit, which implies the condition

$$\frac{S_0}{\hbar} = 2\pi n \quad n = 1, 2, \dots \infty .$$

In order to apply the above condition to integrable systems, it is important to know that trajectories are confined to *invariant tori* in phase-space, whose projection onto the coordinate space has a boundary. We need to make sure that the action is a single-valued function of the coordinates, and this requires that a phase-loss of $\pi/2$ has to be admitted everytime the projection of the closed trajectory reaches this boundary³⁴.

A relevant example of the above is the motion of one particle in a central potential, where the radial coordinate r runs back and forth between the limits (r_{min}, r_{max}) . The boundary is reached precisely at these limits, when the sign of the radial momentum is reversed.

³³in Classical Mechanics with N freedoms, periodic motion is well characterized for both integrable and chaotic systems. In the former case, it should be called more properly *multiperiodic*, since the motion is confined to *invariant tori* in the phase-space of constant energy E , with $N - 1$ independent frequencies. Since rational numbers are a dense set in real numbers, we can always make these frequencies proportional to appropriate integers, so that they are commensurable, and the motion is truly periodic. In chaotic systems no such tori exist, because there are no constants of motion, other than the total energy. But periodic orbits are also meaningful, even if they are isolated or become unstable after many cycles.

³⁴to achieve a thorough comprehension of this statement in Classical Mechanics, some dedicated reading is advised. See for example the course by M. V. Berry, "Semiclassical mechanics of regular and irregular motion", North Holland, 1983.

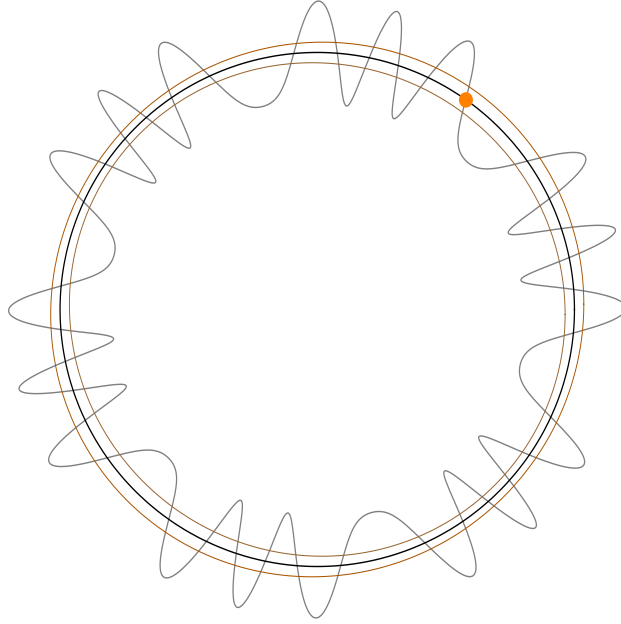


Figure 11: *Illustration of the idea of a stationary state in a 2D coordinate space: quantum fluctuations are of such nature that at each point (orange) the phase of the propagator (wavy line) returns to exactly the same value over the classical trajectories (black line). Many classical orbits of this kind need to be considered to form a stationary state.*

As a consequence, the exact quantization condition actually is: $S_0/\hbar = (n + \beta/4)2\pi$, where β is the (integer) number of boundary crossings, or $S_0 = (n + \beta/4)h$, just the quantization condition we formulated in Section 2. For chaotic systems, periodic trajectories are also enhanced when they are in phase, but their periods are not commensurable, and many trajectories, with very long periods, may contribute to the same energy.

No matter the kind of motion, we may conjecture that states of well defined energy exist in Quantum Mechanics, where the time factor $e^{-iEt/\hbar}$, introduced by the propagation over the classical trajectory, is inherited by the wavefunction. This would be natural, since this factor indicates a frequency in accord with De Broglie's relation $\omega = E/\hbar$, therefore uniquely determined by the energy³⁵. Then we see that, under the assumption that the classical trajectories dominate the exact path integral calculation, the postulate of quantized action comes out naturally from Feynman's propagation, and the formula $S_0 = \oint \mathbf{p}d\mathbf{r} = (n + \alpha)h$ is indeed an excellent approximation to calculate the allowed energies for integrable systems. It is known generically in the literature as the **semiclassical approximation**.

Anyway having an approximate solution is not enough, and we want to have the *exact* solution to the energy problem, since Feynman's theory is exact. But even more importantly, most physical systems of interest (such as multielectronic atoms, molecules, nuclei, or condensed matter in solids or liquids), are chaotic in their classical formulation, and the semiclassical approximation above is not useful anymore. So the most effective way to proceed is to use Schrödinger's equation, and realize that, in the situation previously described, what we want is the particle's wavefunction $\psi(\mathbf{r}, t)$ to have a common periodic phase at all space points³⁶.

³⁵note this frequency differs from the classical one $\omega_{cl} = 2\pi/\Delta t$, Δt being the period.

³⁶in wave motion, this phenomenon is well known: these are the stationary states, characterized by the normal modes of oscillation.

So we want the probability density at each point \mathbf{r} to be constant in time

$$\frac{\partial |\psi(\mathbf{r}, t)|^2}{\partial t} = 0 \quad \forall \mathbf{r} \in \mathbb{R}^3, \quad (44)$$

that is, a stationary probability density, like an unchanging temperature distribution in a thermal medium, or a fluid velocity distribution in a stationary regime.

We can attain solutions of this type to the Schrödinger equation (41) by pursuing the two steps below:

- 1) Find solutions to the eigenvalue problem of the Hamiltonian operator H

$$\left(\frac{-\hbar^2}{2m} \Delta + U(\mathbf{r}) \right) \psi(\mathbf{r}) = E\psi(\mathbf{r}) \quad (45)$$

for some real value of the parameter E (total energy), and impose the condition that $\psi(\mathbf{r})$ makes sense as a wavefunction. That is, it must accomplish:

- a) The normalization condition $\int |\psi(\mathbf{r})|^2 d^3\mathbf{r} = 1$ (convergent integral $< +\infty$).
- b) The continuity of the wavefunction at each space point $\mathbf{r} \in \mathbb{R}^3$. Also the continuity of the space derivatives $\left(\frac{\partial\psi}{\partial\mathbf{r}}\right)$, unless we have assumed an infinite potential at that particular point ³⁷.

It is actually the verification of the two conditions above what really causes a restriction on the energy values E , bringing them to their quantized values.

- 2) Build the following time dependent wavefunction

$$\psi(\mathbf{r}, t) = e^{-iEt/\hbar} \psi(\mathbf{r}), \quad (46)$$

which indeed represents the desired stationary states, for

- a) it is a solution of the Schrödinger equation (41), and
- b) it fulfils condition (44).

We leave as a simple exercise to check that the wavefunction (46) truly accomplishes both of the above statements.

Equation (45) can be written as

$$H\psi = E\psi, \quad (47)$$

³⁷such potentials (impenetrable walls, Coulomb law at the origin, Dirac delta functions, etc.) are never fully realizable in practice, but their introduction may greatly simplify the problem in question, and are customarily used.

and gets the name of **time independent Schrödinger equation**. The operator H is specified by the force field $U(\mathbf{r})$, and the exact calculation of the energies of the stationary states is therefore reduced to a mathematical problem of eigenvalues, which implies a second order differential equation, independent of time. The eigenvalues must be real, of course, since H is self-adjoint.

Initial conditions may be required, for example incident or outgoing plane or spherical waves in a given direction. Also boundary conditions may need to be fulfilled, where the wavefunction is zero at some boundary, which is usually described by setting there an infinite potential.

Of course, all the results obtained from equation (47), with appropriate boundary conditions, bear all the precision of the Feynman path integral we saw in 3.1. As in every eigenvalue problem, according to what we stated in Section 11, it is ensured that the eigenstates fulfill $\Delta E = 0$, that is, their energy is well defined. The resolution of the differential equation $H\psi = E\psi$ for the most elementary force fields in one and several dimensions (impenetrable walls, harmonic oscillator, Coulomb field, etc) will be dealt with in subsequent chapters.

Once the energy eigenvalue problem has been solved for a given potential, the set of eigenfunctions and associated eigenvalues $\{\Phi_{n,k}(\mathbf{r}), E_n, n = 1, \infty, k = 1, N(E_n)\}$ is available to us, where k runs over the quantum numbers necessary to describe the different orthogonal eigenfunctions of equal energy E_n , in the subspace associated with that particular eigenvalue³⁸. The dimension of this subspace (number of orthogonal states of equal energy), gets the name of **quantum degeneracy** $g = N(E_n)$ in the literature. Even if the phenomenon of degeneracy is also there in Classical Mechanics (and it is, in general, infinite), the key issue is that, in the physical reality, it is always a *finite* and calculable number, which plays an essential role in the calculation of the *entropy* in Statistical Mechanics.

Expansion in stationary states

Just as eigenvectors of unit norm of a matrix (Hermitian, in this case) always form an orthonormal set, within the vector space where this matrix operates, every wavefunction at a given time can be expressed as a linear combination of energy eigenstates. If, for the sake of simplicity, we leave out the degeneracy index k , which is not essential for the discussion below, we can write: $\psi(\mathbf{r}) = \sum_n c_n \Phi_n(\mathbf{r})$, with complex numbers $c_n \in \mathbb{C}$ such that $\sum_n |c_n|^2 = 1$.

Taking into account Schrödinger's equation from Eq. (46) at each of the above terms, the time dependence of the wavefunction will be determined by the expansion

$$\psi(\mathbf{r}, t) = \sum_n c_n e^{-iE_n t/\hbar} \Phi_n(\mathbf{r}) . \quad (48)$$

It is important to realize that such function is not, in general, a stationary state, unless all coefficients c_n are zero, except one. In other words, the necessary and sufficient condition for a state to have a well defined energy is that “it does not move”, according to the definition given by expression (44).

³⁸por instance, for a particle of energy E_n enclosed in a rectangular box, the possible orientations of its momentum. For a particle subject to a central potential, those necessary to define the angular momentum state: (l, m) .

Since the scalar product $c_n = \langle \Phi_n | \psi \rangle$ is independent of t , we can write

$$\psi(\mathbf{r}_2, t_2) = \sum_n \langle \Phi_n | \psi \rangle e^{-i\frac{E_n}{\hbar}(t_2-t_1)} \Phi_n(\mathbf{r}_2) = \sum_n \left(\int \Phi_n^*(\mathbf{r}_1) \psi(\mathbf{r}_1) d^3\mathbf{r}_1 \right) \Phi_n(\mathbf{r}_2) e^{-i\frac{E_n}{\hbar}(t_2-t_1)} .$$

By reordering the above factors, and recalling how the propagator operates on the wavefunctions, according to the 3D version of formula (25), we conclude that the exact Feynman propagator can be written as

$$K(\mathbf{r}_2, t_2; \mathbf{r}_1, t_1) = \sum_n \Phi_n(\mathbf{r}_2) \Phi_n^*(\mathbf{r}_1) e^{-i\frac{E_n}{\hbar}(t_2-t_1)} , \quad (49)$$

where the propagation can be considered forward in time ($t_2 > t_1$) or backward in time ($t_2 < t_1$), when using the above expression. However in order to perform the full reverse propagation in time $(\mathbf{r}_2, t_2) \rightarrow (\mathbf{r}_1, t_1)$, the conjugate propagator $K^*(\mathbf{r}_2, t_2; \mathbf{r}_1, t_1)$ is required. The above formula is of great utility in all kinds of problems, including particle scattering under the action of a given potential. It also shows that the stationary states of well defined energy are spatially invariant under the action of the propagator, as we conjectured at the beginning of this Section. To see this, just let K operate on an eigenstate $\Phi_m(\mathbf{r})$ according to (25), and take into account their orthogonality.

13 The Bohr formula

As we have seen, a linear combination of stationary states generates a time dependence, according to Schrödinger's equation, such that the wavefunction is no longer stationary, and takes the form of a moving pulse.

Let us analyze the probability density when the particle finds itself in a state which is a superposition of two different energy states: E_2 (*high* state) and E_1 (*low* state), with $E_2 > E_1$. This situation is quite general and happens in a great deal of physical systems, causing a phenomenon called *quantum oscillation*. We shall see that the particle travels virtually through space in a periodic way, with a frequency ω determined by **Bohr's formula**: $E_2 - E_1 = \hbar\omega$. In case the particle has an electrical charge, the oscillation gives rise to the emission of one photon of the same frequency, in qualitative agreement with the prediction of Classical Electrodynamics, after a certain time Δt . Therefore, Bohr's formula is not just a mere consequence of energy conservation and the existence of photons, but it is rooted in Schrödinger's equation.

Indeed, let us assume $\psi = c_1\psi_1 + c_2\psi_2$, where $\psi_{2,1}$ are the wavefunctions in the *high* and *low* states, respectively, with $c_{1,2} \in \mathbb{C}$. Since the overall phase does not have any physical meaning, we may assume without loss of generality that c_1 is real positive ($c_1 > 0$), and that $c_2 = c_1 e^{i\phi_0}$.

If we single out a given space point \mathbf{r} , the probability density at that point gets a contribution from the interference between both states:

$$|\psi(\mathbf{r}, t)|^2 = |c_1\psi_1 + c_2\psi_2|^2 = |c_1|^2|\psi_1|^2 + |c_2|^2|\psi_2|^2 + 2 \operatorname{Re} \left(|c_1 c_2| |\psi_1 \psi_2| e^{-i\left(\frac{(E_2-E_1)t}{\hbar} - \Phi\right)} \right) ,$$

where $\Phi(\mathbf{r}) = \phi_2(\mathbf{r}) - \phi_1(\mathbf{r}) - \phi_0$ depends on the phase difference at that point between the wavefunctions $\psi_1 = |\psi_1| e^{i\phi_1(\mathbf{r})}$ and $\psi_2 = |\psi_2| e^{i\phi_2(\mathbf{r})}$.

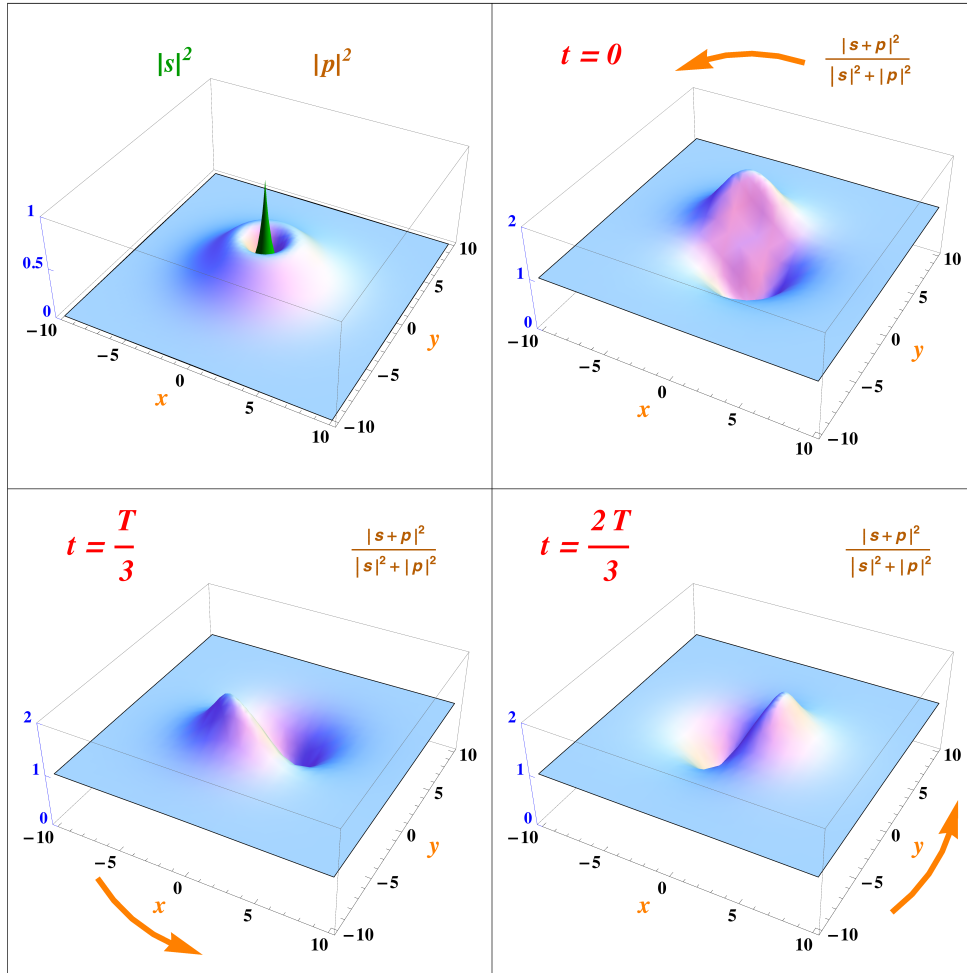


Figure 12: Probability density in the horizontal plane (XY) of the non stationary state that results from superposition of the orbitals $2p$ ($n = 2, l = 1, m = 1$) and $1s$ ($n = 1, l = 0$) of Hydrogen. It can be seen how the interference between them generates an electric dipole which is a function of time, that gyrates around the proton with Bohr's frequency (period $T = \frac{2\pi}{\omega}$). The horizontal scales show units of the Bohr radius a_0 . In the top left figure the $2p$ orbital has been multiplied by a factor of 50.

It can be easily checked that the probability density is then a periodic function of time

$$|\psi(\mathbf{r}, t)|^2 = A(\mathbf{r}) + B(\mathbf{r}) \cos(\omega t - \Phi(\mathbf{r})) ,$$

that oscillates between a maximum value $A + B$ (constructive interference) and a minimum value $A - B$ (destructive interference) with a frequency ω that is independent of the point \mathbf{r} , and it is determined by Bohr's formula.

The functions A and B do depend on \mathbf{r} , as $A(\mathbf{r}) = |c_1|^2 |\psi_1(\mathbf{r})|^2 + |c_2|^2 |\psi_2(\mathbf{r})|^2$ and $B(\mathbf{r}) = 2|c_1 c_2| |\psi_1(\mathbf{r}) \psi_2(\mathbf{r})|$. It is clear that the probability increase at that point necessarily means a decrease at other points, due to the wavefunction normalization, and conversely. Therefore what happens is a global displacement of the particle (oscillation) of periodic character.

The oscillation stops instantly once the particle is localized, or its energy is measured. Note that, during the oscillation process, the energy is not well defined ($\Delta E \neq 0$). It is a useful exercise to calculate ΔE explicitly, and show that $\Delta E = |c_1 c_2| (E_2 - E_1)$.

The energy measurement, for charged particles, is achieved by detecting the emitted photon, which provides evidence that the particle is already in the *down* state. In this case, the time Δt elapsed before photon emission can be estimated on average from the uncertainty principle $\Delta E \Delta t \sim \hbar$ ³⁹.

There are also examples of quantum oscillation with particles that are electrically neutral. Most strikingly, the relativistic case of flavor oscillations of neutrinos of momentum p and different masses $m_1 \neq m_2$ (therefore different energies). What stops the oscillation in this case is neutrino detection, showing a well defined flavor⁴⁰.

A good 3D example of oscillations, of the charged type, is found when the electron in a Hydrogen atom adopts a quantum state which is a superposition of the ground state with $n = 1$ ($1s$ orbital) and the first excited state with $n = 2$, $l = 1$ and $m = 1$ ($2p$ orbital). These wavefunctions are obtained by solving the time-independent Schrödinger equation with the Coulomb field, and will be studied later on. In spherical coordinates, they have the generic form: $\psi = R_{nl}(r)Y_m^l(\theta, \phi)$. The electron density in the horizontal plane is depicted in Figure 12 as a function of time, where it can be seen how it gyrates around the proton, as a consequence of the interference. For the sake of clarity, $c_1 = c_2 = \frac{1}{\sqrt{2}}$ has been assumed, and the density has been divided by the sum of electron densities in both orbitals, also represented in Figure 12.

The above phenomenon is called **spontaneous emission** and the superposition of the wavefunctions actually occurs due to the action of the electromagnetic field of the vacuum at that particular frequency (recall our discussion in Section 2.6, fórmula (13)). The average lifetime is calculable in *Quantum Electrodynamics* from the wavefunctions.

14 Quantum Mechanics in the relativistic framework

In some cases, we have addressed the study of quantum physics under the assumption that the particle velocity is small compared with the light velocity c , although the fully relativistic formalism was historically achieved nearly at the same time as the nonrelativistic approach. The reason not to deal with the full relativistic formalism in this core course is twofold:

- For the electron, Schrödinger's equation $i\hbar \frac{\partial \psi}{\partial t} = H\psi$ is itself fully relativistic, with the proper definition of the H operator, such as it is realized in the *Dirac equation*. The free-motion solutions are still plane waves (called *spinors*), which have extra degrees of freedom (the electron spin), with the additional potentiality of representing the antiparticles (the *positron*), in close relation with the properties of the spatial propagation backwards in time. The formalism requires somewhat lengthier calculations.
- Most applications in Atomic Physics, Molecular Physics, Condensed Matter Physics, and even Nuclear Physics, involve non relativistic velocities, and the calculations with the Dirac equation are unnecessary (except for precision phenomena, such as vacuum polarization). In addition, the handling of many-body interactions becomes much more complicated. Only in Particle Physics is the relativistic formalism widespread.

³⁹the time Δt should not be confused with the oscillation period $T = 2\pi/\omega$.

⁴⁰to handle this particular case, we suggest to assess the exercise proposed in this Course.

Let us recapitulate and realize that, in all the above formalism, only the Feynman propagator and the Hamiltonian in Schrödinger's equation (based on the equation $E = \frac{p^2}{2m}$) were expressed in a non relativistic form. This was in contrast to De Broglie's relations, the uncertainty principle, the orthonormal basis of stationary states, and the time dependence (48) of the expansion onto them. These are all essentially relativistic concepts, and their related formalism can be used in all kinds of problems involving velocities comparable to c , after correct use of relativistic kinematics.

It is clearly not the task of this course to go deeper on the subject. We simply add that one of the most far-reaching consequences of Relativity in Quantum Mechanics is that the uncertainty principle becomes more stringent: the complete localization of a particle in space becomes impossible, no matter its momentum uncertainty.

The maximum spatial location (minimal Δx) that a particle of rest mass m can have is given in Relativity by the so-called **Compton wavelength**:

$$\lambda_C = \frac{h}{mc} ,$$

and no experiment can determine the position of a particle with greater precision than the above. For the electron, $\lambda_C = 0.024 \text{ \AA}$.

It should be pointed out that, in a totally relativistic framework, adequate to describe data from high energy particle accelerators, Quantum Mechanics does not stand as a consistent theory, and must be replaced by a more perfect one, called Quantum Field Theory. This theory extends Quantum Mechanics also in applications not necessarily relativistic, in Condensed Matter Physics. In Electromagnetism, it is called Quantum Electrodynamics.