From Quantum to Molecule

Dr Juan Rojo
VU Amsterdam and Nikhef Theory Group
http://www.juanrojo.com/
j.rojo@vu.nl

Lecture notes, current version: January 31, 2020

Contents

Page

From Quantum to Molecule

Dr Juan Rojo
VU Amsterdam and Nikhef Theory Group
http://www.juanrojo.com/
j.rojo@vu.nl

1 HC1: Introduction to Quantum Theory I

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

Learning goals of this lecture:

- Assess the consequences of the wave-particle duality posited by quantum theory.
- Understand that the state of a quantum system is fully described by the quantum wave-function, which is a solution of the time-independent Schroedinger equation.
- Become familiar the probabilistic interpretation associated to the quantum wave-function and compute the normalisation constants in simple cases.
- Apply Heisenberg's uncertainty principle to pairs of correlated physical observables.

Introduction. In this first two lectures of the course (HC1 and HC2), we will present a concise overview of the basic principles of quantum theory, the mathematical language relevant for the description of small objects such as atoms, molecules, and electrons. We will state these central principles of quantum theory as established facts, avoiding (due to lack of time) the historical discussion of how these principles were developed or what is the experimental evidence that validates them. The interested student can find a brief introduction to the historical developments that lead to the formation of quantum theory on the slides that I have posted in Canvas:

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

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

1.1 Wave-particle duality

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

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

$$\lambda \equiv \frac{h}{p} = \frac{h}{mv}\,, \tag{1.1}$$

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

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

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

$$\lambda = \frac{h}{p} \simeq 0.5 \times 10^{-10}\,\mathrm{m}\,, \tag{1.2}$$

which is the typical separation between atoms in an crystal. Therefore one expects to observe the wave character of electrons when crossing a crystalline lattice.
On the other hand, for a car of mass $m = 1000$ kg moving at a velocity of $v = 100$ km/h, such that its momentum is $p = 2.8 \times 10^4$ kg m/s, we can associate a De Broglie wavelength of

$$\lambda = \frac{h}{p} \simeq 2 \times 10^{-38}\,\mathrm{m}\,, \tag{1.3}$$

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

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

The remarkable wave-particle behaviour of quantum theory is illustrated nicely by the famous double slit

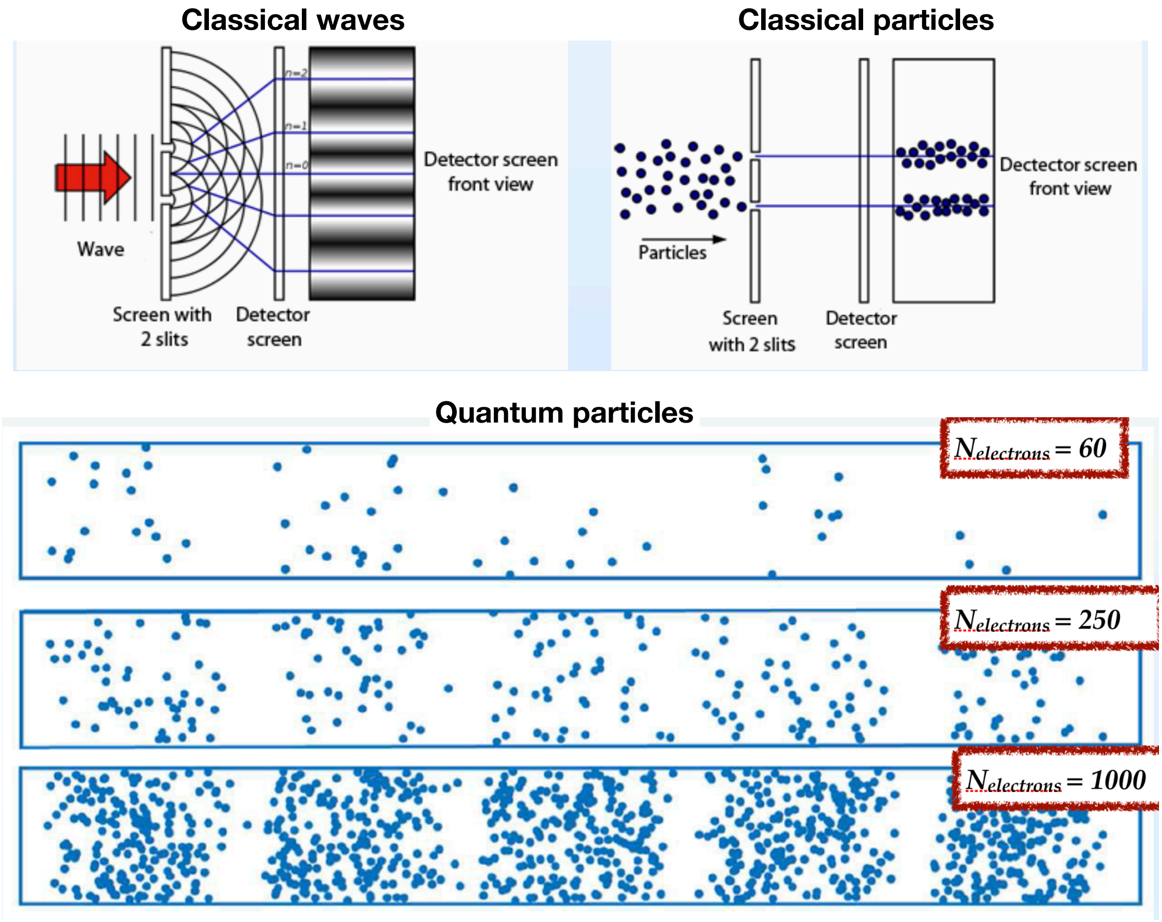


Figure 1.1: In classical theory, the behaviour of waves and particles in the double slit experiment is very different: waves lead to an interference pattern, while particles lead to just two blobs in the detector screen (upper diagrams). In quantum particle, the situation is very different (lower diagrams):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

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

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

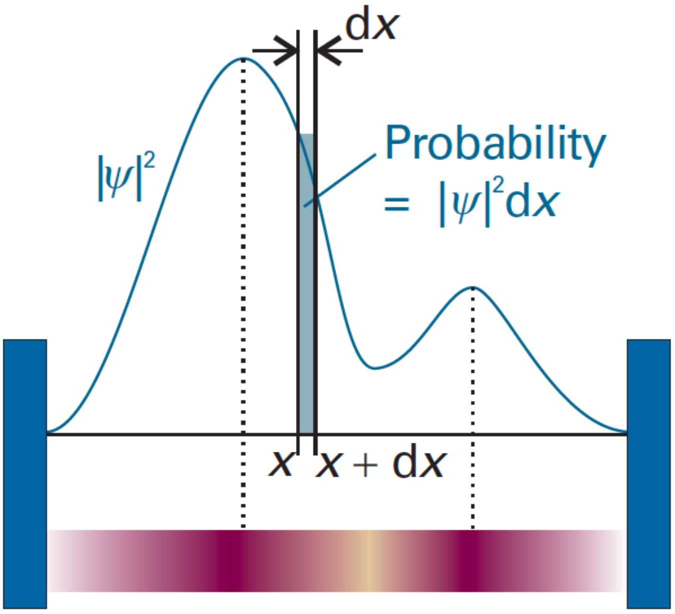


Figure 1.2: The physical interpretation of the quantum wave-function $\Psi(x)$ is that its square $|\Psi(x)|^2$ is the probability density associated to measuring the particle in a position x in space. Therefore, the probability to find the particle at position x in the range dx will be given by $|\Psi(x)|^2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

1.2 The quantum wave-function

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

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

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

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

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

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

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

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

$$|\Psi|^2 = \Psi^*\Psi = \left[\mathrm{Re}(\Psi) - i\mathrm{Im}(\Psi)\right]\left[\mathrm{Re}(\Psi) + i\mathrm{Im}(\Psi)\right] \,, \tag{1.6}$$

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

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

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

one possible wave function allowed is:

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

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

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

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

  as we can check with our specific example:

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

  which is appropriately normalised as expected. In computing this integral, we have used the result that

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

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

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

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

  Note that here we assume that the wave function is always *square-integrable*, namely that integrals of the form Eq. (1.12) are always well defined (else the probabilistic interpretation would be impossible). Wave functions that cannot be normalised are not physical.

Consider the following example: a system is characterised by a wave function of the form

$$\Psi(x) = N\left(\sin\left(\frac{3\pi x}{L}\right) - \sin\left(\frac{4\pi x}{L}\right)\right) , \tag{1.13}$$

for $0 \le x \le L$. We can compute its normalisation constant as follows. We need to impose that

$$1 = |\Psi(x)|^2 = N^2 \int_0^L dx \, \left(\sin^2\left(\frac{3\pi x}{L}\right) + \sin^2\left(\frac{4\pi x}{L}\right) - 2\sin\left(\frac{3\pi x}{L}\right)\sin\left(\frac{4\pi x}{L}\right)\right) \tag{1.14}$$

To compute these integrals, it is useful to change variables, $z = \pi x/L$, so that we get

$$1 = |\Psi(x)|^2 = \frac{N^2 L}{\pi}\int_0^\pi dz \, \left(\sin^2(3z) + \sin^2(4z) - 2\sin(3z)\sin(4z)\right) = N^2 L \, , \tag{1.15}$$

where we have used the result of the definite integral

$$\int_0^\pi \sin(mx)\sin(nx)dx = \pi/2 \ (0) \ \text{ for } \ m = n \ (m \neq n) \, . \tag{1.16}$$

Therefore the normalisation constant of this wave function is $N = L^{-1/2}$.

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

  $$\sin\left(\frac{\pi x}{L}\right)\Big|_{x=0,L} = 0 \, . \tag{1.17}$$

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

  $$\begin{aligned} \Psi'(x) &= \sqrt{\frac{2\pi}{L^2}}\cos\left(\frac{\pi x}{L}\right) \, , \quad 0 \le x \le L \, , \\ \Psi'(x) &= 0 \, , \quad x \le 0 \quad \text{or} \quad x \ge L \, , \end{aligned} \tag{1.18}$$

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

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

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

- In general there is not a unique answer to the question of where exactly a quantum particle is at a given time: all we know is what is the probability density of all possible positions x. However we can compute what is the *most likely value* of a given property to find upon measurement, namely the *maximum* of the associated probability distribution. We can also evaluate its *expectation value*, namely the mean of the same probability distribution.

Recall that given an stochastic random variable x with an associated probability distribution $P(x)$, the *most likely value* of x, denoted as x^*, is given by the global maximum of $P(x)$:

$$\left.\frac{dP(x)}{dx}\right|_{x=x^*} = 0\,, \tag{1.19}$$

while the *expectation value* of x, $\langle x\rangle$, is instead the mean of the distribution, evaluated as

$$\langle x\rangle = \int dx\, x\, P(x)\,. \tag{1.20}$$

In general the most likely value and the expectation value of $P(x)$ will be different.

For example, if we want to compute the expectation value (the mean) of an observable $f(x)$ that depends on the particle position x, we can use the following expression:

$$\langle f(x)\rangle \equiv \int_{-\infty}^{+\infty} dx\, f(x)\, P(x) = \int_{-\infty}^{+\infty} dx\, \Psi^*(x)\, f(x)\, \Psi(x)\,. \tag{1.21}$$

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

$$\langle x\rangle = \int_0^L dx\, x\, \frac{2}{L}\sin^2\left(\frac{\pi x}{L}\right) = \frac{2L}{\pi^2}\int_0^\pi dy\, y\, \sin^2(y) = \frac{2L}{\pi^2}\frac{\pi^2}{4} = \frac{L}{2}\,, \tag{1.22}$$

where we have used the integral in Eq. (1.11). This result implies that if we measure the position of the particle characterised by this wave function, the expected result is that we find it in the middle of the box where is it confined, at $x = L/2$.

We can also evaluate the most likely value associated to this quantum state

$$\left.\frac{d}{dx}\left(\frac{2}{L}\sin^2\left(\frac{\pi x}{L}\right)\right)\right|_{x=x^*} = 0 \quad \to \quad \cos\left(\frac{\pi x^*}{L}\right) = 0 \tag{1.23}$$

whose solution is $x^* = L/2$. In this case x^* and $\langle x\rangle$ coincide due to the specific properties of $P(x) = |\Psi(x)|^2$, but as mentioned above in general they will be different.

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

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

```
npts=100
for i in range(0,npts+1):
    x[i] = i/npts
    phi[i] = (2)**1/2 * math.sin(math.pi*x[i])
```

```
    phi2[i] = phi[i]**2
import matplotlib.pyplot as plt
plt.plot(x,phi,color="blue",label=r"$\phi(x)$")
plt.plot(x,phi2,color="red",label=r"$\phi^2(x)$")
plt.xlabel(r"$x$")
```

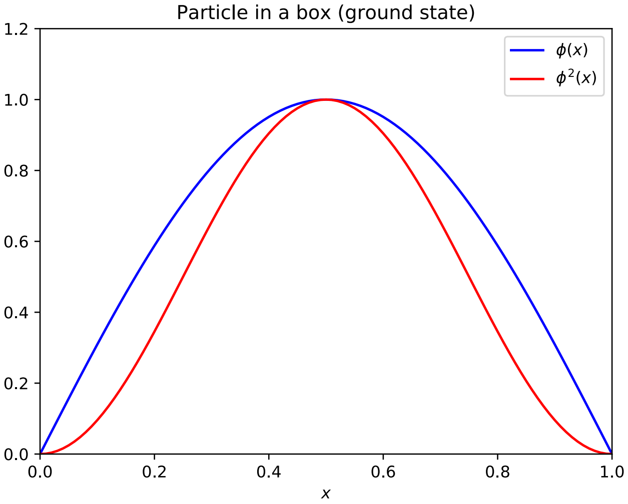


Figure 1.3: Graphical representation of the wave function $\Psi(x)$ in Eq. (1.8) for the ground state of a particle in a box and its corresponding probability density $P(x) = |\Psi(x)|^2$. Here we assume that $L = 1$.

1.3 The Schroedinger equation

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

$$ma = m\frac{d^2x(t)}{dt} = F_{\rm tot}\,, \tag{1.24}$$

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

$$x(t) = x_0 + v(t - t_0)\,, \tag{1.25}$$

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

As we discussed above, for a quantum system all information is provided by its wave function $\Psi(x)$ (now back to the position representation). So we need a different equation that determines the time evolution of the wave function, namely the analog of Newton's Eq. (1.24) for the quantum case. The corresponding dynamical equation in quantum theory is known as the *Schroedinger equation*. Here we will restrict ourselves to the time-independent Schroedinger equation, which determines the wave function of a quantum system in terms of its properties such as the local potential energy. In the simplest case of motion in one dimension, the time-independent Schroedinger equation read

$$-\frac{\hbar^2}{2m}\frac{d^2\Psi(x)}{dx^2} + V(x)\Psi(x) = E\Psi(x)\,, \tag{1.26}$$

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

$$-\frac{\hbar^2}{2m}\left(\frac{d^2}{dx^2}+\frac{d^2}{dy^2}+\frac{d^2}{dz^2}\right)\Psi(\vec{x})+V(x,y,z)\Psi(\vec{x})=E\Psi(\vec{x})\,. \tag{1.27}$$

A general quantum system will be defined by the masses m_i of the particles that compose it and the potential $V(x_1, x_2, \ldots)$ that these particles experience, as well as by suitable boundary conditions.

Boundary conditions are requirements that the wave function $\Psi(x)$ must obey in specific regions of space. One example of boundary condition is that the wave function should be zero in regions where the potential is infinite, that is, where $V(x) = \infty$ one should impose that $\Psi(x)$. Another example is the *continuity* that $\Psi(x)$ should obey when moving between different regions of space. For example, if a given quantum state has wave functions $\Psi_I(x)$ and $\Psi_{II}(x)$ in regions I and II that meet at $x = x_0$, then the continuity of the wave function requires that the boundary condition $\Psi_I(x) = \Psi_{II}(x)$ is satisfied.

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

$$-\frac{\hbar^2}{2m}\frac{d^2\Psi(x)}{dx^2}=E\Psi(x)\,. \tag{1.28}$$

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

$$\Psi(x)=\sin(Bx)\,, \tag{1.29}$$

which is a solution of Eq. (1.28) provided that

$$\begin{aligned}
\frac{d}{dx}\Psi(x) &= B\cos(Bx)\,,\\
-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\Psi(x) &= -\frac{\hbar^2}{2m}\left(-B^2\sin(Bx)\right)=\frac{\hbar^2B^2}{2m}\sin(Bx)\,,\\
E &= \frac{\hbar^2B^2}{2m} \quad\to\quad B=\pm\sqrt{\frac{2mE}{\hbar^2}}\,.
\end{aligned} \tag{1.30}$$

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

$$\Psi(x)=A\cos\left(\sqrt{\frac{2mE}{\hbar}}x\right)+B\sin\left(\sqrt{\frac{2mE}{\hbar}}x\right)\ . \tag{1.31}$$

The coefficients A and B in Eq. (1.31) are free parameters to be fixed by the specific boundary conditions of the problem. This result shows that under exactly the same conditions, a particle propagates rather differently in classical theory, Eq. (1.24) as compared to quantum theory, Eq. (1.31).

In Fig. 1.4 we show the same graphical representation as in Fig. 1.3 now for the wave function of the free particle, Eq. (1.31), for $A = 0$ and $B = 1$, with an energy chosen so that $2mE/\hbar^2 = 1$. We can see clearly the periodic nature of the wave function, with the probability of finding the particle at the position x, $P(x) = |\Psi(x)|^2$, peaking at fixed separations. You might have noticed that the free-particle wave function Eq. (1.31) cannot be normalised: the integral of $|\Psi(x)|^2$ between $-\infty$ and ∞ is clearly infinite. This means that a free particle is not really a physical state. This fact is related to the Heisenberg uncertainty principle, which we discuss next.

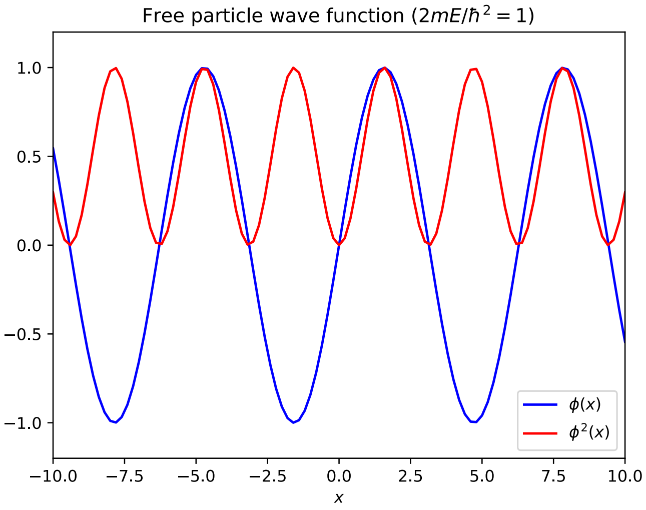


Figure 1.4: Same as Fig. 1.3 for the wave function of the free particle, Eq. (1.31), for $A = 0$ and $B = 1$, with an energy chosen so that $2mE/\hbar^2 = 1$. Note that this wave function cannot be normalised, highlighting that these solutions do not correspond to physical systems.

1.4 Heisenberg's uncertainty principle

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

Perhaps the most important incarnation of the Heisenberg's uncertainty principle is the one that relates the position and the linear momentum of a particle. If we denote by Δx the uncertainty associated to the position of a given particle, and Δp_x the uncertainty associated to its linear momentum (in the same direction), quantum theory tells us that both Δx and Δp_x cannot be arbitrarily small at the same time. Instead, they need to satisfy the following inequality:

$$\Delta x \cdot \Delta p_x \geq \hbar \,, \tag{1.32}$$

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

$$\Delta x \geq \frac{h}{2\pi} \frac{1}{\Delta p_x} \,. \tag{1.33}$$

We emphasize again that Eq. (1.32) is not merely a restriction due to the imprecision of our experimental measurement apparatus: this is a fundamental limitation about the information that can be extracted from a quantum system even with a perfect measurement. The same principle holds for other variables, such as energy and time, where we have that

$$\Delta E \cdot \Delta t \geq \hbar\,. \tag{1.34}$$

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

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

$$\Delta y \cdot \Delta p_y \geq \hbar\,, \quad \Delta z \cdot \Delta p_z \geq \hbar\,, \tag{1.35}$$

this restriction is not present to measure the position in a given direction and its linear momentum in an orthogonal direction, for example we can have that

$$\Delta y \cdot \Delta p_x \geq 0\,, \quad \Delta x \cdot \Delta p_z \geq 0\,. \tag{1.36}$$

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

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

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

$$\Delta x = \hbar/\Delta p = \left(1.05 \times 10^{-34}\,\mathrm{m^2kg/s}\right) / \left(27.8 \times 10^{-8}\,\mathrm{kg}\cdot\mathrm{m/s}\right) = 3.8 \times 10^{-28}\,\mathrm{m}\,, \tag{1.37}$$

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

$$\Delta x = \hbar/\Delta p = \left(1.05 \times 10^{-34}\,\mathrm{m^2kg/s}\right) / \left(2.73 \times 10^{-25}\right) = 3.8 \times 3.8^{-10}\,\mathrm{m}\,, \tag{1.38}$$

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

Heisenberg's uncertainty principle is also useful to understand what happens with the free-particle wave function. We saw that this wave function, Eq. (1.31), could not be normalised. The reason is that this wave function corresponds to a particle with well defined kinetic energy E and thus well-defined linear momentum $p_x = \sqrt{2mE}$ (since for a free particle $E = mv^2/2 = (mv)^2/2m = p^2/2m$). Therefore, the free-particle wave function corresponds to a quantum state with a well-definite momentum, and therefore characterised by $\Delta p_x = 0$. However, in this case Heisenberg's uncertainty principle implies that the uncertainty in the position of the particle will be

$$\Delta x \geq \hbar/\Delta p_x \geq \infty \tag{1.39}$$

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

Summary

We can now recapitulate what we have learned in this first lecture about some of the basic ideas of quantum theory. These ideas will be extensively used in the rest of the course, and applied to a wide variety of different quantum systems.

I/ All the physical information about a quantum system is contained in its wave-function $\Psi(x)$.

II/ The square of the wave-function $|\Psi(x)|^2$ represents the probability density for finding the particle at the position x upon a measurement. We cannot ascertain the exact position of a particle, but we can evaluate for example its expectation value $\langle x \rangle$.

III/ The wave-function $\Psi(x)$ must be continuous, have a continuous first derivative (unless the potential is infinite at the boundary), be single valued, and be squared-integrable. Probability conservation implies that the wave function should be normalised to unity.

IV/ The wave function is a solution of a differential equation called the Schroedinger equation, which depends on the potential $V(x)$ under which the particle moves.

V/ In quantum theory there is an intrinsic limitation on how well we can measure specific pairs of physical observables, such as position and momentum. This property is quantified by Heisenberg's uncertainty principle.

From Quantum to Molecule

Dr Juan Rojo
VU Amsterdam and Nikhef Theory Group
http://www.juanrojo.com/
j.rojo@vu.nl

2 HC2: Introduction to Quantum Theory II

In this lecture we continue with the introduction to the basic concepts of quantum theory. We will present the mathematical language required to extract information on physical properties from the wave function of a quantum state. In particular, we will show how in quantum theory there is a correspondence between physical observables and operators, and how the action of these operators can be expressed in the framework of linear algebra.

Learning goals of these two lectures:

- Become familiar with the mathematical formalism of quantum physics, including Hermitian operators, eigenvalue equations, and orthogonality.
- Express the measurement process of quantum states in the mathematical language of linear algebra.
- Determine how experimental observables can be calculated from the wave-function.
- Compute the expectation values of physical quantities in selected quantum states.
- Differentiate between the most important types of radioactive processes.

2.1 Observables and operators in quantum theory

As we have discussed in HC1, the wave-function $\Psi(x)$ of a quantum system contains the complete physical information on the system. In particular, the various properties of the system should be calculable only from the knowledge of the wave-function, without any additional inputs required.

In quantum theory, we denote as an *observable* a given property of a quantum system (energy, momentum, angular momentum, electric charge, ...) that can be extracted from a *experimental measurement* of this system. Mathematically, the tools that we will use to compute the expected outcome of a measurement of a quantum system are known as *operators*, which can be expressed in the language of *eigenfunctions* and *eigenvectors* of linear algebra.

Before discussing the role that operators have in quantum theory, let us briefly review the concept of an eigenvalue system with matrices that you have learned in your linear algebra courses.

Eigenvalue equations with matrices. An eigenvalue equation is a mathematical equation of the form

$$A\mathbf{v} = \lambda\mathbf{v}. \tag{2.1}$$

where A is an square matrix of dimensions $n \times n$ and $\mathbf{v}$ is a column vector with n dimensions. The scalar λ is known as the *eigenvalue* of the equation, while the vector $\mathbf{v}$ is known as the associated *eigenvector*. The key feature of Eq. (2.8) is that applying a matrix A to the vector $\mathbf{v}$ returns the original vector with an overall rescaling, $\lambda\mathbf{v}$. In order to compute the eigenvalues of a matrix, we need to evaluate the solutions of the *characteristic equation* of the matrix A, defined as

$$\det\left(A - \lambda \cdot I\right) = 0\,, \tag{2.2}$$

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

To illustrate how to compute eigenvalues, one can consider the following matrix

$$A = \left(\begin{array}{cc} 1 & -3 \\ 3 & -5 \end{array}\right)\,, \tag{2.3}$$

which has associated the following characteristic equation

$$\det\left(A - \lambda \cdot I\right) = \left|\begin{array}{cc} 1-\lambda & -3 \\ 3 & -5-\lambda \end{array}\right| = \lambda^2 + 4\lambda + 4 = 0\,. \tag{2.4}$$

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

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

$$A\mathbf{v}_i = \lambda\mathbf{v}_i. \tag{2.5}$$

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

$$\left(\begin{array}{cc} 1 & -3 \\ 3 & -5 \end{array}\right)\left(\begin{array}{c} v_{1,1} \\ v_{1,2} \end{array}\right) = \lambda_1 \left(\begin{array}{c} v_{1,1} \\ v_{1,2} \end{array}\right) \tag{2.6}$$

$$\begin{aligned} v_{1,1} - 3v_{1,2} &= -2v_{1,1} \qquad (2.7) \\ 3v_{1,1} - 5v_{1,2} &= -2v_{1,1} \end{aligned}$$

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

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

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

Eigenvalue equations in quantum systems. Formally, an *operator* represents the action of a specific mathematical function onto a given wave-function $\Psi(x)$. For instance, Schroedinger's equation Eq. (1.27) can be expressed in operator form as follows

$$\widehat{H}\Psi(x) = E\Psi(x)\,, \tag{2.8}$$

where the "hat" $(\widehat{\ })$ symbol indicates an operator (as opposed to just a standard function), in this case the *Hamiltonian operator* defined as

$$\widehat{H} \equiv -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)\,. \tag{2.9}$$

Operators in quantum theory act on wave function and return either numbers or functions. An operator equation of the form of Eq. (2.8) has the same form as the eigenvalue equations that we saw before in Eq. (2.8), replacing the matrix A by the Hamiltonian operator $\widehat{H}$ and the eigenvector $\mathbf{v}$ by the quantum wave function $\Psi(x)$. Actually the analogy is more transparent for those quantum systems where the number of quantum states is finite, and where the Hamiltonian operator can be written as a square matrix. We will see examples of such systems when discussing the quantum mechanics of molecules.

An *operator* is a mathematical object that is defined by its action upon some test function. For example, the action of the operator $\widehat{\mathcal{O}}_1 = d/dx$ is defined as taking the derivative on the function it acts upon, $\widehat{\mathcal{O}}_1 f(c) = df(x)/dx$. A specific class of operators are those which just add a multiplicative pre-factor, for instance the action of the operator $\widehat{\mathcal{O}}_2 = x^3$ is defined by $\widehat{\mathcal{O}}_1 f(x) = x^3 f(x)$.

In the case of Eq. (2.8), the application of the Hamiltonian operator $\widehat{H}$ to the wave-function returns the total energy E of the quantum state. The *correspondence* between operators and observables implies that $\widehat{H}$ is the operator that represents the total energy of a given quantum system. Therefore, we can determine the energy of a quantum system by applying the operator $\widehat{H}$ to its wave function. Note that not all wave functions are eigenvalues of $\widehat{H}$, meaning that one can construct wave functions for which

$$\widehat{H}\Psi(x) \neq E\Psi(x)\,. \tag{2.10}$$

In general, solving a quantum system corresponds to determining the eigenvalues and eigenvectors of

Eq. (2.8), which is the equivalent to solving the Schroedinger equation.

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

$$\widehat{\Omega}\,\Psi_k(x) = \omega_k\,\Psi_k(x)\,, \quad k = 1, \ldots, n \tag{2.11}$$

where we have:

- $\widehat{\Omega}$ represents a generic operator associated to the observable property Ω (such as the energy or momentum) of the quantum system.
- Ψ_k is the k-th eigenfunction, corresponding to the k-th eigenvalue ω_k. It can be physically interpreted as the wave function of a quantum system where the observable Ω associated to the operator $\widehat{\Omega}$ takes a value ω_k.
- n is the number of eigenvalues that this equation has.

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

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

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

$$\widehat{\Omega}\Psi = \frac{d}{dx}e^{\alpha\,x} = \alpha e^{\alpha\,x} = \alpha\Psi\,, \tag{2.12}$$

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

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

$$\widehat{\Omega}\Psi = \frac{d}{dx}\left(e^{\alpha x} + e^{\alpha\,x^2}\right) = \alpha e^{\alpha x} + 2\alpha x e^{\alpha\,x^2} \neq \omega\Psi\,, \tag{2.13}$$

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

Observables and operators. Therefore, in quantum theory any observable property Ω of a quantum system will be represented by an operator $\widehat{\Omega}$. We can then determine the value of this property associated to the specific quantum system Ψ by solving the corresponding eigenvalue equations $\widehat{\Omega}\Psi_k = \omega_k\Psi_k$. We list here the most important cases for this *correspondence* between observables and operators, for simplicity restricted to the one-dimensional case:

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

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

Commutation relations. Heisenberg's uncertainty principle illustrates an important concept of quantum theory: the *complementarity between physical observables.* We define two observables Ω_1 and Ω_2 to be *complementary* if the sequential application of the corresponding operators $\widehat{\Omega}_1$ and $\widehat{\Omega}_2$ onto a generic wave function Ψ does not *commute*, that is,

$$\widehat{\Omega}_1 \left(\widehat{\Omega}_2 \Psi \right) \neq \widehat{\Omega}_2 \left(\widehat{\Omega}_1 \Psi \right) , \tag{2.14}$$

or in other words, the results of applying the two operators $\widehat{\Omega_1}$ and $\widehat{\Omega_2}$ to a generic wave-function depends on the *order in which they have been applied.* It can be demonstrated that for each pair of complementary observables there will be a relation of the form of the Heisenberg uncertainty principle, Eq. (1.32), implying that a simultaneous measurement of the physical quantities Ω_1 and Ω_2 with arbitrary precision is not possible. As mentioned above, two examples of complementary variables are position and momentum in the same direction, $\Omega_1 = x$ and $\Omega_2 = p_x$, as well as time and total energy, $\Omega_1 = t$ and $\Omega_2 = E$.

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

$$\left[\widehat{\Omega}_1, \widehat{\Omega}_2 \right] \equiv \widehat{\Omega}_1 \widehat{\Omega}_2 - \widehat{\Omega}_2 \widehat{\Omega}_1 \, , \tag{2.15}$$

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

$$[\widehat{x}, \widehat{p}_x] = i\hbar \, , \tag{2.16}$$

as is easy to verify explicitly. Indeed, since

$$\widehat{x}\widehat{p}_x \Psi = x \left(\frac{\hbar}{i} \frac{d}{dx} \right) \Psi = \frac{\hbar}{i} x \frac{d\Psi}{dx} \, , \tag{2.17}$$

$$\widehat{p}_x \widehat{x} \Psi = \left(\frac{\hbar}{i} \frac{d}{dx} \right) (x\Psi) = \frac{\hbar}{i} \Psi + \frac{\hbar}{i} x \frac{d\Psi}{dx} \, , \tag{2.18}$$

then their commutator gives

$$[\widehat{x}, \widehat{p}_x] \; \Psi = -\frac{\hbar}{i} \Psi = i\hbar \Psi \, , \tag{2.19}$$

which is the sought-for result Eq. (2.16). Therefore, x and p are *complementary observables* (their operators do not commute) and thus they cannot be measured simultaneously with arbitrary precision. This is another way of representing Heisenberg's uncertainty principle.

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

$$\left[\widehat{\Omega}_1, \widehat{\Omega}_2 \right] \neq 0 \, , \tag{2.20}$$

that is, that the two operators do not commute, then the physical observables to which these two operators are associated are complementary and have associated a Heisenberg uncertainty relation. In other words, they cannot be measured with arbitrary precision at the same time.

2.2 The quantum superposition principle and the free particle revisited

In general not all quantum wave functions will be the solution of an eigenvalue equation. Going back to the Schroedinger equation expressed as an eigenvalue equation, Eq. (2.8), we can write its solutions (eigenvalues and eigenfunctions) as

$$\widehat{H}\Psi_k(x) = E_k\Psi_k \, . \tag{2.21}$$

and now we can present a powerful principle of quantum theory, known as the *superposition principle*:

If $\Psi_1, \Psi_2, \ldots, \Psi_n$ are solutions of a quantum eigenvalue equation, $\widehat{\Omega}\Psi_k = \omega_k\Psi_k$, for example the Schroedinger equation, then the quantum state defined by their linear superposition

$$\Psi(x) = \sum_{k=1}^{n} c_k\Psi_k(x) \; , \tag{2.22}$$

is also a physically acceptable quantum state, although it will not have associated a unique value of the physical observable Ω as the eigenfunctions do.
The coefficients c_k can be determined from measurements of Ω in this quantum system: the probability of measuring ω_k is $P_k = |c_k|^2$, that is, the square of the corresponding coefficient. For example, if we measure ω_1 16% of the times, we know that $c_1 = \sqrt{P_1} = \sqrt{0.16} = 0.4$. Note that since the wave function should be normalised the sum of all probabilities should add up to one, and therefore the coefficients c_k should satisfy $\sum_k |c_k|^2 = 1$.

Applying the superposition principle, we know that the wave function

$$\Psi(x) = \sum_k c_k\Psi_k(x) \, , \tag{2.23}$$

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

$$\widehat{H}\Psi(x) = \sum_k c_k\widehat{H}\Psi_k(x) = \sum_k c_k E_k\Psi_k(x) \neq \omega\Psi(x), \tag{2.24}$$

showing how there exist physically allowed quantum systems that are not solutions of Schroedinger's equations. The reason is that these quantum states do not have a well-defined energy, and that different measurements of E will return different values.

The free particle revisited. We can now revisit the free-particle solution of the Schroedinger's equation, Eq. (1.31). We would like to compute which is the linear momentum associated to this quantum state. For quantum states with well-defined momentum, we know using the above correspondence that we should use the corresponding eigenvalue equation:

$$\widehat{p}_x\Psi(x) = \frac{\hbar}{i}\frac{d}{dx}\Psi(x) = p_x\Psi(x) \, , \tag{2.25}$$

with p_x being the sought-for result. Considering the $B = 0$ solution, if we apply Eq. (2.25) to the free particle wave function we find:

$$\widehat{p}_x \Psi(x) = \frac{\hbar}{i} \frac{d}{dx} \left[A \cos\left(\sqrt{\frac{2mE}{\hbar}} x \right) \right] = -\frac{\hbar}{i} A \sqrt{\frac{2mE}{\hbar^2}} \sin\left(\sqrt{\frac{2mE}{\hbar^2}} x \right) \neq p_x \Psi(x) \,, \tag{2.26}$$

so we find that a plane wave solution of the form of Eq. (1.31) with $B = 0$ is not an eigenvector of the linear momentum operator: we cannot associate a well-defined value of p_x to this quantum state.

On the other hand, if we choose that $B = iA$ in Eq. (1.31) we have that the wave function reads

$$\Psi(x) = A \cos\left(\sqrt{\frac{2mE}{\hbar^2}} x \right) + iA \sin\left(\sqrt{\frac{2mE}{\hbar^2}} x \right) = A \exp\left(i \sqrt{\frac{2mE}{\hbar^2}} x \right) \,, \tag{2.27}$$

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

$$\widehat{p}_x \Psi(x) = \frac{\hbar}{i} \frac{d}{dx} \left[A \exp\left(i \sqrt{\frac{2mE}{\hbar^2}} x \right) \right] = \sqrt{2mE}\, \Psi(x) \tag{2.28}$$

so the momentum along the x direction p_x that can be associated to the free particle with wave function Eq. (2.27) is $p_x = \sqrt{2mE}$. One can easily show that the solution where $B = -iA$ is also an eigenvalue of the linear momentum operator with eigenvector $p_x = -\sqrt{2mE}$. Therefore, the general solution of the Schroedinger equation for the free particle is a linear combination of plane waves moving in the positive direction with well defined momentum and the corresponding plane waves moving in the negative direction.

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

Wave-packet solutions. So does this mean that free particles always have well-defined values of their linear momentum p_x? Does this imply that the position of a free particle is always maximally uncertain? No, if we take into account that physically, from Eq. (1.32), there should be an uncertainty associated also to the expectation value of $\widehat{p}$, the momentum of the quantum state, if we want to have the particle localised in a finite region of space. A wave function for a free particle with a *finite momentum resolution* (and therefore a certain amount of spatial localisation) can be constructed by means of a *superposition* of free-particle solutions, each with *different wave numbers* k, namely

$$\Psi(x) = \sum_{k}^{N} c_k e^{ikx} \,. \tag{2.29}$$

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

$$\Psi(x) = \sum_{n=1}^{N} \cos(n\pi x) \,, \tag{2.30}$$

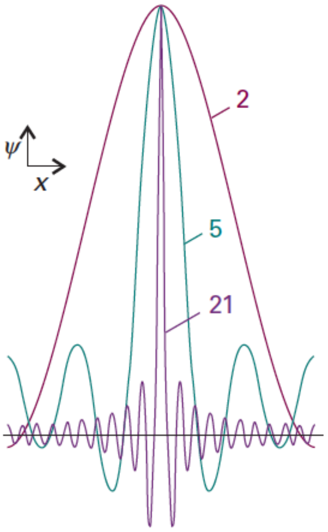


Figure 2.1: The wave function Eq. (2.30) corresponding to the superposition of N plane-wave free particle solutions, each with a different value of $k = n\pi$. We show the results from the addition of $N = 2, 5, 21$ terms in Eq. (2.30), showing that the more terms we include, the better the localization of the free particle (since the higher is the indetermination of its momentum p_x).

which is shown in Fig. 2.1: the more terms we add in the sum, the more values the momentum $\hbar k$ of the particle can take, hence Δp is higher (more uncertain) and Δx smaller (increased localization in space).

2.3 Hermiticity and orthogonality.

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

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

What is the defining characteristic of an Hermitian operator? We say that an operator $\widehat{\Omega}$ is Hermitian provided that, given two arbitrary wave-functions Ψ_i and Ψ_j, it satisfies the following property:

$$\int dx \Psi_i^* \widehat{\Omega} \Psi_j = \left(\int dx \Psi_i^* \widehat{\Omega} \Psi_j \right)^\dagger , \tag{2.31}$$

where the "dagger" symbol † indicates to to interchange i and j (that is, taking the transpose matrix), and then taking the complex conjugate, that is

$$\left(\int dx \Psi_i^* \widehat{\Omega} \Psi_j \right)^\dagger = \int dx \left(\Psi_j^* \widehat{\Omega} \Psi_i \right)^* . \tag{2.32}$$

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

$$\int dx \Psi_i^* \, \widehat{p} \, \Psi_j = \int dx \Psi_i^* \left(\frac{\hbar}{i} \frac{d}{dx} \right) \Psi_j = \frac{\hbar}{i} \left(\Psi_i^* \Psi_j \Big|_{-\infty}^{+\infty} - \int dx \Psi_j \frac{d}{dx} \Psi_i^* \right) = \int dx \Psi_j \left(-\frac{\hbar}{i} \right) \frac{d}{dx} \Psi_i^* \tag{2.33}$$

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

$$\int dx \Psi_i^* \, \widehat{p} \, \Psi_j = \int dx \Psi_j \left(-\frac{\hbar}{i} \right) \frac{d}{dx} \Psi_i^* = \left(\int dx \Psi_i^* \, \widehat{p} \, \Psi_j \right)^\dagger . \tag{2.34}$$

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

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

The key property that the eigenvalues of an Hermitian operator $\widehat{\Omega}$ are real can be demonstrated from its definition Eq. (2.31) as follows. Let us assume that $\Psi_i = \Psi_j = \psi$ is an eigenfunction of this operator with eigenvalue ω, that is, the relation $\widehat{\Omega}\psi = \omega\psi$ holds. Then we have that

$$\int dx \psi^* \Omega \psi = \int dx \psi^* \omega \psi = \omega \int dx \psi^* \psi = \omega \, , \tag{2.35}$$

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

$$\left(\int dx \psi^* \Omega \psi \right)^\dagger = \left(\omega \int dx (\psi^* \psi)^* \right) = \omega^* \tag{2.36}$$

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

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

$$\int dx \, \Psi_i^*(x) \, \Psi_j(x) = \delta_{ij} \, , \tag{2.37}$$

that is, the integral vanishes unless the eigenfunctions are the same, $i = j$, in which case the integral equals one because of the normalization condition (the eigenvectors can always be normalised to ensure that Eq. (2.37) is satisfied). This important property allows to project a general quantum state as a *linear superposition* of the eigenfunctions of an Hermitian operator, which form a complete basis of the corresponding vector space.

2.4 Expectation values of physical quantities

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

$$\langle b \rangle = \frac{1}{n} \sum_{i=1}^{n} b_i \,, \tag{2.38}$$

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

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

$$\langle \Omega \rangle = \int dx \, \Psi^* \widehat{\Omega} \Psi \,, \tag{2.39}$$

Here we can have two possible situations:

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

  $$\langle \Omega \rangle = \int dx \Psi^* \widehat{\Omega} \Psi = \int dx \Psi^* \omega \Psi = \omega \int dx \Psi^* \Psi = \omega \,, \tag{2.40}$$

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

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

  $$\widehat{\Omega}\Psi_k = \omega_k \Psi_k \,, \quad k = 1, \ldots, n \tag{2.41}$$

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

  $$\Psi(x) = \sum_{k=1}^{n} c_k \Psi_k(x) \,. \tag{2.42}$$

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

  $$\int dx \, \Psi^*(x) \Psi_j(x) = \int dx \left(\sum_{k=1}^{n} c_k \Psi_k(x) \right)^* \Psi_j(x) = \sum_{k=1}^{n} c_k^* \int dx \, \Psi_k^*(x) \Psi_j(x) = c_j^* \,, \tag{2.43}$$

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

Therefore, in full generality, we can always expand a quantum wave function as in Eq. (2.42) in terms of the eigenvectors of the operator associated to the physical observable that we want to measure. In this case, the expectation value $\langle \Omega \rangle$ will be given by the weighted sum of eigenvalues, with weight $|c_k|^2$:

$$\langle \Omega \rangle = \int dx \left(\sum_k c_k \Psi_k \right)^* \widehat{\Omega} \left(\sum_j c_j \Psi_j \right) = \sum_{k,j} c_k^* c_j \omega_j \int dx \Psi_k^* \Psi_j = \sum_{k,j} c_k^* c_j \omega_j \delta_{ij} = \sum_k |c_k|^2 \omega_k \,, \tag{2.44}$$

where we have use the orthogonality property of the eigenfunctions of an Hermitian operator Eq. (2.37). Note that in this derivation we assume that the coefficients of the linear superposition Eq. (2.42) are canonically normalized, that is, they satisfy $\sum_k |c_k|^2 = 1$, as implied by the condition that the original wave function $\Psi(x)$ is appropriately normalised.

Therefore, if we know the expansion of a given wave function in terms of the eigenvectors of an Hermitian operator, Eq. (2.42), we can readily compute the expectation value of this operator as a weighted sum of its eigenvalues as indicated by Eq. (2.44). In other words, if we express the wave function of a quantum system $\Psi(x)$ as a linear superposition of the eigenvalues of an operator $\widehat{\Omega}$,

$$\Psi(x) = \sum_k c_k \Psi_k(x) \,, \qquad \widehat{\Omega} \Psi_k = \omega_k \Psi_k \,, \tag{2.45}$$

then evaluating the expectation value of the physical observable Ω is particularly simple:

$$\langle \Omega \rangle = \sum_k |c_k|^2 \omega_k \,. \tag{2.46}$$

That implies that the coefficients c_k completely determine the corresponding expectation values. These coefficients can be determined by experimental measurements of Ω in this system: the probability P_k to finding the eigenvalue ω_k is proportional to $|c_k|^2$, so if the wave function is normalised then $P_k = |c_k|^2$.

Assume a quantum system, characterised by energy eigenstates with wave functions $\Psi_0(x), \Psi_1(x), \Psi_2(x), \ldots$ and the corresponding eigenvalues $E_0, E_1, E_2, \ldots$. In 50% of the measurements of the energy of the system, we find E_1, in 10% of the measurements, we find E_3, and in all other measurements we find E_5. We would like to determine the expectation value $\langle E \rangle$ for the energy of the system. First of all we need to know the coefficients c_n of the wave function of the system,

$$\Psi(x) = \sum_{n=0}^{\infty} c_n \Psi_n(x) \,, \tag{2.47}$$

and for this we will use that the probability P_n to find an energy E_n upon a measurement in this system is the given by $|c_n|^2$, the square of the corresponding coefficient in the wave function. Therefore from the data in the problem we have $c_1 = \sqrt{P_1} = \sqrt{0.5}$, $c_3 = \sqrt{P_3} = \sqrt{0.1}$, $c_5 = \sqrt{P_5} = \sqrt{0.4}$, where the value of P_5 has been determined from the condition that $P_1 + P_3 + P_5$: the probability of all possible outcomes must add up to unity. We can now evaluate the expectation value of E using

$$\langle E \rangle = \sum_{n=0}^{\infty} |c_n|^2 E_n = \sum_{n=0}^{\infty} P_n E_n = 0.5 E_1 + 0.1 E_3 + 0.4 E_5 \,. \tag{2.48}$$

Note that here E_n, as opposed to Eq. (2.47), is multiplied by $P_n = |c_n|^2$ rather than by the c_n itself.

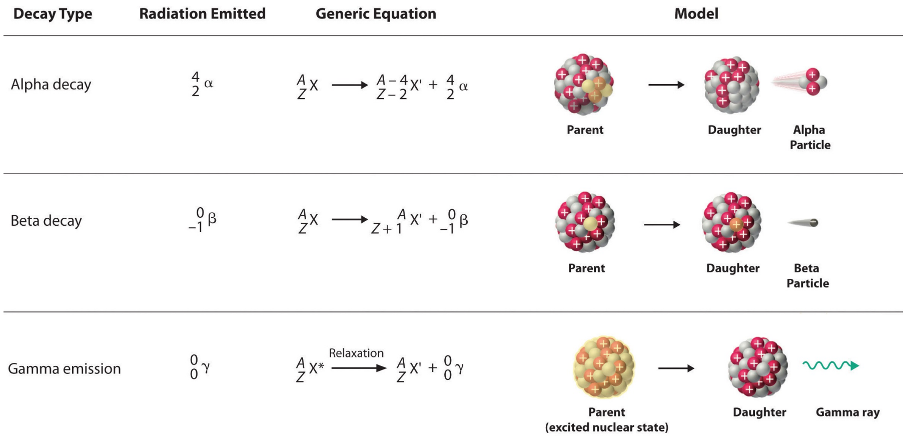


Figure 2.2: The three main types of radioactive decay processes. In alphas decay, mediated by the strong interaction, a He nucleus (2 protons and 2 neutrons) is emitted. In beta decay, mediated by the weak interaction, either an electron or a positron are emitted (together with a neutrino). In gamma decay, mediated by electromagnetism, a high energy photon is emitted.

2.5 Radioactivity

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

There are three main types of radioactive processes:

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

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

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

  This radioactive decay process is mediated by the weak interaction. If the initial unstable element is ^A_ZX, for this process the final element will be $^A_{Z\pm1}Y$, depending on whether an electron or a positron has been emitted.

- γ radiation: the emission of a high energy photon γ.

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

Therefore each of these three radioactive processes is mediated by a different fundamental interaction. The mean features of these three kinds of radioactive processes are summarized in Fig. 2.2.

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

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

$$dN = -\lambda N(t)dt \quad \rightarrow \quad N(t) = N_0 e^{-t/\tau}\,, \tag{2.49}$$

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

$$\langle t\rangle = \frac{\int_0^\infty dt\, t\, N(t)}{\int_0^\infty dt\, N(t)} = \tau\,. \tag{2.50}$$

Therefore, we see from Eq. (2.49) that the number of nuclei of a given sample that undergo radioactive decays decreases exponentially with time. One sometimes also defines the activity of a radioactive sample, defined as (minus) the rate of change of $N(t)$ per unit time,

$$A(t) \equiv -\frac{dN(t)}{dt} = \frac{N_0}{\tau}\exp\left(-\frac{t}{\tau}\right)\,. \tag{2.51}$$

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

The value of the decay constant λ is different for each atomic element and isotope. This provides among other things a rather useful method to determine the age of objects, the so-called *radiocarbon dating method*. This method is based on the fact that one of the isotopes of carbon, ^{14}C, has a decay constant of a few thousand years, while the more frequent isotope ^{12}C is stable. This means that if we know somehow the initial abundance of ^{14}C in a given sample, and measure the current abundance, since we know τ we can determine t from Eq. (2.49). In other words, we can determine in a rather reliable way the age of this specific sample. The original abundance of ^{14}C can be determined for instance by comparing with the current one of ^{12}C, since the ratio between the abundances of the two isotopes in various systems is rather well understood.

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

For instance, assume that we find that a sample with only 10% of ^{14}C atoms as compared to its original abundance. By applying Eq. (2.49), we have that

$$0.1\, N_0 = N_0 e^{-t/(8267\,\mathrm{yr})} \qquad \rightarrow \qquad t = 19000\,\mathrm{yr}\,, \tag{2.52}$$

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

Summary

We can now recapitulate what we have learned in this lecture about some of the most important principles and concepts of quantum mechanics. As in the case of those principles that we covered in the previous lecture, the ideas presented here will be extensively used in the rest of the course, and applied to a wide variety of different quantum systems.

I/ Physical observables Ω are represented by Hermitian operators $\widehat{\Omega}$ built upon the position $\widehat{x}$ and momentum $\widehat{p}$ operators, that act on the wave function of a quantum system. Examples of this are the total energy $\widehat{H}$ and the linear momentum $\widehat{p}_x$.

II/ The correspondence between observables and operators allows one to determine physical properties from a given quantum state.

III/ By means of the quantum superposition principle, we can always express a general wave function as a combination of eigenvectors of Schroedinger's equation,

$$\Psi(x) = \sum_n c_k \Psi_k(x)\,, \qquad \widehat{H}\Psi_k(x) = E_k \Psi_k(x)\,. \tag{2.53}$$

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

IV/ The knowledge of the wave function of a system allows us to evaluate the expectation value $\langle \Omega \rangle$ of any observable quantity Ω by computing matrix elements of its associated operator $\widehat{\Omega}$.

V/ The expectation value of a physical observable Ω can be expressed in terms of its eigenvalues and the coefficients of the wave function expressed as a linear superposition of their eigenvectors.

VI/ Quantum theory plays a central role in the description of radioactive processes, whereby unstable atomic nuclei radiate particles such as photons, electrons, and He nucleus.

Further reading

Further reading material about the topics covered in this lecture can be found in the following sections of the course textbook (*Physical Chemistry*, Atkins, De Paula & Keeler, 11th edition):

Chapters in textbook

- **7A.2**: Wave-particle duality.
- **7B.1**: The Schroedinger equation.
- **7B.2**: The Born interpretation of the wave function.
- **7C.1**: Operators.
- **7C.2**: Superpositions and expectation values.
- **7C.3**: The uncertainty principle.
- **7D.1**: Free motion in one dimension.

From Quantum to Molecule

Dr Juan Rojo
VU Amsterdam and Nikhef Theory Group
http://www.juanrojo.com/
j.rojo@vu.nl

3 HC3: The quantum mechanics of simple systems

In the previous lectures we have studied the solutions of the Schroedinger equation of the simplest possible quantum system: the free particle in one dimension. In this lecture, we discuss quantum mechanics applied to other important systems such as a particle in a confining box and the quantum harmonic oscillator. We will study some remarkable phenomena that appear in these systems that do hot have an analog in classical mechanics, such as that the *the quantization of energies* and the *quantum tunneling* effect.

The **learning goals** of this lecture are:

(a) Learn how to solve the Schroedinger equation for simple quantum systems.

(b) Understand that confinement of a quantum particle in space leads to the quantization of its energy levels and to a non-vanishing energy for the ground state.

(c) Interpret the physical content of the wave-functions from the solutions of the Schroedinger equation.

(d) Understand and applying the mathematical technique of separation of variables in differential equations.

(e) Verify that quantum particles can occupy regions of space which are classically forbidden.

(f) Understand and apply the phenomenon of quantum tunneling that arise in the presence of finite potential barriers.

3.1 The particle in a box and energy quantization

In the HC2, when we solved the Schroedinger equation for a free particle in absence of boundary conditions, we found that its energy E could take any value. Therefore, for a free particle allowed to move anywhere in space, its energy levels are continuous: there is no restriction on the values they can take. We now will see how once the particle is confined into a limited region of space, energy levels become automatically

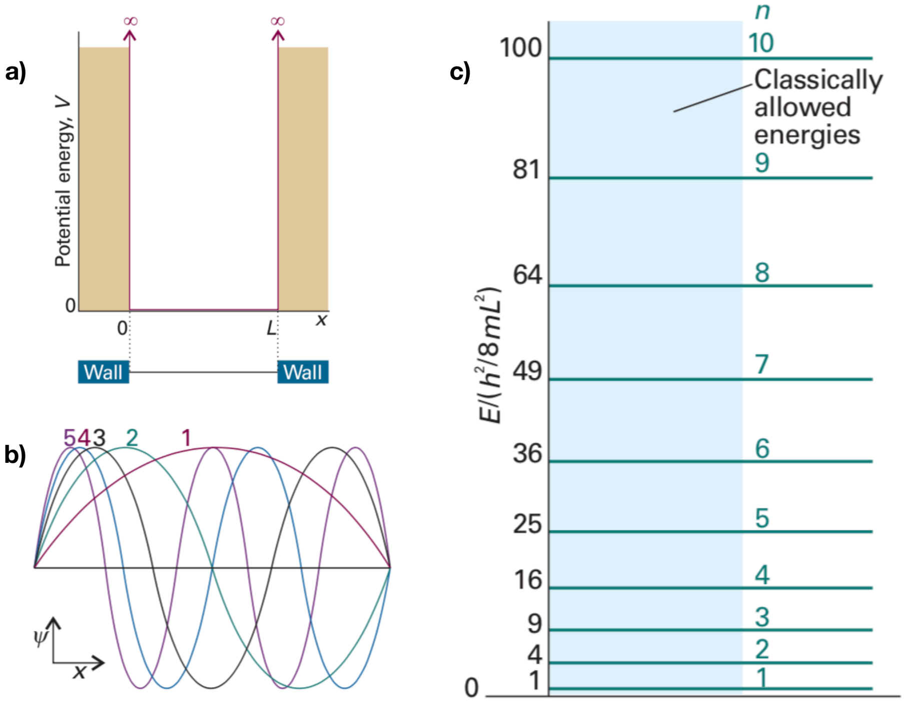


Figure 3.1: a) The potential $V(x)$ for the particle in a box system. b) the normalised wave functions for the first five energy levels of this quantum system. c) The corresponding values of the quantized energies E_n. The filled blue band indicates the classically allowed values of the energy.

discretised, or in the quantum jargon, *quantized*. This is one of the most distinctive features of quantum theory that make it uniquely different to the classical picture.

By quantization we mean that the values of a given physical observable, such as the energy of a system, cannot take any continuous value but are instead restricted to a finite set of discrete values. One then says that the energy of the system is quantized: it can only take one of a finite set of value.

Perhaps the simplest system for which energy quantization arises is for the so-called *particle in a box* system. This system is defined by a single particle moving under the effects of a potential of the form

$$\begin{aligned} V(x) &= 0 \quad \text{for} \quad 0 \le x \le L\,, \\ V(x) &= +\infty \quad \text{for} \quad x < 0 \quad \text{and} \quad x > L\,, \end{aligned} \tag{3.1}$$

as illustrated in Fig. 3.3a. In other words, the particle undergoes free motion in the region $0 \le x \le L$, but cannot move outside this range because it is *confined* by the infinite potential barrier Eq. (3.1) (since the particle would need an infinite energy to overcome that potential barrier). Recall that, as discussed in HC1, in the presence of infinite potentials the wave function is still continuous but its derivate can be discontinuous.

Inside the region limited by the confining potential, $0 \le x \le L$, the solution of Schroedinger's equation will be the same as for a free particle (since the potential vanishes there) and thus we have

$$\Psi_k(x) = Ae^{ikx} + B^{-ikx} = (A+B)\cos(kx) + (A-B)i\sin(kx) \equiv D\cos(kx) + C\sin(kx)\,, \tag{3.2}$$

where we have expanded the exponentials using $e^{ix} = \cos(x) + i\sin(x)$ and then redefined the (arbitrary) integration coefficients for reason that will become apparent below. For the time being, k is a real constant that can take any value: we know that for a free particle the energies are not quantized.

Since in the region outside the box, $x > L$ and $x < 0$, we have that $V(x) = \infty$, the particle cannot travel to this region: it would require an infinite energy! This implies that the wave-function will be zero in that region: $\Psi(x) = 0$ for $x > L$ and $x < 0$. This means that there is a zero probability of finding the particle in the region outside the box.

Classically, a particle cannot occupy a region with potential $V(x)$ unless $E \geq V(x)$. The reason is that the total energy E is the sum of the kinetic T and potential V energies, $E = T + V$, and T is positive definite. However, in quantum theory this restriction does not hold, and particle with $E < V(x)$ can still occupy this region. As we will see below, however the probability that this happens is exponentially suppressed. The exception is when $V(x) = \infty$, in this case no matter the value of E no particle can occupy this region of x.

From these considerations, it follows that, since as discussed in Sect. 1.2 the wave function is continuous, we have that the following *boundary conditions* must be satisfied:

$$\Psi_k(x=0) = 0\,, \quad \Psi_k(x=L) = 0\,. \tag{3.3}$$

Therefore, the continuity requirement of the wave function leads to boundary conditions that can be used to fix the values of the integration constants that appear in Eq. (3.2):

$$\Psi_k(x=0) = D \to D = 0\;, \qquad \Psi_k(x=L) = C\sin(kL) = 0 \to k = \frac{n\pi}{L}\;, \tag{3.4}$$

where n is an arbitrary *integer number.* The value of the overall coefficient C can be determined from requiring the normalization of the wave-function:

$$1 = \int_{-\infty}^{\infty} dx\,|\Psi_k(x)|^2 = C^2\int_0^L dx\,\sin^2(n\pi x/L) \to C = \sqrt{\frac{2}{L}}\,. \tag{3.5}$$

Combining these results, and recalling that $\widehat{H}\Psi_n(x) = -(\hbar^2/2m)d^2/dx^2\Psi_n(x) = E_n\Psi_n(x)$, we find that:

for a free particle confined to a box, the quantum wave-functions and energies are given by

$$\Psi_n(x) = \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right)\;, \quad E_n = \frac{\hbar^2\pi^2 n^2}{2mL^2}\;. \tag{3.6}$$

Therefore, we now find that the *energies of the particle are quantized* (can only take a discrete set of values) and labeled by an integer number n. This can be compared to the case of the unbounded free-particle, where there were no such restrictions on the values that E could take.

In Fig. 3.3b we show the normalised wave functions for the first five energy levels of this quantum system, and in Fig. 3.3c the corresponding values of the quantized energies E_n, where the filled blue band indicates the classically allowed values of the energy.

A further interesting finding of this analysis is that the lowest energy that a particle can have in this system is not zero, but rather

$$E_{\rm min} = E_1 = \hbar^2\pi^2/2mL^2 \neq 0\,, \tag{3.7}$$

since $n = 0$ is not a valid quantum state since the wave function $\Psi_0(x) = 0$ everywhere. This is known as the *zero-point energy*, and is a consequence of the fact that a quantum particle in a confining potential cannot be completely at rest. Indeed, if the particle was at rest (vanishing kinetic energy), we would then know its momentum with arbitrary precision (if $p_x = 0$ then $\Delta p_x = 0$), contradicting Heisenberg's uncertainty principle: we have some information about the position of the particle, namely that it will be found between $x = 0$ and $x = L$.

The qualitative results found from the particle in a box system are fully general and apply to other systems: in quantum mechanics, *energy quantization* arises from the wave nature of the wave-function in the presence of boundary conditions, including periodic ones.

Let us now evaluate the expectation value of the linear momentum p_x for this system. As we have shown, the wave-function that solves the Schroedinger equation accounting for the boundary conditions of the system is given by

$$\Psi_n(x) = \sqrt{\frac{2}{L}}\sin\left(\frac{\pi n x}{L}\right)\,, \tag{3.8}$$

and if we compute the expectation value of p_x using Eq. (2.39) we find that

$$\langle p_x\rangle = \frac{2}{L}\int_0^L dx\sin\left(\frac{\pi n x}{L}\right)\left(\frac{\hbar}{i}\frac{d}{dx}\right)\sin\left(\frac{\pi n x}{L}\right) = \frac{2\hbar n\pi}{iL^2}\int_0^L \sin\left(\frac{\pi n x}{L}\right)\cos\left(\frac{\pi n x}{L}\right) = 0\,, \tag{3.9}$$

since the integral vanishes for any value of n, as can be checked using trigonometric identities:

$$\int dx\sin(ax)\cos(ax) = \frac{1}{2a}\sin^2(ax)\,. \tag{3.10}$$

So therefore we find that the expectation value of the momentum for the particle in a box is $\langle p_x\rangle = 0$. This result can be understood if we expand the solution Eq. (3.8) in terms of exponentials:

$$\Psi_n(x) = \sqrt{\frac{2}{L}}\sin\left(\frac{\pi n x}{L}\right) = \sqrt{\frac{1}{2L}}\frac{1}{i}\left(e^{i\pi n x/L} - e^{-i\pi n x/L}\right)\,, \tag{3.11}$$

which correspond to the superposition (with equal amplitude) of a plane wave moving in the positive direction with momentum $p_x = \hbar\pi n/L$ and another moving in the opposite direction with $p_x = -\hbar\pi n/L$, hence when averaging the two components of the wave-function, they cancel among them leading to $\langle p_x\rangle = 0$.

Finally, we note that in the $n \to \infty$ limit, the energies of the particle become *effectively continuous*, as expected in classical physics. This is the realization of the so-called *correspondence principle* of quantum theory: for large values of the quantum numbers, the behaviour of the quantum theory becomes effectively classical.

3.2 Particle in a two-dimensional box

The next system that we will consider is similar than the previous one, but now the box has *two dimensions* in space, which we will denote by x and y. Therefore, the confining 2D potential of this system will take the following form:

$$\begin{aligned} V(x,y) &= 0 \quad \text{for} \quad 0 \le x \le L_x \quad \text{and} \quad 0 \le y \le L_y \,, \\ V(x,y) &= +\infty \quad \text{for} \quad y < 0\,, \quad y > L_y\,, \quad x < 0\,, \quad x > L_x\,, \end{aligned} \tag{3.12}$$

where we allowed the dimensions of the box to be different, $L_X \neq L_Y$. Inside the box, the Schroedinger equation is the same as that of the free particle of the previous example but now in two dimensions, namely:

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right)\Psi(x,y) = E\Psi(x,y)\ , \tag{3.13}$$

where note that now the wave-function depends on two variables, x and y, and thus the derivatives that appear are *partial derivatives* rather than total derivatives.

To solve this differential equation, we need to adopt the method of *separation of variables*. In this method, one assumes that the full wave-function $\Psi(x,y)$ can be expressed as a product of two functions, each depending separately on x and y only, that is, one tries a solution of the form:

$$\Psi(x,y) = \Psi_X(x)\Psi_Y(y)\,. \tag{3.14}$$

If we plug this *ansatz* on the two-dimensional Schroedinger equation, Eq. (3.13), we obtain the following expression

$$-\frac{\hbar^2}{2m}\Psi_Y(y)\left(\frac{\partial^2}{\partial x^2}\right)\Psi_X(x) - \frac{\hbar^2}{2m}\Psi_X(x)\left(\frac{\partial^2}{\partial y^2}\right)\Psi_Y(y) = E\Psi_X(x)\Psi_Y(y)\,, \tag{3.15}$$

and now, if we divide each side of the equation by $\Psi(x,y)$, we find that

$$-\frac{\hbar^2}{2m}\frac{1}{\Psi_X(x)}\left(\frac{\partial^2}{\partial x^2}\right)\Psi_X(x) - \frac{\hbar^2}{2m}\frac{1}{\Psi_Y(y)}\left(\frac{\partial^2}{\partial y^2}\right)\Psi_Y(y) = E\,. \tag{3.16}$$

In Eq. (3.16), the right-hand side (RHS) is independent of both x and y, and in the left-hand side (LHS) we have the sum of two pieces, the first one depending *only on* x and the second one depending *only on* y. Therefore, the only way the equation can be true is if each piece is separately equal to a *constant*. If these two constants are denoted respectively by E_X and E_Y respectively, we find

$$-\frac{\hbar^2}{2m}\frac{1}{\Psi_X(x)}\left(\frac{\partial^2}{\partial x^2}\right)\Psi_X(x) = E_X\ , \tag{3.17}$$

$$-\frac{\hbar^2}{2m}\frac{1}{\Psi_Y(y)}\left(\frac{\partial^2}{\partial y^2}\right)\Psi_Y(y) = E_Y\ , \tag{3.18}$$

which are of course nothing but *two separate Schroedinger equations*, one for the x component of the wave function, $\Psi_X(x)$, and another for the y component of the wave function, $\Psi_Y(y)$. The total energy of the system is then $E = E_X + E_Y$, which justifies our choice of notation for the integration constants.

From the discussion above, we see that the solution of the Schroedinger equation for a particle in a 2D box will be given by the product of solutions to the same equation in a 1D box. That is, we will have that the x- and y-components of the wave functions are

$$\Psi_x(x) = \sqrt{\frac{2}{L_x}} \sin\left(\frac{n_x \pi x}{L_x}\right) , \tag{3.19}$$

$$\Psi_y(y) = \sqrt{\frac{2}{L_y}} \sin\left(\frac{n_y \pi y}{L_y}\right) , \tag{3.20}$$

and thus the *quantum state of the system* is now being defined by *two independent integer numbers* (n_x, n_y) (the two quantum numbers of the system), and therefore the total wave-function is

$$\Psi(x, y) = \Psi_x(x)\Psi_x(y) = \sqrt{\frac{4}{L_x L_y}} \sin\left(\frac{n_x \pi x}{L_x}\right) \sin\left(\frac{n_y \pi y}{L_y}\right) . \tag{3.21}$$

The total energy of a given quantum state of the system will be specified by the quantum numbers of this state, n_x and n_y, and thus if we take into account the result for the one-dimensional case, Eq. (3.6), we have that

$$E_{n_x,n_y} = \frac{\hbar^2}{2m}\left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2}\right) . \tag{3.22}$$

Note that in the limit in which $L_x = L_y = L$ there will be a *degeneracy* of quantum states, meaning that different quantum states, defined by different pairs of quantum numbers (n_x, n_y) will have associated the *same total energy.* In this limit indeed the total energy becomes

$$E_{n_x,n_y} = \frac{h^2}{8\pi^2 m}\left(\frac{n_x^2 + n_y^2}{L^2}\right) , \tag{3.23}$$

so for example the quantum state $(n_x = 1, n_y = 2)$ will correspond to a state with the same energy as that with $(n_x = 2, n_y = 1)$. Degeneracy is a generic property of quantum systems: in general, many different states can have associated the same total energy.

3.3 The quantum harmonic oscillator

In classical physics, when we have a particle with total energy E moving inside a conservative potential $V(x)$, the particle will *confined* to the region defined by $E \geq V(x)$. Indeed, from energy conservation we have that the sum

$$E = T + V(x) = \frac{1}{2}mv^2 + V(x) , \tag{3.24}$$

where T is the particle's kinetic energy, is a constant of motion and must hold for all values of x. Therefore, we have that

$$v^2 = \frac{2}{m}\left(E - V(x)\right) \tag{3.25}$$

can only be satisfied if $E \geq V(x)$, else the velocity would be an unphysical complex number. Therefore, the particle cannot move in the region of x for which $V(x) > E$: we know that this region is *classically forbidden.* However, in quantum physics this is *not* necessarily the case: a particle can occupy a region of space x where $E < V(x)$. This phenomenon is known as *quantum tunneling* and again has no classical counterpart. As we will see, such particle will have a exponentially suppressed probability of being found in the classically forbidden region.

Here we will study a extremely important quantum system, the quantum harmonic oscillator, which exhibits explicitly this tunneling behaviour. In classical mechanics, an *harmonic oscillator* is defined as particle moving under the effects of a *quadratic potential*, that is, a potential $V(x)$ of the form

$$V(x) = \frac{1}{2}\kappa x^2 \,, \tag{3.26}$$

where κ is known as the *spring constant* or *Hooke's constant.* Though physically this potential is usually associated to a system based on a frictionless body attached to a flexible spring, the form Eq. (3.26) is fully general and applies to many other potentials. In particular, any potential can be approximated by Eq. (3.26) in the region near local minima (as can be seen by doing a Taylor expansion), so harmonic oscillators are ubiquitous in quantum mechanics.

The harmonic potential Eq. (3.26) vanishes at $x = 0$, the *equilibrium* position of the particle. Note that this potential is *confining*, since it increases quadratically as $|x|$ increases, and thus a particle in this potential would never be able to completely escape from it, no matter how large its energy is. From this potential, at the classical level we can compute the force that the particle will experience, namely

$$F = -\frac{dV(x)}{dx} = -\kappa x \,, \tag{3.27}$$

which is known as *Hooke's law*: in an harmonic oscillator (or in general, for a quadratic potential) the force is attractive and proportional to the deviation with respect to the equilibrium position.

Let us now study the behaviour of a quantum particle under the effects of the potential Eq. (3.26), that is, a *quantum harmonic oscillator*. The Schroedinger equation associated to this system will now be:

$$-\frac{\hbar^2}{2m}\frac{d^2\Psi}{dx^2} + \frac{1}{2}\kappa x^2\Psi = E\Psi \,. \tag{3.28}$$

Solving this equation is beyond the scope of this course, though for completeness let me show here the explicit form of the solutions for the wave function:

$$\Psi_n(x) = \frac{1}{\sqrt{2^n n!}}\left(\frac{m\omega}{\pi\hbar}\right)^{1/4} e^{-m\omega x^2/2\hbar} H_n\left(\sqrt{\frac{m\omega}{\hbar}}x\right) \,, \tag{3.29}$$

where $H_n(x)$ are as special family of orthogonal polynomials known as *Hermite polynomials*, and we have defined the *frequency* of the oscillator as $\omega \equiv \sqrt{\kappa/m}$, in analogy with the classical treatment. The solutions of Eq. (3.28) are labeled by the quantum number n, which takes only integer values $n = 0, 1, 2, 3, \ldots$.

As a consequence of the potential barrier that confines the particle, the energies of the quantum harmonic oscillator are *quantized*, and it is possible to show that they are given by

$$E_n = \hbar\omega\left(n + \frac{1}{2}\right) \,. \tag{3.30}$$

There are two important consequences of this result. First of all, we note that the difference in energy between two adjacent quantum levels n and $n + 1$ is constant, that is

$$E_{n+1} - E_n = \hbar\omega \,, \tag{3.31}$$

independently of the value of n. Secondly we find that, in the same way as for the particle confined in a box, the energy of the *ground state* (that is, the *vacuum*) of the system, the eigenfunction with the smallest associated energy, is *different from zero*. Indeed we find that for $n = 0$ we get

$$E_0 = \frac{1}{2}\hbar\omega \,, \tag{3.32}$$

which is known as the *zero-point energy* of a quantum harmonic oscillator.

This is a direct consequence of Heisenberg's uncertainty principle: if the energy and momentum were zero, the particle would be at rest, and we would know p_x with arbitrary precision and thus $\Delta p_x = 0$. But then the indetermination on its position x would be maximal, as in the free particle case, and this is not possible due to the confining harmonic potential.

For small values of n, the Hermite polynomials that appear in the quantum wave-function Eq. (3.29) take relatively simple forms, and we list the first few of those:

$$\begin{aligned} H_0(y) &= 1\,, \\ H_1(y) &= 2y\,, \\ H_2(y) &= 4y^2 - 2\,, \\ H_3(y) &= 8y^3 - 12y\,, \end{aligned} \tag{3.33}$$

and so on. Therefore, for the ground state of the system, $n = 0$, the wave-function is

$$\Psi_0(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} e^{-m\omega x^2/2\hbar} \,, \tag{3.34}$$

which is known as a *Gaussian function*. It is easy to check explicitly that these wave-function is correctly normalized (as is the case for other values of n), by verifying that

$$\int_{-\infty}^{\infty} dx \, |\Psi_0(x)|^2 = 1 \,. \tag{3.35}$$

To show this, first one should make the change of variable $y \equiv \sqrt{m\omega/\hbar}x$ and then use the result for the Gaussian integral that

$$\int_{-\infty}^{\infty} dx \, e^{-x^2} = \sqrt{\pi} \,. \tag{3.36}$$

It is interesting to compare the probability densities for the position x for the first two energy levels, namely $|\Psi_0(x)|^2$ with $|\Psi_1(x)|^2$, where

$$\Psi_1(x) = \sqrt{2}\left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \sqrt{\frac{m\omega}{\hbar}} \, x \, e^{-m\omega x^2/2\hbar} \,, \tag{3.37}$$

This comparison is shown in Fig. 3.2, where we show the wave-function $\Psi_n(x)$ and its square $|\Psi_n(x)|^2$ (which remember represents the probability density for the position x) in the quantum harmonic oscillator for the first two eigenstates, $n = 0$ (left plot) and $n = 1$ (right plot).

We observe that while for $n = 0$ (the ground state) the maximum of the probability density $|\Psi|^2$ is found for $x = 0$ (the classical equilibrium position), for $n = 1$ (the first excited state) it is rather more likely to find the particle far from the equilibrium position. This property holds for other excited states: the higher the value of n, the more likely is to find the particle far from $x = 0$. This behaviour is consistent with the

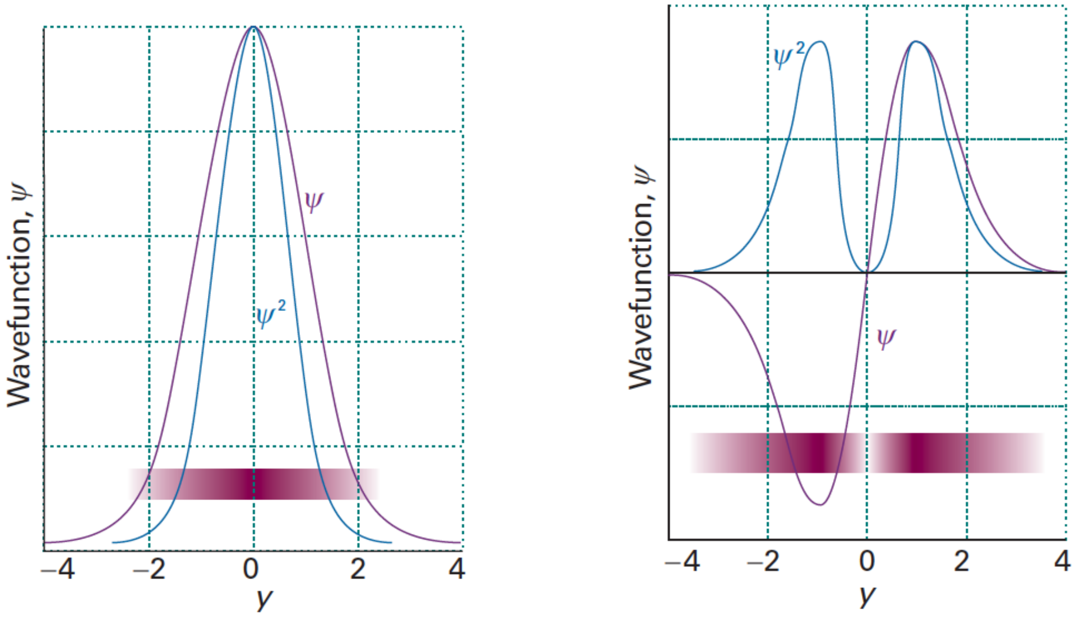


Figure 3.2: The wave-function $\Psi_n(x)$ and its square $|\Psi_n(x)|^2$ (which represents the probability density for the position x) in the quantum harmonic oscillator for the first two eigenstates, $n = 0$ (left plot) and $n = 1$ (right plot). We observe that while for $n = 1$ (the ground state) the maximum probability $|\Psi|^2$ is found for $x = 0$, for the excited state $n = 1$ it is rather more likely to find the particle far from the equilibrium position.

classical theory, where the harmonic oscillator spends more time in the turning points than in the equilibrium point because its velocity is the smallest in the former positions.

The exponential suppression in the wave function of the quantum harmonic oscillator, Eq. (3.29) implies that it goes to zero for $x \to \pm\infty$, no matter the value of n (that is, of how energetic is the particle). This is because the particle has a oscillatory behaviour in the region $E > V(x)$, but then decays exponentially in the classically forbidden region $E < V(x)$, which is eventually reached no matter how large is E (because of the form of the potential).

In classically forbidden regions, where $E < V(x)$, the wave function is always exponentially suppressed, for example with a behaviour of the form $\Psi(x) \propto e^{-Ax}$ or $\Psi(x) \propto e^{-Ax^2}$.

To gain intuition on the behaviour of quantum systems, it is always useful to plot graphically the wave functions and the associated probability distributions. In plotting a function $f(x)$, it is always useful to consider *(i)* which are the zeros of this function, $f(x)$, *(ii)* which are the local maxima and minima of this function, $df(x)/dx = 0$, and *(iii)* what are the asymptotic limits when $x \to \infty$. Let us consider as an example the first excited state of the harmonic oscillator, and for simplicity set $m\omega/\hbar = 1$, so that we wave function and the associated probability density read (ignoring overall constants):

$$\Psi_1(x) = xe^{-x^2/2}\,, \qquad P_1(x) = x^2 e^{-x^2}\,. \tag{3.38}$$

Note that in these units while the potential is proportional to $V(x) \propto x^2/2$ and the energy to $E_1 \propto 3/2$. We show in Fig. 3.3 the wave function $\Psi_1(x)$ and the associated probability density $P_1(x) = |\Psi_1(x)|^2$ for

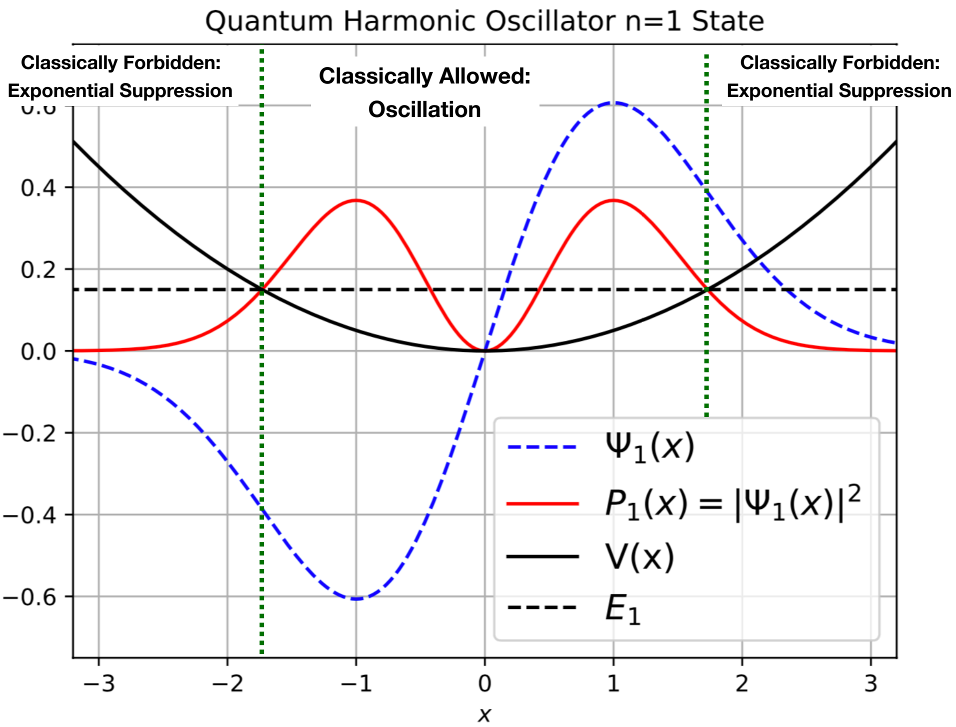


Figure 3.3: The wave function $\Psi_1(x)$ and the associated probability density $P_1(x) = |\Psi_1(x)|^2$ for the $n = 1$ level of the quantum harmonic oscillator. We also show (in suitably rescaled units) the potential $V(x)$ and the energy E_1. In the classically allowed region both $\Psi_1(x)$ and $P_1(x)$ exhibit an oscillatory behaviour, but in the classically forbidden region instead one observes an exponential suppression.

the $n = 1$ level of the quantum harmonic oscillator. We also show (in suitably rescaled units) the potential $V(x)$ and the energy E_1. One can see that in the classically allowed region both $\Psi_1(x)$ and $P_1(x)$ exhibit an oscillatory behaviour, but in the classically forbidden region instead one observes an exponential suppression.

Properties of the quantum harmonic oscillator. Since we have the wave-functions for all values of n, Eq. (3.29), we know that we have a complete knowledge of this quantum system, and thus we can compute the expectation values of arbitrary physical observables. First of all, we can show that the expectation value of the position x of the harmonic oscillator is, for any value of the quantum number n,

$$\langle x \rangle = 0 \,, \tag{3.39}$$

in other words, the particle has a symmetric distribution of positions around the classical equilibrium position $x = 0$. This can be easily shown by noting that

$$\langle x \rangle = \int_{-\infty}^{\infty} dx \, x \, |\Psi(x)|^2 \sim \int_{-\infty}^{\infty} dx \, x \, e^{-m\omega x^2/\hbar} \left[H_n \left(\sqrt{\frac{m\omega}{\hbar}} x \right) \right]^2 = 0 \,, \tag{3.40}$$

since the *integrand is an odd function*, $f(x) = f(-x)$, and the integration range is symmetrical. To see this, note that $H_n(-x) = \pm H_n(x)$ for any values of n.

Having established that in the quantum harmonic oscillator the particle can be found with equal probability at the right and at the left of the equilibrium position, it is perhaps more interesting to now compute its *mean square displacement*, given by

$$\left\langle x^2 \right\rangle = \left(n + \frac{1}{2} \right) \frac{\hbar}{\sqrt{m k_f}} \, . \tag{3.41}$$

Therefore, the *standard deviation* of the position x is

$$\Delta x \equiv \sqrt{\langle x^2 \rangle - \langle x \rangle^2} = \sqrt{\left(n + \frac{1}{2} \right) \frac{\hbar}{(m k_f)^{1/2}}} \tag{3.42}$$

which for large values of n grows like $\Delta x \sim \sqrt{n}$: the likelihood of finding the particle at a greater distance from $x = 0$ increases as the square root of the quantum number n, despite the fact that on average the expectation value will still be $\langle x \rangle = 0$. These results are consistent with the previous discussion above, based on the behaviour of the wave functions Ψ_n. From Heisenberg's uncertainty principle, Eq. (1.32) we can determine the standard deviation associated to measurements of the linear momentum of the quantum harmonic oscillator in this limit,

$$\Delta p_x \sim \frac{\hbar}{\Delta x} \sim \frac{\hbar}{n^{1/2}} \, , \tag{3.43}$$

so the higher the value of n, the better the momentum of the harmonic oscillator can be predicted (in the *correspondence limit*, we recover the classical expectation that p_x can be determined with vanishingly small uncertainty.)

There are other properties of this quantum system that are useful to compute. The expectation value of the potential energy is given by

$$\langle V \rangle = \frac{1}{2} k_f \left\langle x^2 \right\rangle = \frac{1}{2} \left(n + \frac{1}{2} \right) \hbar \left(\frac{k_f}{m} \right)^{1/2} = \frac{1}{2} \left(n + \frac{1}{2} \right) \hbar\omega \, , \tag{3.44}$$

where we have used the fact that the expectation value of an operator is *linear*, and the result for $\left\langle x^2 \right\rangle$ just computed above. Therefore, given that the complete energy of the quantum harmonic oscillator was Eq. (3.30), we find that $\langle V \rangle = E_n/2$, and thus for the kinetic energy $\langle E_k \rangle = E_n/2$. So in the quantum harmonic oscillator, the energy is *equally shared* between kinetic and potential, for any value of n. This is actually a consequence of a deep principle called the *equipartition theorem.* In other words, we have that for this quantum system

$$\langle E \rangle = \langle E_k \rangle + \langle V \rangle = \frac{1}{2} \langle E \rangle + \frac{1}{2} \langle E \rangle \, . \tag{3.45}$$

so on average half the total energy corresponds to the kinetic energy and the other half to the potential energy.

3.4 Quantum tunneling

As has been discussed in the case of the quantum harmonic oscillator, in quantum theory particles have small but finite probabilities of being found in classically forbidden regions with $E \leq V(x)$. This has the remarkable consequence that particles can cross potential barriers in a way that is not possible classically. In Newton's mechanics, if a particle with energy E encounters a potential barrier with $V > E$ it will be completely deflected. However in quantum theory there is a finite possibility that the particle will be able to jump to the other side of the barrier.

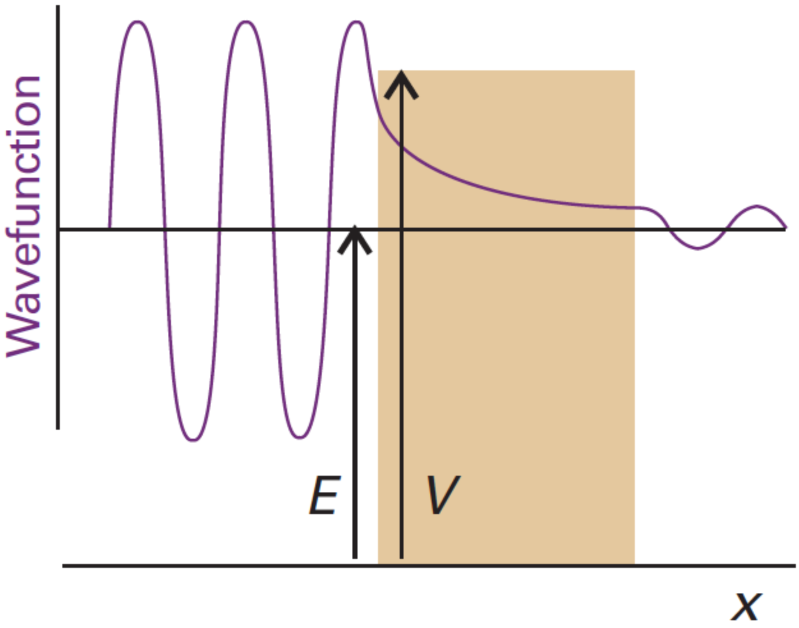


Figure 3.4: Schematic representation of the *quantum tunneling effect*: the wave-function of a particle with kinetic energy E_k is non-zero inside a barrier with potential energy $V > E_k$, and therefore has a finite probability (non-zero wave-function) to be found at the other side of the barrier. Note that the probability of finding the particle at the right side of the barrier is exponentially suppressed.

This remarkable phenomenon, the *quantum tunneling* effect, and is schematically represented in Fig. 3.4, where we show how the wave function of a particle is non-zero even in the classically forbidden region with $V > E_k$, and thus leads to a finite probability of finding the particle at the right of the potential barrier.

The quantum tunneling effect is a direct consequence of the wave-like nature of the wave function. We can now quantify and compute explicitly the value of the wave-function inside and on the other side of the potential barrier. As indicated in Fig. 3.4, at the left of the barrier we have $V = 0$, and thus the solution of the Schroedinger equation there is the usual free-particle solution, namely

$$\Phi_k(x) = Ae^{ikx} + Be^{-ikx} \, , \tag{3.46}$$

where the kinetic energy is $E_k = \hbar^2 k^2/2m$ and thus the linear momentum is $p_x = k\hbar = \sqrt{2mE_k}$. In the region *inside the barrier*, the Schroedinger equation is instead given by:

$$-\frac{\hbar^2}{2m}\frac{d^2\Psi}{dx^2} + V\Psi = E_k\Psi \, , \quad \text{with} \quad V \geq E_k \, . \tag{3.47}$$

Note that here I have identified the total energy of the particle E with the kinetic energy at the left side of the barrier, $E = E_k$, in order to *energy conservation* to be satisfied. Moreover, since the potential V is constant, this equation can be rewritten as

$$-\frac{\hbar^2}{2m}\frac{d^2\Psi}{dx^2} = -(V - E_k)\Psi \, , \tag{3.48}$$

which has the form of a free-particle equation, but this time with a *negative energy*, $\widetilde{E} = -(V - E_k)$. Using the same method as solution as for a free particle, we get that the wave-function inside the barrier is now

$$\Psi = C\, e^{\kappa x} + D\, e^{-\kappa x}\,, \quad \kappa \equiv \sqrt{2m\,(V - E_k)}/\hbar \geq 0\,, \tag{3.49}$$

which as an *exponential solution*, rather than the oscillatory solution of the free particle equation. Therefore, the wave-function is non-zero inside the barrier, despite $V > E_k$ and thus of being forbidden in classical physics: it was a finite probability of being found in the classically forbidden region.

Finally, in the region right to the barrier, we have again a free-particle solution for a particle moving in the positive x direction, that is

$$\Psi = A' e^{ikx}\,, \quad k = \sqrt{2mE_k}/\hbar\,, \tag{3.50}$$

with equal momentum and energy as in the left side of the barrier due to the principle of energy conservation. In order to determine the values of the five integration constants introduced above, A, B, C, D, A', we need exploit two properties of the wave-function: it is *continuous everywhere*, and its *derivative is also continuous* for any value of x in the presence of finite potentials.[1] If we label as $x = 0$ and $x = L$ the start and end points of the potential barrier, continuity of the wave-function there implies that

$$\begin{aligned} A + B &= C + D\,, \\ Ce^{\kappa L} + De^{-\kappa' L} &= A'e^{ikL}\,, \end{aligned} \tag{3.51}$$

while the continuity of the first derivative of the wave-function at the same endpoints implies that

$$\begin{aligned} ikA - ikB &= \kappa C - \kappa D\,, \\ \kappa Ce^{\kappa L} - \kappa De^{-\kappa L} &= ikA'e^{ikL}\,. \end{aligned} \tag{3.52}$$

Note that we have five unknowns and four equations, and therefore we can express four of these unknowns in terms of a single integration constant, say A, that can then be fixed from the overall normalisation condition.

Transmission and reflection coefficients. As we saw in the free-particle case, for the solution in the left side of the barrier, Eq. (3.46) we could make the interpretation that the Ae^{ikx} component of the wave function can be associated with the *incident wave* (since its momentum was $p_x = +\hbar k$), while the Be^{-ikx} instead would be the *reflected wave* (with momentum $p_x = -\hbar k$ pointing in the negative x direction). Therefore, we can define a ratio $T = A'/A$ which physically can be interpreted as the ratio of the amplitude of the *transmitted* wave over the *incident* wave, see Fig. 3.5. This *transmission coefficient* T can be computed using the values of the integration coefficients B, C, D, A' obtained as explained above, resulting in the following expression:

$$T\,(\kappa L, \epsilon) = \left(1 + \frac{\left(e^{\kappa L} - e^{-\kappa L}\right)^2}{16\epsilon(1-\epsilon)}\right)^{-1}\,, \quad \epsilon \equiv E/V\,, \tag{3.53}$$

and where κ has been defined in Eq. (3.49). The transmission amplitude T has a number of important limiting cases. When taking the various limits, note that κ depends implicitly on ϵ as well, since

$$\kappa\hbar = \sqrt{2m(V - E_k)} = \sqrt{2mV}\sqrt{1-\epsilon}\,. \tag{3.54}$$

With this caveat, it is possible to derive the following important properties of the transmission amplitude T:

---

[1] The first derivative of the wave function can be discontinuous in the case of infinite potential wells.

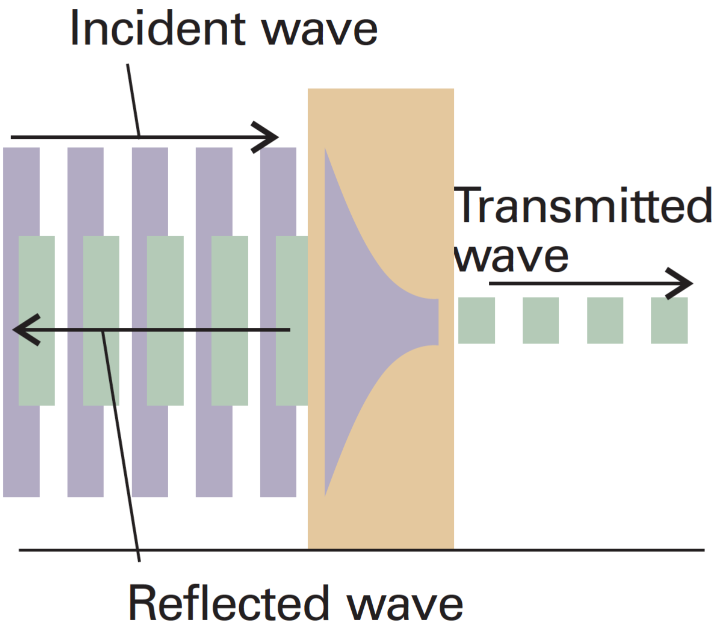


Figure 3.5: The physical interpretation of the quantum tunneling effect: an incident wave Ae^{ikx} left to the barrier is partially transmitted to the other side of the barrier with wave function $A' = e^{ikx}$ and partially reflected, with momentum in the opposite direction as compared to the incident wave, Be^{-ikx}. The ratio $T = A'/A$ of the transmitted over the incident amplitude is known as the *transmission coefficient.*

- In the limit $L \to 0$ for fixed κ, then the transmission coefficient $T \to 1$.

  This limit corresponds either to *very short barriers* L. In this two cases, it makes sense physically that the probability of tunneling becomes very high (and the amplitude of the *reflected way* conversely very small).

- In the limit $\kappa \to 0$ ($\epsilon \to 1$) for fixed L, then the transmission coefficient goes to

$$T \to \left(1 + \frac{mVL^2}{\hbar}\right)^{-1}, \qquad (3.55)$$

  so it does *not* tend to one even if $E_k \lesssim V$ (only in the case of very short barriers $L \to 0$ then $T \to 1$).

- For $E_k \ll V$, or what is the same $\epsilon \to 0$, we find that $T \to 0$.

  This can be physically understood from the fact that for a steep enough barrier, eventually the probability of transmission will become vanishingly small, in agreement with the *classical expectation.*

- As $E_k \to V$ ($\epsilon \to 1$), the value of the transmission amplitude increases monotonically, until the limiting value Eq. (3.55) is achieved.

- in the limit $\kappa L \gg 1$ the transmission amplitude Eq. (3.53) becomes

$$T \simeq 16\epsilon(1-\epsilon)e^{-2\kappa L}\,. \qquad (3.56)$$

  This limit corresponds to either very steep ($\kappa \to \infty$) or very long ($L \to \infty$) barriers, or the two at the same time. In this case we intuitively expect that the transmission probability will be small, and what Eq. (3.56) indeed shows is that T is *exponentially small* in this limit. We also note that $T \sim e^{-2L\sqrt{2mV}/\hbar}$, and thus that *lighter particles* will have a higher probability of tunneling that heavier particles.

The fact that the transmission coefficient Eq. (3.53) is different from zero is a striking deviation of quantum theory with respect to classical physics. The quantum tunneling effect indicates that for instance a naive particle picture of electrons or other quantum particles is far from adequate to describe the phenomena of the microcosm.

To conclude this discussion of the tunneling effect, recall that in HC2 we mentioned the *correspondence principle* of quantum theory, namely that in the appropriate limits the quantum behaviour should become effectively classical. In the case of the quantum tunneling effect, since we have that

$$\kappa = \frac{1}{\hbar}\sqrt{2m(V - E_k)}\,, \tag{3.57}$$

we find that, for fixed values of V and E_k, if $\kappa \to \infty$ then from Eq. (3.53) we see that $T \to 0$. This limit can be realized if

$$\hbar \ll \sqrt{2m(V - E_k)}\,. \tag{3.58}$$

Therefore, in this limit (where Planck's constant can be set to zero) we find that the tunneling probability goes to zero and this recover the classically expected behaviour.

Summary

To summarize, some of the important concepts that we have learned in this lecture are the following:

- The boundary conditions on the wave-function induced by a confining potential lead to the *quantization of the allowed energy levels.*
- This energy quantization is a generic property of quantum systems in the presence of boundary conditions, as shown also in other systems such as the particle in a box with finite barriers and the quantum harmonic oscillator.
- In several quantum systems, the energy of the ground state is different to zero, unlike in classical physics. We denote this effect as the *zero-point energy*, and it is a direct consequence of Heisenberg's uncertainty principle.
- Quantum particles have a non-zero probability of being measured *within classically forbidden regions*, and to tunnel potential barriers even when their kinetic energy is smaller than the energy of the barrier. This probability will however be very small, since it is exponentially suppressed.
- In some circumstances, quantum states can be *degenerate*, meaning that different states, characterized by different quantum numbers, can have associated the *same total energy.*
- In the *correspondence limit*, usually associated to high values of the quantum numbers of the system, quantum theory predictions should *reproduce their classical counterparts.*

Further reading

Further reading material about the topics covered in this lecture can be found in the following sections of the course textbook (*Physical Chemistry*, Atkins and De Paula, 11th edition):

Chapters in textbook

- **7D.2**: Confined motion in one dimension.
- **7D.3** Confined motion in two or more dimensions.
- **7D.4**: Tunneling.
- **7E.1**: The harmonic oscillator.
- **7E.2**: The properties of oscillators

From Quantum to Molecule

Dr Juan Rojo
VU Amsterdam and Nikhef Theory Group
http://www.juanrojo.com/
j.rojo@vu.nl

4 HC4: Rotational motion in quantum mechanics

In this lecture, we discuss the quantum mechanics of systems characterised by rotational symmetry. In particular, we solve the Schroedinger equation for particles confined to a ring and to the surface of a sphere. We show how adopting a different coordinate system than Cartesian coordinates simplifies dramatically the solution of these problems. We also study the role that angular momentum plays for this systems. These systems are important in order to understand the quantum mechanics of the hydrogen atom as well as more complex atoms and molecules, as will be discussed in the following lectures.

The **learning goals** of this lecture are the following:

(a) Become familiar with the concept of angular momentum in classical mechanics.

(b) Demonstrate the quantization of both the total angular momentum and of its individual components in systems characterised by rotational symmetry.

(c) Solve Schroedinger's equation for a free particle in a ring.

(d) Solve Schroedinger's equation for a free particle in a sphere.

Introduction. Quantum systems characterised by rotational symmetry are of great importance for the study of the physics of atoms and molecules. The obvious example is the hydrogen atom, a system composed by a proton and an electron bound together by the electrical force: since the Coulomb force depends only on the modulus of the separation $\vec{r}$ between the electron and the proton

$$F_C = -k\frac{Q_e Q_p}{|\vec{r}|^2} \tag{4.1}$$

then the system is characterised by an invariance under rotations that determines many of its most important properties, such as which specific quantum states are allowed.

With this motivation, both in this chapter and in the following ones we will study the implications of quantum mechanics for systems exhibiting rotational symmetry, both in two and in three spatial dimensions.

For these systems the use of Cartesian coordinates is not practical, so first of all we will have to introduce more suitable coordinate systems that fully exploit the benefits of rotational symmetry.

4.1 Polar and spherical coordinates

The solution of Schroedinger's equation in systems that exhibit rotational symmetry is greatly facilitated by using polar or spherical coordinates rather than Cartesian coordinates. The use of spherical coordinates makes also more transparent the physical interpretation of the corresponding results. With this motivation, we begin this lecture with a review of polar and spherical coordinates.

Polar coordinates. Let us start with polar coordinates, that are relevant for problems where the particles in the system are confined to the two-dimensional (x, y) plane. As illustrated in Fig. 4.2 (left), a point in the two-dimensional (x, y) plane can be represented in terms of its distance from the coordinate origin, r, and the angle with the x-axis, φ. The explicit expression for the coordinate transformation between polar and Cartesian coordinates is given by

$$\begin{aligned} x &= r\cos\varphi\,, \\ y &= r\sin\varphi\,, \end{aligned} \tag{4.2}$$

where the radius r satisfies $x^2 + y^2 = r^2$, and where the polar angle is restricted to the range $0 \le \varphi < 2\pi$. The inverse coordinate transformation is given by

$$\begin{aligned} r &= \sqrt{x^2+y^2}\,, \\ \varphi &= \arctan\left|\frac{y}{x}\right|, \end{aligned} \tag{4.3}$$

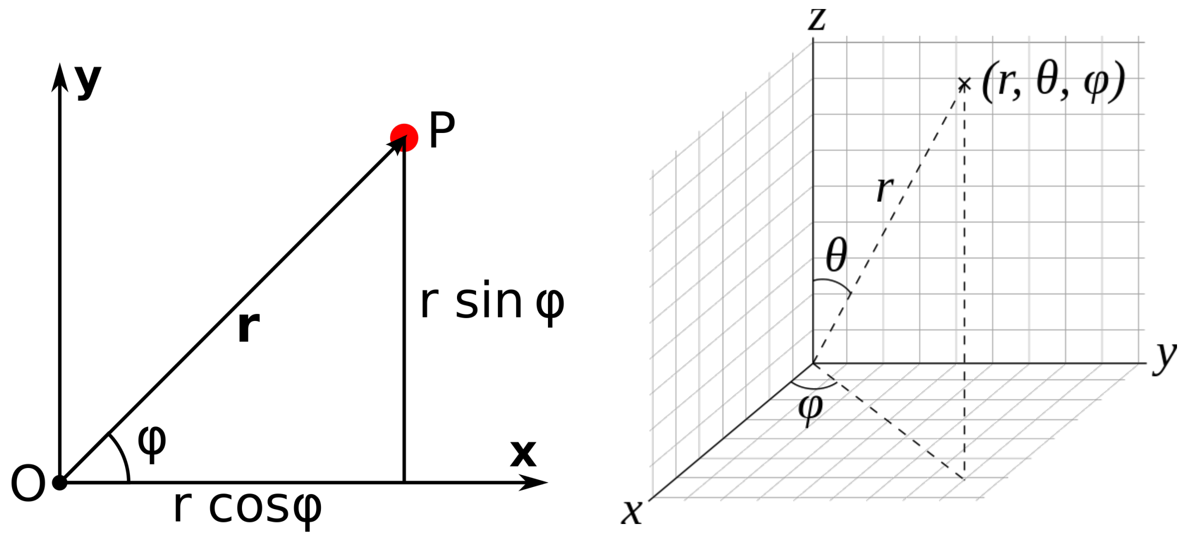
for φ lying in the first quadrant.

When computing transformations between Cartesian and spherical coordinates, it is useful to know the *Jacobian matrix* of the transformation, namely the set of partial derivatives between one set of coordinates with respect to the others. In this case, the Jacobian matrix is given by the following:

$$\begin{aligned} \frac{\partial r}{\partial x} &= \frac{\partial}{\partial x}\sqrt{x^2+y^2} = \frac{x}{\sqrt{x^2+y^2}} = \frac{x}{r} = \cos\varphi\,, \\ \frac{\partial r}{\partial y} &= \frac{\partial}{\partial y}\sqrt{x^2+y^2} = \frac{y}{\sqrt{x^2+y^2}} = \frac{y}{r} = \sin\varphi\,, \\ \frac{\partial \varphi}{\partial y} &= \frac{\partial}{\partial x}\arctan\left|\frac{y}{x}\right| = \frac{1}{1+y^2/x^2}(-y/x^2) = -\frac{y}{r^2} = -\frac{\sin\varphi}{r}\,, \\ \frac{\partial \varphi}{\partial y} &= \frac{\partial}{\partial y}\arctan\left|\frac{y}{x}\right| = \frac{1}{1+y^2/x^2}(1/x) = \frac{x}{r^2} = \frac{\cos\varphi}{r}\,, \end{aligned} \tag{4.4}$$

which can be used when doing the conversion between the two sets of coordinates, as will be illustrated below.

Spherical coordinates. Analogously to the definition of polar coordinates, for a particle moving in the three-dimensional space (x, y, z), one can define *spherical coordinates* as represented schematically in Fig. 4.2. In addition to r and φ (which in this context is referred to as the *azimuthal angle*) we now have a second angle called the *polar angle* θ. The equations for the coordinate transformation between Cartesian and spherical



Polar coordinates *Spherical coordinates*

Figure 4.1: Left: in two dimensions, a point in the (x, y) plane can be represented by the polar coordinates (r, φ). Right: in three-dimensions, a point in the (x, y, z) space can be represented by the spherical coordinates (r, θ, φ). See text for more details.

coordinates in three dimensions are given by

$$\begin{aligned} x &= r \sin\theta \cos\varphi \,, \\ y &= r \sin\theta \sin\varphi \,, \\ z &= r \cos\theta \,, \end{aligned} \tag{4.5}$$

where analogously to the case of polar coordinates we have the relation $r^2 = x^2 + y^2 + z^2$. The spherical coordinates have the following ranges:

$$0 \le r \le \infty \,, \qquad 0 \le \theta \le \pi \,, \qquad 0 \le \varphi \le 2\pi \,. \tag{4.6}$$

The inverse transformation, namely from Cartesian coordinates to spherical coordinates, takes the form

$$\begin{aligned} r &= \sqrt{x^2 + y^2 + z^2} \,, \\ \theta &= \arccos\left(\frac{z}{\sqrt{x^2 + y^2 + z^2}} \right) = \arccos\left(\frac{z}{r} \right) \,, \\ \varphi &= \arctan \frac{y}{x} \,. \end{aligned} \tag{4.7}$$

The usefulness of spherical coordinates for problems with rotational symmetry, as we will see, stems for the simplification of the corresponding Schroedinger equation when using variables that reflect the underlying symmetries of the problem. In particular, the three-dimensional Schroedinger equation for a system with rotational symmetry can be *separated* as a modified one-dimensional equation for the radial coordinate r and a universal differential equation for the angular variables θ and φ, as we will show shortly.

We can now use the equations of the polar and spherical coordinates to solve Schroedinger's equation for two important quantum systems: a particle that is confined to move in a *ring*, and a particle which is confined to move in the *surface of a sphere*.

4.2 Quantum mechanics of a particle in a ring

In HC3, we have applied Schroedinger's equation to determine the wave function $\Psi(x)$ of a variety of quantum systems. In particular, we considered the quantum mechanics of a particle confined in a box. There we found that the quantization of both the particle energy and of the allowed wave functions was a direct consequence of the boundary conditions required at the walls of the box due to the infinite potential barrier present.

Now we move to consider another quantum system of great importance for the understanding of the behaviour of atoms and molecules, namely the quantum mechanics of a particle undergoing rotational motion. We will start with the two-dimensional case (particle in a ring) and then move to the three-dimensional case (particle confined in the surface of the sphere). As we will see, also for these systems both the energy and the allowed wave functions are quantized. Here the underlying reason for the quantization will be not the presence of an infinite potential barrier, but rather the *periodic boundary conditions* that the wave function should satisfy due to the rotational symmetry.

Classical description and angular momentum. Let us first review the classical system. We consider here a particle following circular motion with a fixed radius R. As you have seen in the Mechanics course, the *angular momentum* associated to the motion of this particle is given by

$$\vec{J} = \vec{r} \times \vec{p} \, , \tag{4.8}$$

where $\vec{p} = m\vec{v}$ is the linear momentum, m is the mass, and $\vec{r}$ is the position vector with respect the origin of coordinates. In this equation, $\times$ stands for the cross-product between two vectors $\vec{v}_1$ and $\vec{v}_2$, defined for a three-dimensional vector space as

$$\vec{v}_1 \times \vec{v}_2 = \left(|\vec{v}_1||\vec{v}_2|\sin\theta\right)\vec{n} = \left(v_{1,y}v_{2,z} - v_{1,z}v_{2,y}\right)\hat{i} + \left(v_{1,z}v_{2,x} - v_{1,x}v_{2,z}\right)\hat{j} + \left(v_{1,x}v_{2,y} - v_{1,y}v_{2,x}\right)\hat{k} \, , \tag{4.9}$$

where θ is the angle between the two vectors in the plane that contains them, $\vec{n}$ is a unit vector perpendicular to the same plane, and $\hat{i}, \hat{j}, \hat{k}$ are the unit vectors in the x, y, and z directions respectively.

The angular momentum $\vec{J}$ of a particle undergoing a circular motion will be perpendicular both to the position vector $\vec{r}$ and the linear momentum $\vec{p}$, as illustrated in Fig. 4.2. For example, in the case of circular motion in the (x, y) plane, the angular momentum points in the z direction, $\vec{J} = (0, 0, J_z)$ where $J_z = \pm R|\vec{p}|$ and R is the radius of the circular motion. The sign of J_z depends on whether the circular motion is clockwise or counterclockwise.

In classical mechanics, the kinetic energy for a particle undergoing circular motion is given by

$$E_{\rm kin} = \frac{J^2}{2mR^2} = \frac{J^2}{2I} \, , \tag{4.10}$$

with $I = mR^2$ is the *moment of inertia* and $J \equiv |\vec{J}|$. This can be compared with the kinetic energy for a particle undergoing linear motion, where we have the usual expression of

$$E_{\rm kin} = \frac{1}{2}mv^2 = \frac{p^2}{2m} \, . \tag{4.11}$$

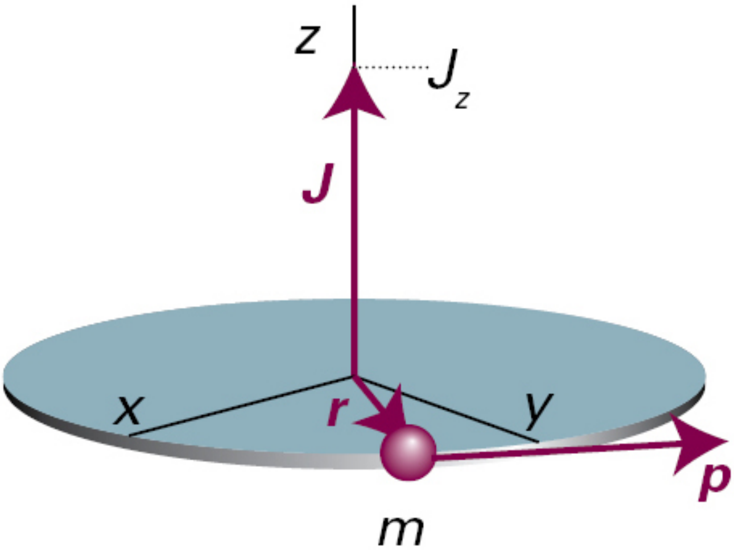


Figure 4.2: The angular momentum $\vec{J}$ of a particle undergoing a circular motion in the (x, y) plane is perpendicular both to the position vector $\vec{r}$ and the linear momentum $\vec{p}$, and therefore it points into the z direction, $\vec{J} = (0, 0, J_z)$.

Note that of course the two expressions are equivalent for circular motion, where $J = Rp$ and therefore Eq. (4.10) reads $E_{\rm kin} = J^2/2I = R^2p^2/2mR^2 = p^2/2m$.

Note that in the classical case both the kinetic energy E and the total angular momentum $\vec{J}$ of the particle in a ring can take any values. As we will see now, this is not true in the quantum case where both physical quantities will be quantised. Similarly as the case of a particle in a box, this quantization will arise once we impose boundary conditions on the quantum wave function of the system.

Quantum description. Let us now study the particle in a ring from the point of view of quantum mechanics. For a particle moving in the (x, y) plane, the time-independent Schroedinger's equation reads

$$\widehat{H}\Psi(x, y) = E\Psi(x, y) \,, \tag{4.12}$$

where the Hamiltonian operator for a free particle in two dimensions is given by

$$\widehat{H} = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right) \,. \tag{4.13}$$

In order to exploit the rotational symmetry of the system, we will perform a coordinate transformation from Cartesian to polar coordinates, Eq. (4.2). In polar coordinates, it can be shown that the Hamiltonian will be given by

$$\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} = \frac{\partial^2}{\partial r^2} + \frac{1}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\frac{\partial^2}{\partial \varphi^2} \,, \tag{4.14}$$

and therefore Schroedinger's equation in polar coordinates reads

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial r^2} + \frac{1}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\frac{\partial^2}{\partial \varphi^2}\right)\Psi(r, \varphi) = E\Psi(r, \varphi) \,. \tag{4.15}$$

To obtain the expression of the Hamiltonian in polar coordinates, one needs to apply the chain rule of derivation and use the Jacobian matrix for the change of coordinates, Eq. (4.4). We now need to solve this equation to determine the allowed values of the energy and the wave function for a particle confined to move in a ring.

In order to solve this differential equation, first of all we note since since for a particle in a ring the radial coordinate, $r = R$, is constant, then the wave function can depend only on the polar angle: $\Psi = \Psi(\varphi)$. This property can also be derived by noting that $r = R$ is not a dynamical variable of the system but only an external parameter. Therefore, the derivatives of the wave function with respect to the radial coordinate r will vanish. With this simplification, the general expression of Schroedinger's equation in polar coordinates, Eq. (4.15), reads

$$-\frac{\hbar^2}{2I}\frac{d^2}{d\varphi^2}\Psi(\varphi) = E\Psi(\varphi)\,, \tag{4.16}$$

where we have used the fact that $mR^2 = I$ is the moment of inertia of the particle. Formally, Eq. (4.16) is the same type of differential equation as that of a one-dimensional free-particle, Eq. (1.28). Therefore, it admits the same form of solutions, namely a linear combinations of exponentials of the form:

$$\Psi(\varphi) = A\exp\left(i\sqrt{\frac{2IE}{\hbar^2}}\varphi\right) + B\exp\left(-i\sqrt{\frac{2IE}{\hbar^2}}\varphi\right)\,, \tag{4.17}$$

where A and B are integration constants to be determined by the boundary conditions and the normalization of the wave function. In Eq. (4.17) the particle energy E can take in principle any value. However, we need to make sure that the wave function satisfies the boundary conditions of the problem.

In the case of the particle in a box, we imposed the *continuity boundary conditions* $\Psi(x = 0) = \Psi(x = L) = 0$ which stem from the fact that the wave function vanished outside the box. For a particle restricted to move in a ring, the wave function should satisfy the *periodicity condition boundary conditions* instead, which in this case read

$$\Psi(\varphi + 2\pi) = \Psi(\varphi)\,, \tag{4.18}$$

given that the angles φ and $\varphi + 2\pi$ are identical and thus the quantum state should be the same.

What are the implications of these periodicity boundary condition? For the wave function Eq. (4.17) to be invariant over the transformation Eq. (4.18), we need to impose that

$$\exp\left(i\sqrt{\frac{2IE}{\hbar^2}}(\varphi+2\pi)\right) = \exp\left(i\sqrt{\frac{2IE}{\hbar^2}}\varphi\right) \quad\to\quad \exp\left(2\pi i\sqrt{\frac{2IE}{\hbar^2}}\right) = 1\,, \tag{4.19}$$

which in turn implies that only a specific discrete set of values of the energy E will lead to physically acceptable solutions, namely those that satisfy

$$\sqrt{2IE_m}/\hbar = m \tag{4.20}$$

with m an integer number. Therefore we find that

The energy of a free particle confined to a ring is *quantized* due to the periodic boundary conditions. This means that we can label the physically allowed wave functions as $\Psi_m(x)$, with m being an angular quantum number that labels each eigenvector and eigenvalue of the Hamiltonian.

Therefore the solutions of the Schroedinger equation for a particle confined to a ring will be of the form of Eq. (4.17) subject to the condition Eq. (4.20), that is, they will have the form

$$\Psi_m(\varphi) = A\exp\left(im\varphi\right)\,, \qquad m = 0, \pm 1, \pm 2, \ldots\,, \tag{4.21}$$

where m is the angular integer (positive or negative) quantum number labeling the solutions, each with an associated kinetic energy with value

$$E_m = \frac{m^2\hbar^2}{2I}\,. \tag{4.22}$$

Moreover, using the relation between energy and angular momentum, $E = J_z^2/2I$, we find that also the angular momentum is quantised,

$$J_{z,m} = m\hbar\,, \tag{4.23}$$

and therefore the quantization of the energy of the particle implies that also its angular momentum is quantized. We observe here that $\hbar$ plays the role of the *quantum* of angular momentum: for all the states of the particle in a ring, the angular momentum is an integer multiple of $\hbar$. States with positive (negative) m correspond to positive (negative) angular momenta. Note also that the ground state is $m = 0$, where $\Psi_0 = (2\pi)^{-1/2}$ is independent of the value of φ, and the angular momentum (and the energy) vanishes.

In general the solutions in Eq. (4.21) will not be normalised. We can however easily normalise them by applying the normalisation condition,

$$\int_0^{2\pi} d\varphi\, \Psi_m^*(\varphi)\Psi_m(\varphi) = A^2\int_0^{2\pi} d\varphi\, e^{\mp im\varphi}e^{\pm im\varphi} = A^2 2\pi = 1 \quad \to \quad A = \frac{1}{\sqrt{2\pi}}\,, \tag{4.24}$$

where we integrate over all the allowed values that the polar angle φ can take.

We have seen explicitly how for the particle in a ring the periodic boundary conditions that the wave-function must satisfy imply that both the energy and the angular momentum are quantised. Before moving forward, let us study in a bit more detail the role than angular momentum plays in quantum mechanics.

4.3 Angular momentum in quantum mechanics

The analysis of the quantum mechanics of a particle undergoing circular motion in a ring has demonstrated that the angular momentum is quantized. Let us now take a closer look at the interpretation of these results. At the classical level, for a particle following a circular motion in the (x, y) plane, its angular momentum is given, using the definition of the cross-product between two vectors, by

$$\vec{J} = \vec{r}\times\vec{p} = (x, y, 0)\times(p_x, p_y, 0) = (0, 0, xp_y - yp_x) = (0, 0, J_z)\;. \tag{4.25}$$

In quantum theory, physical observables have associated operators that act on the wave function. What is therefore the operator $\hat{J}_z$ associated to the z component of the angular momentum J_z?

To determine the expression of $\hat{J}_z$, we need to exploit the fact that J_z is expressed in terms of the position $\vec{x}$ and linear momentum $\vec{p}$ vectors, for which we know which are the corresponding operators. Thus we need to start with the classical expression

$$J_z = xp_y - yp_x \,, \tag{4.26}$$

and implement the following replacements:

Observable	**Operator**
x	$\hat{x} = x$
y	$\hat{y} = y$
p_x	$-i\hbar\frac{\partial}{\partial x}$
p_y	$-i\hbar\frac{\partial}{\partial y}$

and this way we can identify what is the expression for the angular momentum operator in quantum mechanics:

$$\widehat{J}_z = \frac{\hbar}{i}\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right) \,, \tag{4.27}$$

where note that we use partial rather than total derivatives, since the wave function depends now on the two spatial coordinates x and y.

Angular momentum in polar coordinates. As we have seen in the discussion of Sect. 4.2, the quantum description of the motion in a particle in a system with rotational symmetry is most transparent when using polar coordinates. So we want to express the angular momentum operator Eq. (4.27) in polar coordinates rather than in Cartesian coordinates. For this we will use the chain rule of the derivative, so that for a general function $f(x, y)$ one has:

$$\begin{aligned}
\frac{\partial}{\partial x} f(x,y) &= \frac{\partial}{\partial x} f\left(r(x,y), \varphi(x,y)\right) = \frac{\partial f}{\partial r}\frac{\partial r}{\partial x} + \frac{\partial f}{\partial \varphi}\frac{\partial \varphi}{\partial x} = \cos\varphi\frac{\partial f}{\partial r} - \frac{\sin\varphi}{r}\frac{\partial f}{\partial \varphi} \,, \\
\frac{\partial}{\partial y} f(x,y) &= \frac{\partial}{\partial y} f\left(r(x,y), \varphi(x,y)\right) = \frac{\partial f}{\partial r}\frac{\partial r}{\partial y} + \frac{\partial f}{\partial \varphi}\frac{\partial \varphi}{\partial y} = \sin\varphi\frac{\partial f}{\partial r} + \frac{\cos\varphi}{r}\frac{\partial f}{\partial \varphi} \,,
\end{aligned} \tag{4.28}$$

where we have exploited the expressions for the Jacobian matrix associated to the change of coordinates, Eq. (4.4). Therefore, once we include also the contribution from the position operator we find

$$x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x} = r\cos\varphi\left(\sin\varphi\frac{\partial}{\partial r} + \frac{\cos\varphi}{r}\frac{\partial}{\partial \varphi}\right) - r\sin\varphi\left(\cos\varphi\frac{\partial}{\partial r} - \frac{\sin\varphi}{r}\frac{\partial}{\partial \varphi}\right) = \frac{\partial}{\partial \varphi} \,, \tag{4.29}$$

where note that the contribution proportional to the partial derivative with respect to r vanishes. Therefore, we find that for a particle moving in the (x, y) plane, its angular momentum operator Eq. (4.27) has the following expression in polar coordinates:

$$\widehat{J}_z = \frac{\hbar}{i}\frac{\partial}{\partial \varphi} \,. \tag{4.30}$$

What are the eigenvalues and eigenvectors that we can associate to $\hat{J}_z$? First of all, we note that since we have constructed it in terms of $\hat{\vec{x}}$ and $\hat{\vec{p}}$, then $\hat{J}_z$ is automatically an Hermitian operator and thus it satisfies all the properties that were presented in Sect. 2.3. Second, if we construct the eigenvalue equation associated to $\hat{J}_z$ we have

$$\hat{J}_z\Psi_m(\varphi) = \frac{\hbar}{i}\frac{\partial}{\partial \varphi}\Psi_m(\varphi) = j_m\Psi_m(\varphi) \,, \tag{4.31}$$

where Ψ_m and j_m are the eigenfunctions and eigenvectors of the angular momentum operator respectively, labelled by the quantum number m. What are the solutions of this eigenvalue equation? We can try again a solution of the plane wave form

$$\Psi(\varphi) = A\exp(\pm iB\varphi)\,, \quad \rightarrow \quad \frac{\hbar}{i}\frac{\partial}{\partial\varphi}\Psi(\varphi) = \frac{\hbar}{i}A\,(\pm iB)\exp(\pm iB\varphi)\,, \tag{4.32}$$

which is indeed a solution of Eq. (4.31) with eigenvalue $j = \pm\hbar B$. In addition, as in the case of the Schroedinger equation, these wave functions should satisfy the periodicity boundary condition $\Psi(\varphi + 2\pi) = \Psi(\varphi)$, which is satisfied provided that $B = m$ is an integer number. Putting everything together, we find that the eigenvectors and eigenvalues of the angular momentum operator in polar coordinates, $\hat{J}_z$ in Eq. (4.30), are labelled by the quantum number m and are given by

$$\Psi_m(\varphi) = A\exp\left(im\varphi\right)\,, \quad j_m = m\hbar\,, \qquad m = 0, \pm1, \pm2, \dots \tag{4.33}$$

For a free particle confined to a ring, the eigenfunctions of the angular momentum and Hamiltonian (Schroedinger equation) operators are identical, and therefore, these quantum states have well defined values both of the kinetic energy and of the angular momentum.

We also note that the quantization conditions for the angular momentum that we found when solving Schroedinger equation for the free particle, Eq. (4.23) are the same than when solving the eigenvalue equation for the angular momentum operator.

4.4 Quantum mechanics of a particle in spherical motion

Following this discussion of the quantum mechanics of the particle in a ring, and in particular of the role played by the angular momentum, we now move to discuss the case of a quantum particle confined to move in the surface of a sphere of constant radius $r = R$. Such configuration is important to describe the electronic wave functions of atoms and molecules, as we will see in the subsequent lectures. As in the case of the particle in a ring, it is advantageous to use a coordinate system that exploits the rotational symmetry of the problem, and therefore here we will adopt spherical coordinates as represented in Fig. 4.3 and defined by the coordinate transformations of Eq. (4.5).

Once we transform the free-particle Hamiltonian in three space dimensions from Cartesian to spherical coordinates, the Schroedinger equation for a free particle reads

$$-\frac{\hbar^2}{2m}\left[\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\left(\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2} + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}\right)\right]\Psi(r,\theta,\varphi) = E\Psi(r,\theta,\varphi)\,. \tag{4.34}$$

This equation can be simplified by taking into account the fact that the wave function cannot depend on r since it is restricted to move in the surface of the sphere defined by $r = R$. Therefore, the differential equation that needs to be solved is:

$$-\frac{\hbar^2}{2mR^2}\left(\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2} + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}\right)\Psi(\theta,\varphi) = E\Psi(\theta,\varphi)\,. \tag{4.35}$$

In order to solve this equation, we will use the method of *separation of variables*. In this method, one *assumes* that the full wave function is the product of a function of the polar angle θ only, $\Psi_\theta(\theta)$, and another function of the azimuthal angle φ only, $\Psi_\varphi(\varphi)$, namely we have that our *ansatz* reads

$$\Psi(\theta,\varphi) = \Psi_\theta(\theta)\Psi_\varphi(\varphi)\,, \tag{4.36}$$

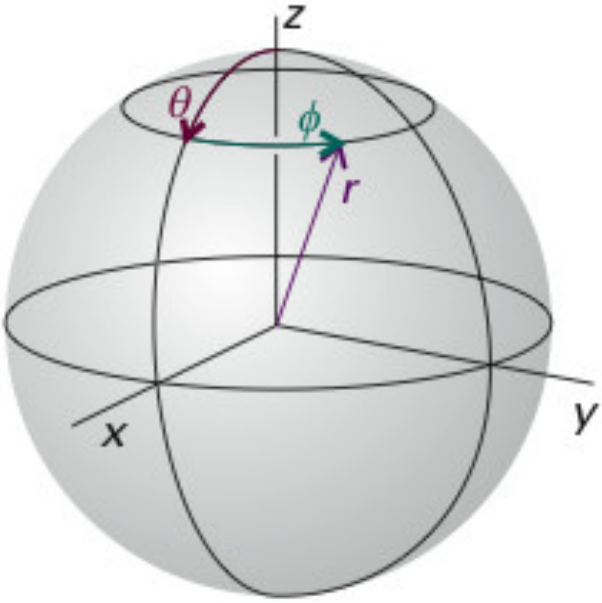


Figure 4.3: The motion of a particle confined to the surface of a sphere with fixed radius r are best described using spherical coordinates, see also Fig. 4.2.

and now we need to try if this *ansatz* satisfies Eq. (4.35). By plugging this ansatz it into the Schroedinger equation, one finds that

$$\frac{\Psi_\theta}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\Psi_\varphi + \frac{\Psi_\varphi}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}\Psi_\theta = -\frac{2mER^2}{\hbar^2}\Psi_\theta\Psi_\varphi\,, \tag{4.37}$$

which can be simplified to read

$$\frac{1}{\Psi_\varphi}\frac{\partial^2}{\partial\varphi^2}\Psi_\varphi + \frac{\sin\theta}{\Psi_\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}\Psi_\theta = -\frac{2mER^2}{\hbar^2}\sin^2\theta\,. \tag{4.38}$$

In the above equation, the first term of the LHS depends only on φ, while the second term of the LHC as well as the RHS depend only on θ. Therefore, the only way that this equation can be satisfied is if both the φ-dependent piece and the θ-dependent piece are equal to the same constant value, which we will denote for convenience m_l^2 for reasons that will become clear later. For the time being, m_l^2 just stands for a real positive constant, with no other restrictions about the values that it can take.

Therefore, we end up with two separate ordinary differential equations, each depending on a single variable, that we need to solve:

$$\frac{1}{\Psi_\varphi}\frac{\partial^2}{\partial\varphi^2}\Psi_\varphi = -m_l^2\,, \tag{4.39}$$

$$\frac{\sin\theta}{\Psi_\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}\Psi_\theta + \frac{2mER^2}{\hbar^2}\sin^2\theta \ = m_l^2. \tag{4.40}$$

For simplicity, in the following we will define

$$\epsilon \equiv \frac{2mR^2}{\hbar^2}E\,, \tag{4.41}$$

which is now a dimensionless number proportional to the total energy of the particle E. Our goal is to separately determine the expressions of $\Psi_\theta(\theta)$ and $\Psi_\varphi(\varphi)$ so that we can reconstruct the whole wave function Eq. (4.36).

Let us now solve these two independent differential equations. First of all, we want to solve the equation for the azimuthal angle, which can be rearranged to read

$$\frac{\partial^2}{\partial\varphi^2}\Psi_\varphi(\varphi) = -m_l^2\Psi_\varphi(\varphi) \tag{4.42}$$

but this is nothing but the Schroedinger equation for a free particle in a ring, Eq. (4.16). Therefore we know that m_l will be quantised, in the sense that it can only adopt integer numbers, and that the wave function will be of the form

$$\Psi_{\varphi,m_l}(\varphi) = \frac{1}{\sqrt{2\pi}}\exp(im_l\varphi)\,, \tag{4.43}$$

where m_l can only take only integer values and the wave function is normalised.

Now we need to solve the second differential equation, the one that determines the dependence of the wave function on the polar angle θ:

$$\frac{\sin\theta}{\Psi_\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}\Psi_\theta + \epsilon\sin^2\theta\ = m_l^2. \tag{4.44}$$

This differential equation is of a type called *Associated Legendre* equations. It is beyond the scope of the course to determine its solutions, and here we will just take them as given. As in the case of Ψ_φ, Ψ_θ must also obey periodic boundary conditions, in this case we have that

$$\Psi_\theta(\theta+2\pi) = \Psi_\theta(\theta)\,, \tag{4.45}$$

and this leads to introducing another quantum number related to angular momentum, which we denote by l. The values that these two quantum numbers, l and m_l, can take, are not independent, and it can be shown that the only allowed values are

$$\begin{aligned} l &= 0,1,2,3,\ldots \\ m_l &= -l,-l+1,-l+2,\ldots,l-2,l-1,l\,, \end{aligned} \tag{4.46}$$

so that for a quantum state characterised by the quantum number l, then m_l can only take $(2l+1)$ values, and one has that $|m_l| \le l$. As the values of the quantum numbers l and m_l increases, the expressions for the spherical Harmonics becomes more complicated.

Putting everything together, we find that the solutions of the Schroedinger equation for a particle in a sphere, Eq. (4.35), are given by

$$\Psi(\theta,\varphi) = \Psi_{\theta,l,m_l}(\theta)\Psi_{\varphi,l}(\varphi) \equiv Y_{l,m_l}(\theta,\varphi)\,, \tag{4.47}$$

where the functions $Y_{l,m_l}(\theta,\varphi)$ are called the *spherical harmonics.* The explicit expressions for the first few spherical harmonics are given in Table 1. It can be checked that all spherical harmonics are appropriately normalised, as corresponds to a quantum wave function. Note that for the ground state, the spherical harmonic with values $(l,m_l) = (0,0)$ is just a constant.

Let us discuss some important properties of the solution of Schroedinger equation for the particle in the sphere, that follow from the solution of the corresponding differential equations subject to the appropriate

l	m_l	$Y_{l,m_l}(\theta,\varphi)$
0	0	$\left(\frac{1}{4\pi}\right)^{1/2}$
1	0	$\left(\frac{3}{4\pi}\right)^{1/2}\cos\theta$
1	±1	$\mp\left(\frac{3}{8\pi}\right)^{1/2}\sin\theta e^{\pm i\varphi}$
2	0	$\left(\frac{5}{16\pi}\right)^{1/2}\left(3\cos^2\theta-1\right)$

Table 1: The first four spherical harmonics $Y_{l,m_l}(\theta,\varphi)$.

boundary conditions.

- Quantum states are labelled by a pair of quantum numbers (l, m_l), which have to satisfy the restrictions of Eq. (4.46).
- A quantum state characterised by the quantum numbers (l, m_l) has associated a kinetic energy E_l and *total angular momentum* J_l given by

  $$E = l(l+1)\frac{\hbar^2}{2mR^2}\,, \qquad J_l = \sqrt{l(l+1)}\hbar\,, \tag{4.48}$$

  as can be checked by recalling that $E = J^2/2mR^2$. Note that both J_l and E_l are independent of m_l.

  The total angular momentum $J_l \equiv |\vec{J}_l|$ should not be mixed with its component in the z direction J_z, since in general for a particle moving in three dimensions as in this case these can be different.[2]
- States with larger l correspond to greater angular momentum and kinetic energy E_l and J_l, as well as shorter de Broglie wavelengths.

  In Fig. 4.4 we show a schematic representation of the wave function of a particle in a sphere (the spherical harmonics defined in Eq. (4.47)) for the $l = 0, 1, 2, 3$. The distance of a point on the surface from the origin is proportional to the square modulus of the amplitude of the wave-function at that point.
- The value of m_l determines the *component of the angular momentum in the z direction*, as opposed to its total magnitude,:

  $$J_z = m_l\hbar\,, \tag{4.49}$$

  that can take $2l+1$ possible values. Therefore we find that both the *total magnitude* and the *orientation* of the angular momentum $\vec{J}$ are quantised for this system.

  In Fig. 4.5 we illustrate the allowed orientations of angular momentum vector $\vec{J}$ when $l = 2$, and only the values $m_l = -2, 1, 0, 1, 2$ are allowed. Recall that m_l determines the value of $J_z = m\hbar$, and that the total magnitude of the vector is fixed, $J = \sqrt{l(l+1)}\hbar = \sqrt{6}\hbar$ for $l = 2$.

---

[2] For a particle moving in two dimensions, then J_l and J_z coincide since they represent the same physical quantity.

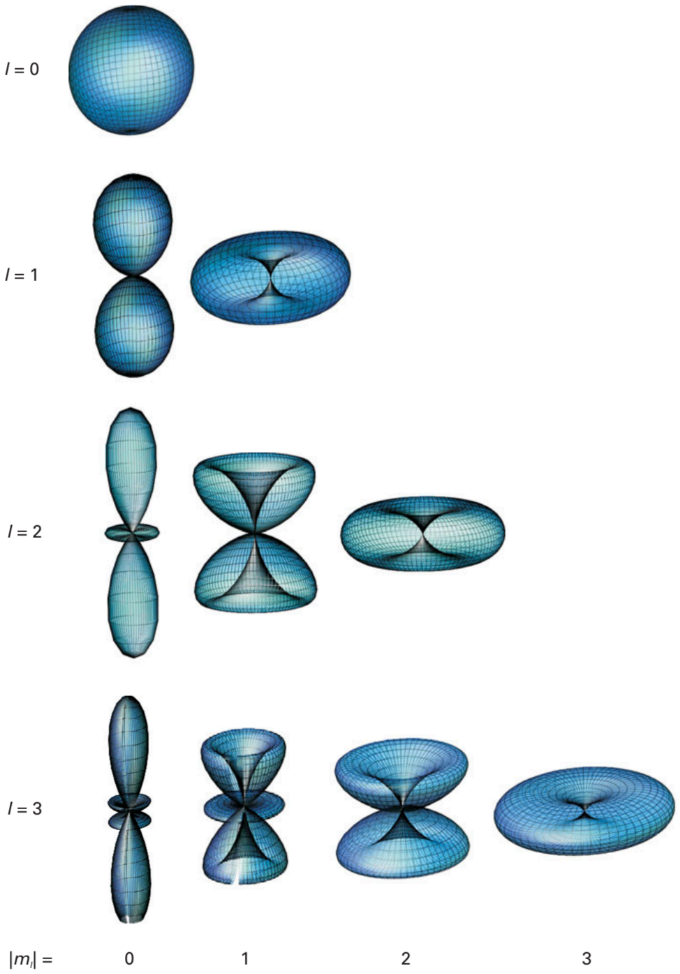


Figure 4.4: Schematic representation of the wave function of a particle in a sphere (the spherical harmonics defined in Eq. (4.47)) for the $l = 0, 1, 2, 3$. The distance of a point on the surface from the origin is proportional to the square modulus of the amplitude of the wave-function at that point.

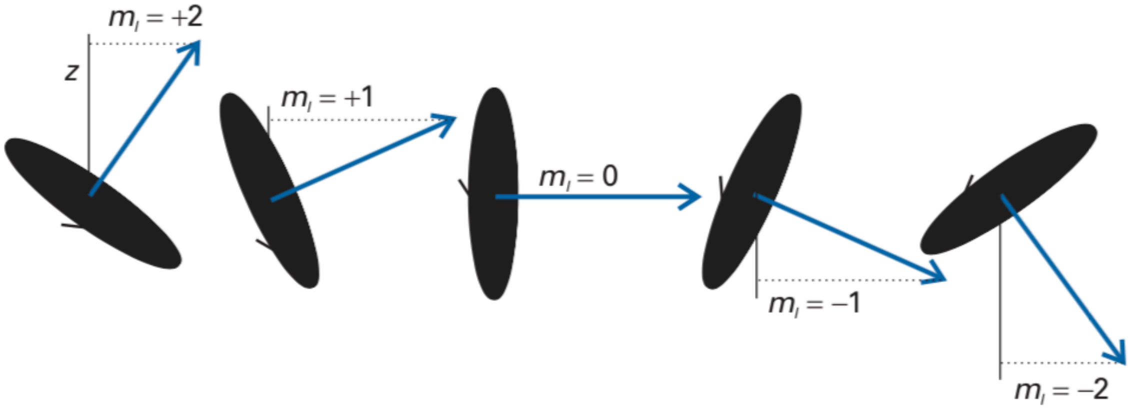


Figure 4.5: The permitted orientations of angular momentum vector $\vec{J}$ when $l = 2$, and only the values $m_l = -2, 1, 0, 1, 2$ are allowed. Recall that m_l determines the value of $J_z = m\hbar$, and that the total magnitude of the vector is fixed, $J = \sqrt{l(l+1)}\hbar = \sqrt{6}\hbar$ for $l = 2$.

4.5 Probabilistic interpretation in spherical coordinates

As for the case of all other quantum systems, the wave functions associated to the particle restricted to move in the surface of a sphere, Eq. 4.47, admit a probabilistic interpretation. In particular, it provides information about what should be the most likely location of a particle upon a measurement. However the use of spherical coordinates introduces some subtleties in the discussion.

Consider a particle moving in two-dimensions, that is, restricted to the (x, y) plane. The wave function will depend on the two coordinates, $\Psi(x, y)$, and the associated probability density is then $P(x, y) = |\Psi(x, y)|^2$. For example, the probability of finding the particle within a box of size $2L$ centered in the origin would be

$$\int_{-L}^{L} dx \int_{-L}^{L} dy \; P(x,y) = \int_{-L}^{L} dx \int_{-L}^{L} dy |\Psi(x,y)|^2 \, . \tag{4.50}$$

Likewise, the most likely values where to find the particle are given by the maxima of the probability distribution, given by the usual optimisation conditions,

$$\frac{\partial P(x,y)}{\partial x} = \frac{\partial P(x,y)}{\partial y} = 0 \, . \tag{4.51}$$

In the case of spherical coordinates, one might naively think that the corresponding probability density was simply $P(\theta, \varphi) = |Y_{l,m_l}|^2$. However, this is not correct, since one is missing the Jacobian factor due to the change of coordinates. The appropriate relation between probability densities in Cartesian and spherical coordinates for the particle restricted to the surface of the sphere is given by

$$P(x,y,z)dxdydz = P(x(\theta,\varphi), y(\theta,\varphi), z(\theta,\varphi))R^2 \sin\theta d\theta d\varphi \, , \tag{4.52}$$

and therefore the probability density associated to the angular variables will be instead

$$P_{l,m_l}(\theta,\varphi) = |Y_{l,m_l}(\theta,\varphi)||^2 \, \sin\theta \, , \tag{4.53}$$

with the additional factor of $\sin\theta$ arising from the Jacobian of the coordinate transformation. Using Eq. (4.55) one can now compute most likely values and expectation values for the position of a particle over the surface of the sphere. For example, the most likely values of θ and φ will now the defined by the condition

$$\frac{\partial P_{l,m_l}(\theta,\varphi)}{\partial \theta} = \frac{\partial P_{l,m_l}(\theta,\varphi)}{\partial \varphi} = 0 \, , \tag{4.54}$$

for a given pair of values of the angular quantum numbers m and m_l. Note that these conditions return both local maxima and minima, so one need to tell them apart. This is in general easy since the probability density of the angular variables $P_{l,m_l}(\theta, \varphi)$ usually vanishes at minima.

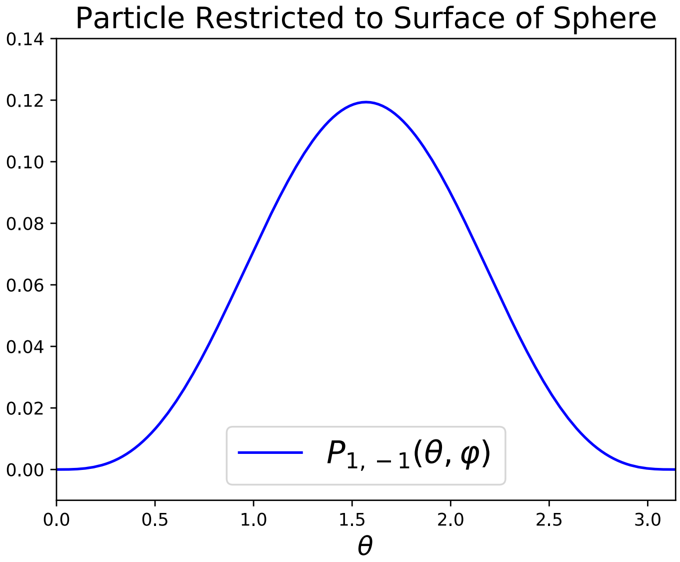


Figure 4.6: The probability density associated to the state $(l, m_l) = (1, -1)$ of a particle restricted to the surface of a sphere, as a function of the polar angle θ.

Assume that a particle in the surface of a sphere has the quantum numbers $l = 1$ and $m_l = -1$. We would like to compute the most likely position of the particle in the sphere's surface. Using Eq. (4.55), the corresponding probability density will be

$$P_{1,-1}(\theta,\varphi) = |Y_{1,-1}(\theta,\varphi)||^2 \sin\theta = \frac{3}{8\pi}\sin^3\theta\,. \tag{4.55}$$

Therefore the most likely value of θ will be given by the solutions of the condition

$$\frac{\partial}{\partial\theta}\left(\frac{3}{8\pi}\sin^3\theta\right) = 0 \quad \rightarrow \quad \sin^2\theta\cos\theta = 0 \tag{4.56}$$

which is satisfied by $\theta = 0, \pi/2, \pi$. Since $\theta = 0, \pi$ correspond to minima (the probability $P(\theta,\varphi)$ vanishes there), it turns out that $\theta = \pi/2$ is the only maximum and thus the most likely value of the polar angle. Furthermore, since $P_{1,-1}(\theta,\varphi)$ does not depend explicitly on φ, any value between 0 and 2π will be as likely as any other: the particle is completely delocalised in the azimuthal direction. Note that this probability distribution is appropriately normalised, since

$$\int_0^\theta d\theta \int_0^{2\pi} P_{1,-1}(\theta,\varphi) = 2\pi\frac{3}{8\pi}\int_0^\theta d\theta\sin^3\theta = 2\pi \times \frac{3}{8\pi} \times \frac{4}{3} = 1\,. \tag{4.57}$$

In Fig. 4.6 we represent graphically $P_{1,-1}(\theta,\varphi)$ as a function of the polar angle θ.

Summary

To summarize, some important concepts that we have learned in this lecture about the application of quantum theory to a particle moving either in circular or in spherical motion are the following:

- The description of quantum systems with rotation symmetry simplifies in a marked way when the dynamics of the system are expressed in polar (cylindrical) or spherical coordinates.
- Imposing cyclical boundary conditions leads to the quantization of the angular momentum associated to the rotating particle.
- The eigenstates of the energy and of the total angular momentum coincide. For a particle moving in a ring, the total angular momentum coincides with its z-component, but in general these two magnitudes are different.
- The wave function of a particle in a sphere is given by the spherical harmonics, whose shape is determined by the values of the angular quantum numbers (l, m_l) associated to each state.
- The spherical harmonics admit the standard probabilistic interpretation once the Jacobian factor from the coordinate transformation is taken into account.

In the next lecture, we will extensively use these concepts to the study of the solutions of the Schroedinger equation applied to the hydrogen atom. The interested student might want to consult the lectures notes of the 2018-2019 course as well as the further reading indicated below to learn more about angular momentum in quantum mechanics. Two important concepts in this respect that we do not have time to cover are the following. First of all, in the same way as Heisenberg's uncertainty principle prevents the simultaneous determination of the position and linear momentum of a particle, it is not possible to determine simultaneously the angular momentum and the angular position of a particle. Second, that only the total magnitude of the angular momentum $|\vec{J}|$ and its component in a given direction J_i can be simultaneously determined. Indeed, it is not possible to determine simultaneously the values of two different components of $\vec{J}$.

Further reading

Further reading material about the topics covered in this lecture can be found in the following sections of the course textbook (*Physical Chemistry*, Atkins and De Paula, 11th edition):

Chapters in textbook

- **7F.1**: Rotation in two dimensions.
- **7F.2**: Rotation in three dimensions.

From Quantum to Molecule

Dr Juan Rojo
VU Amsterdam and Nikhef Theory Group
http://www.juanrojo.com/
j.rojo@vu.nl

5 HC5: The hydrogen atom

In this lecture, we discuss the quantum mechanics of the hydrogen atom, one of the most important systems for our understanding of atomic and molecular phenomena. A crucial property of this system is that its Schroedinger equation can be solved analytically, and this allows us to understand in a detailed way the resulting properties of the wave functions of the hydrogen atom. This knowledge will represent the building block for our subsequent studies, first of more complicated atoms composed by more than one electron, and then of molecules composed by two atoms or more.

The **learning goals** of this lecture are:

(a) Solving the Schroedinger equation for the hydrogen atom.

(b) Interpreting physically the radial and angular wave functions of the hydrogen atom.

(c) Understanding how the concept of probability density is modified in spherical coordinates as compared to Cartesian coordinates.

(d) Being able to draw graphically and identify the main qualitative features of the electronic orbitals of the hydrogen atom.

5.1 The Schroedinger equation for the hydrogen atom

The hydrogen atom plays a central role in this course for a number of reasons:

- It is the *simplest possible atom* that exists, composed by only one proton and one electron.
- The Schroedinger equation of the hydrogen atom can be *solved exactly*, so we can study its properties in great detail without the need of any numerical approximations.
- The main features of the atomic orbitals of the hydrogen atom can then be applied to the description of other more complex atoms, in particular of *multi-electron atoms* (HC6).

- The hydrogen atom forms the basis for our understanding of *molecular* bonds and *molecular structure*, which is the main topic of the second part of the course.

The hydrogen atom is composed by one proton with electric charge $Q_p = +e$ and one electron with the opposite charge $Q_e = -e$ bound by the electric force attraction, the Coulomb force. Within a hydrogen atom, the electrostatic potential that the electron experiences is given by

$$V(r) = -\frac{1}{4\pi\epsilon_0}\frac{e^2}{r}\,, \tag{5.1}$$

where r is the distance that separates the electron and the proton, and ϵ_0 is the dielectric constant of the vacuum. Given that the mass of the proton is much larger than the mass of the electron, $m_p \simeq 1800\, m_e$, one can consider to very good approximation that the proton is at rest in this system. Therefore the motion of the proton can be neglected and only considering the motion of the electron around it is required.

Spherical symmetry

A central feature of the Coulomb potential Eq. (5.1) is that it exhibits *spherical symmetry*: it depends only on the distance $r = |\vec{r}|$ between the electron and the proton, but not on the values of the polar θ and azimuthal φ angles of the distance vector $\vec{r}$ that connects them. We will therefore now be able to exploit everything that we learned in HC4 concerning the quantum mechanics of systems with spherical symmetry, in particular the solutions of the Schroedinger equation for a particle confined in the surface of a sphere that we presented in Sect. 4.4.

The Hamiltonian for the hydrogen atom, which as usual corresponds to the operator associated to the total energy of the system, takes the following form:

$$\begin{aligned} \widehat{H} &= \widehat{E}^{p}_{\rm kin} + \widehat{E}^{e}_{\rm kin} + \widehat{V}(r) \\ &= -\frac{\hbar^2}{2m_p}\nabla^2_p - \frac{\hbar^2}{2m_e}\nabla^2_e - \frac{e^2}{4\pi\epsilon_0 r}\,, \end{aligned} \tag{5.2}$$

where the *Laplacian operator* is defined as the sum of the second derivatives with respect to the particle coordinates,

$$\nabla^2 \equiv \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)\,, \tag{5.3}$$

and we denote by ∇^2_p the Laplacian acting on the proton spatial coordinates and ∇^2_e on those of the electron. In the same way as in the two-body problem in classical mechanics, the problem is simplified if we express the coordinates of the proton and the electron relative to the center of mass of the system. Since $m_p \gg m_e$, the position of the center of mass coincides basically with the position of the proton, which can therefore be considered to be stationary (to be more precise, the center-of-mass of the system is freely moving since no forces act upon it). In the coordinates with respect the center of mass of the system, the Schroedinger equation reads

$$-\frac{\hbar^2}{2\mu}\nabla^2\Psi(r,\theta,\varphi) - \frac{e^2}{4\pi\epsilon_0 r}\Psi(r,\theta,\varphi) = E\Psi(r,\theta,\varphi)\,, \tag{5.4}$$

where we have introduced the reduced mass of the proton-electron system,

$$\frac{1}{\mu} = \frac{1}{m_e} + \frac{1}{m_p} \simeq \frac{1}{m_e}\,, \tag{5.5}$$

given the fact that the proton is much more massive than the electron. From the numerical point of view, using m_e instead of μ is in general a very good approximation. Note that Eq. 5.4 is being expressed in the spherical coordinates defined in Sect. 4.1: as was shown there, the problem simplifies when adopting these coordinates that reflect the underlying symmetries of the system. Crucially, note that Eq. (5.4) is now one-particle differential equation, as compared to the two-particle equation that we started with.

In order to solve the differential equation Eq. (5.4), we will try the same method of *separation of variables* as the one used in HC4. That is, we want to express the total wave function of the system, $\Psi(r, \theta, \varphi)$, as a product of functions that depend separately on r, θ, and φ. Note that, as opposed to the problem that we discussed in Sect. 4.4, the electron now is *not confined* to the surface of a sphere, so we also need to account here for the radial dependence of the wave function. Therefore we adopt the following *ansatz* for the electron wave function:

$$\Psi(r, \theta, \varphi) = R(r) Y(\theta, \varphi) \, , \tag{5.6}$$

with $R(r)$ representing the radial part of the wave function and the angular dependence is contained on the *spherical harmonics* $Y(\theta, \phi)$, which as we know correspond to the solution of the Schroedinger equation for a particle confined in the surface of a sphere. Our choice of the spherical harmonics is Eq. (5.6) is justified since, as we will show, now the angular part of the wave function satisfies the same differential equation as the particle in the surface of a sphere of Sect. 4.4.

Using this ansatz, we obtain that the Schroedinger equation in spherical coordinates reads

$$-\frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\Lambda^2\right) RY + V(r) RY = ERY \, , \tag{5.7}$$

where we have used the expression of the Laplacian in spherical coordinates, and where we have defined

$$\Lambda^2 \equiv \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2} + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} \, . \tag{5.8}$$

Next, we use the fact that the radial function $R(r)$ is independent of the angular variables and that the spherical harmonics $Y(\theta, \varphi)$ do not depend on the radius r, so that the above equation can be written as

$$-\frac{\hbar^2}{2\mu}\left(Y\frac{\partial^2 R^2}{\partial r^2} + \frac{2Y}{r}\frac{\partial R}{\partial r} + \frac{R}{r^2}\Lambda^2 Y\right) + V(r) RY = ERY \, , \tag{5.9}$$

which can be simplified by multiplying both sides by r^2/RY, leading to

$$-\frac{\hbar^2}{2\mu R}\left(r^2\frac{d^2 R}{dr^2} + 2r\frac{dR}{dr}\right) + V(r) r^2 - \frac{\hbar^2}{2\mu Y}\Lambda^2 Y = Er^2 \, . \tag{5.10}$$

From this expression, we can determine that our ansatz Eq. (5.6) with the separation of variables has been successful: the last term on the left hand side of Eq. (5.10) depends only on the angular variables, while the rest of the equation depends only on r or on constants. Therefore, the only way in which this condition can be satisfied is provided that

$$-\frac{\hbar^2}{2\mu R}\left(r^2\frac{d^2 R}{dr^2} + 2r\frac{dR}{dr}\right) \quad + \quad Vr + A = Er^2 \, , \tag{5.11}$$

$$-\frac{\hbar^2}{2\mu Y}\Lambda^2 Y \quad = \quad A \, , \tag{5.12}$$

which A some unspecified constant, that will be fixed later. Therefore, we end up with two independent differential equations: one for the radial part of the wave function $R(r)$ and another for the angular part $Y(\theta, \varphi)$, which must be solved separately.

Angular dependence. From our study of the quantum mechanics of a particle confined in the surface of a sphere in HC4, we already know how to solve the angular equation:

$$-\frac{\hbar^2}{2\mu Y(\theta,\varphi)}\Lambda^2 Y(\theta,\varphi) = A\,, \tag{5.13}$$

since using the definition of Λ^2 we have that it is written as

$$-\frac{\hbar^2}{2\mu}\left(\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2} + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}\right)Y(\theta,\varphi) = AY(\theta,\varphi)\,, \tag{5.14}$$

but this is nothing but Schroedinger's equation for a particle confined to the surface of a sphere, Eq. (4.35), with mass μ. From this identification, it follows that $A = Er^2$, with r being the radial coordinate, and then the solutions of this equation are indeed the spherical harmonics $Y_{l,m_l}(\theta,\varphi)$, labelled by the two angular quantum numbers (l, m_l). Therefore, since we know that the kinetic energy of the particle in a sphere is given by Eq. (4.48), we can conclude that the constant A must be quantised and is given by

$$A = l(l+1)\frac{\hbar^2}{2\mu}\,, \tag{5.15}$$

where l is the principal angular quantum number. Due to the periodic boundary conditions applied to the angular component of the wave function, this quantum number can only take positive integer values: $l = 0, 1, 2, 3, \ldots$. Note that Eq. (5.15) automatically implies that the radial solutions of the hydrogen atom will also be quantised and at least will be labelled by angular quantum number l.

Radial dependence and the effective potential. We can now turn to solve the radial part of Schroedinger's equation for the hydrogen atom. Using Eq. (5.15), the radial differential equation reads

$$\frac{\hbar^2}{2\mu R}\left(r^2\frac{d^2R}{dr^2} + 2r\frac{dR}{dr}\right) + V(r)r^2 + \frac{\hbar^2 l(l+1)}{2\mu} = Er^2\,. \tag{5.16}$$

This differential equation can be written in a physically more transparent way using the rescaling $R(r) = u(r)/r$, which makes possible to simplify the above equation using

$$\left(r^2\frac{d^2R}{dr^2} + 2r\frac{dR}{dr}\right) = r\frac{d^2u(r)}{dr^2}\,, \tag{5.17}$$

which in turn leads to a simpler differential equation

$$-\frac{\hbar^2}{2\mu}\frac{d^2u}{dr^2} + V_{\rm eff}(r)u = Eu\,, \tag{5.18}$$

where we have defined an *effective interaction potential* $V_{\rm eff}(r)$ by

$$V_{\rm eff}(r) \equiv -\frac{e^2}{4\pi\epsilon_0 r} + \frac{l(l+1)\hbar^2}{2\mu r^2}\,, \tag{5.19}$$

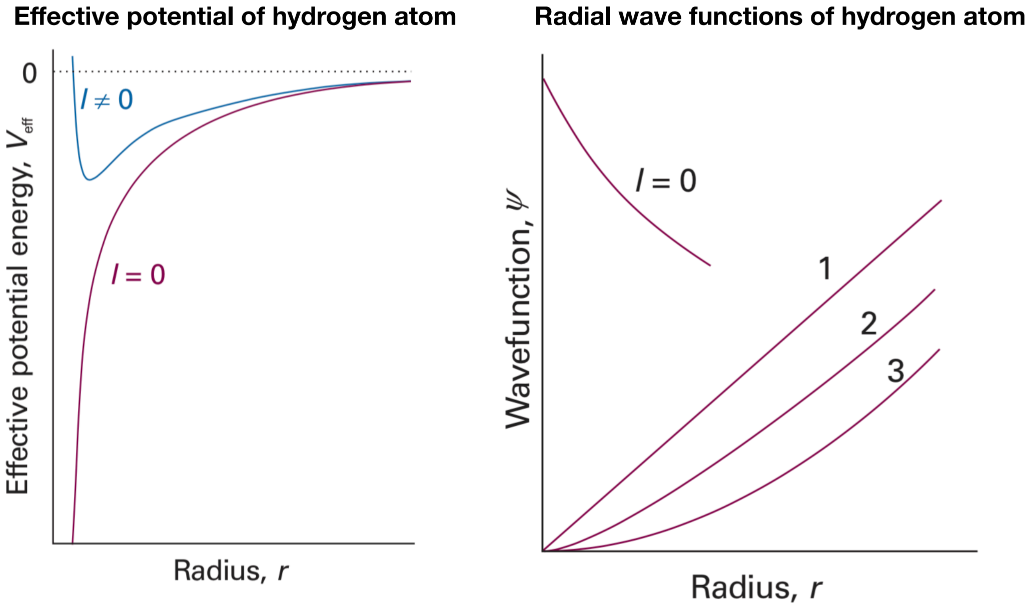


Figure 5.1: Left: the effective interaction potential of the hydrogen atom $V_{\rm eff}(r)$, Eq. (5.19) includes contributions from the Coulomb potential and from the centrifugal force which is proportional to the electron angular momentum. Here we show its values both for $l \neq 0$ (finite angular momentum) and $l = 0$ (vanishing angular momentum). Right: schematic representation of the radial part of the wave function of the hydrogen atom for different values of the angular quantum number l.

which includes the contributions both from the Coulomb force as well as from the angular momentum of the electron (namely the centrifugal force that grows with l). After these manipulations, we can see how Eq. (5.18) formally corresponds to the Schroedinger equation for a particle of mass μ moving in one dimension r under the effects of the potential $V_{\rm eff}(r)$.

The effective potential Eq. (5.19) has different behaviors when $l = 0$ (vanishing angular momentum) and when $l > 0$ (finite angular momentum), as shown in Fig. 5.1. Indeed, for $l = 0$ we recover the Coulomb *attractive* potential, that tends to $V_{\rm eff} \to -\infty$ when $r \to 0$. However, in the presence of angular momentum $l \neq 0$, the effective potential becomes *repulsive* at small distances, $V_{\rm eff} \to +\infty$ when $r \to 0$, therefore disfavoring small values of r in the energy budget of the problem. At large values of r, $r \to \infty$, the Coulomb potential always dominates since it is characterised by a gentle fall-off with r.

The physical interpretation of the effective potential $V_{\rm eff}(r)$ Eq. (5.19) is the following:

- First of all, we see that the term that depends on the angular momentum l has the opposite sign as the Coulomb potential, implying that it corresponds to a *repulsive effective force* rather than an attractive one. So it has the opposite effect than the Coulomb interaction.

- Second, we observe that when the distance becomes small $V(r) \propto +r^{-2}$, and therefore the electron and the proton cannot get too close to each other.

- This effective potential also appears in the classical description of the two body problem, and its second term corresponds to the contribution of the *centrifugal force*.

- Indeed, while the radial equation Eq. (5.18) describes an effective one dimensional motion, the original physical particle is three-dimensional, and the remnants of this rotating motion are present in the effective potential though the contribution of the centrifugal force.

- We see that in the case that the angular momentum quantum number vanishes, $l = 0$, then the effective potential boils down to the Coulomb potential.
- For small values of the radial coordinate r, then $V_{\rm eff} \simeq l(l+1)r^{-2}$, meaning that the larger the value of the angular momentum l the farther than on average the electron will be from the nucleus (because of the bigger centrifugal force).
- We see that for large separations r the effective potential goes to zero, with both the Coulomb attraction and the centrifugal force becoming vanishingly small, with the former dominating as discussed above.

Introducing the effective potential therefore highlights the different qualitative behaviors that can be expected from the radial solutions of the Schroedinger equation for the hydrogen atom.

5.2 The radial wave functions of the hydrogen atom

The previous discussion indicates that the radial wave functions $u(r)$ of the hydrogen atom can be derived by solving Eq. (5.18). It is beyond the scope to show how to explicitly solve this differential equation, and here we will limit ourselves to present its solutions and discuss their main features. First of all, when solving Eq. (5.18) one finds that the allowed energy levels are *quantised*, and that they are given in terms a new quantum number n, called the *principal quantum number*, as follows:

$$E_n = -\frac{\mu e^4}{32\pi^2\epsilon_o^2\hbar^2}\frac{1}{n^2}\,, \tag{5.20}$$

where n is a positive integer number: $n = 1, 2, 3, \ldots$. Note that $n = 0$ is not allowed since it corresponds to an unphysical solution.

As in previous quantum systems, the quantisation of the wave function and thus of the allowed energy states follows from *imposing boundary conditions* that need to be respected by the system from physical considerations. In this case, the quantisation of the energy levels indicated in Eq. (5.20) can be shown to be a consequence of the boundary condition that require that $R(r) \to 0$ for $r \to \infty$, namely that the radial component of the wave function must vanish at infinity. This boundary condition is necessary since else the probability distribution associated with the electron would not be well defined, in particular it would not be possible to assign to it a well-defined *probabilistic interpretation*.

Another important observation related to Eq. (5.20) is the fact that $E_n \le 0$ reflects that the electron and the proton in a hydrogen atom form a *bound state*. That is, the energy of the electron+proton system together is smaller than the separate energies of the electron and the proton, and therefore the formation of an hydrogen atom is energetically favored. For this reason, E_n is also known as the *binding energy* of the electron, namely the energy that needs to be provided to free the electron from this bound state.

The quantum states with energies Eq. (5.20), labelled by the principal quantum number n, can be shown to have associated the following radial wave functions:

$$R_{n,l}(r) = N_{n,l}\rho^l L_{n+1}^{2l+1}(\rho)\exp\left(-\rho/2\right)\,, \tag{5.21}$$

where we have defined the following variables:

$$\rho \equiv \frac{2r}{na}\,, \qquad a = \frac{m_e}{\mu}a_0\,, \qquad a_0 = \frac{4\pi\epsilon_0\hbar^2}{m_e e^2}\,. \tag{5.22}$$

Therefore, we see that each of the radial solutions $R_{n,l}(r)$ is labelled in terms of two quantum numbers: (n,l). Each pair of values of (n,l) then corresponds to a different quantum state, though note that for a given value of n the states with different angular quantum number l will be *degenerate* since they have the same energy, see Eq. (5.20).

In the context of atomic and molecular physics, these quantum states are known as *electronic orbitals.*

Note that since $m_e \simeq \mu$, then $a \simeq a_0$ to very good approximation. In Eq. (5.22) we have defined a new constant a_0 with units of length, known as the *Bohr radius*, and whose physical interpretation will become transparent now. One important property is that the quantisation conditions imply that the quantum numbers n and l are not independent, but that that have to satisfy the following condition:

For an orbital characterised by the principal quantum number n, the angular quantum number l can only take the following values: $l = 0, 1, 2, \ldots, n-1$. For example, if $n = 3$, the second excited states of the hydrogen atom, then l can be either 0,1, or 2. Therefore a given principal quantum number n has associated $n-1$ states each with a different value of l.

Let us now discuss the general structure and properties of these solutions, Eqns. (5.21) and (5.22):

- The values of the overall constants $N_{n,l}$ are fixed by the normalisation conditions of the wave functions.
- The radial wave functions $R_{n,l}(r)$ depend on both the radial n and the angular l quantum numbers. Note that the dependence in l arises from the effective potential Eq. (5.19) in the differential equation that determines $R(r)$.
- For small values of r, the wave functions can be shown to scale as $R_{n,l}(r) \simeq r^l$. Therefore, we see that the radial wave function vanishes at the origin except for $l = 0$ (for a system with vanishing angular momentum).

  We also see that the larger the value of l, the smaller the probability of finding the electron close to the proton. This behaviour is a direct consequence of the centrifugal component of the effective potential $V_{\text{eff}}(r)$, which tends to push the electron away for the proton if l is large.

  The small-r behaviour of the radial wave functions is schematically represented in Fig. 5.1. For $l = 1$, the radial wave function grows linearly, $R_1 \simeq r$, for $l = 2$, it grows quadratically, $R_1 \simeq r^2$, and so on. For a system with vanishing angular momentum instead, $l = 0$, we have that the wave function is constant for $r = 0$ and then decreases as r is increased.
- At large distances, the radial wave function falls off exponentially

  $$R_{n,l}(r) \simeq \exp\left(-r/na\right)\,, \tag{5.23}$$

  ensuring that the wave function *vanishes at infinity* as required by the boundary conditions. Recall that an exponential dominates over any fixed-order polynomial.

Note that here the product na provides a measure of the *size of the hydrogen atom*: given the steeply-falling character of the exponential, the electron is confined to the region with $r \lesssim na$. We also note that the effective size of this atom increases with the main quantum number n.

Therefore, we can identify a_0, namely the Bohr radius, with the *radius of the hydrogen atom* when the electron occupies the ground state ($n = 1$, the state with smallest energy).

- The interpolation between the limiting small-r and large r limit is determined by a series of special functions called the *Associated Laguerre polynomials* $L_{n+1}^{2l+1}(\rho)$. These functions depend on the two quantum numbers n and l. For integer values of n and l, these polynomials are smooth functions of ρ, for instance the first few ones are given by

$$\begin{aligned} L_0^k(x) &= 1\,, \\ L_1^k(x) &= -x+k+1\,, \\ L_2^k(x) &= \frac{1}{2}\left[x^2-2(k+2)x+(k+1)(k+2)\right]\,. \end{aligned} \tag{5.24}$$

  Note in particular that these associated Laguerre polynomials $L_p^k(x)$ tend to a constant as $x \to 0$ and then grows at most as a power p, x^p, as $x \to \infty$. Therefore, at large values of the radius r, the asymptotic behaviour of the radial wave function is dominated by the exponential in Eq. (5.23).

Putting together Eq. (5.21) with the expressions for the Associated Laguerre polynomials, one can construct the explicit form of radial wave functions for any value of n and l. For instance, the three lowest energy states (labelled by $n = 1$ and $n = 2$) will have associated the following wave functions:

$$\begin{aligned} R_{1,0}(\rho) &= 2\left(\frac{1}{a}\right)^{3/2} e^{-\rho/2}\,, \\ R_{2,0}(\rho) &= \frac{1}{\sqrt{8}}\left(\frac{1}{a}\right)^{3/2}(2-\rho)e^{-\rho/2}\,, \\ R_{2,1}(\rho) &= \frac{1}{\sqrt{24}}\left(\frac{1}{a}\right)^{3/2}\rho e^{-\rho/2}\,. \end{aligned} \tag{5.25}$$

In particular, $R_{1,0}(r)$ represents the radial wave function associated to the ground state of the hydrogen atom. One can check that all these wave functions are normalised by integrating their squares over the allowed ranges for the r, θ, and φ coordinates. Note also that, as mentioned above, these wave functions vanish at $\rho = 0$ unless $l = 0$, where they take constant values. For instance, for $n = 1$ and $n = 2$, the value of the $l = 0$ wave functions at the origin are given by

$$\begin{aligned} R_{1,0}(r=0) &= 2\left(\frac{1}{a}\right)^{3/2}\,, \\ R_{2,0}(r=0) &= \frac{2}{\sqrt{8}}\left(\frac{1}{a}\right)^{3/2}\,. \end{aligned} \tag{5.26}$$

As will be shown shortly, this does not mean that the electron has a non-zero probability of being found at $r = 0$ in the same position as the proton. This would be problematic since quantum mechanics would not be able to describe such configuration.

Generalisation to hydrogen-like atoms This discussion can be generalised to *hydrogen-like atoms*, which are defined as atoms that have Z protons and $A-Z$ neutrons but only a single electron. One example of this would be the Helium atom if one of its two electrons has been stripped off. For hydrogen-like atoms, the only difference would be to replace e^2 by Ze^2 in the effective potential of the radial wave function, Eq. (5.19). Therefore the only difference at the level of radial wave functions would be to replace Bohr's radius a_0 by

$$a_0 = \frac{4\pi\epsilon_0\hbar^2}{m_e Z e^2} \tag{5.27}$$

or in other words, replacing a_0 in the solution of the hydrogen atom for a_0/Z in the case of hydrogen-like atoms. For the three lowest energy states, the expression for the radial wave functions of hydrogen-like atoms are given by

$$\begin{aligned} R_{1,0}(\rho) &= 2\left(\frac{Z}{a}\right)^{3/2} e^{-Z\rho/2}\,, \\ R_{2,0}(\rho) &= \frac{1}{\sqrt{8}}\left(\frac{Z}{a}\right)^{3/2} (2-\rho)e^{-Z\rho/2}\,, \\ R_{2,1}(\rho) &= \frac{1}{\sqrt{24}}\left(\frac{Z}{a}\right)^{3/2} \rho e^{-Z\rho/2}\,. \end{aligned} \tag{5.28}$$

On the other hand, the angular part of the wave function, given by the spherical harmonics $Y_{l,m_l}(\theta,\varphi)$, is the same for hydrogen and hydrogen-like atoms.

In hydrogen-like atoms, the atomic size now will be smaller than the one of the hydrogen atom by a factor $1/Z$. This can be understood from the fact that having now Z protons instead of one creates a stronger electrical attraction with the electron, and therefore the electron is more likely to be found closer to the atomic nucleus.

Allowed electronic transitions in the hydrogen atom. We can express the values of the energy levels of the hydrogen atom Eq. (5.20) in a more physically transparent way as follows:

$$E_n = -\frac{hc}{n^2}\widetilde{R}_h\,, \tag{5.29}$$

where we have defined

$$\widetilde{R}_h = \frac{\mu e^4}{32\pi^2\epsilon_0\hbar^2}\,, \quad \widetilde{R}_h \equiv \frac{\mu}{m_e}\widetilde{R}_\infty\,, \tag{5.30}$$

and where the so-called *Rydberg constant* is given as

$$\widetilde{R}_\infty = \frac{m_e e^4}{8\epsilon_0^2 h^3 c}\,. \tag{5.31}$$

From Eq. (5.29) is clear that this Rydberg constant, neglecting proton mass effects, is minus the energy associated to the ground state of the hydrogen atom. In other words, it is a measure of the binding energy of the electron in the $n=1$ state of the hydrogen atom.

If we define the *ionisation energy of the hydrogen atom*, I, as the energy that needs to be supplemented to such an atom in its ground state in order to ionize it, in terms of the Rydberg constant it will be given by

$$I = hc\widetilde{R}_h = 13.6\,\mathrm{eV}\,, \tag{5.32}$$

which is consistently also denoted as *one Rydberg.* So the Rydberg is a unit suitable to describe ionisation energies in hydrogen-like atoms.

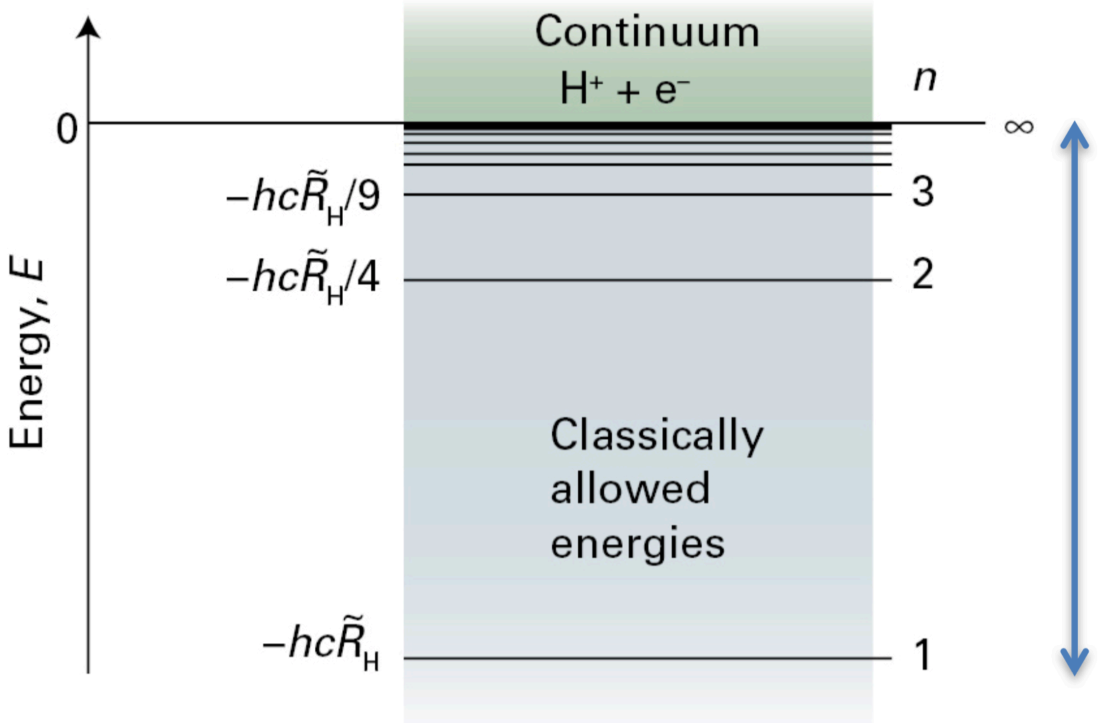


Figure 5.2: Schematic representation of the energy levels of the hydrogen atom. The ground state ($n = 1$) has energy $E_1 = -hc\widetilde{R}_H$, the first excited state ($n = 2$) has energy $E_2 = -hc\widetilde{R}_H/4$ and so on, expressed in terms of the Rydberg constant. As n keeps increasing, the difference between energy levels becomes smaller and smaller. If the atoms finds itself in the energy level n and absorb energy (say from a photon) with $E \geq -E_n$, then the hydrogen atom will ionize and dissociate into a proton and a electron, not bounded by the electromagnetic interaction anymore. Recall that the fact that $E_n < 0$ indicate that the electron and the proton form a *bound state*.

Note that from the distribution of energy levels of the hydrogen atom, Eq. (5.29), one finds that the difference between two neighboring energy levels decreases as n is increased. Indeed, if one has two adjacent levels E_n and E_{n-1}, then their energy difference is given by

$$\Delta E_n = E_{n-1} - E_n = -\frac{hc}{(n+1)^2}\widetilde{R}_h + \frac{hc}{n^2}\widetilde{R}_h = hc\widetilde{R}_h\frac{2n+1}{(n^2+n)^2}\,, \tag{5.33}$$

and therefore in the limit of a highly excited state, $n \to \infty$, one as that this energy difference ΔE_n becomes vanishingly small.

This behaviour is illustrated in Fig. 5.2, where we display the schematic representation of the energy levels of the hydrogen atom in terms of the Rydberg constant. The ground state ($n = 1$) has energy $E_1 = -hc\widetilde{R}_H$, the first excited state ($n = 2$) has energy $E_2 = -hc\widetilde{R}_H/4$ and so on. As n keeps increasing, the difference between energy levels becomes smaller and smaller. If the atoms finds itself in the energy level n and absorbs energy (say from a photon) with $E \geq -E_n$, then the hydrogen atom will ionize and dissociate into a proton and a electron, not bounded by the electromagnetic interaction anymore. The higher the value of n, the smaller the energy of the photon that will be needed to dissociate an hydrogen atom. As mentioned above, for $n = 1$ this energy is known as the ionisation energy I of the hydrogen atom.

As is clear from Fig. 5.2 the fact that $E_n < 0$ indicate that the electron and the proton form a *bound state*. Positive energies of the unbounded electron+proton system can take any value (since they are not subjected to the quantisation conditions) and we say that they form a *continuum*.

5.3 The orbital structure of the hydrogen atom

We now have all the ingredients that we need in order to take a closer look at the orbital structure of the hydrogen atom. Recall that by *electronic orbitals* we mean simply the allowed quantum states for the electrons in this system, labelled by the pair of quantum numbers (n, l). First of all, we note that the values of the energy E_n are independent of the values of the angular quantum numbers l and m_l, and depend only on the values of the principal (radial) quantum number n. This means that, in general, there will be several orbitals sharing the same value of the energy E_n: in particular, for a given n, all orbitals with different values of l and m_l will have the same energy. Recall that for a fixed value of n, the allowed values of l are

$$l = 0, 1, 2, \ldots, n-1\,, \tag{5.34}$$

while in turn for a given value of l, the allowed values of m_l are given by

$$m_l = -l, -l+1, \ldots, l-1, l\,, \tag{5.35}$$

where the value of m_l determines the orientation of the angular momentum with respect to the z axis. So for each value of n there exist a number of orbitals that share the same energy E_n, and this number can be computed as

$$N_n = \sum_{l=0}^{n-1} (2l+1) = n^2 - n + n = n^2\,, \tag{5.36}$$

where we have used the expression for the arithmetic sum

$$\sum_{k=1}^{n} k = \frac{1}{2} n(n+1)\,. \tag{5.37}$$

Therefore, we have $N_1 = 1$ orbitals for the ground state, $N_2 = 4$ orbitals for the first excited state, $N_3 = 9$ orbitals for the second excited state, and so on.

For historical reasons, the electronic energy levels $n = 1, 2, 3, 4, \ldots$ in the hydrogen atom are denoted as the $K, L, M, N, \ldots$ *electronic shells*. In turn, orbitals with angular momentum $l = 0, 1, 2, 3, 4, \ldots$ are labelled by the letters $s, p, d, f, g, \ldots$. For instance, an s orbital in the L shell corresponds to $(n, l) = (2, 0)$, while a p orbital in the M shell corresponds to $(n, l) = (3, 1)$.

Following this convention, here we will use the following notation to denote the orbitals of the hydrogen atom in terms of their radial n and angular n quantum numbers:

n	l	notation
1	0	$1s$
2	0	$2s$
2	1	$2p$
3	0	$3s$
3	1	$3p$
3	2	$3d$

A graphical representation of the distribution of the orbitals of the hydrogen atom in shells (labelled by the value of n) and sub-shells (labelled by the value of l) is schematically represented in Fig. 5.3. Each shell

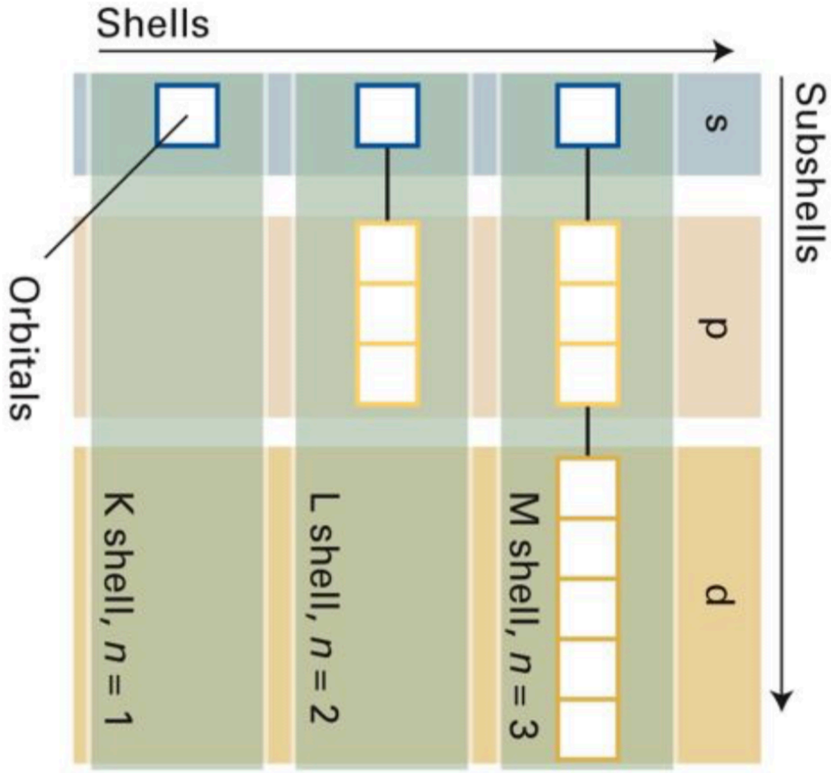


Figure 5.3: The distribution in shells and sub-shells of the orbitals of the hydrogen atom. Each shell corresponds to a different main quantum number n: the K shell is $n = 1$, the L shell is for $n = 2$, and so in. Within each shell, there is a division in subshells labelled by the value of the angular quantum number l. For example, the M shell ($n = 3$) has three subshells: s ($l = 0$), p ($l = 1$), and d ($l = 2$). A subshell with quantum number l contains $(2l - 1)$ orbitals. The total number of orbitals in a shell with principal quantum number n is n^2.

corresponds to a different principal quantum number n: the K shell is $n = 1$, the L shell is for $n = 2$, and so in. Within each shell, there is a division in subshells labelled by the value of the angular quantum number l. For example, the M shell ($n = 3$) has three subshells: s ($l = 0$), p ($l = 1$), and d ($l = 2$). For each subshell there are $2l - 1$ orbitals, corresponding to the possible values of the quantum number m_l can take in that subshell. The total number of orbitals in a shell with principal quantum number n is n^2. Both in the hydrogen and in hydrogen-like atoms, there is a single electron that can occupy any of the orbitals shown in Fig. 5.3.

5.4 Radial probability distributions

An important feature of using spherical coordinates in the description of the hydrogen atom is that one needs some care when constructing the radial probability distributions out of the corresponding radial wave functions. To illustrate this point, let us consider first of all the ground state of the hydrogen atom (orbital $1s$, with $n = 1$ and $l = 0$). The corresponding radial wave function is given by

$$R_0(r) = \frac{2}{a_0^{3/2}} e^{-r/a_0} \, , \tag{5.38}$$

and the associated angular part of the wave function is given by

$$Y_{0,0}\left(\theta,\varphi\right) = (4\pi)^{-1/2}\,, \tag{5.39}$$

which can be combined to construct the total electronic wave function of the ground state of the hydrogen atom:

$$\Psi_0(r,\theta,\varphi) = R_0(r)Y_{0,0}\left(\theta,\varphi\right) = \frac{1}{\sqrt{\pi a_0^3}}e^{-r/a_0}\,. \tag{5.40}$$

This wave function has a maximum for $r = 0$ and then decays exponentially for $r > 0$. Note that this wave function does not depend on the angles θ and φ, and is thus *spherically symmetric*.

As has been discussed above, the fact that the wave function has a maximum at the origin is characteristic of the electronic orbitals of type s, that is, those quantum states for which the angular momentum quantum number vanishes ($l = 0$). As we will now show, this property does *not* imply that the electron has a finite probability of being found at $r = 0$ (which would mean that the proton and the electron are at the same position), as a consequence of the properties of spherical coordinates. Indeed, the probability to find a electron at a position (x, y, z) specified in Cartesian coordinates is given by

$$P(x,y,z) = |\Psi(x,y,z)|^2 dxdydz\,, \tag{5.41}$$

where $dxdydz$ represent the spatial volume where the electron is allowed to be found upon measurement. To obtain the corresponding expression in the case of spherical coordinates, one needs to take into account the *Jacobian matrix* for the change of variables given by

$$dxdydx = \left|\frac{\partial(x,y,z)}{\partial(r,\theta,\varphi)}\right| drd\theta d\varphi = r^2 dr\sin\varphi d\varphi d\theta\,. \tag{5.42}$$

Therefore we find that we need to add an extra prefactor when constructing the probability densities in spherical coordinates.

Relation between probability densities and wave functions

In Cartesian coordinates, the relation between probability density and wave functions is

$$P(x,y,z) = |\Psi(x,y,z)|^2\,, \tag{5.43}$$

that is, the probability density is proportional to the wave function squared. In spherical coordinates, the radial and angular probability functions in terms of the corresponding wave-functions are

$$P(r) = r^2|R_{n,l}(r)|^2\,, \qquad P(\theta,\varphi) = \sin\theta|Y_{l,m_l}(\theta,\varphi)|^2 \tag{5.44}$$

with additional pre-factors arising from the Jacobian of the transformation between Cartesian and spherical coordinates. Note also that due to separation of variables both $P(r)$ and $P(\theta,\varphi)$ are individually normalised,

$$\int_0^\infty dr\,P(r) = 1\,, \qquad \int_0^\pi d\theta\int_0^{2\pi} d\varphi\,P(\theta,\varphi) = 1\,. \tag{5.45}$$

Exploiting this information, we can now compute the probability density associated to the wave function for the ground state of the hydrogen atom, Eq. (5.38), finding

$$\begin{aligned} P_0(r)dr &= \int_0^{2\pi} d\varphi \int_0^{\pi} d\theta |\Psi_0(r)|^2 r^2 dr \sin\theta \\ &= \frac{1}{\pi a_0^3}\int_0^{2\pi} d\varphi \int_0^{\pi} \sin\theta d\theta r^2 e^{-2r/a_0} dr = \frac{4}{a_0^3} r^2 e^{-2r/a_0} dr \,, \end{aligned} \tag{5.46}$$

and therefore the radial probability density $P_0(r)$ associated to the ground state of the hydrogen atom is:

$$P_0(r) = \frac{4}{a_0^3} r^2 e^{-2r/a_0} \,, \tag{5.47}$$

where we have integrated over the angular variables, exploiting the fact that Ψ_0 does not depend on the angles (in statistics, we call this process *marginalisation*). When integrating over the angular variables, the following relation is useful:

$$\int_0^{2\pi} d\varphi \int_0^{\pi} d\theta \sin\theta = 4\pi \,, \tag{5.48}$$

which is known as the total *solid angle* in three dimensions.

The result Eq. (5.46) indicates the probability of finding the electron in an interval of size dr at a distance r from the proton. Note that while the wave function itself peaked at $r = 0$, $\Psi_0(r = 0) \neq 0$, the associated probability vanishes at the origin, $P_0(r = 0) = 0$. This implies that the electron has *a vanishing probability* of being found at the same position as the nucleus of the hydrogen atom.

By weighting with the probability Eq. (5.46), one can compute various average properties of the ground state of the hydrogen atom. For instance, one can evaluate the *expectation value* for the distance r between the electron and the proton in the ground state by means of the weighted average:

$$\langle r \rangle = \int_0^{\infty} dr\, r\, P_0(r) = \frac{4}{a_0^3}\int_0^{\infty} dr\, r^3 e^{-2r/a_0} dr = \frac{4}{a_0} \times \frac{6a_0^4}{16} = \frac{3a_0}{2} \,. \tag{5.49}$$

This result justifies why the Bohr radius a_0 is good estimate for the average size of the hydrogen atom when this occupies its ground state. To compute this integral, we have used the following result:

$$\int_0^{\infty} dx\, x^n \exp(-bx) = \frac{n!}{b^{n+1}} \,. \tag{5.50}$$

It is also interesting to compute which is the *most likely value* of r, denoted by r^*, where the electron will be found. Note that in general this value will be *different* from the expectation value $\langle r \rangle$. To determine this, we need to determine where the radial probability density $P_0(r)$ has a maximum by imposing the condition:

$$\frac{dP_0(r)}{dr} = 0 = \frac{4}{a_0}\left(2r^* + r^{*2}(-2/a_0)\right) e^{-2r^*/a} = \frac{8r^*}{a_0}(1 - r^*/a_0)e^{-2r^*/a} \,, \tag{5.51}$$

which is satisfied by $r^* = a_0$. Therefore we find that the Bohr radius a_0 is *the most likely value* where the electron will be found in the ground state of the hydrogen atom.

We show in Fig. 5.4 the radial probability distributions $P(r)$ Eq. (5.46) for different electronic orbitals of the hydrogen atom as a function of r/a_0. There are a number of interesting features that can be observed:

- The higher the value of n, the more likely it will be to find the electron far from the atomic nucleus.

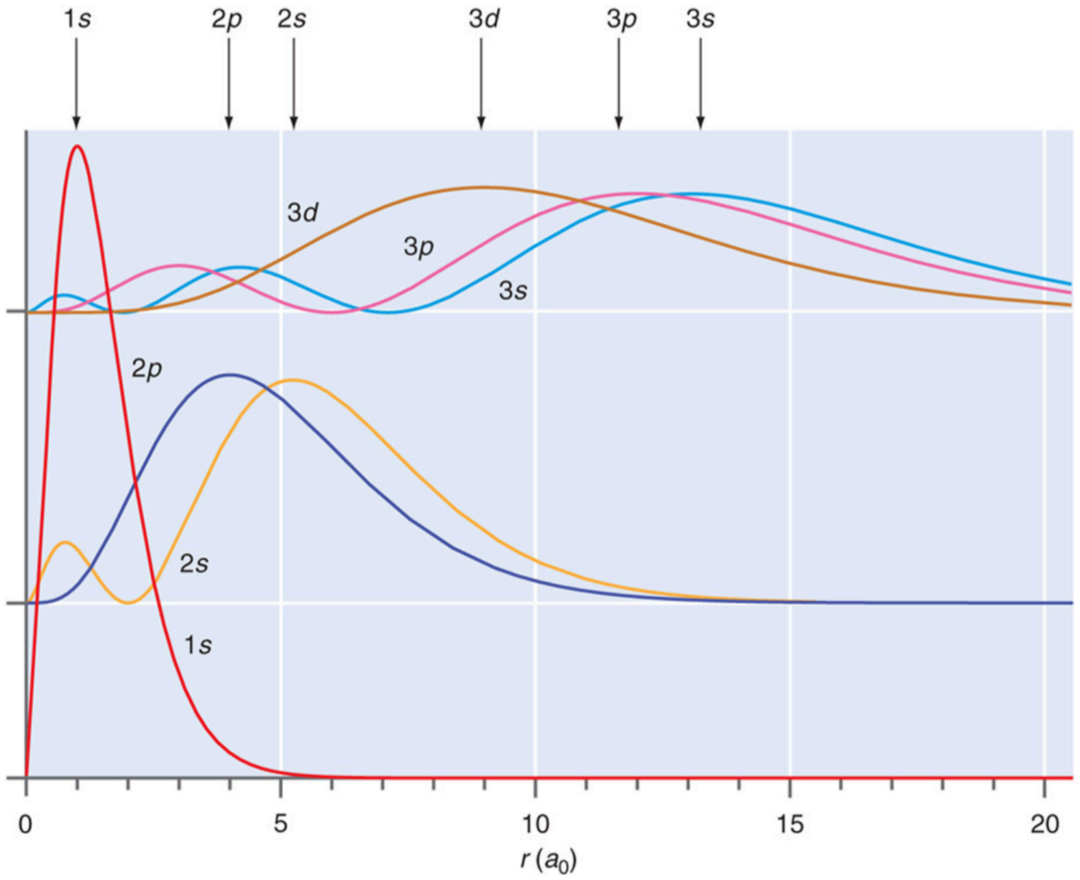


Figure 5.4: The radial probability distributions $P(r)$, Eq. (5.46), for different electronic orbitals of the hydrogen atom as a function of r/a_0. We find that the higher the value of n, the more likely it will be to find the electron far from the atomic nucleus. We also find that for a given n, electrons occupying orbitals with $l = 0$ have a larger probability of being found near the nucleus. All probability distributions vanish at the coordinate origin $P(r = 0) = 0$.

- For a given n, electrons occupying orbitals with $l = 0$ have a larger probability of being found near the nucleus. Note that in all cases the probability distributions vanish at the origin of coordinates, $P(r = 0) = 0$.

- s-type orbitals peak at a distance r *larger* than that of the p-type and other types of orbitals. This means that the higher the value of l, the less spread a given electronic orbital is. In other words, d-type orbitals are less spread than p-type orbitals which in turn are less spread than s-type orbitals.

Using a similar strategy as the one used for the ground state, it is possible to determine the radial coordinate expectation value $\langle r\rangle$ and the most likely radius r^* for any (n, l) orbital of the hydrogen (or hydrogen-like) atoms using the corresponding radial probability densities.

Graphical representation of radial probability distributions

Consider a hydrogen atom in a quantum state defined by $n = 3$, $l = 2$, and $m_l = -2$. We would like to determine the most likely value of the radial coordinate r and sketch graphically the radial probability distribution $P(r)$ as a function of r/a_0. Up to overall normalisation factors, one has

$$R_{3,3}(r) \propto \frac{r^2}{a_0^2} e^{-r/3a_0} \,, \tag{5.52}$$

and therefore the corresponding radial probability distribution will be given by

$$P_{3,2}(r) = |R_{3,2}(r)|^2 r^2 \propto \frac{r^6}{a_0^4} e^{-2r/3a_0} \,. \tag{5.53}$$

To determine the most likely value of the radial coordinate r, define variable $y = r/a_0$ so that

$$P_{3,2}(y) \propto y^6 e^{-2y/3} \,, \tag{5.54}$$

whose local extrema are given by

$$\frac{dP_{3,2}(y)}{dy} = 0 = 6y^5 \, e^{-2y/3} - (2/3) y^6 \, e^{-2y/3} \,. \tag{5.55}$$

This equation has two solutions, $y^* = 0$ and $y^* = 9$. Since the wave function vanishes for $r^* = 0$, we know that this is a minimum. Therefore the only maximum of the radial probability distribution function is $r^* = 9a_0$. With this information, and using the fact that $P(r)$ vanishes at both $r = 0$ and $r \to \infty$, we can sketch this function in Fig. 5.5.

5.5 Hydrogen-like atoms

The solutions that we have found for the hydrogen atom can be easily generalised to the case of *hydrogen-like atoms*, which are defined as atoms that have Z protons and $A - Z$ neutrons but only a single electron. One example of this would be the Helium atom if one of its two electrons has been stripped off, or Lithium if two of its electrons have been removed.

In hydrogen-like atoms, the only difference as compared to the derivation of the hydrogen atom would be to replace e^2 by Ze^2 in the effective potential of the radial wave function, Eq. (5.19). Therefore the only difference at the level of radial wave functions would be to replace Bohr's radius a_0 by

$$a_{Z,0} = \frac{4\pi\epsilon_0 \hbar^2}{m_e Z e^2} = \frac{a_0}{Z} \,, \tag{5.56}$$

or in other words, replacing a_0 in the solution of the hydrogen atom for a_0/Z in the case of hydrogen-like atoms. For the three lowest energy states, the expression for the radial wave functions of hydrogen-like atoms

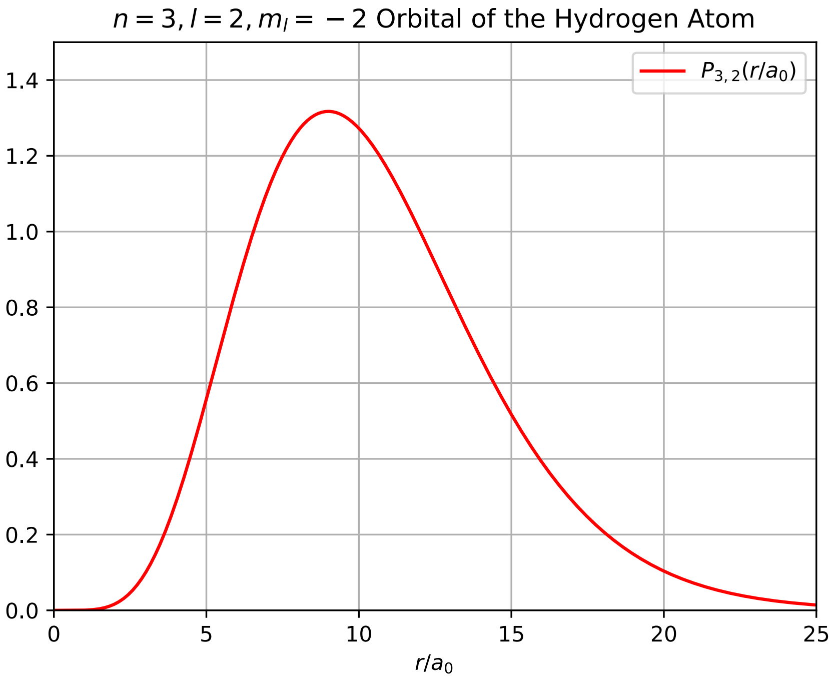


Figure 5.5: Graphical representation of the radial probability distribution for the $(3, 2, -2)$ orbital of the hydrogen atom. Note how this distribution is peaked for $r^* = 9a_0$.

are given by

$$\begin{aligned} R_{1,0}(Z,\rho) &= 2\left(\frac{Z}{a_0}\right)^{3/2} e^{-Z\rho/2} \, , \\ R_{2,0}(Z,\rho) &= \frac{1}{\sqrt{8}}\left(\frac{Z}{a_0}\right)^{3/2} (2-\rho)e^{-Z\rho/2} \, , \\ R_{2,1}(Z,\rho) &= \frac{1}{\sqrt{24}}\left(\frac{Z}{a_0}\right)^{3/2} \rho e^{-Z\rho/2} \, . \end{aligned} \tag{5.57}$$

On the other hand, the angular part of the wave function, given by the spherical harmonics $Y_{l,m_l}(\theta,\varphi)$, is the same for hydrogen and hydrogen-like atoms.

In hydrogen-like atoms, the atomic size now will be smaller than the one of the hydrogen atom by a factor $1/Z$. This can be understood from the fact that having now Z protons instead of one creates a stronger electrical attraction with the electron, and therefore the electron is more likely to be found closer to the atomic nucleus.

5.6 General properties of the p- and d-type orbitals

Since we have devoted some attention to the discussion of the s-type orbitals of the hydrogen atom, including the ground state of the system, let us now discuss some of the general properties of the p-type and d-type orbitals, starting with the former, and then continuing with the later.

p-type orbitals. The p-type orbitals are defined by an angular quantum number $l = 1$, and therefore a p-type subshell contains three orbitals, with $m_l = -1, 0$ and 1 respectively. The corresponding wave functions can be constructed by combining the radial $R_{n,l}(r)$ and angular $Y_{l,m_l}(\theta, \varphi)$ components of the wave function. For example, for the $2p$ orbital, defined by the $n = 2$ and $l = 1$ quantum wave numbers, in the case that $m_l = 0$ we have that

$$R_{2,1}(\rho) = \frac{1}{24^{1/2}} \left(\frac{1}{a}\right)^{3/2} \rho e^{-\rho/2} \tag{5.58}$$

$$Y_{1,0}(\theta, \varphi) = \left(\frac{3}{4\pi}\right)^{1/2} \cos\theta \,, \tag{5.59}$$

so here the wave function is symmetric with respect to the azimuthal angle φ. Combining the radial and angular components, we have the following wave function for the $2p_0$ orbital of the hydrogen atom.

$$\Psi_{2p_0}(r, \theta) = R_{2,1}(r) Y_{1,0}(\theta) = \frac{1}{4(2\pi)^{1/2}} \left(\frac{1}{a_0}\right)^{5/2} r\cos\theta e^{-r/2a_0} = r\cos\theta f(r) = z f(r) \,, \tag{5.60}$$

where we have used that in spherical coordinates $z = r\cos\theta$, and we have defined the function $f(r)$ that depends only on the radial coordinate $f(r)$ as follows:

$$f(r) \equiv \frac{1}{4(2\pi)^{1/2}} \left(\frac{1}{a_0}\right)^{5/2} e^{-r/2a_0} \,. \tag{5.61}$$

Note that denote the orbital with quantum numbers $(n, l, m_l) = (2, 1, 0)$ as $2p_0$, which is a more compact notation. So we find that the wave function can be written as a radial function $f(r)$ multiplied by z.

As discussed above, the wave functions for hydrogen-like atoms can be readily obtained from the wave functions of the hydrogen atom by means of the replacement $a \to a/Z$. To illustrate this, the wave function for the $2p_0$ orbital of an hydrogen-like atom with atomic number Z would be given by

$$\Psi_{2p_0}(r, \theta) = R_{2,1}(r) Y_{1,0}(\theta) = \frac{1}{4(2\pi)^{1/2}} \left(\frac{Z}{a_0}\right)^{5/2} r\cos\theta e^{-Zr/2a_0} = r\cos\theta f(r) = z f(r) \,. \tag{5.62}$$

The wave function of the $2p_0$ orbital, Eq. (5.60), vanishes everywhere in the plane $z = 0$, which is for this reason called a *nodal plane*. We also see that the wave function is positive for $z > 0$ and negative for $z < 0$, and that moreover it satisfies the reflection property that $\Psi_{2p_0}(r, z) = -\Psi_{2p_0}(r, -z)$.

From its mathematical structure, we also see that for a given value of z, the wave function of the $2p_0$ orbital will be symmetric with respect to the distance from the origin of coordinates r (the distance to the atomic nucleus), with

$$f(r) \propto e^{-r/2a_0} \,, \tag{5.63}$$

and that the wave function vanishes exponentially for $r \gg 2a_0$. Putting together all these properties, we can represent graphically the $2p_0$ orbitals of the hydrogen atom as in Fig. 5.6. To be precise, there we represent the *boundaries* or the orbitals, defined as the volumes that contain a given fraction of the total electron probability. Formally, the electronic orbitals extend to arbitrary high r.

We can observe the following properties of the $2p_0$ orbitals displayed in Fig. 5.6:

- The orbitals vanish in the nodal plane $z = 0$.

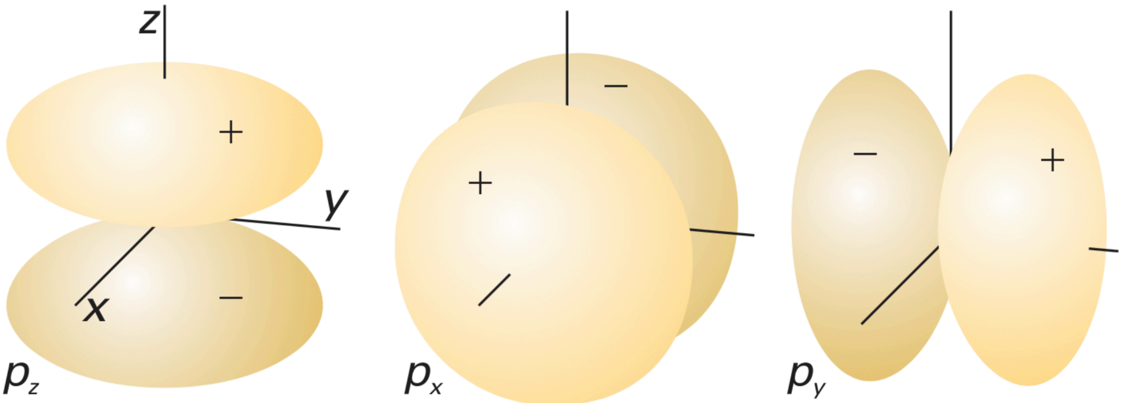


Figure 5.6: Schematic representation of the $2p_0$ (also denoted as $2p_z$), $2p_x$, and $2p_y$ orbitals of the hydrogen atom. Note that each of these orbitals exhibits a nodal plane for $z = 0$, $x = 0$, and $y = 0$ respectively.

- The orbitals are symmetric with respect to this nodal plane, since $|\Psi_{2p_0}(r,z)|^2 = |\Psi_{2p_0}(r,-z)|^2$.
- The orbitals vanish for large r.
- The orbitals exhibit polar symmetry for a given value of z: they depend only on r but not on the angular variables.

Similar symmetry properties apply for the other $2p$ orbitals. For orbitals with quantum numbers $m_l = 1$ and $m_l = -1$, the corresponding wave functions for the hydrogen atom will be given by:

$$\Psi_{2p_{\pm 1}} = R_{2,1}(r) Y_{1,\pm 1}(\theta,\varphi) = \mp \frac{1}{8\pi^{1/2}} \left(\frac{1}{a_0} \right)^{5/2} r \sin\theta e^{\pm i\varphi} e^{-Zr/2a_0} \propto \mp r \sin\theta e^{\pm i\varphi} f(r) \,, \qquad (5.64)$$

These wave functions are now complex quantities, so they cannot be plotted directly. To facilitate their interpretation, we note that since Ψ_{2p_1} and $\Psi_{2p_{-1}}$ are two degenerate eigenfunctions (meaning that they have associated the same energy), then by the properties of quantum mechanics we known that any linear combination of them will also be an eigenfunction of the Schroedinger equation. With this motivation, we define the following two linear combinations:

$$\Psi_{2p_x} \equiv -\frac{1}{\sqrt{2}} \left(\Psi_{2p_1} - \Psi_{2p_{-1}} \right) = r \sin\theta \cos\varphi f(r) = x f(r) \,, \qquad (5.65)$$

$$\Psi_{2p_y} \equiv \frac{i}{\sqrt{2}} \left(\Psi_{2p_1} + \Psi_{2p_{-1}} \right) = r \sin\theta \sin\varphi f(r) = y f(r) \,, \qquad (5.66)$$

again using the definition of spherical coordinates. Therefore we observe that these $2p_x$ and $2p_y$ orbitals share the same symmetry property as the $2p_0$ ($2p_z$) orbitals, namely having a nodal place for which the wave function vanishes. Moreover, this nodal plane is also a *symmetry plane*: the wave function is symmetric (up to an overall sign) with respect to this nodal plane. Therefore, as shown in Fig. 5.6, the p_x and p_y orbitals are nothing but a rotated version of the p_z orbitals (left panel in the Figure).

As opposed to the s-type orbitals, the p-type orbitals are not rotationally symmetric. It can be shown that instead all the orbitals of the hydrogen atom on the s-type orbitals are rotationally symmetric.

General results for the nodal planes. It can be shown that the radial part of the electron wave function $R_{n,l}(r)$ has $n-l-1$ nodal planes, that is, planes where the wave function vanishes. This follows from the mathematical structure of the wave functions of the hydrogen atom. For example, p orbitals with $l=1$, will have associated $n-1$ nodal planes, and indeed we have seen that the $n=2$ p-type orbitals have a single nodal plane associated. On the other hand, the angular wave function Y_{l,m_l} has l nodal planes. So in total, we see that an orbital defined by the quantum numbers n and l has $(n-l-1)+(l)=n$ nodal planes in its wave function. You can verify explicitly this property with the explicit expressions of the wave functions that we have presented in this section.

Summary

To summarize, some important concepts that we have learned in this lecture are the following:

- The allowed quantum states for the electrons in a hydrogen (or hydrogen-like) atom are called *electronic orbitals*, and are characterised by three quantum numbers: (n, l, m_l).
- The principal quantum number n determines the energy of the orbital and the average distance $\langle r\rangle$ with respect to the nucleus. It fixes the main electronic shell structure.
- Despite the fact that for $l=0$ the radial part of the electron wave function vanishes for $r=0$, the associated probability density is $P(r=0)=0$ due to the Jacobian of the transformation from Cartesian to spherical coordinates.
- The angular momentum quantum numbers l and m_l determine the subshell structure. Within each shell defined by n, there will be l subshells each filled by $2l+1$ orbitals.
- The s-type orbitals ($l=0$) exhibit rotational symmetry, while the p-type orbitals are instead symmetric with respect to a nodal plane where the wave function vanishes.

In the next lecture, we will study the electronic structure of the rest of the atoms that define the other elements of the periodic table: we will move from single-electron atoms to multi-electron atoms.

Further reading

Further reading material about the topics covered in this lecture can be found in the following sections of the course textbook (*Physical Chemistry*, Atkins and De Paula, 11th edition):

Chapters in textbook

- **8A.1**: The structure of hydrogenic atoms.
- **8A.2**: Atomic orbitals and their energies.

van Quantum tot Molecuul

Dr Juan Rojo
VU Amsterdam and Nikhef Theory Group
http://www.juanrojo.com/
j.rojo@vu.nl

6 HC6: Multi-electron atoms and the electron spin

In this lecture, we discuss how to apply the concepts that we learned in HC5 about the quantum mechanics of the hydrogen atom to more complex elements, in particular to multi-electron atoms. Since moving beyond the two-body problem the Schroedinger equation does not admit an analytical solution, we will need to adopt a number of approximations. We will start by Helium, composed by two electrons, and then study atoms with three electrons or more.

The **learning goals** of this lecture are:

(a) Applying the quantum mechanics of the hydrogen atom to the understanding of the electronic structure of multi-electron atoms.

(b) Using well-motivated approximations to express the orbitals of multi-electron atoms in terms of those of the hydrogen system.

(c) Becoming familiar with the concepts of spin, Pauli exclusion principle, and fermions and bosons, and the role they play in the quantum mechanics of the electrons.

(d) Using the building up principle and Hund's role to determine the electronic structure of multi-electron atoms.

6.1 The helium atom

In the previous lecture, we have studied the quantum mechanics of simplest possible of all chemical elements: the hydrogen atom, composed only by one proton and one electron. We have derived the wave functions for this system as well as for hydrogen-like atoms, that is, heavier elements with only one electron. Now we move to study more complicated atoms, in particular atoms with multiple electrons. We will start with the helium atom, which is the next-to-simplest atom since it contains only two electrons, and then apply the same ideas to atoms with more electrons. As we will show, we will base our study heavily on applying the same ideas and concepts that have appeared in the case of the hydrogen atom, and construct the wave functions of multi-electron atoms using the hydrogen atom wave functions as building blocks, in terms of the so-called *orbital approximation*.

We start this lecture with the next-to-simplest atom after the hydrogen atom: the helium (He) atom. A helium atom is composed by a nucleus with two protons and two neutrons (hence $Z = 2$ and $A = 4$) and two electrons. Since we always assume the atomic nucleus to be point-like (the nuclear radius is much smaller than the atomic radius), we have to solve in principle a *three-body problem*: the coupled motion of the two electrons and the atomic nucleus. As opposed to the two-body problem (the hydrogen atom) where a fully analytical solution was possible, for the case of the three-body problem it will become necessary to introduce a number of approximations.[3]

The associated Schroedinger equation for the helium atom is given by

$$\widehat{H}\Psi = \left(-\frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{2e^2}{4\pi\epsilon_0 r_1} - \frac{\hbar^2}{2m_e}\nabla_2^2 - \frac{2e^2}{4\pi\epsilon_0 r_2} + \frac{e^2}{4\pi\epsilon_0 r_{12}} \right) \Psi = E\Psi \,, \tag{6.1}$$

where r_1 is the distance between the nucleus and the first electron, r_2 is the distance between the nucleus and the second electron, and r_{12} is the distance between the two electrons. The kinetic terms ∇_1^2 and ∇_2^2 act on the coordinates of the first ($\vec{r}_1$) and second ($\vec{r}_2$) electrons respectively, see Eq. (5.3) for their definition. In addition to the kinetic terms for the two electrons, we also have the two Coulomb potentials representing the attraction between each of the two electrons and the atomic nucleus, as well as the repulsive Coulomb potential between the two electrons (since they are both negatively charged). Note that we have used $Z = 2$ in the Coulomb potential between each of the electrons and the He nucleus.

The main difference between the Schroedinger equations for the hydrogen and for the helium atoms, Eq. (6.1), is that while the former admits an analytical solution, this is not possible for the latter, and therefore we are forced to adopt a number of approximations. The method that we will adopt in this discussion is the so-called *orbital approximation*:

The orbital approximation

In this approximation, one assumes the wave function of the two-electron system can be expressed as the product of the wave function of the individual electrons, namely one writes

$$\Psi(\vec{r}_1, \vec{r}_2) = \Psi(\vec{r}_1)\Psi(\vec{r}_2) \,. \tag{6.2}$$

This assumption is based on neglecting the repulsive interaction between the two electrons. Indeed, the orbital approximation is exact if the term $e^2/4\pi\epsilon_0 r_{12}$ is removed from Eq. (6.1).

Within this approximation, the Schroedinger equation Eq. (6.1) for this system simplifies to:

$$\widehat{H}\Psi = \left(-\frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{2e^2}{4\pi\epsilon_0 r_1} - \frac{\hbar^2}{2m_e}\nabla_2^2 - \frac{2e^2}{4\pi\epsilon_0 r_2} \right) \Psi = E\Psi \,, \tag{6.3}$$

which now can be solved analytically. To see this, note that we can write using Eq. (6.2)

$$\widehat{H}\Psi = \left(\widehat{H}_1 + \widehat{H}_2 \right) \Psi(\vec{r}_1, \vec{r}_2) = \left(\widehat{H}_1 + \widehat{H}_2 \right) \Psi_1(\vec{r}_1)\Psi_2(\vec{r}_2) \,, \tag{6.4}$$

where $\widehat{H}_1$ is the Hamiltonian of a hydrogen-like atom with $Z = 2$ for the first electron and $\widehat{H}_2$ the same for

---

[3] Actually there does not exist a known solution of the three body problem: the system is inherently chaotic.

the second electron. In this situation, it is clear that then $\Psi_1(\vec{r}_1)$ will be the wave functions of the hydrogen atom, since Eq. (6.4) can be written in that case as

$$\widehat{H}\Psi = \left(\widehat{H}_1\Psi_1(\vec{r}_1)\right)\Psi_2(r_2) + \Psi_1(\vec{r}_1)\left(\widehat{H}_2\Psi_2(r_2)\right) = (E_1 + E_2)\,\Psi_1(\vec{r}_1)\Psi_2(r_2)\,. \tag{6.5}$$

Therefore, we have shown that if we neglect the repulsive Coulomb interaction between the two electrons of the helium atom, we can derive an analytic solution for the wave function in terms of the wave functions of the hydrogen atom, with the total energy of the system being given by

$$E = E_1 + E_2\,, \tag{6.6}$$

namely the sum of the individual energies of the two electrons. However, one still needs to account in some form for the effect that each electron has on the other, and this is achieved by means of a concept known as the *effective electric charge*.

The effective electric charge $Z_{\rm eff}$. The basic assumption that underlies the orbital approximation that we have used in Eq. (6.4) is that the motion of the two electrons in the system is *uncorrelated* between them: it is not affected by its mutual repulsive interaction. However, we know that this is not the case: the mutual repulsion between the two electrons will modify their motion around the nucleus to some extent. While we cannot compute fully this effect, we can account for it in an approximate manner.

The effective electric charge

In multi-electron atoms, one electron feels the *average* presence of the other electron. For example, for some configurations the two electrons will have little overlap, while for other configurations they will be on average closer. So effectively, the total positive electric charge felt by the electron will be smaller than the value Z from the protons in the nucleus, since the presence of the other electron will be reducing it. One then defines the *effective charge of the atomic nucleus* as the one that one electron experiences due to the *smearing* induced by the presence of the other electron.

In the case of the helium atom, we will have that this smearing will lead to an effective charge $Z_{\rm eff} < Z = 2$ smaller than the number of protons in the nucleus. This effect is also known as *shielding*: the positive charge of the nucleus felt by a given electron is partially shielded by the other electrons that are also orbiting around it. In this case, this effective electric charge of the nucleus turns out to be $Z_{\rm eff} = 1.62$. Note that in principle the value of $Z_{\rm eff}$ can be different depending on the specific orbital, but for the He atom with only two electrons it is the same for all electronic orbitals. Putting everything together, combining the orbital approach for the Helium wave function in Eq. (6.2) with the concept of effective charge of the atomic nucleus, we can construct our approximation for the electronic wave functions of the helium atom. For instance, if the two electrons occupy the $1s$ orbital, then the wave function of the helium atom will be given by

$$\begin{aligned}\Psi(\vec{r}_1,\vec{r}_2) &= \Psi_{1s}(\vec{r}_1)\times\Psi_{1s}(\vec{r}_2) = \frac{Z_{\rm eff}^{3/2}}{(\pi a_0^3)^{1/2}}e^{-Z_{\rm eff}r_1/a_0}\times\frac{Z_{\rm eff}^{3/2}}{(\pi a_0^3)^{1/2}}e^{-Z_{\rm eff}r_2/a_0}\\ &= \frac{Z_{\rm eff}^3}{\pi a_0^3}e^{-Z_{\rm eff}(r_1+r_2)/a_0}\,,\end{aligned} \tag{6.7}$$

with $Z_{\rm eff} = 1.62$. Therefore, we have shown how within the orbital approximation one can construct the wave functions for the electronic orbitals of the helium atom in terms of the wave functions that we derived

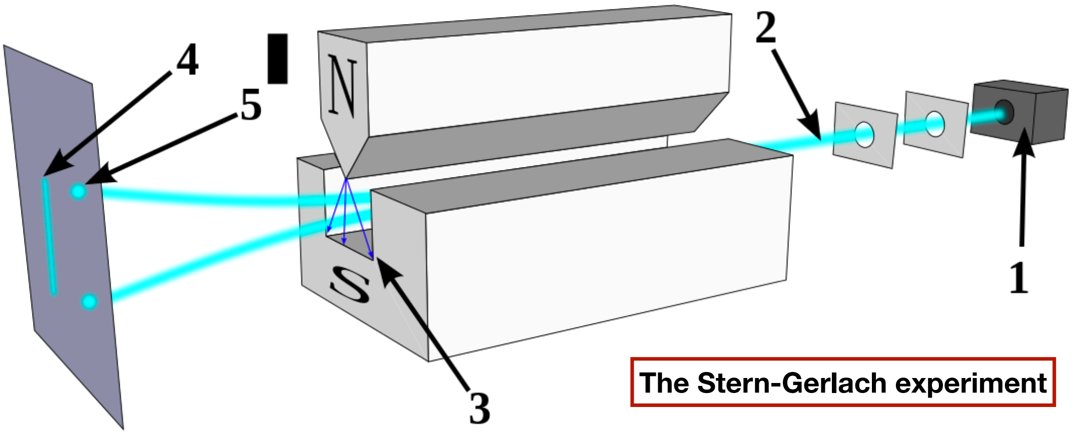


Figure 6.1: Schematic representation of the Stern-Gerlach experiment. A beam of atoms passes through a magnetic field perpendicular to their direction of motion. The beam is then deflected in two possible ways, indicating that the silver atoms are characterised by some form of internal angular momentum that can take only two values of same size but opposite sign, rather than a continuum of values as one could expect from classical theory.

in the previous chapter for the hydrogen-like atoms.

Before we can discuss how to generalise these ideas to more complex atoms such as Li ($Z = 3$, composed by three electrons), we need to discuss in some detail one of the foundational concepts of quantum mechanics: *spin*. The reason is that we have stated above as an obvious fact that two electrons can *occupy the same quantum orbital*, but actually this is not possible unless we introduce a new property, spin, that does not have an analog in classical theory.

6.2 Spin in quantum mechanics

Many introductions to quantum mechanics trace back the discovery of quantum property of *spin* to the *Stern-Gerlach experiment*. In this experiment, a bunch of silver atoms was beamed through a magnetic field $\vec{B}$ perpendicular to their direction of motion, as represented schematically in Fig. 6.1, therefore being deflected before impacting on a detector screen. Classically, the atoms could be deflected in principle in any direction, since the force that the magnetic field exerts on the silver atoms. The reason is that the torque acting on the magnetic moment $\vec{\mu}$ of the silver atoms in the presence of a external magnetic field $\vec{B}$ is

$$\vec{\tau} = \vec{\mu} \times \vec{B} \, . \tag{6.8}$$

where $\vec{\mu} \propto \vec{J}$ proportional to the total angular momentum of the silver atoms. Classically, the angular momentum of the silver atoms can take any value so one expects a continuum values for the torque and thus for the direction of deflection.

However, what the experiment found was that the silver atoms where deflected only in two directions (as opposed to a continuum), symmetrically with respect their original direction of motion. This result implies the silver atoms are characterised by some form of *angular momentum* that can take only *two values of same size but opposite sign.*

It was later understood that this angular momentum associated to silver atoms arises from the *intrinsic magnetic moment* of the electron in the outer atomic shell. We denote by *spin* this intrinsic angular momentum of the electron. We can naively think of spin as the angular momentum arising from the rotation of the electron along some axis, but this classical picture cannot really be true in the case of point particles and quantum mechanics. It is better to think of the spin as *another type of charge of the electron*, not unlike the electric charge. Therefore one can state that in quantum mechanics:

- Particles such as electrons and protons have associated a *new quantum number* denoted by spin s, which corresponds to a form of intrinsic angular momentum.
- For a particle characterised by a spin quantum number s, its spin can be aligned in $2s-1$ different directions (in the same way as for the orbital angular momentum), given by $-s, -s+1, \ldots, s-1, s$.
- Therefore, since an electron has spin quantum number $s = \hbar/2$, the component of the spin vector in the z direction can be either $+\hbar/2$ and $-\hbar/2$. As we will see, in the same way as that orbital angular momentum had associated the (l, m_l) pair of quantum numbers, also for spin we have the (s, m_s) combination, where for an electron $m_s = \pm 1/2$, since $s = \hbar/2$ and its component in the z-direction $s_z = \pm\hbar/2$.

This discussion about the properties of the electron spin will provide useful when constructing the electronic structure of multi-electron atoms: in addition to the the three quantum numbers (n, l, m_l) that define the wave functions of the electron atom, we will need now to specific also the value of spin quantum number m_s of the electron (that is, the projection of its spin along the z direction) in order to uniquely identify a given electronic orbital. Indeed, the existence of the electron spin is an important factor to determine the electronic orbital structure of multi-electron atoms.

The vector model of spin. As illustrated in Fig. 6.2, one can represent the spin of a $s = \hbar/2$ particle as a vector $\vec{s}$ restricted to a cone pointing in the z direction. This model is defined by the following properties:

- For a particle with spin s, then m_s can take $2s+1$ values, which means 2 values for an electron (since $s = 1/2$ in units of $\hbar$).
- The projection of $\vec{s}$ along the z axis is always either $s_z = +\hbar/2$ or $s_z = -\hbar/2$, depending on whether the corresponding *spin quantum number* m_s is $m_s = 1/2$ or $m_s = -1/2$.
- The size of this vector is $|\vec{s}| = \sqrt{s(s+1)}\hbar$, which corresponds to the total magnitude of spin angular momentum of the electron. For a spin 1/2 particle this is $|\vec{s}| = \sqrt{3/4}\hbar$.

  This property can be understood as follows. Any measurement of one of the three components of the spin vector will always return either $+\hbar/2$ or $-\hbar/2$. Therefore, if we add them together, the total magnitude of the spin vector can be obtained from using Pythagoras's theorem, which gives:

  $$|\vec{s}| = \left((\hbar/2)^2 + (\hbar/2)^2 + (\hbar/2)^2\right)^{1/2} = \left(3 \times (\hbar/2)^2\right) = \sqrt{3/4}\hbar\,, \tag{6.9}$$

  as we wanted to demonstrate.
- Note that in this model the projections along the x and y axis are not defined, and would be determined at random upon the corresponding measurement: even if m_s is fixed, the spin vector $\vec{s}$ can still take any position in the corresponding cone.

Visualizing spin as in Fig. 6.2 is not completely rigorous, but will prove to be rather useful in the following.

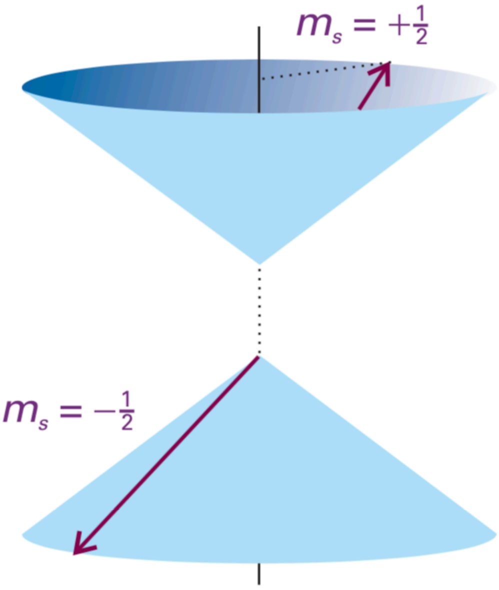


Figure 6.2: One can represent the spin of a $s = \hbar/2$ particle as a vector $\vec{s}$ sitting in a cone along the z direction. The projection of $\vec{s}$ along the z axis is always either $s_z = +\hbar/2$ or $s_z = -\hbar/2$, depending on whether $m_s = 1/2$ or $m_s = -1/2$. The magnitude of this vector is $|\vec{s}| = \sqrt{s(s+1)}\hbar$, which corresponds to the total spin angular momentum of the electron. Note that the projections along the x and y axis are not defined, and would be determined at random upon the corresponding measurement: even if m_s is fixed, the spin vector $\vec{s}$ can still take any position in the corresponding cone.

6.3 Fermions and bosons: spin and statistics

In quantum mechanics, the spin of a particle determines several of its most important properties. In terms of their spin, particles can be divided into *two classes*:

- *Fermions*: particles with *half-integer spin*: $\hbar/2$, $3\hbar/2$, ...

- *Bosons*: particles with *integer spin*: 0, $\hbar$, ...

Concerning the particles that will be relevant for this course, we have that both electrons, protons, and neutrons are *fermions* with spin $s = \hbar/2$. On the other hand, the total spin of an atom will be determined by the vectorial sum of the spin of its component electrons, leading to the fact that atoms can be either bosons (integer spin) or fermions (half-integer spin) depending on the specific electron configuration. In most cases, the configurations of the outermost electronic orbitals are the ones that determine the overall value of the spin of an atom.

The main difference between fermions and bosons is related to the fact of whether or not *two identical particles* can *occupy the same quantum state*. To illustrate this property, let us consider a simple system composed by two *identical particles*, say two electrons, one at position x_1 and the other at position x_2. For this system composed by two particles, its wave function can be separated in terms of the individual wave functions:

$$\Psi_{\rm tot}(x_1, x_2) = \Psi_1(x_1)\Psi_2(x_2)\,. \tag{6.10}$$

Now let us exchange the positions of the two particles $x_1 \to x_2$ and $x_2 \to x_1$. The new wave function of the system will be

$$\widetilde{\Psi}_{\rm tot}(x_1, x_2) = \Psi_1(x_2)\Psi_2(x_1)\,. \tag{6.11}$$

However, since the particles are identical, all physical information that I can extract from the system should be the same as before exchanging their positions. This requirement implies square of the wave function (which determines the probability of finding the system in a given quantum state) should be unchanged, that is,

$$|\Psi_{\rm tot}(x_1,x_2)|^2 = |\widetilde{\Psi}_{\rm tot}(x_1,x_2)|^2\,, \tag{6.12}$$

which implies that the wave function itself can only vary up to a complex phase,

$$\widetilde{\Psi}_{\rm tot}(x_1,x_2) = e^{i\phi}\Psi_{\rm tot}(x_1,x_2)\,. \tag{6.13}$$

Moreover, if we exchange back again the positions of the two particles, one is back to the starting configuration Eq. (6.10), and then the wave function should be the same as before. This implies that

$$e^{2i\phi} = 1 \qquad \to \qquad e^{i\phi} = \pm 1\,. \tag{6.14}$$

This exercise tells us that identical quantum particles can behave only on two ways if they exchange positions (or more in general, if they exchange quantum states) within a system:

- either the wave function of the system remains unchanged,
- or else it gets a minus sign.

We denote the first class of particles as *bosons*. Therefore, the wave function of a system composed by bosons is *symmetric* upon the exchange of two identical particles:

$$\widetilde{\Psi}_{\rm bosons}(x_1,x_2) = \Psi_{\rm bosons}(x_1,x_2)\,, \tag{6.15}$$

while we denote the second class of particles as *fermions*, for which under the same operation the wave function is instead *antisymmetric*:

$$\widetilde{\Psi}_{\rm fermions}(x_1,x_2) = -\Psi_{\rm fermions}(x_1,x_2)\,. \tag{6.16}$$

Note that there is no other option: upon the interchange of two identical particles, the wave function of the system is either *symmetric* (for bosons) or *antisymmetric* (for fermions).

6.4 The Pauli exclusion principle and two-electron systems

The most important implication of this difference between fermions and bosons is the so-called *Pauli exclusion principle*. Its derivation follows directly from the previous discussion. Consider the wave function of a system composed by two identical fermions that occupy the same position (again, more in general, that they occupy the same quantum state). We know that the total wave function will be antisymmetric upon the exchange of these two fermions, and therefore one finds that

$$\psi_{\rm fermions}(x_1,x_1) = -\psi_{\rm fermions}(x_1,x_1) = 0\,, \tag{6.17}$$

implying that:

The Pauli exclusion principle

Two fermions cannot occupy simultaneously the same quantum state.

This principle implies a given quantum state, characterised by a set of quantum numbers, can only be occupied by *one fermion at a time*. Since electrons are fermions, this principle has important consequences for the electronic structure of multi-electron atoms. On the other hand, bosons can occupy the same quantum state without no limitations, since they have a symmetric wave function upon the exchange of two identical particles

$$\psi_{\rm bosons}(x_1,x_1) = +\psi_{\rm bosons}(x_1,x_1) \neq 0\,. \tag{6.18}$$

In the context of the orbital structure of multi-electron atoms, the Pauli exclusion principle tells us that two electrons cannot occupy the same quantum state. This implies that a given orbital, defined by the quantum numbers (n,l,m_l), can contain *at most two electrons*, one with spin quantum number $m_s=+1/2$ and the other with spin quantum number $m_s=-1/2$. It follows that if two electrons occupy the same orbital then they must have *spins pointing in opposite direction*.

Paired and unpaired electrons

We define as *paired electrons* two electrons with opposite spin that occupy the same quantum state. *Unpaired electrons* are those with spins pointing in the same direction, and that therefore due to the Pauli exclusion principle cannot occupy the same electronic orbital. A given atomic orbital can therefore be occupied at most by a couple of paired electrons, else the Pauli exclusion principle would not be satisfied.

From the Pauli exclusion principle, it follows that each electronic orbital can at most be occupied by two electrons at the same time. Therefore, the two-electron system plays an important role in the study of multi-electron atoms. Here we now discuss the various ways in which we can combine two electrons taking into account the contributions from their spin.

In the following, we indicate by $|+\rangle$ the quantum state corresponding to an electron with spin pointing in the positive direction along the z axis (thus $m_s=+1/2$), and by $|-\rangle$ the same electron pointing in the negative direction (thus $m_s=-1.2$). Within the vector model of the electron spin, represented schematically in Fig. 6.2, any state for which the spin vector lies in the upper cone will have associated a $|+\rangle$ while if we vector lies in the lower cone they will have associated a $|-\rangle$. With this notation, we can then construct the following combinations for the two-electron system

- Two electrons pointing upwards: $|+\rangle_1|+\rangle_2 \equiv |++\rangle$.
- Two electrons pointing downwards: $|-\rangle_1|-\rangle_2 \equiv |--\rangle$.
- One electron upwards, another downwards: $|+\rangle_1|-\rangle_2 \equiv |+-\rangle$ or $|-\rangle_1|+\rangle_2 \equiv |-+\rangle$.

Recall that quantum particles such as electrons are *indistinguishable*: we cannot really label one electron as "1" and the other as "2", since it is not possible to tell them apart. Therefore the spin configurations $|+-\rangle$ and $|-+\rangle$ are not physically meaningful, since they assume that we can tell one electron apart from the other. We should instead construct linear combinations of these which have a more transparent physical interpretation. With this motivation we define:

$$\sigma_+ \equiv \frac{1}{\sqrt{2}}\left(|{+}{-}\rangle + |{-}{+}\rangle\right) , \tag{6.19}$$

$$\sigma_- \equiv \frac{1}{\sqrt{2}}\left(|{+}{-}\rangle - |{-}{+}\rangle\right) . \tag{6.20}$$

The rationale between choosing these combinations is the following. The first combination, σ_+, is *symmetric* under the exchange of the two particles of the system. The second combination, σ_-, is instead *antisymmetric* with respect to such exchange. Note that in these combinations specifying which ones is "electron 1" and "electron 2" is irrelevant: the same property holds irrespective of how one does the assignment. The overall factor $1/\sqrt{2}$ has been added to ensure the normalisation of the two-electron wave function.

Summarizing, the four possible spin configurations that can be physically constructed for a two electron system are the following:

$$\begin{aligned} & |{+}{+}\rangle \\ & |{-}{-}\rangle \\ \sigma_+ &= \frac{1}{\sqrt{2}}\left(|{+}{-}\rangle + |{-}{+}\rangle\right) , \\ \sigma_- &= \frac{1}{\sqrt{2}}\left(|{+}{-}\rangle - |{-}{+}\rangle\right) . \end{aligned} \tag{6.21}$$

One should emphasize that the fact that we can construct these four combinations does not mean that all of them can be realised in an specific physical system. Indeed, out of these four configurations, only σ_- is antisymmetric under the exchange of the two electrons as required by the Pauli exclusion principle. Therefore, we obtain the following important result:

For two electrons that occupy the same atomic orbital Ψ_{n,l,m_l}, only one specific combination of radial and spin wave functions can be constructed, $\Psi_{n,l,m_l}(\vec{r_1})\Psi_{n,l,m_l}(\vec{r_2})\sigma_-$ in s way that satisfies the Pauli exclusion principle. Indeed, we see that despite the fact that the spatial part of the wave function, $\Psi_{n,l,m_l}(\vec{r_1})\Psi_{n,l,m_l}(\vec{r_2})$, is symmetric under the exchange of the two electrons, the total wave function is antisymmetric as required for a system of fermions since $\sigma_- \to -\sigma_-$ upon the exchange of the two electrons. On the other hand, for electrons that occupy different orbitals this restriction does not apply, and for example $\Psi_{n_1,l,m_l}(\vec{r_1})\Psi_{n_2,l,m_l}(\vec{r_2})\sigma_+$ with $n_1 \neq n_2$ is an allowed wave function.

Depending on the relative orientation of the spins of a two electron system, we can divide them as:

- A system of *two paired electrons* is called a *singlet state*, it has total spin $S = 0$, and the spin component of the wave function is σ_-, Eq. (6.20). Note we use upper case notation, S, to denote the total spin of the two electron system.
- A system of *two unpaired electrons* is called a *triplet state*. Such triplet state has a total spin of $S = 1$. The spin configurations of the triplet states $|{+}{+}\rangle, \sigma_+$, and $|{-}{-}\rangle$ have associated a value of the total spin component in the z direction of $S_Z = +1, 0, -1$, respectively.

The way how the total spin S and its z-projection S_z are constructed from the spins of the two individual electrons for the various configurations is represented schematically in Fig. 6.3. There we use the same representation of $\vec{s}$ as a vector restricted to lie in the surface of a cone along the z direction as was used in

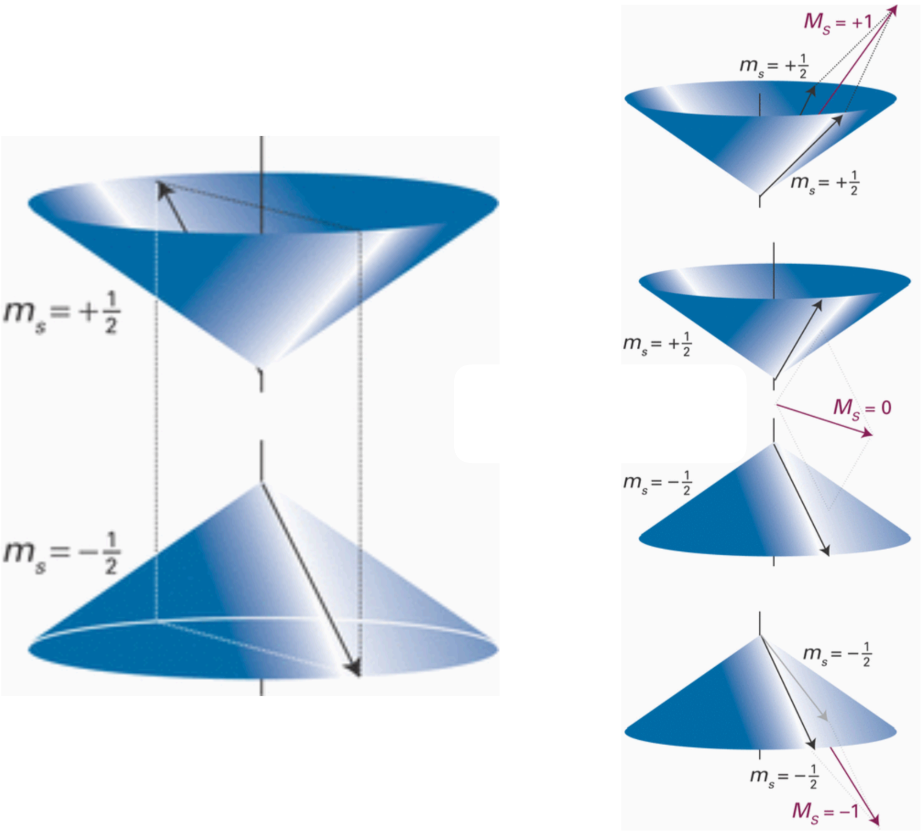


Figure 6.3: Schematic representations of the different possible spin configurations in a two-electron system in terms of the vector model for the spin. In the left plot, we show the *singlet state* of paired electrons, where the total spin of the system is $S = 0$. The first electron has $m_s = +1/2$ (thus lying in the upper cone) and the second electron has $m_s = -1/2$ (thus lying in the lower cone). Note that also their spin components in the x and y directions are the opposite. In the right plot of the figure, we show the three possible *triplet configurations*, each with total spin $S = 1$. They differ in the values of the spin projections along the z axis, s_z. From top to bottom we have the configurations with $m_s = +1$, $m_s = 0$, and $m_s = -1$ respectively. Note how the total value of m_s of the two electron system is the sum of that of the individual electrons.

Fig. 6.2 and in the corresponding discussion. In the left plot, we show the *singlet state* of paired electrons, where the total spin of the system is $S = 0$. The first electron has $m_s = +1/2$ (thus lying in the upper cone) and the second electron has $m_s = -1/2$ (thus lying in the lower cone). Note that also their spin components in the x and y directions are the opposite. In the right plot of the figure, we show the three possible *triplet configurations*, each with total spin $S = 1$. They differ in the values of the spin projections along the z axis, s_z. From top to bottom we have the configurations with $M_S = +1$, $M_S = 0$, and $M_S = -1$ respectively. Note how the total value of M_s of the two electron system is the sum of that of the individual electrons. For example, for the upper configuration, we have $M_S = m_s + m_s = 1/2 + 1/2 = +1$.

6.5 Multi-electron atoms and the building-up principle

The above discussion on the electronic spin completes our study of the helium atom, the next-to-simplest chemical element with $Z = 2$. We now to discuss how the electrons distribute themselves among the electronic orbitals of more complex elements, with $Z \geq 3$. In this discussion, we will keep using the *orbital approximation*, which assumes that the electronic orbitals of multi-electron atoms can be written as a combination of the orbitals of hydrogen-like atoms with suitable modifications such as that the the *effective electric charge*.

Shielding in multi-electron atoms. We have already introduced the concept of *effective electric charge* $Z_{\rm eff}$ in multi-electron atoms in Sect. 6.1. The idea is that in an multi-electron atoms with Z protons, the effective charge that one electron experiences is $Z_{\rm eff} < Z$ due to the combined effect of the smearing from the other electrons. This same idea can be expressed in terms of *shielding*: namely, each of the electrons in an atom partially shields the positive electric charge of the atomic nucleus for all other electrons. We therefore define the shielding constant σ as follows:

$$Z_{\rm eff} = Z - \sigma \,, \qquad (6.22)$$

where the specific value of σ is different element by element and also varies within orbitals.

To illustrate this point, we know already that s-type orbitals have a higher likelihood to be found close to the nucleus at $r = 0$ (see Fig. 5.4 and the corresponding discussion), and therefore the effective charge that they experience will be larger than that of the p-type orbitals, which on average are further away from the protons in the nucleus. This effect can be observed from the table below, which compares the value of the effective electric charge $Z_{\rm eff}$ of Helium with that associated to the different orbitals of Carbon (with $Z = 6$):

Element	Z	Orbital	$Z_{\rm eff}$
He	2	$1s$	1.6875
C	6	$1s$	5.6727
		$2s$	3.2166
		$2p$	3.1358

For similar reasons, the value of the shielding constant for d-type orbitals will also be different than for the s- and d-type orbitals: an electron in a d-type orbital is on average more likely be found farther from the nucleus than that of an p-type orbital, and thus one expects a more intense shielding. We can also see that for a given type of orbital, say a s-type orbital, the shielding constant will be larger for more excited states with larger n, which on average are found farther from the atomic nucleus.

Therefore, if we denote by $\sigma_{n,l}$ the shielding constant associated to an orbital with quantum numbers (n, l), we will have the following rules of thumb:

- For orbitals with a fixed principal quantum number n, the larger the value of l the higher the value of the shielding constant, for example we have that

$$\sigma_{3,s} \le \sigma_{3,p} \le \sigma_{3,l} \,. \qquad (6.23)$$

- For orbitals with a fixed angular quantum number l, the larger the value of the principal quantum number n the higher the value of the shielding constant, for example we have that

$$\sigma_{1,s} \le \sigma_{2,s} \le \sigma_{3,s} \,. \qquad (6.24)$$

Note also that this is not a fundamental rule and that there are exceptions to the above general principle.

The building up (aufbau) principle. In order to fill the electron orbitals of a given multi-electron atom, one must follow the so-called *building up* or *aufbau principle*, which determines the filling order of the orbitals

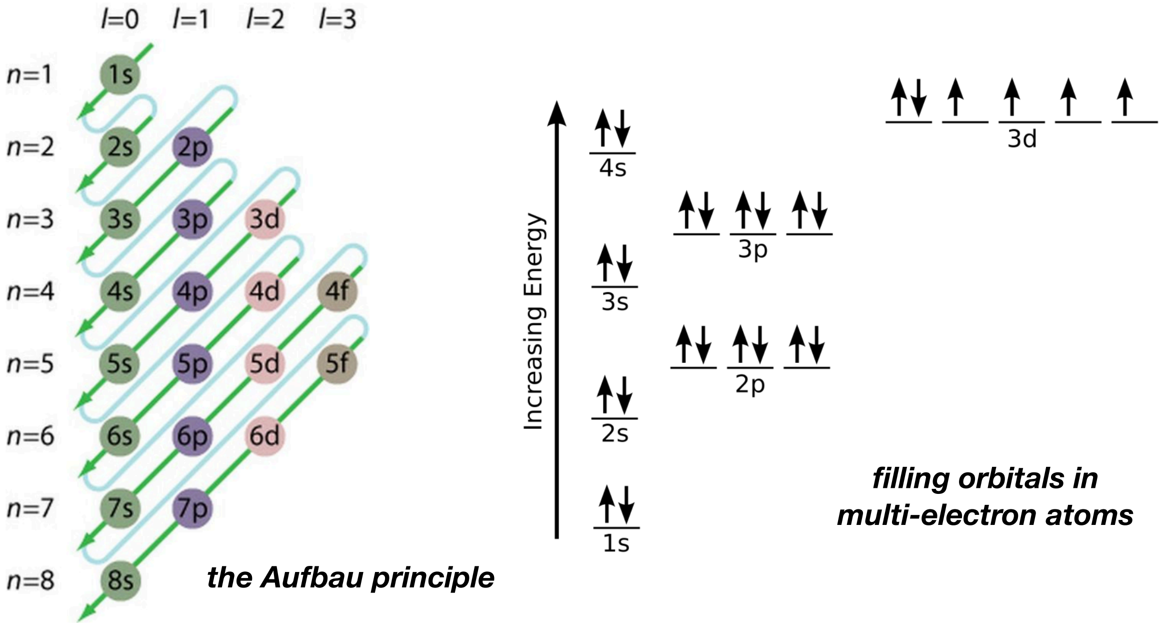


Figure 6.4: Left panel: the building up principle determines the ordering of the filling of electronic orbitals in multi-electron atoms. This order is determined by the values of the quantum numbers n and l, and ensures that the free orbitals with lower energies are always filled first. Right panel: example of the filling of atomic orbitals for iron (Fe), with $Z = 26$. Note that within a given sub-shell, electrons first occupy empty orbitals before starting to pair within the same orbital. For a subshell with angular quantum number l, there are $2l + 1$ orbitals that can be occupied (each by at most two electrons).

as a function of their energy::

The building up principle

In a multi-electron atom, electrons will always fill the free orbital which has the lowest energy. Once this orbital is completely filled, electrons will start to occupy the next free orbital with the lowest energy, and so on.

We should be careful since this is *not a fundamental principle* but rather a rule of thumb, and the order of the filling of electronic orbitals in some atoms differs from that indicated by the aufbau principle. The specific order in which electronic shells should be filled according to the building up principle is represented in Fig. 6.4. When expressing orbitals in terms of their quantum numbers (n, l), we see that the filling order will be:

$$1s \to 2s \to 2p \to 3s \to 3p \to 4s \to 3d \to 4p \to \ldots \, . \tag{6.25}$$

Note that depending on the value of l, some orbitals with $n_2 > n_1$ will be filled before the n_1 shell is complete. For example, the $4s$ orbital should be filled before the $3d$ orbital according to the building up principle. Recall also that the number of electrons that fill a given subshell depends on the value of l: for $s-$type orbitals we can fit two electrons, for p-type orbitals we can fit six electrons and so on. Orbitals with angular quantum number l can accommodate up to $4l + 2$ electrons once we take their spin into account.

It is instructive to show how the building up principle is applied for different elements. As we will show, the results of this filling of electronic shells also provides useful information to understand the chemical behaviour of the different elements.

- The electronic structure of lithium (Li, $Z = 3$) is $1s^2 2s^1$.
- The electronic structure of beryllium (Be, $Z = 4$) is $1s^2 2s^2$.
- The electronic structure of nitrogen (N, $Z = 7$) is $1s^2 2s^2 2p^3$.
- The electronic structure of neon (Ne, $Z = 10$) is $1s^2 2s^2 2p^6$.
- The electronic structure of phosphorus (P, $Z = 15$) is $1s^2 2s^2 2p^6 3s^2 3p^3 = [\mathrm{Ne}]3s^2 3p^3$.
- The electronic structure of sulphur (S, $Z = 16$) is $1s^2 2s^2 2p^6 3s^2 3p^4 = [\mathrm{Ne}]3s^2 3p^4$.

where [Ne] represents the electronic structure of Ne with its $n = 1$ and $n = 2$ filled shells. We observe that both He and Ne have all shells filled ($n = 1$ for He, and $n = 1$ and $n = 2$ for Ne). This explains why these two elements, which belong to the family of *noble gases*, have a very low chemical reactivity: their electronic structure is complete and thus very stable.

In Fig. 6.4 we show as an example the filling of atomic orbitals for iron (Fe), with $Z = 26$. Note that within a given sub-shell, electrons first occupy empty orbitals before starting to pair within the same orbital - this is called the *Hund rule* and will be discussed below. This diagram illustrates how the electronic orbitals are filled in order of increasing energy, starting from the ground state ($1s$), then filling the first excited state ($2s$), and then subsequently the next free orbital with the lowest energy.

Hund's rule. The *Hund's rule* for the filling of atomic orbitals states that:

> When filling orbitals, electrons first occupy *the empty degenerate orbitals* before they occupy an orbital where another electron is already present.

This effect is illustrated in Fig. 6.4 for the case of the Fe atom ($Z = 26$). Note that, following Pauli's exclusion principle, two electrons that occupy the same orbital must have their spins *paired* (that is, pointing in opposite directions). A direct consequence of this rule is that the *ground state of an atom* with a given value of Z is the one that contains *the maximum number of unpaired electrons*, since this is the one that has associated the smallest total energy. An explanation of this rule is provided by the concept of *spin correlations*: electrons with unpaired spin (pointing in the same direction) stay away from each other, since this reduces their mutual repulsion and thus decreases the total energy of the system.

Let us see what are some of the practical consequences of the application of Hund's rule. According to this rule, the electrons that occupy the p-type orbitals in C, N, and O atoms should be distributed as follows:

Element	Atomic structure	Orbital filling
C ($Z = 6$)	$1s^2 2s^2 2p^2$	$1s^2 2s^2 2p_x^1 2p_y^1$
N ($Z = 7$)	$1s^2 2s^2 2p^3$	$1s^2 2s^2 2p_x^1 2p_y^1 2p_z^1$
O ($Z = 8$)	$1s^2 2s^2 2p^4$	$1s^2 2s^2 2p_x^2 2p_y^1 2p_z^1$

So we see that, to begin with, degenerate orbitals within a given subshell (in this case the $2p_x$, $2p_y$, and $2p_z$ orbitals) are occupied by only one electron. Only when these three degenerate orbitals contain one electron each, they will start to accommodate the second electron in a way that their spins are paired.

Summary

To summarize, some important concepts that we have learned in this lecture about

- Within the orbital approximation, the electronic structure of multi-electron atoms can be understood in terms of that of the hydrogen atoms with suitable modifications, such as the effective electric charge.
- Spin is a fundamental property of particles such as electrons and protons that does not have classical analog. It can be understood by means of the vector model of spin.
- The Pauli exclusion principle indicates that two fermions cannot occupy the same quantum state, and has important implication to understand the electronic structure of multi-electron atoms.
- The building-up principle and Hunds's rule determine the order in this the electronic shells will be filled in multi-electron atoms.

This lecture completes our study of the electronic structure of individual chemical elements. We have started from the simplest possible element, hydrogen, and then studied the electronic structure of multi-electron atoms first with Helium and then for atoms with $Z > 3$. In the second part of the course, we will exploit and generalize these concepts to the study of the electronic structure of *molecules*, bound states composed by two or more atoms.

Further reading

Further reading material about the topics covered in this lecture can be found in the following sections of the course textbook (*Physical Chemistry*, Atkins and De Paula, 11th edition):

Chapters in textbook

- **8B.1**: *The orbital approximation.*
- **8B.2**: *The Pauli exclusion principle.*
- **8B.3**: *The building-up principle.*