van Quantum tot Molecuul

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3 HC3: Quantum mechanics of simple systems

Quantum mechanics of simple systems: the particle in a box, quantum tunneling, the quantum harmonic oscillator, particle in a box with finite potential barriers.
Based on Atkins and de Paula, *Physical Chemistry*, 10th edition, Chapter 8.

In this lecture we discuss quantum mechanics applied to relatively simple systems such as the 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*.

The *learning goals* of this lecture are:

(a) Solving the Schroedinger equation for simple quantum systems.

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

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

(d) Understanding and applying the mathematical technique of separation of variables.

(e) Understanding and applying the phenomenon of quantum tunneling.

3.1 Particle in a box and energy quantization

In HC2, when we solved the Schroedinger equation for a free particle, we found that its energy was given by $E_k = k^2\hbar^2/2m$, where k was a real parameter that could take any value. Therefore, for a free particle, energy levels *are not quantized*. We now will see how once the particle is confined into a limited region of space, energy levels become automatically quantized. One of the simplest system in 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

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

In other words, the particle undergoes free motion for $0 \le x \le L$, but cannot move outside this range because it is *confined* by the potential Eq. (3.1) (since the particle would need an infinite energy to overcome that potential barrier).

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

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

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.

Since for $x > L$ and $x < 0$ we have that $V(x) = \infty$, the particle cannot travel to this region (since it would require infinite energy) and thus the wave-function will be zero there. In particular this means that

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

Now, since as discussed in HC2, the wave-function must be *continuous*, we can use the *boundary conditions* Eq. (3.3) to fix the coefficients in Eq. (3.2):

$$\Psi_k(x=0) = D \to D = 0\;, \tag{3.4}$$

$$\Psi_k(x=L) = C\sin(kL) = 0 \to k = \frac{n\pi}{L}\;, \tag{3.5}$$

where n is an arbitrary *integer number*. Therefore we find that for a particle in a box the quantum wave-functions and energies are given by

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

Therefore, we now find that the *energies of the particle are quantized*, and labeled by an integer number n rather than by a real number k as was the case for a free particle. Finally, the coefficient $C = (2/L)^{1/2}$ can be determined from requiring the normalization of the wave-function.

Remarkably, we note that the lowest energy that a particle can have in this system is not zero, but rather $E_1 = \hbar^2\pi^2/2mL^2 \neq 0$. 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 at rest (because else we would know its momentum with arbitrary precision, contradicting Heisenberg's uncertainty principle). Note also that the solution $n = 0$ corresponds to $\Psi_0 = 0$, that is, the absence of any particle in the system, so it cannot really be associated with the group state (which is instead the $n = 1$ state).

The conclusions that we can extract 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.

Let us now computes the expectation value of the 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

$$\Psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{\pi n x}{L}\right) , \tag{3.7}$$

and if we compute the expectation value of p_x, using the definition of Eq. (2.37), we find that

$$\langle p_x \rangle = \frac{2}{L}\int_0^L dx \sin\left(\frac{\pi n x}{L}\right)\left(\frac{\hbar}{i}\frac{d}{dx}\right)\sin\left(\frac{\pi n x}{L}\right) = \frac{2\hbar n\pi}{iL^2}\int_0^L \sin\left(\frac{\pi n x}{L}\right)\cos\left(\frac{\pi n x}{L}\right) = 0 \,, \tag{3.8}$$

since the integral vanishes for any value of n, as can be checked using trigonometric identities. So therefore we find that the expectation value of the momentum for the particle in a box is $\langle p_x \rangle = 0$. This can be understood if we expand the solution Eq. (3.7) as follows

$$\Psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{\pi n x}{L}\right) = \sqrt{\frac{1}{2L}}\frac{1}{i}\left(e^{\pi n x/L} - e^{-\pi n x/L}\right) , \tag{3.9}$$

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 cancel to each other leading to $\langle p_x \rangle = 0$.

Note also that in the limit where $n \to \infty$ the energies of the particle become *effectively continous*, 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:

$$\begin{aligned} V(x,y) &= 0 \quad \text{for} \quad 0 \le x \le L_x \quad \text{and} \quad 0 \le y \le L_y \\ V(x,y) &= +\infty \quad \text{for} \quad y < 0\,, \quad y > L_y\,, \quad x < 0\,, \quad x > L_x \end{aligned} \tag{3.10}$$

Inside the box, the Schroedinger equation is the same as that of the free particle but now in two dimensions, namely

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right)\Psi(x,y) = E\Psi(x,y) , \tag{3.11}$$

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*, namely assuming 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,

$$\Psi(x, y) = \Psi_X(x)\Psi_Y(y) \,. \tag{3.12}$$

If we plug this *ansatz* on the two-dimensional Schroedinger equation Eq. (3.11), we find that

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

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

$$-\frac{\hbar^2}{2m}\frac{1}{\Psi_X(x)}\left(\frac{\partial^2}{\partial x^2}\right)\Psi_X(x) - \frac{\hbar^2}{2m}\frac{1}{\Psi_Y(y)}\left(\frac{\partial^2}{\partial y^2}\right)\Psi_Y(y) = E \,. \tag{3.14}$$

In Eq. (3.14), the RHS is independent of both x and y, and in the 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

$$-\frac{\hbar^2}{2m}\frac{1}{\Psi_X(x)}\left(\frac{\partial^2}{\partial x^2}\right)\Psi_X(x) = E_X \,, \tag{3.15}$$

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

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

$$\Psi_x(x) = \sqrt{\frac{2}{L_x}}\sin\left(\frac{n_x\pi x}{L_x}\right) \,, \tag{3.17}$$

$$\Psi_y(y) = \sqrt{\frac{2}{L_y}}\sin\left(\frac{n_y\pi y}{L_y}\right) \,, \tag{3.18}$$

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

$$\Psi(x, y) = \Psi_x(x)\Psi_x(y) = \sqrt{\frac{4}{L_xL_y}}\sin\left(\frac{n_x\pi x}{L_x}\right)\sin\left(\frac{n_y\pi y}{L_y}\right) \,. \tag{3.19}$$

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_2, and thus reads

$$E_{n_x,n_y} = \frac{h^2}{8m}\left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2}\right) \,. \tag{3.20}$$

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

$$E_{n_x,n_y} = \frac{h^2}{8m}\left(\frac{n_x^2 + n_y^2}{L^2}\right) , \tag{3.21}$$

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 states: in general, many different states can have associated the same total energy.

3.3 Quantum tunneling

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

$$E = E_k + V(x) = \frac{1}{2}mv^2 + V(x) , \tag{3.22}$$

where E_k is the particle's kinetic energy, is a constant of motion and must hold for all values of x. Therefore, we have that

$$v^2 = \frac{2}{m}(E - V(x)) \tag{3.23}$$

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 cross a potential barrier even when its kinetic energy is smaller than the potential energy of the barrier. This remarkable phenomenon is known as the *quantum tunneling* effect, and is schematically represented in Fig. 3, 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, 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

$$\Phi_k(x) = Ae^{ikx} + Be^{-ikx} , \tag{3.24}$$

where the kinetic energy is $E_k = \hbar^2k^2/2m$ and thus the linear momentum is $p_x = k\hbar = \sqrt{2mE_k}$.

Now, in the region *inside the barrier* the Schroedinger equation looks like

$$-\frac{\hbar^2}{2m}\frac{d^2\Psi}{dx^2} + V\Psi = E_k\Psi , \quad \text{with} \quad V \geq E_k . \tag{3.25}$$

Note that here I have identified the total energy 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

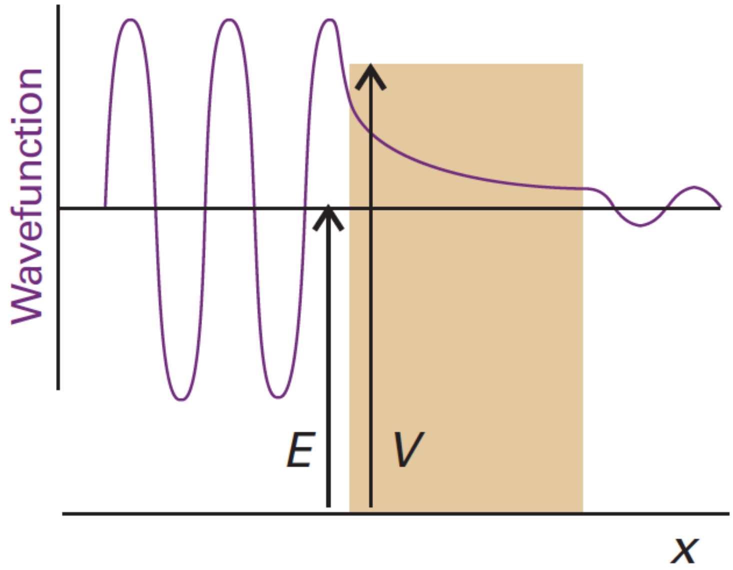

Figure 3: Schematic representation of the *quantum tunneling effect*: the wave-function of a particle with kinetic energy E_k is non-zero inside a barrier with potential energy $V > E_k$, and therefore has a finite probability (non-zero wave-function) to be found at the other side of the barrier.

equation can be rewritten as

$$-\frac{\hbar^2}{2m}\frac{d^2\Psi}{dx^2} = -(V - E_k)\Psi\,, \tag{3.26}$$

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

$$\Psi = C\,e^{\kappa x} + D\,e^{-\kappa x}\,, \quad \kappa\hbar = \sqrt{2m\,(V - E_k)} \geq 0\,, \tag{3.27}$$

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.

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

$$\Psi = A'e^{ikx}\,, \quad k\hbar = \sqrt{2mE_k}\,, \tag{3.28}$$

with equal momentum and energy as in the left side of the barrier. 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 *continous everywhere*, and its *derivative is also continous* for any value of x. 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

$$\begin{aligned} A + B &= C + D\,, \\ Ce^{\kappa L} + De^{-\kappa' L} &= A'e^{ikL}\,, \end{aligned} \tag{3.29}$$

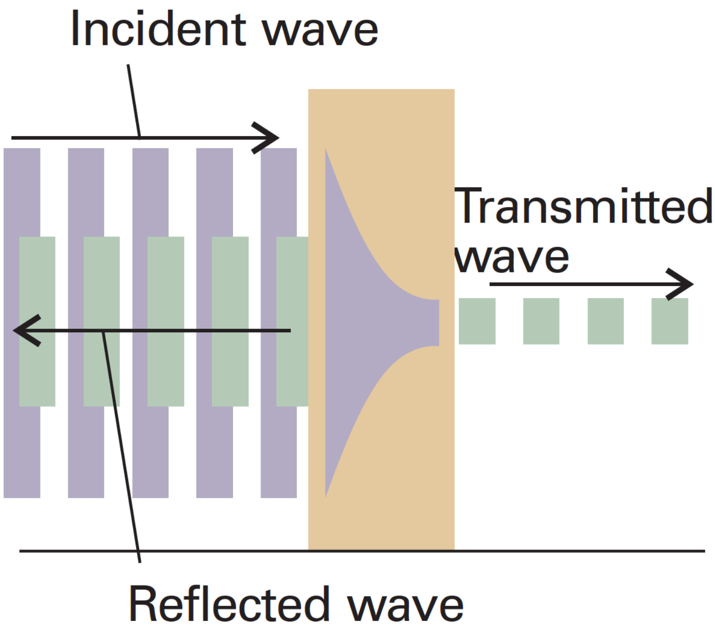

Figure 4: The physical interpretation of the quantum tunneling effect: an incident wave Ae^{ikx} left to the barrier is partially transmitted to the other side of the barrier with wave function $A' = e^{ikx}$ and partially reflected, with momentum in the opposite direction as compared to the incident wave, Be^{-ikx}. The ratio $T = A'/A$ of the transmitted over the incident amplitude is known as the *transmission coefficient*.

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

$$\begin{aligned} ikA - ikB &= \kappa C - \kappa D\,, \\ \kappa C e^{\kappa L} - \kappa D e^{-\kappa L} &= ikA' e^{ikL}\,. \end{aligned} \tag{3.30}$$

Note that we have five unknowns and four equations, and therefore we can express four of these unknowns in terms of a single one, say A.

As we saw in the free-particle case, for the solution in the left side of the barrier, Eq. (3.24) 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. 4. 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:

$$T(\kappa L, \epsilon) = \left(1 + \frac{\left(e^{\kappa L} - e^{-\kappa L}\right)^2}{16\epsilon(1-\epsilon)}\right)^{-1}\,, \quad \epsilon \equiv E/V\,, \tag{3.31}$$

and where κ has been defined in Eq. (3.27). 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

$$\kappa\hbar = \sqrt{2m(V - E_k)} = \sqrt{2mV}\sqrt{1-\epsilon}\,. \tag{3.32}$$

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

- 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

$$T \to \left(1 + \frac{mVL^2}{\hbar}\right)^{-1}, \tag{3.33}$$

  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. (3.33) is achieved.

- in the limit $\kappa L \gg 1$ the transmission amplitude Eq. (3.31) becomes

$$T \simeq 16\epsilon(1-\epsilon)e^{-2\kappa L}. \tag{3.34}$$

  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. (3.34) 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. (3.31) 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

$$\kappa = \frac{1}{\hbar}\sqrt{2m(V-E_k)}, \tag{3.35}$$

we find that, for fixed values of V and E_k, if $\kappa \to \infty$ then from Eq. (3.31) we see that $T \to 0$. This limit can be realized if

$$\hbar \ll \sqrt{2m(V-E_k)}. \tag{3.36}$$

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.

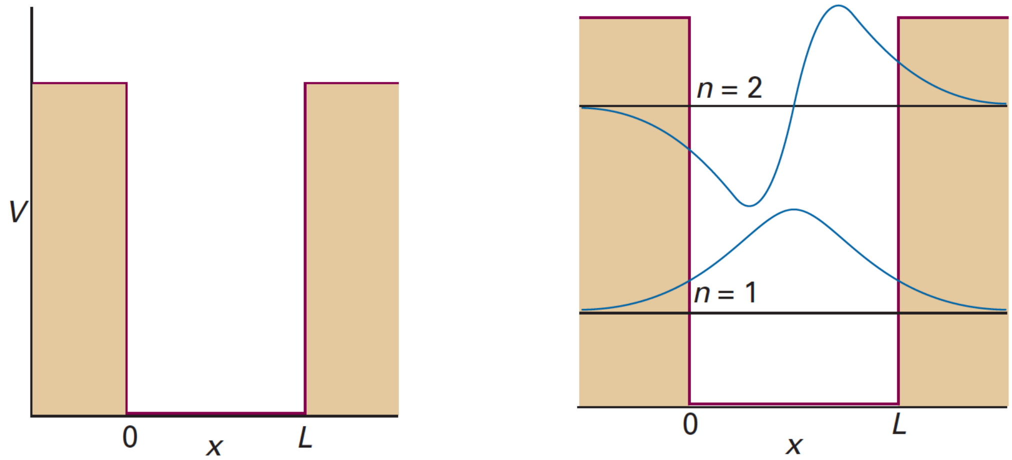

Figure 5: Schematic representation of the particle-in-a-box quantum system, characterized by finite potential barriers V at the two sides of the box (left plot). In the right plot we show the wave function for the first two quantum states of the system, $n = 1$ and $n = 2$, which exhibit oscillatory behaviour inside the box but decay exponentially fast in the classically forbidden region with $E < V$.

3.4 Particle in a box with finite potential walls

The next quantum system that one could study is a modification of the particle-in-a-box system discussed above, with the difference that the potential barriers V at the two sides of the box now are *finite* (as opposed to infinite as before). In other words, the potential function in this system now reads

$$\begin{aligned} V(x) &= 0 \quad \text{for} \quad 0 \le x \le L\,, \\ V(x) &= +|V| \quad \text{for} \quad x < 0 \quad \text{and} \quad x > L\,. \end{aligned} \tag{3.37}$$

Although we will not work out this case explicitly in the lectures, the solution to the Schroedinger equation here follows quite directly the tunneling derivation that was presented above. Indeed, one has to solve the Schroedinger equation both inside the potential well (where we have the free-particle, oscillatory, solution) and in the classically forbidden regime *inside* the left and the right barriers, where we find a exponentially decaying solution. The integration constants of this problem can be uniquely determine by the conditions condition that the wave-function and its derivate should be continuous at both sides of the potential barrier, $x = 0$ and $x = L$, as well as by the overall normalization of the wave function.

In Fig. 5 we show in the left plot the schematic representation of the particle-in-a-box quantum system, characterized by finite potential barriers V at the two sides of the box. In the right plot, we show the wave function for the first two quantum states of the system, $n = 1$ and $n = 2$, which exhibit oscillatory behaviour inside the box but *decay exponentially fast* in the classically forbidden region with $E < V$. Note that, as in the quantum tunneling case discussed above, the wave-function is non-zero even inside the potential barrier, where $V > E_k$ with E_k being the kinetic energy of the particle inside the box, but quickly becomes very small if $V \gg E_k$.

3.5 The harmonic oscillator in quantum mechanics

In classical mechanics, an *harmonic oscillator* is defined in general as particle moving under the effects of a *quadratic potential*, that is

$$V(x) = \frac{1}{2} k_k x^2 \,, \tag{3.38}$$

where k_f 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. (3.38) is fully general and applies to many other potentials. In particular, any potential can be approximated by Eq. (3.38) in the region near local minima (as can be seen by doing a Taylor expansion).

The harmonic potential Eq. (3.38) 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, we can compute the force that the particle will experience, namely

$$F = -\frac{dV(x)}{dx} = -\kappa_f x \,, \tag{3.39}$$

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. (3.38), that is, a *quantum harmonic oscillator*. The Schroedinger equation associated to this system will now be:

$$-\frac{\hbar^2}{2m}\frac{d^2\Psi}{dx^2} + \frac{1}{2}k_f x^2 \Psi = E\Psi \,. \tag{3.40}$$

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:

$$\Psi_n(x) = \frac{1}{\sqrt{2^n n!}} \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} e^{-m\omega x^2/2\hbar} H_n\left(\sqrt{\frac{m\omega}{\hbar}} x\right) \,, \tag{3.41}$$

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 $\omega \equiv \sqrt{k/m}$, in analogy with the classical treatment. The solutions of Eq. (3.40) 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

$$E_n = \hbar\omega\left(n + \frac{1}{2}\right) \,. \tag{3.42}$$

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

$$E_{n+1} - E_n = \hbar\omega \,, \tag{3.43}$$

independently of the value of n. Second, and more strikingly, we find that 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

$$E_0 = \frac{1}{2}\hbar\omega \,, \tag{3.44}$$

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 with arbitrary precision. 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. (3.41) take relatively simple forms,

$$\begin{aligned} H_0(x) &= 1\,, \\ H_1(x) &= 2y\,, \\ H_2(x) &= 4y^2 - 2\,, \\ H_3(x) &= 8y^3 - 12y\,, \end{aligned} \tag{3.45}$$

and so on. Therefore, for the ground state of the system, $n = 0$, the wave-functions takes the particularly simple form

$$\Psi_0(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} e^{-m\omega x^2/2\hbar} \,, \tag{3.46}$$

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

$$\int_{-\infty}^{\infty} dx\, |\Psi_0(x)|^2 = 1\,. \tag{3.47}$$

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

$$\int_{-\infty}^{\infty} dx\, e^{-x^2} = \sqrt{\pi}\,. \tag{3.48}$$

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

$$\Psi_1(x) = \sqrt{2}\left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \sqrt{\frac{m\omega}{\hbar}}\, x\, e^{-m\omega x^2/2\hbar} \,, \tag{3.49}$$

This comparison is shown in Fig. 6, 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 $n = 1$ (the ground state) the maximum probability $|\Psi|^2$ is found for $x = 0$ (the classical equilibrium position), for the excited state $n = 1$ 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 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.

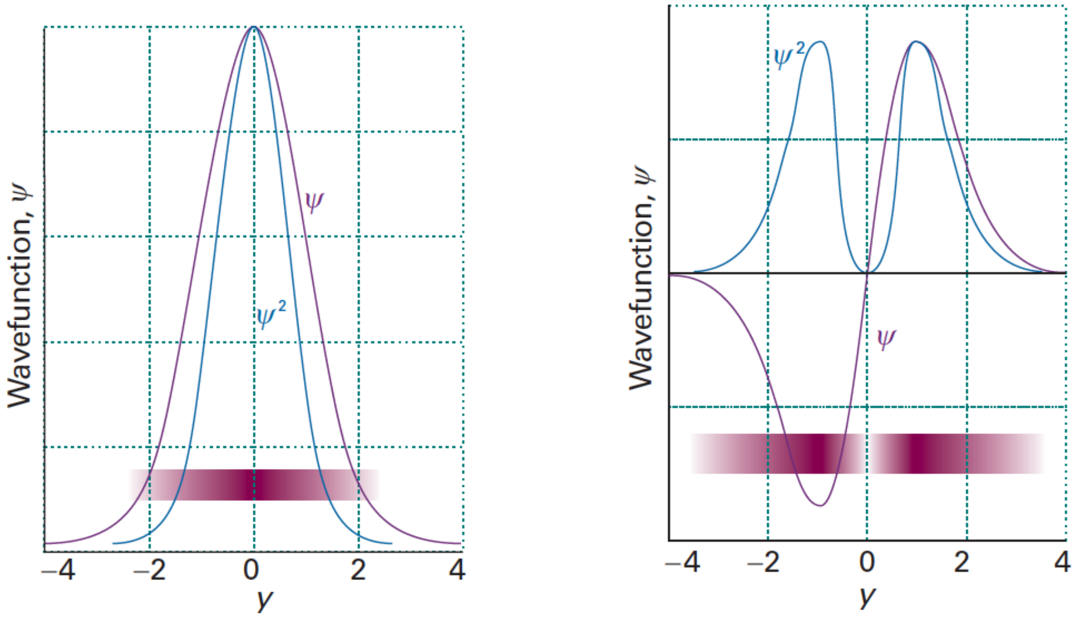

Figure 6: The wave-function $\Psi_n(x)$ and its square $|\Psi_n(x)|^2$ (which represents the probability density for the position x) in the quantum harmonic oscillator for the first two eigenstates, $n = 0$ (left plot) and $n = 1$ (right plot). We observe that while for $n = 1$ (the ground state) the 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.

The exponential suppression in the wave function of the quantum harmonic oscillator, Eq. (3.41) 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).

Since we have the wave-functions for all values of n, Eq. (3.41), 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,

$$\langle x \rangle = 0\,, \tag{3.50}$$

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

$$\langle x \rangle = \int_{-\infty}^{\infty} dx\, x\, |\Psi(x)|^2 \sim \int_{-\infty}^{\infty} dx\, x\, e^{-m\omega x^2/\hbar} \left[H_n\left(\sqrt{\frac{m\omega}{\hbar}} x \right) \right]^2 = 0\,, \tag{3.51}$$

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

$$\langle x^2 \rangle = \left(n + \frac{1}{2} \right) \frac{\hbar}{\sqrt{m k_f}} \, . \quad (3.52)$$

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

$$\Delta x \equiv \sqrt{\langle x^2 \rangle - \langle x \rangle^2} = \sqrt{\left(n + \frac{1}{2} \right) \frac{\hbar}{(m k_f)^{1/2}}} \quad (3.53)$$

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. (2.43) we can determine the standard deviation associated to measurements of the linear momentum of the quantum harmonic oscillator in this limit,

$$\Delta p_x \sim \frac{\hbar}{\Delta x} \sim \frac{\hbar}{n^{1/2}} \, , \quad (3.54)$$

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

$$\langle V \rangle = \frac{1}{2} k_f \langle x^2 \rangle = \frac{1}{2} \left(n + \frac{1}{2} \right) \hbar \left(\frac{k_f}{m} \right)^{1/2} = \frac{1}{2} \left(n + \frac{1}{2} \right) \hbar\omega \, , \quad (3.55)$$

where we have used the fact that the expectation value of an operator is *linear*, and the result for $\langle x^2 \rangle$ just computed above. Therefore, given that the complete energy of the quantum harmonic oscillator was Eq. (3.42), 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

$$\langle E \rangle = \langle E_k \rangle + \langle V \rangle = \frac{1}{2} \langle E \rangle + \frac{1}{2} \langle E \rangle \, . \quad (3.56)$$

3.6 Summary

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

- The boundary conditions on the wave-function induced by a confining potential lead to the *quantization of the allowed energy levels*. This is a generic property of quantum systems, as we have seen in various examples such as the particle in a box with finite barriers and the quantum harmonic oscillator.

- In many quantum systems, the energy of the ground state is different to zero, unlike classical physics. We denote this effect as the *zero-point energy*.

- 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.
- 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.