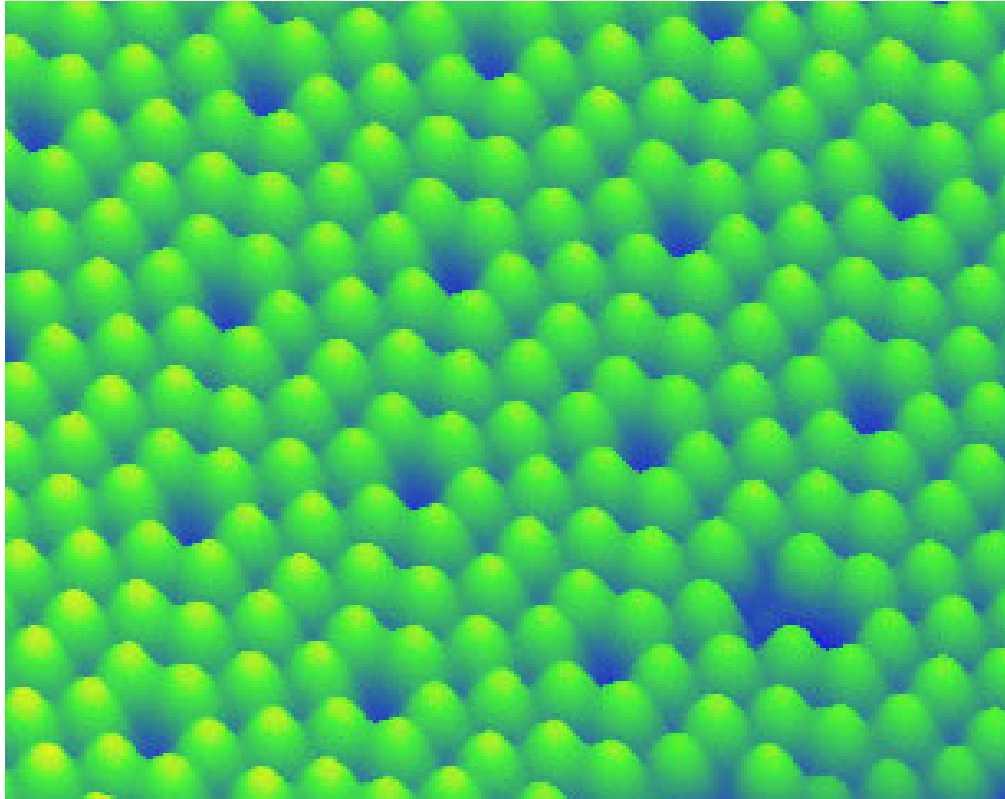


11 QUANTUM MECHANICS

How is it possible to have a microscope able to zoom so much so that individual atoms can be seen?



www.aip.org/history/einstein/atoms.htm

Discover the answer to this question in this chapter.

In 1925, Erwin Schrödinger further develops the ideas of de Broglie to arrive at an equation that can be used to calculate the amplitude of the wave as a function of the position. The result depends on the energy of the particle and on the potential energy, which also varies with the position. This equation is the Schrödinger equation.

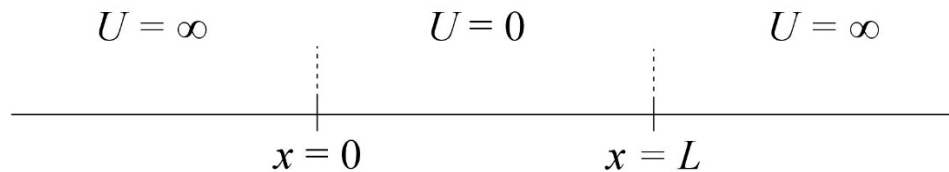
$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}(E - U)\psi = 0$$

There is a slightly more complex version in three dimensions. Rest assured; you will not have to solve this differential equation to find the amplitude of the wave. However, the solutions of this equation for simple or important situations will be shown.

11.1 A PARTICLE IN A BOX

1-Dimensional Box

We will start with a situation where the potential energy is zero between $x = 0$ and $x = L$ and infinite outside the region between $x = 0$ and $x = L$.



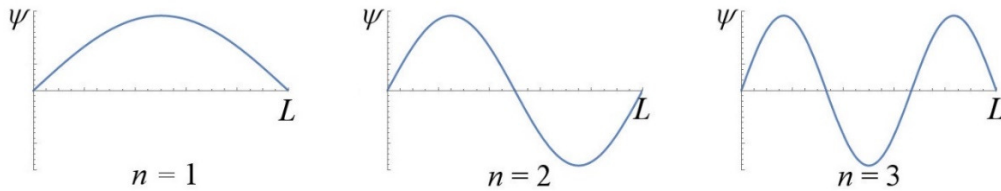
In this situation, a particle is trapped in the space between $x = 0$ and $x = L$. This particle cannot come out of this region, regardless of the energy given to it since a particle cannot go at the positions where U is larger than the mechanical energy of the particle. This situation is also called *a particle in an infinite potential well* because the graph of potential looks like a well with sides of infinite height.

The solutions of the Schrödinger equation are relatively simple when the potential energy is constant. The solutions are:

- A sine wave between $x = 0$ and $x = L$.
- 0 for $x < 0$ and $x > L$.

Moreover, as the wave function must be continuous, the sine wave must be zero at $x = 0$ and $x = L$.

Therefore, a situation quite similar to the one obtained with standing waves is obtained. The possible waves are (the first three actually)



The following values of wavelengths are thus possible.

Possible Wavelengths for a Particle Trapped in a One-Dimensional Box

$$\lambda_n = \frac{2L}{n}$$

As the wavelength is

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

The possible momenta for the particle are given by

$$\begin{aligned} p_n &= \frac{h}{\lambda_n} \\ &= \frac{nh}{2L} \end{aligned}$$

To find the energy, the kinetic energy is needed. To easily find it, this link between momentum and kinetic energy when the speed is much smaller the speed of light (found in mechanics) is used.

$$E_k = \frac{1}{2} \frac{p^2}{m}$$

Therefore, the energy is

$$\begin{aligned} E_n &= E_k + U \\ &= \frac{1}{2} \frac{p_n^2}{m} + 0 \end{aligned}$$

Using the value of the momentum, the final result is

Possible Energies for a Particle Trapped in a 1-Dimensional Box

$$E_n = n^2 \frac{h^2}{8mL^2}$$

These are the only values of energy allowed for the particle in the box. The energy is therefore quantified, which means that it can only take certain specific values.

Example 11.1.1

An electron is trapped in a one-dimensional box 0.7 nm wide. What are the four lowest values of energy that this electron can have?

The energies are given by

$$\begin{aligned}
 E_n &= n^2 \frac{h^2}{8mL^2} \\
 &= n^2 \cdot \frac{(6.626 \times 10^{-34} \text{ Js})^2}{8 \cdot 9.11 \times 10^{-31} \text{ kg} \cdot (0.7 \times 10^{-9} \text{ m})^2} \\
 &= n^2 \cdot 1.23 \times 10^{-19} \text{ J} \\
 &= n^2 \cdot 0.767 \text{ eV}
 \end{aligned}$$

Therefore, the energy levels are

$$\begin{aligned}
 E_1 &= 1^2 \cdot 0.767 \text{ eV} \\
 &= 0.767 \text{ eV}
 \end{aligned}$$

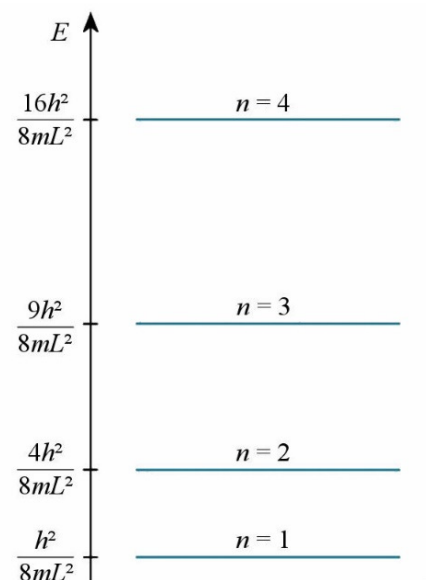
$$\begin{aligned}
 E_2 &= 2^2 \cdot 0.767 \text{ eV} \\
 &= 3.070 \text{ eV}
 \end{aligned}$$

$$\begin{aligned}
 E_3 &= 3^2 \cdot 0.767 \text{ eV} \\
 &= 6.907 \text{ eV}
 \end{aligned}$$

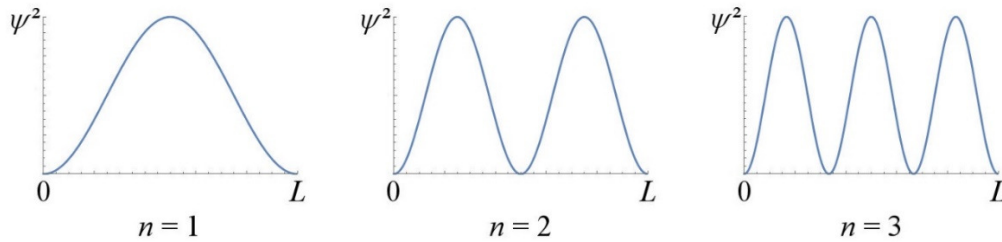
$$\begin{aligned}
 E_4 &= 4^2 \cdot 0.767 \text{ eV} \\
 &= 12.279 \text{ eV}
 \end{aligned}$$

These energies can be represented by the following diagram (four levels are shown, but there is an infinite number).

In this diagram, there is only one axis (which is the vertical axis used for energy).



The graphs of ψ^2 for the first three levels are as follows.



These graphs show the probability of finding the particle at a specific location in the box if its position is measured. For example, when the particle is at the third level, there are three locations where there is a good chance of finding the particle while it is impossible to find the particle at $x = L/3$ and $x = 2L/3$.

Remember that, according to the Copenhagen interpretation, the particle is everywhere at the same time in the box (except in places where ψ^2 is zero). The particle will be at a specific location chosen at random among all possibilities by following the laws of probabilities only if the position of the particle is measured.

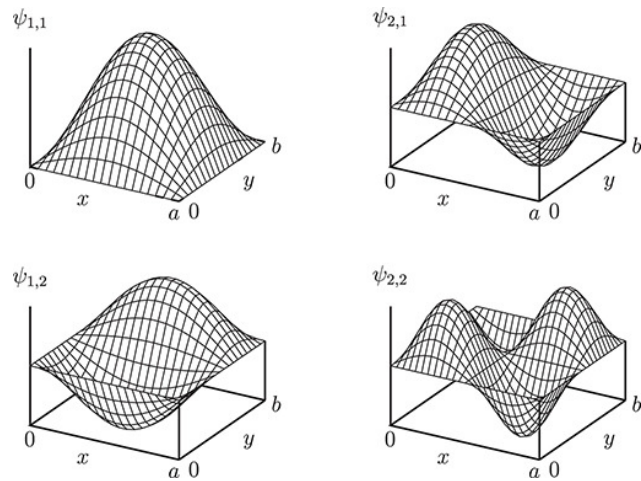
3-Dimensional Box

Let's start by going to a 2-dimensional box. In this case, we have the following waves.

The solution is now characterized by 2 numbers. These numbers, n_x and n_y , indicates the number of half wavelengths that there are in x and y -directions. The possible waves are denoted by ψ_{n_x, n_y} . For example, the wave $\psi_{1,2}$ is the solution when $n_x = 1$ and $n_y = 2$.

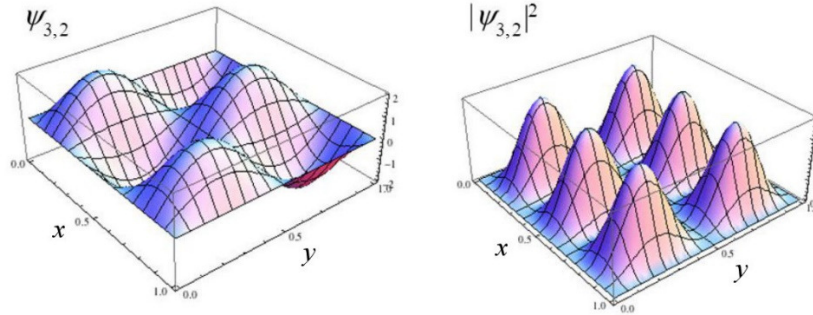
In this case, the energy is

$$E_n = (n_x^2 + n_y^2) \frac{h^2}{8mL^2}$$



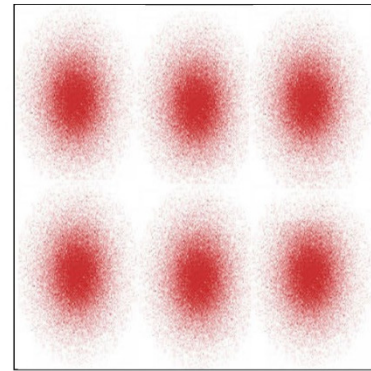
iopscience.iop.org/book/978-1-6817-4637-1/chapter/bk978-1-6817-4637-1ch4

Again, these waves can be used to calculate the probability of finding the particle at a specific location in the box. For example, here is the graph of the probability of finding the particle at different locations for the wave $\psi_{3,2}$. (This is recognized by the fact that there are 3 probability maximums in the x -direction and 2 in the y -direction.)



slideplayer.com/slide/4751950/

This probability can also be represented as in the right diagram. This diagram shows what would be obtained if the position of the particle in the box is measured several thousand times. Of course, more positions are obtained where the probability is greater.



In three dimensions, the solution is now characterized by 3 numbers. These numbers, n_x , n_y and n_z , indicate the number of half wavelengths that there are in the x , y and z -directions. The possible waves are denoted by ψ_{n_x, n_y, n_z} . For example, the wave is $\psi_{1,2,4}$ when $n_x = 1$, $n_y = 2$ and $n_z = 4$.

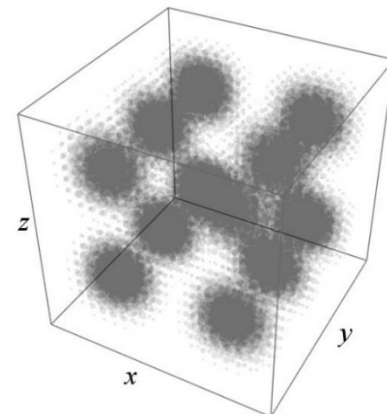
In this case, the energy is

Possible Energies for a Particle Trapped in a 3-Dimensional Box

$$E_n = (n_x^2 + n_y^2 + n_z^2) \frac{h^2}{8mL^2}$$

The square of the wave amplitude ψ^2 still gives the probability of finding the particle. For example, the diagram on the right shows where it is more likely to find the particle for the wave $\psi_{2,3,2}$. (This is recognized by the fact that there are 2 probability maximums in the x -direction, 3 in the y -direction, and 2 in the z -direction.)

The diagram shows the positions that would be obtained if the position of the particle in the box were measured several thousand times.



Made with demonstrations.wolfram.com/ParticlesIn1DAnd3DBoxes/

Example 11.1.2

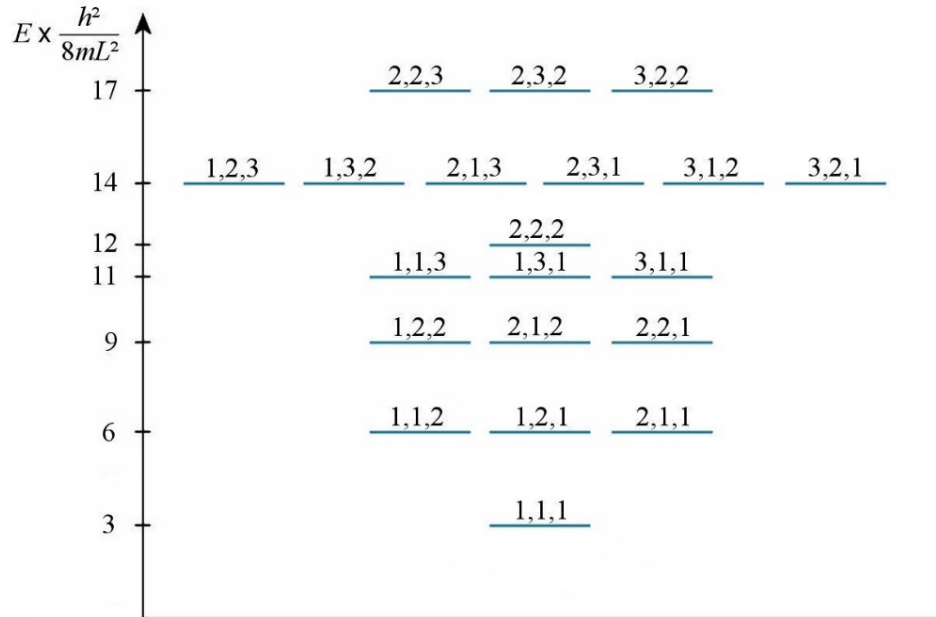
An electron is trapped in a three-dimensional box having sides 0.7 nm long. What is the energy of the electron if it is at the level characterized by $n_x = 1$, $n_y = 3$ and $n_z = 2$?

The energy is

$$\begin{aligned}
 E_n &= (n_x^2 + n_y^2 + n_z^2) \frac{h^2}{8mL^2} \\
 &= (1^2 + 3^2 + 2^2) \cdot \frac{(6.626 \times 10^{-34} \text{ Js})^2}{8 \cdot 9.11 \times 10^{-31} \text{ kg} \cdot (0.7 \times 10^{-9} \text{ m})^2} \\
 &= 1.72 \times 10^{-18} \text{ J} \\
 &= 10.74 \text{ eV}
 \end{aligned}$$

There are now levels that have the same energy. For example, the level characterized by $n_x = 1$, $n_y = 1$, $n_z = 2$, the level characterized by $n_x = 1$, $n_y = 2$, $n_z = 1$, and the level characterized by $n_x = 2$, $n_y = 1$, $n_z = 1$, all have the same energy. When several levels have the same energy, they are said to be *degenerate*.

The following diagram represents those energies.



Note that if a particle has an energy for which there are several levels, the particle is in all levels at the same time. For example, with an energy of $6h^2/8mL^2$, the particle is at the same time in the three states denoted by $\psi_{1,1,2}$, $\psi_{1,2,1}$ and $\psi_{2,1,1}$. The specific level will be decided only if the state of the particle is measured.

11.2 SPIN

What is Spin?

During the 1920s, we discovered that several particles had an angular momentum.

The angular momentum of the particle is called the *spin*. It's as if the electron is turning on itself but this image cannot be true since the electron doesn't even have a size in the current theory. (Even though we often see this kind of representation in popular works.) Virtually all known particles, such as electrons, protons and neutrons, have an angular momentum but nobody knows why these particles have an angular momentum. The spin of a particle is an intrinsic property of the particle, as is its electrical charge and mass. Just as we don't know why a particle has a specific electrical charge, we don't know why particles have a specific angular momentum. The particle has an angular momentum, that's all we can say, and we have no explanation for that.

The magnitude of the kinetic moment of a particle, noted S , is given by the formula

$$S = \sqrt{s(s+1)} \frac{h}{2\pi}$$

where s can take the values 0, $\frac{1}{2}$, 1, $1\frac{1}{2}$, 2, ... This s is also called, by a shortcut, the spin of the particle. The electron, the proton and the neutron have a spin of $\frac{1}{2}$ and the photon has a spin of $s = 1$.

What's even more amazing is that spin can't take any direction. Thus, when the magnitude of the spin component is measured along an axis, the number of possibilities is limited. For a particle with a spin s , the number of possible values for the spin component is $2s + 1$. For a particle with a spin $\frac{1}{2}$ (such as the electron, proton and neutron), only 2 values are possible, i.e. $+\frac{1}{2}h/2\pi$ (often called a spin up), or $-\frac{1}{2}h/2\pi$ (often called a spin down).

A charged particle that has an angular momentum also has a magnetic moment. The magnetic moment measures whether the atom acts as a small magnet. The greater the magnetic moment, the greater the effect of a magnetic field on the particle. Note that if it is assumed that the electron is a uniformly charged sphere, the magnetic moment can be calculated from the angular momentum. In doing so, a magnetic moment of only half the real magnetic moment of the electron is obtained. This is another sign that the representation of the electron as a rotating charged sphere cannot be true.

Pauli Exclusion Principle

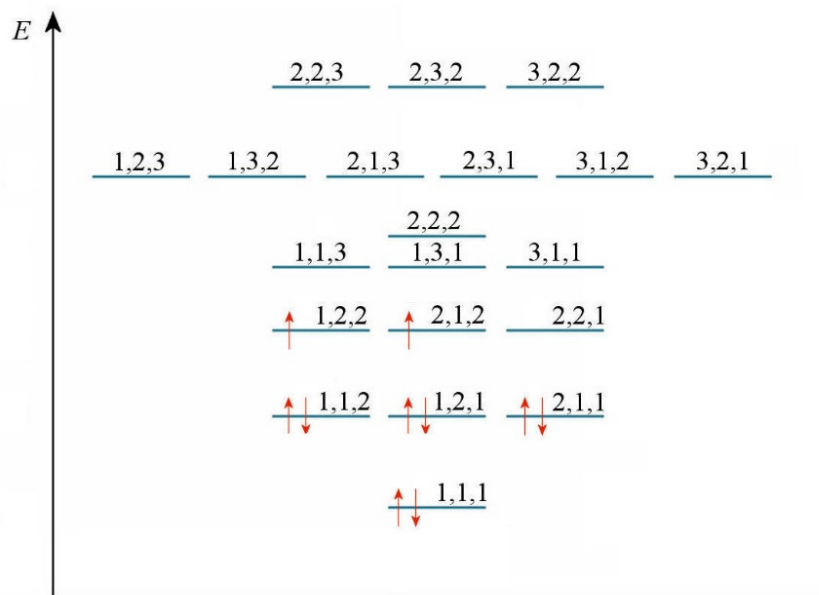
In 1925, Pauli discovered that particles that had a half-integer spin ($\frac{1}{2}$, $1\frac{1}{2}$, $2\frac{1}{2}$, ...) could not be in the same state. This is Pauli exclusion principle.

Let's take the example of the 3-dimensional box to illustrate what this means. Suppose we 10 electrons are put in the box. In this case, the energy levels are still described by the same numbers n_x , n_y and n_z but the energy of the levels is no longer the same as when there was a single electron in the box. The repulsion between the electrons adds potential energy, and this energy increases the energy of the levels a little compared to what we had with a single electron. We will not calculate the new values of these energies.

The exclusion principle tells us that 10 electrons cannot be placed at the lowest level. The electrons would then be in the same state, and this is forbidden by the principle of exclusion. Each electron must have a distinct state.

With a $\frac{1}{2}$ spin, an electron has two distinct states depending on the orientation of the spin. This means 2 electrons can be placed on each energy level. (If the particle had a $1\frac{1}{2}$ spin, 4 particles could be placed on each level.)

Here is the smallest energy configuration for 10 electrons in the box.



In a stable state, the electrons always place themselves at the lowest possible energy level. In the event of a tie, any level can be taken. In our example, there are 2 electrons on the three levels $\psi_{1,2,2}$, $\psi_{2,1,2}$ and $\psi_{2,2,1}$. No matter what choice you make, both electrons are actually in a state that is a superposition of the three levels anyway.

When electrons are placed on levels that have the same energy (such as levels $\psi_{1,2,2}$, $\psi_{2,1,2}$ and $\psi_{2,2,1}$), always start by placing a single electron on each of the levels with spins all oriented in the same direction. Electrons with spin in the opposite direction can only be placed on each level after all the levels are filled with one electron. The electrons thus place themselves with spins in the same direction because it forces them to be further away from each other since they cannot occupy the same state if they have spins in the same direction. By being further away from each other, the potential electrical energy is smaller and the system, at equilibrium, is always at the lowest energy. Should the spin up or down be chosen first? It doesn't change anything because even if 2 spins up are chosen, the system is really in a state that is superimposing 2 spins up and 2 spins down! The direction of the 2 spins will be decided only if the direction of the spins is measured.

The exclusion principle was postulated by Pauli in 1925 to explain why all the electrons of an atom were not at the lowest level. The principle was later confirmed with quantum mechanics since it was shown that the addition of 2 identical waves of half-integer spin particles gives a null result. This null result means that two particles can't be in the same state.

11.3 PASSING FROM ONE ENERGY LEVEL TO ANOTHER

Decrease of Energy

A particle on an energy level can move to a lower energy level. The lost energy is then emitted as a photon.

Initially, the particle is at the energy level E_i . After the level change, the particle is at the energy level E_f and there is a photon with an energy E_γ . According to the principle of energy conservation, we have

$$E = E'$$

$$E_i = E_f + E_\gamma$$

which gives

Energy of the Photon Emitted When a Particle Loses Energy and Passes from an Energy Level E_i to an Energy Level E_f

$$E_\gamma = E_i - E_f$$

Example 11.3.1

An electron is trapped in a one-dimensional box with a length of 0.7 nm. What is the wavelength of the light emitted if the electron passes from the third to the first energy level?

The energy of the photon is

$$\begin{aligned}
 E_\gamma &= E_3 - E_1 \\
 &= \frac{3^2 h^2}{8mL^2} - \frac{1^2 h^2}{8mL^2} \\
 &= (9-1) \frac{h^2}{8mL^2} \\
 &= 8 \cdot \frac{(6.626 \times 10^{-34} \text{ Js})^2}{8 \cdot 9.11 \times 10^{-31} \text{ kg} \cdot (0.7 \times 10^{-9} \text{ m})^2} \\
 &= 9.84 \times 10^{-19} \text{ J} \\
 &= 6.139 \text{ eV}
 \end{aligned}$$

Therefore, the wavelength of the light is

$$\begin{aligned}
 \lambda &= \frac{hc}{E_\gamma} \\
 &= \frac{1240 \text{ eVnm}}{6.139 \text{ eV}} \\
 &= 202 \text{ nm}
 \end{aligned}$$

Increase of Energy

A particle on an energy level cannot pass on its own at a higher energy level. In order for the particle to rise to a higher energy level, energy must be given to the particle. This can be done by absorbing a photon or by receiving energy during a collision.

Absorb a Photon

The particle can gain energy by absorbing a photon. However, the photon must have exactly the energy needed to move from one level to another. For example, to move a particle from an energy level of 3.2 eV to an energy level of 8.4 eV, the particle can absorb a photon, but the photon must have an energy exactly equal to 5.2 eV.

Initially, the particle is on an energy level E_i , and there is a photon coming in. After the level change, the particle is at the energy level E_f . According to the principle of energy conservation, we have

$$E = E'$$

$$E_i + E_\gamma = E_f$$

which gives

Energy of the Photon Absorbed When a Particle Gain Energy and Passes from an Energy Level E_i to an Energy Level E_f

$$E_\gamma = E_f - E_i$$

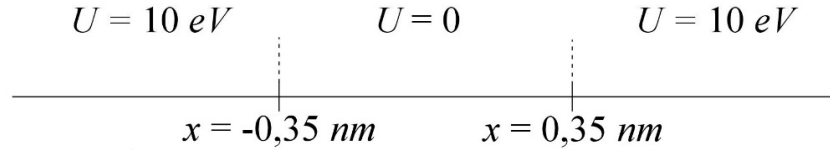
Gain Energy in a Collision

If another particle A collides with particle B on an energy level, particle B can gain just enough energy to allow it to move to a higher level.

In this case, particle A that collides with particle B on an energy level does not necessarily need to have the exact energy that corresponds to the energy required to rise to the new energy level. Let's take an example by assuming that there is a neutron locked in a box, that it needs 5.2 eV to rise to a higher energy level, and that this neutron is bombarded with electrons. During the collision, the electron will give some of its energy to the neutron. If the electrons have less than 5.2 eV, then the neutron will not be able to climb to the new energy level since none of the electrons will be able to give the necessary 5.2 eV. If the arriving electrons have more than 5.2 eV, then it is possible that exactly 5.2 eV will be transferred to the neutron during one of the collisions to allow it to move to the higher level. In fact, probably several electrons will make an elastic collision with the neutron (which gives it no energy) before an electron gives exactly the 5.2 eV needed to move to the higher level.

11.4 A PARTICLE IN A BOX (FINITE POTENTIAL WELL)

In this case, the particle is trapped in a region between $x = -L/2$ and $x = L/2$, but it could come out of the box if its energy is large enough. Let's take an example with values. Suppose the potential energy is 0 eV between $x = -0.35$ nm and $x = 0.35$ nm and it is 10 eV for $x < -0.35$ nm and $x > 0.35$ nm.



Thus, if the particle's energy is less than 10 eV, it is trapped in the region between $x = -0.35 \text{ nm}$ and $x = 0.35 \text{ nm}$ (remember that objects cannot go to places where the potential energy is greater than mechanical energy according to classical mechanics). On the other hand, if its energy is greater than 10 eV, the particle can be anywhere, and it can therefore come out of the box. This situation is called a *particle in a finite potential well* because the potential graph resembles a well whose sides have a height that is not infinite.

The solutions of the Schrödinger equation are completely different in both regions if the particle has an energy of less than 10 eV. The solutions are:

- A sinusoidal function for the region between $x = -0.35 \text{ nm}$ and $x = 0.35 \text{ nm}$. With an $x = 0$ in the centre of the well, this is a symmetrical situation. The sinusoidal functions in the well must therefore be either a cosine or a sine function.

$$\psi = A \cos kx \quad \text{or} \quad \psi = B \sin kx$$

where

$$k = \frac{2\pi}{\lambda} = \frac{2\pi p}{h} = \frac{2\pi\sqrt{2mE}}{h} = \frac{\pi\sqrt{8mE}}{h}$$

- Exponential functions for regions $x < -0.35 \text{ nm}$ and $x > 0.35 \text{ nm}$.

$$\psi = Ce^{-\alpha x} \quad (\text{to the right of the box}) \quad \text{and} \quad \psi = De^{\alpha x} \quad (\text{to the left of the box})$$

where

$$\alpha = \frac{\pi\sqrt{8m(U-E)}}{h}$$

As the wave function and the derivative of the wave function must be continuous, there are only a few possible solutions to make the sinusoidal function and exponential functions fit together. Easier said than done. Let's do it by looking at what is happening at the border to the right of the box (as this situation is symmetrical, the left border gives the same equations).

At the border, the cosine or sine function must have the same value as the exponential function. As the border is at $x = L/2$, we have the following 2 possibilities.

$$A \cos\left(\frac{kL}{2}\right) = Ce^{-\frac{\alpha L}{2}} \quad \text{or} \quad B \sin\left(\frac{kL}{2}\right) = Ce^{-\frac{\alpha L}{2}}$$

The derivatives of the functions must also be equal at the border. As derivatives are

$$\psi' = -Ak \sin kx \quad \text{or} \quad \psi' = Bk \cos kx$$

$$\psi' = -C\alpha e^{-\alpha x}$$

the equality of derivatives at the right border gives us the following two possibilities.

$$-Ak \sin\left(\frac{kL}{2}\right) = -C\alpha e^{-\frac{\alpha L}{2}} \quad \text{or} \quad Bk \cos\left(\frac{kL}{2}\right) = -C\alpha e^{-\frac{\alpha L}{2}}$$

Let's take the first case (when ψ is a cosine function). Then we have the following two equations.

$$A \cos\left(\frac{kL}{2}\right) = C e^{-\frac{\alpha L}{2}} \quad \text{and} \quad -Ak \sin\left(\frac{kL}{2}\right) = -C\alpha e^{-\frac{\alpha L}{2}}$$

By dividing the second equation by the first, we get

$$\frac{-Ak \sin\left(\frac{kL}{2}\right)}{A \cos\left(\frac{kL}{2}\right)} = \frac{-C\alpha e^{-\frac{\alpha L}{2}}}{C e^{-\frac{\alpha L}{2}}}$$

$$k \tan\left(\frac{kL}{2}\right) = \alpha$$

However, as

$$\alpha^2 = \frac{\pi^2 8m(U - E)}{h^2}$$

$$= \frac{\pi^2 8mU}{h^2} - \frac{\pi^2 8mE}{h^2}$$

we get to

$$k \tan\left(\frac{kL}{2}\right) = \sqrt{\frac{\pi^2 8mU}{h^2} - \frac{\pi^2 8mE}{h^2}}$$

Since

$$k = \frac{\pi \sqrt{8mE}}{h}$$

the equation is

$$\frac{\pi \sqrt{8mE}}{h} \tan\left(\frac{L}{2} \frac{\pi \sqrt{8mE}}{h}\right) = \sqrt{\frac{\pi^2 8mU}{h^2} - \frac{\pi^2 8mE}{h^2}}$$

In this equation, we often find the combination $h^2/8mL^2$ which is the energy of the first level for the infinite well. This energy will be denoted as

$$E_{1\infty} = \frac{h^2}{8mL^2}$$

The equation can then be written in the following form.

$$\pi \sqrt{\frac{E}{E_{1\infty}}} \tan\left(\frac{L\pi}{2} \sqrt{\frac{E}{E_{1\infty}}}\right) = \sqrt{\frac{\pi^2 U}{E_{1\infty}} - \frac{\pi^2 E}{E_{1\infty}}}$$

Then, we set

$$E_n = v^2 E_{1\infty} \quad \text{and} \quad U = u^2 E_{1\infty}$$

To arrive at

$$\begin{aligned} \frac{\pi v}{L} \tan\left(\frac{\pi v}{2}\right) &= \sqrt{\frac{\pi^2 u^2}{L^2} - \frac{\pi^2 v^2}{L^2}} \\ v \tan\left(\frac{\pi v}{2}\right) &= \sqrt{u^2 - v^2} \end{aligned}$$

If the same is done for the second case (when ψ is a sine function), the result is $-v \cot\left(\frac{\pi v}{2}\right) = \sqrt{u^2 - v^2}$.

Thus, the energy is found with

Possible Energies for a Particle Trapped in a 1-Dimensional Box (Finite Potential Well)

$$E_n = v^2 E_{1\infty}$$

where v is obtained by solving the following equations

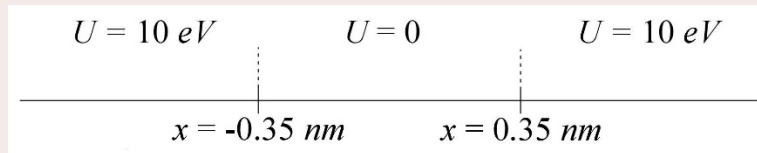
$$\begin{aligned} v \tan\left(\frac{\pi v}{2}\right) &= \sqrt{u^2 - v^2} \\ -v \cot\left(\frac{\pi v}{2}\right) &= \sqrt{u^2 - v^2} \end{aligned}$$

in which the value of u is given by

$$U = u^2 E_{1\infty}$$

Example 11.4.1

What are the possible energy levels of an electron trapped in this box?



The energy levels are given by

$$E_n = v^2 E_{1\infty}$$

In this case, we have

$$E_{1\infty} = \frac{h^2}{8mL^2}$$

$$\begin{aligned}
 &= \frac{(6.626 \times 10^{-34} \text{ Js})^2}{8 \cdot 9.11 \times 10^{-31} \text{ kg} \cdot (0.7 \times 10^{-9} \text{ m})^2} \\
 &= 1.2295 \times 10^{-19} \text{ J} = 0.7674 \text{ eV}
 \end{aligned}$$

The values of v are obtained by solving the following equations.

$$\begin{aligned}
 v \tan\left(\frac{\pi v}{2}\right) &= \sqrt{u^2 - v^2} \\
 -v \cot\left(\frac{\pi v}{2}\right) &= \sqrt{u^2 - v^2}
 \end{aligned}$$

where u is

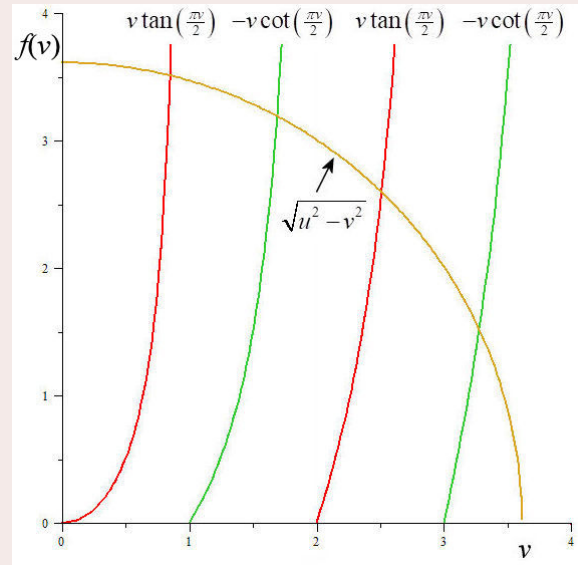
$$\begin{aligned}
 U &= u^2 E_{\infty} \\
 10 \text{ eV} &= u^2 \cdot 0.7674 \text{ eV} \\
 u &= 3.610
 \end{aligned}$$

Thus, we must solve the following 2 equations.

$$\begin{aligned}
 v \tan\left(\frac{\pi v}{2}\right) &= \sqrt{3.610^2 - v^2} \\
 -v \cot\left(\frac{\pi v}{2}\right) &= \sqrt{3.610^2 - v^2}
 \end{aligned}$$

The solution is obtained by finding the intersection points of the function $\sqrt{3.610^2 - v^2}$ and the functions $v \tan(v)$ and $-v \cot(v)$ (graph to the right).

All that remains to do is to solve the equations. The problem is that there are no analytical solutions to these equations! That does not matter, these equations can be easily solved with a computer.



The first equation is

$$v \tan\left(\frac{\pi v}{2}\right) = \sqrt{3.610^2 - v^2}$$

The wolfram website gives us the solutions to this equation.

https://www.wolframalpha.com/input/?i=solve+v*tan%28Pi*v%2F2%29%3D%E2%88%9A%283.610%5E2-v%5E2%29

$$v = 2.510 \quad \text{and} \quad v = 0.849$$

This gives the following energy levels.

$$E_1 = v^2 E_{1\infty} = 0.849^2 \cdot 0.767 \text{ eV} = 0.553 \text{ eV}$$

$$E_3 = v^2 E_{1\infty} = 2.511^2 \cdot 0.767 \text{ eV} = 4.836 \text{ eV}$$

The second equation is

$$-v \cot\left(\frac{\pi v}{2}\right) = \sqrt{3.610^2 - v^2}$$

The wolfram website gives us the solutions to this equation.

https://www.wolframalpha.com/input/?i=solve+-v*cot%28Pi*v%2F2%29%3D%E2%88%9A%283.610%5E2-v%5E2%29

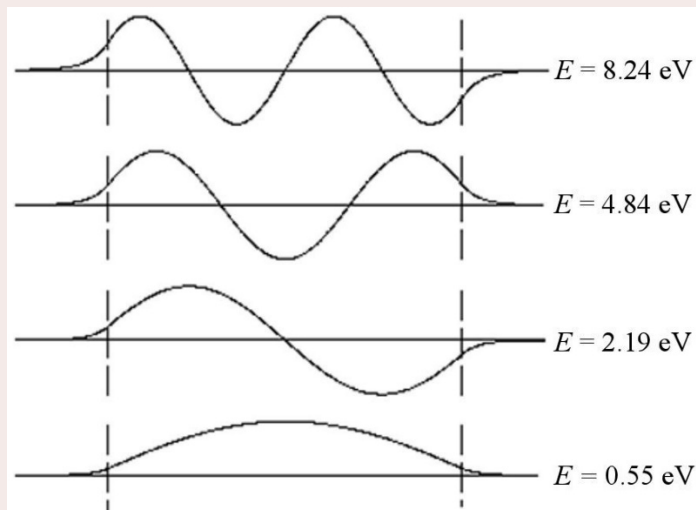
$$v = 3.276 \quad \text{and} \quad v = 1.690$$

This gives the following energy levels.

$$E_2 = v^2 E_{1\infty} = 1.690^2 \cdot 0.767 \text{ eV} = 2.191 \text{ eV}$$

$$E_4 = v^2 E_{1\infty} = 3.276^2 \cdot 0.767 \text{ eV} = 8.236 \text{ eV}$$

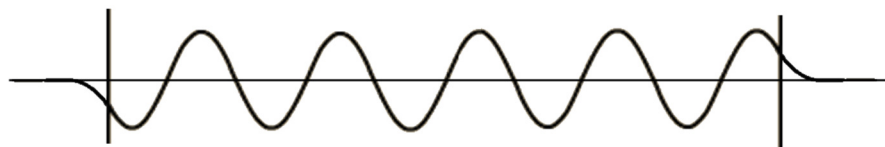
So here are the possible energy levels, with the wave functions associated with these levels.



tccc.iesl.forth.gr/education/local/quantum/vqm/figs/5fwf.gif

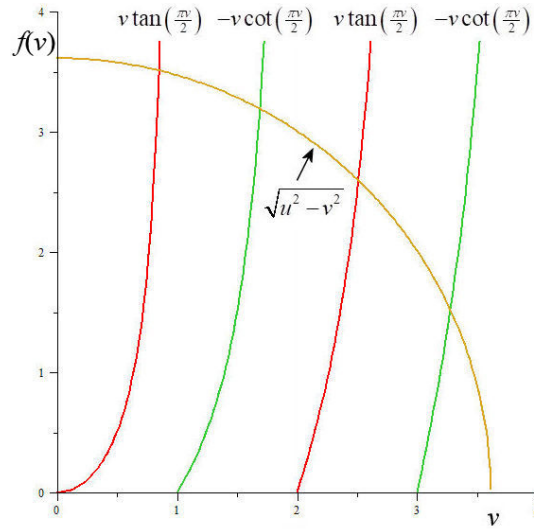
Note that there will always be a value v between 0 and 1, one between 1 and 2, one between 2 and 3 and so on.

Also note that a node is added to the wave each time you move to a higher energy level. The level number is equal to the number of nodes + 1. For example, the following image



represents the 10th level wave since there are 9 nodes inside the box. (In our example, there were only 4 levels. This 10th level does not exist in this case.)

The number of levels can easily be found by finding the number of intersecting points on the graph to the right. There is a crossing point for each tan or cot curve that starts from the v -axis inside the circle. Since there is one of these curves starting at each integer values and the circle has a radius of u , you just have to find the integer smaller than or equal to $u + 1$ (1 must be added for the tan curve that starts from 0).



Number of Energy Levels for a Particle Trapped in a 1-Dimensional Box (Finite Potential Well)

The integer smaller than or equal to $u + 1$

Example 11.4.2

An electron is trapped in a box with a width of 2 nm and a depth of 18 eV. How many energy levels are possible for the particle?

The number of levels is equal to the integer smaller than or equal to $u + 1$, where u is given by

$$U = u^2 E_{1\infty}$$

Since

$$\begin{aligned} E_{1\infty} &= \frac{h^2}{8mL^2} \\ &= \frac{(6.626 \times 10^{-34} \text{ Js})^2}{8 \cdot 9.11 \times 10^{-31} \text{ kg} \cdot (2 \times 10^{-9} \text{ m})^2} \\ &= 1.506 \times 10^{-20} \text{ J} = 0.09401 \text{ eV} \end{aligned}$$

the value of u is

$$\begin{aligned} U &= u^2 E_{1\infty} \\ 18 \text{ eV} &= u^2 \cdot 0.09401 \text{ eV} \\ u &= 13.84 \end{aligned}$$

Thus,

$$u + 1 = 14.84$$

Since the integer smaller than or equal to this number is 14, there are 14 possible energy levels.

The following observations can then be made:

- 1- The number of energy levels is limited if U is not infinite outside the box.
- 2- The energies for which the particle is trapped in the box are slightly lower than those obtained with the infinite potential well (compare example 11.1.1 and 11.4.1), because the sinusoidal function is a little more stretched, which increases the wavelength, which decreases the momentum and, at the same time, the energy.
- 3- Curious thing: the wave goes a little inside the prohibited zones. In example 11.4.1, the wave goes outside the box for the four levels below 10 eV. This means that there is a certain probability of finding the particle in the regions $x < -0.35$ nm and $x > 0.35$ nm, even if this is completely impossible according to classical mechanics.

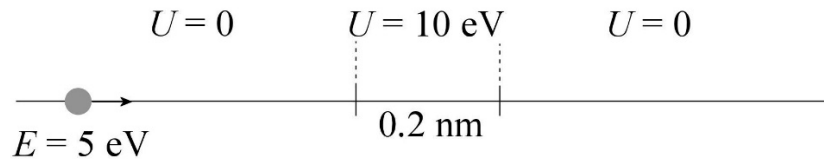
The particle is not trapped inside the box if its energy is greater than U . In this case, the particle can have any energy, provided it is larger than U . The energy is quantified if the particle is trapped inside the box, but it is not quantified if it gets out of the box.

With quantum mechanics, they quickly realized that the atomic nucleus model of the time could not be good. At that time, it was thought that the atomic nucleus was composed of protons and electrons. With quantum mechanics, a fairly rudimentary model of the nucleus can be made in which the particles are trapped in a finite potential well with a width of about 10^{-15} m and a potential well height of about 10 MeV. They realized then that there is only one solution where the electron is trapped in the potential well, and that the energy is far too close to the height of the well. Therefore, no more than 2 electrons could be in the nucleus, and the energy of the level is so close to the height of the well that it is almost impossible for the electrons to remain in the atomic nucleus. This result forced them to assume, in the 1920s, that a neutral particle with almost the same mass as the proton exist (the neutron), whose existence was proven in 1932 by James Chadwick.

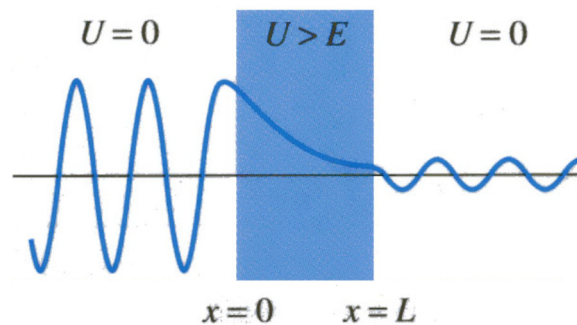
11.5 QUANTUM TUNNELLING

It was noted in the previous section that the particle has a certain probability of being in places prohibited by classical mechanics (the particle had a probability of being outside the

box even if the energy of the particle was less than U). An even more surprising result is obtained if quantum mechanics is used to examine the case of a particle coming to a barrier. Here is a situation representing that.



An electron with an energy of 5 eV is in an area where the potential energy is zero. It is heading towards a fairly thin (0.2 nm) section where the potential energy is 10 eV. As the potential energy of this area (10 eV) is larger than the total energy of the particle (5 eV), the particle should not be able to enter this region according to classical mechanics and, therefore, should not be able to cross this barrier. But the quantum mechanical solution is different. As before, the solution is a sine function for the areas where the energy of the particle is larger than the potential energy and an exponential function for the area where the energy of the particle is smaller than the potential energy. The graph to the right represents the solution.



Harris Benson, Physique 3: Ondes, optique et physique moderne, ERPI, 2009

In the barrier, the exponential function decreases rapidly, but it does not vanish when it reaches the other side. As the wave function must be continuous, the sine function has a non-vanishing amplitude across the barrier. Since the wave function is not zero to the right of the barrier, there is a certain probability of finding the particle across the potential barrier while it should have been impossible to find it there according to classical mechanics. In this example, the probability to cross the barrier is 4.1% (see the calculation a bit further).

This probability of crossing areas that would have been impossible to cross according to classical mechanics is called *quantum tunnelling*.

To calculate the probability, it is necessary to find the amplitudes of the waves before and after the barrier by matching the values of wave functions and the derivatives of the wave functions at the limits of the barrier knowing that one has sine functions outside the barrier and an exponential function inside the barrier (not to mention that the left wave is a superposition of an incident wave and a reflected wave). Once you have the amplitudes, the probability of transmission can be found with the squares of the amplitude. Details of this calculation will not be given. The solution leads to the following formula.

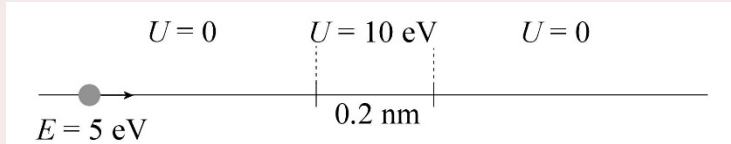
Probability of Crossing a Barrier Potential

$$T = \frac{16E(U - E)}{U^2} e^{-2\alpha L} \quad \text{where } \alpha = \frac{\pi\sqrt{8m(U - E)}}{h}$$

Basically, the probability decreases when U increases and when L increases.

Example 11.5.1

What is the probability that the particle will cross the barrier in this situation?



The probability is found with

$$T = \frac{16E(U - E)}{U^2} e^{-2\alpha L}$$

Here, α is

$$\begin{aligned} \alpha &= \frac{\pi\sqrt{8m(U - E)}}{h} \\ &= \frac{\pi\sqrt{8 \cdot 9.11 \times 10^{-31} \text{ kg} \cdot (10 \text{ eV} - 5 \text{ eV}) \cdot 1.602 \times 10^{-19} \frac{\text{J}}{\text{eV}}}}{6.626 \times 10^{-34} \text{ Js}} \\ &= 1.146 \times 10^{10} \text{ m}^{-1} \end{aligned}$$

Therefore, the probability is

$$\begin{aligned} T &= \frac{16E(U - E)}{U^2} e^{-2\alpha L} \\ &= \frac{16 \cdot 5 \text{ eV} \cdot (10 \text{ eV} - 5 \text{ eV})}{(10 \text{ eV})^2} \cdot e^{-2 \cdot 1.146 \times 10^{10} \text{ m}^{-1} \cdot 0.2 \times 10^{-9} \text{ m}} \\ &= 0.0409 \end{aligned}$$

The probability of crossing the barrier is 4,1%.

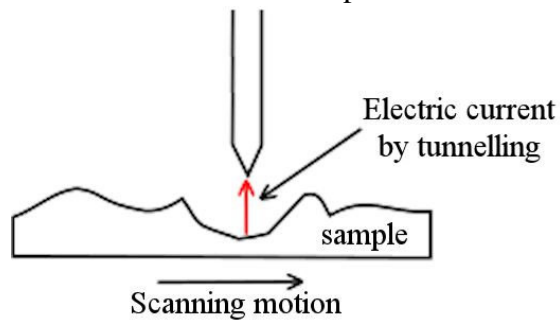
(This formula is only an approximation, valid only if the probability is low, say less than 10%. If the probability is higher, the formula is

$$T = \left(1 + \frac{U_0^2}{4E(E - U_0)} \sinh^2 \left(\frac{L}{\hbar} \sqrt{2m_0(U_0 - E)} \right) \right)^{-1}$$

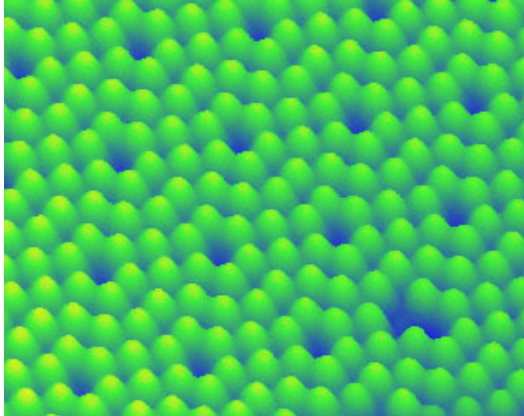
where \sinh is a hyperbolic sine function, a function which is on your calculator.)

One might wonder if this probability to cross a barrier is important for everyday life objects. For example, let's assume that a 100 g object having a 4 J energy is trying to cross a 1 mm wide region where the potential energy is 5 J. In this case, the probability of crossing the barrier is one chance in $10^{1\,000\,000\,000\,000\,000\,000\,000\,000\,000\,000\,000\,000}$. In other words, it's pretty impossible. Do not try to walk through walls by quantum tunnelling...

Quantum tunnelling is the basis for the operation of tunnelling microscopes (really!). This apparatus with unmatched precision was invented in 1981. A very sharp tip (there is only a single atom at the end) passes over a surface. The tip is loaded with electrons, and the surface is positively charged. The electrons are, therefore, attracted to the surface but they cannot go to this surface according to classical mechanics because they don't have enough energy to cross the space between the tip and surface. However, with quantum tunnelling, some electrons are able to cross this space and reach the surface. If the space between the tip and the surface decreases, more electrons can cross the gap. The number of electrons crossing is fairly easy to measure with the electric current passing through the tip. If the current is larger, the surface is closer to the tip because more electrons are then able to pass to the other surface. By scanning the surface, one can determine the shape of the surface.



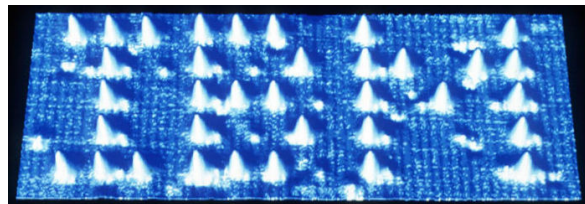
fr.wikipedia.org/wiki/Microscope_à_effet_tunnel



The precision is quite remarkable as the following picture shows. This image represents a silicon surface. The green dots are silicon atoms. A missing atom in the structure can be noticed at the bottom right of the picture.

www.aip.org/history/einstein/atoms.htm

Since the beginning of the 1990s, individual atoms can even be moved one at a time with some tunnelling microscopes. This image, made in April 1990, is the result of the first manipulation of atoms with the microscope at IBM. Atoms have been moved to write the letters IBM on a metal surface.



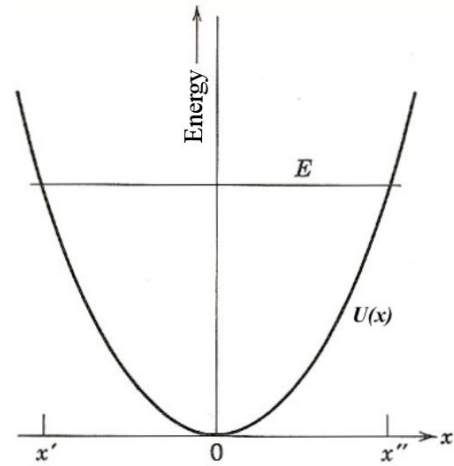
www-03.ibm.com/ibm/history/exhibits/vintage/vintage_4506VV1003.html

They even created a small movie with atoms.

www.youtube.com/watch?v=oSCX78-8-q0

11.6 HARMONIC OSCILLATOR

The potential energy of a particle in harmonic oscillation is $\frac{1}{2}kx^2$. If a particle subjected to such a potential energy has a mechanical energy E , then, according to classical mechanics, it undergoes a harmonic oscillation between points x' and x'' and its speed is the largest at $x = 0$. In addition, it should be impossible, always according to classical mechanics, for the particle to go in the region $x > x''$ or in the region $x < x'$ (since U is greater than E in these regions).

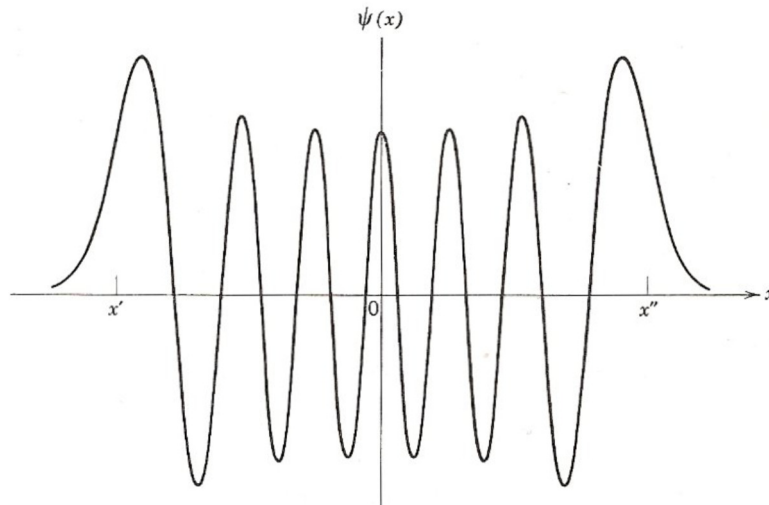


To find out what is happening in this case according to quantum mechanics, the Schrödinger equation with this potential energy must be solved.

Eisberg, Resnick, Quantum physics, John Wiley, 1985

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2} (E - \frac{1}{2}kx^2)\psi = 0$$

It may seem easy at first glance, but this is a mathematical challenge since the solutions are Hermite polynomials (that you probably don't know). For example, the graph of the wave for the thirteenth energy level is



Eisberg, Resnick, Quantum physics, John Wiley, 1985

Even if the details of these solutions are not known, some elements show that these solutions are consistent with what was learned up to now.

1. The amplitude of the wave increases as the potential energy increases. This is quite normal because the kinetic energy decreases when the potential energy increases. Thus, the particle moves at a lower speed and spends more time there than in places where the potential energy is low. If it spends more time at this place, then the

probability of finding the particle at this place is larger and so the wave has a greater amplitude.

2. The wavelength increases as the potential energy increases. When the potential energy increases, the kinetic energy must decrease and the momentum must also decrease. As the wavelength is h/p , the wavelength must also increase as U increases.

These two remarks do not only apply to a particle undergoing a harmonic oscillation. They are valid regardless of the way the potential energy changes.

Despite the complexity of the solutions, the possible energy values are surprisingly quite simple. They are given by

Energy Levels for a Particle in Harmonic Oscillations

$$E_n = \left(n + \frac{1}{2} \right) hf$$

Starts at $n = 0$

The energy levels are, therefore, all evenly spaced in energy. The gap between the levels is always hf .

Example 11.6.1

An electron is undergoing a harmonic oscillation. The lowest energy level is 0.4 eV. What is the wavelength of the light emitted if the electron passes from the 5th to the 3rd energy level?

The energy of the photon is

$$\begin{aligned} E_\gamma &= E_4 - E_2 \\ &= \left(4 + \frac{1}{2} \right) hf - \left(2 + \frac{1}{2} \right) hf \\ &= 2hf \end{aligned}$$

(Note that for a particle undergoing a harmonic oscillation, n starts at 0. Thus, the 5th level has $n = 4$ and the 3rd level has $n = 2$.)

To find the energy of the photon, the value of hf is needed. As the energy of the first level is 0.4 eV, we have

$$\begin{aligned} E_0 &= \left(0 + \frac{1}{2} \right) hf \\ 0.4 \text{ eV} &= \left(0 + \frac{1}{2} \right) hf \\ 0.8 \text{ eV} &= hf \end{aligned}$$

Therefore, the energy of the photon is

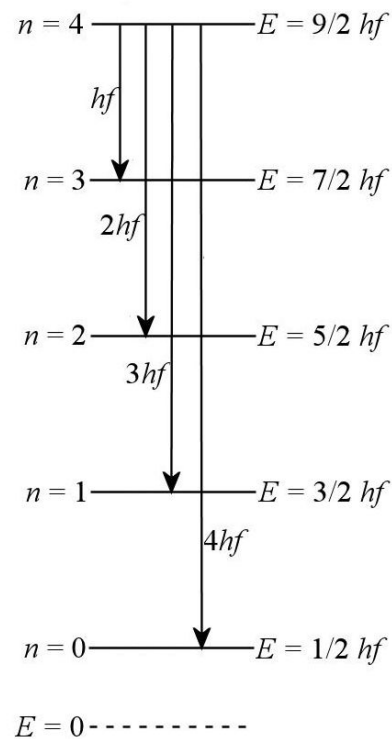
$$\begin{aligned} E_\gamma &= 2hf \\ &= 2 \cdot 0.8eV \\ &= 1.6eV \end{aligned}$$

Thus, the wavelength of the light is

$$\begin{aligned} E_\gamma &= \frac{hc}{\lambda} \\ 1.6eV &= \frac{1240eVnm}{\lambda} \\ \lambda &= 775nm \end{aligned}$$

A Look Back at Planck's Hypothesis

The atoms in a solid are subject to forces such that every atom is doing a harmonic oscillation (when the amplitudes are small). When the energy of an atom drops by one level, the energy of the emitted photon is hf . If the energy of the atom drops by 2 levels, the emitted photon has energy $2hf$. If the energy of the atom drops by three levels, the energy of the emitted photon is $3hf$, and so on. It is easy to see that the energy of the emitted photons must be nhf , where n is an integer. Therefore, hot objects can only emit photons whose energy is nhf . This is exactly what Planck assumed in 1900 to explain the radiation of hot objects. This is an incredible luck to have energy levels evenly spaced like this for a particle undergoing a harmonic oscillation. If the energy differences had been irregular, the energy of the photons would have been very different from nhf and it is unlikely that Planck would have guessed the energy formula and solve the hot body problem.

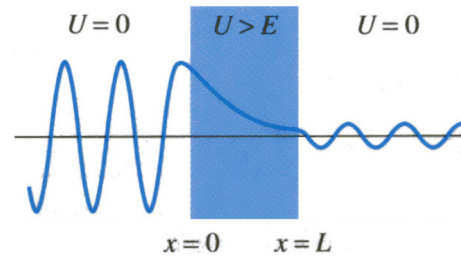


Energy at Absolute Zero

When the temperature of a body becomes very low, the atoms go down to the lowest energy levels, so that they all are at the level lowest at 0 K. However, it can be seen that, even on the first level $n = 0$, the energy is not zero ($E = \frac{1}{2}hf$). So, even at 0 K, there is some energy left and the atoms are still oscillating.

A Common Misconception

For virtually all types of waves, the amplitude increases with the energy of the wave. However, this is not the case with the wave in quantum mechanics. To illustrate the conceptual error often made, let's look again at the wave in quantum tunnelling. Here's what would be a misinterpretation of this wave:

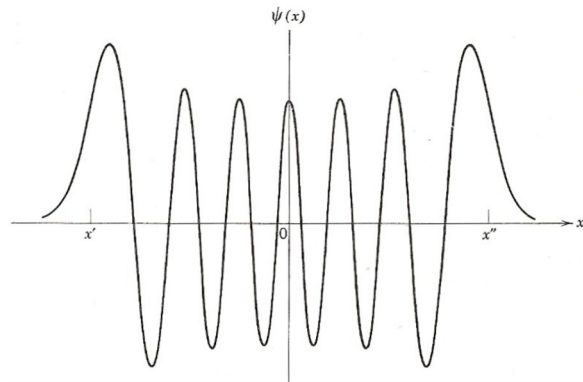


Common Mistake: Thinking that the Energy Decreases if the Amplitude Decreases

In quantum tunnelling, as the amplitude is smaller on the other side of the barrier, one would then think that the electron loses energy as it crosses the barrier.

The electron does not lose energy at all when crossing the barrier. In fact, the electron has exactly the same energy after crossing the barrier as before crossing since the potential energy is exactly the same on each side. As the amplitude is linked with the probability of finding the electron at this location, the amplitude is smaller because few electrons manage to cross the barrier, not because the energy of the electrons has decreased.

This does not mean that there is no link between energy and amplitude at all. When the harmonic oscillator was studied, it was noticed that the amplitude increases when the potential energy increases (because the kinetic energy is then smaller, which means that the particle goes slower there and, therefore, is more likely to be found there).



This link is generally true, unless there is a barrier as in quantum tunnelling. In this case, the amplitudes could be different on either side of the barrier even if the potential energies are the same.

11.7 HYDROGEN ATOM

Electrons and Nucleus

After 1905, there were virtually no scientists doubting the existence of atoms. (One of the last arguments was made by Einstein in 1905 with his doctoral thesis on Brownian motion.

He produces this thesis the same year he wrote his papers on relativity and on the photoelectric effect. He also had a 1-year-old son, Hans Albert. No wonder 1905 is called *Einstein's miraculous year.*)

However, at this time, very few details were known about the internal structure of the atom. There was little doubt that electrons (discovered in 1897) were present in the atom but not much more was known. After 1906, they started to suspect that the number of electrons in the atom is equal to the atomic number of the element.

In 1908, Geiger and Marsden made helium nuclei (also known as alpha particles) pass through a very thin gold foil to observe how these nuclei are deflected. They got very different results from what they were expecting. While they expected small deflections, they sometimes observed very significant deflections ranging up to 180° . Ernest Rutherford found, in 1911, an explanation for the results of this experiment: in the atom, there is a very small positive nucleus (10^{-14} m approx.) where almost all the mass of the atom is found and there are negative electrons around the nucleus.

Rutherford never said that the electrons circled around the nucleus like planets around the Sun. He knew that there are serious problems with such a model. Hantaro Nagaoka had already proposed a similar model in 1904, but it was quickly rejected on the grounds that the electrons in orbit would emit electromagnetic radiation (because accelerating charges emit such radiation) and would lose energy. This loss of energy would bring the electrons closer to the nucleus, and they would lose energy so fast that the electrons would crash on the nucleus in a millionth of a second. The end result is not a very stable atom. Rutherford knew this and avoided the question by simply saying that there are electrons around the nucleus, without specifying their movement or position.

If the electrons can't circle around the nucleus, then what do they do?

Wave Functions for Hydrogen

Early on, Schrödinger used his equation to find the electron's wave functions in hydrogen. In this case, the value of the potential energy of the electron when subjected to the electrical force of the nucleus must be used in Schrödinger's equation.

$$U = \frac{-ke^2}{r}$$

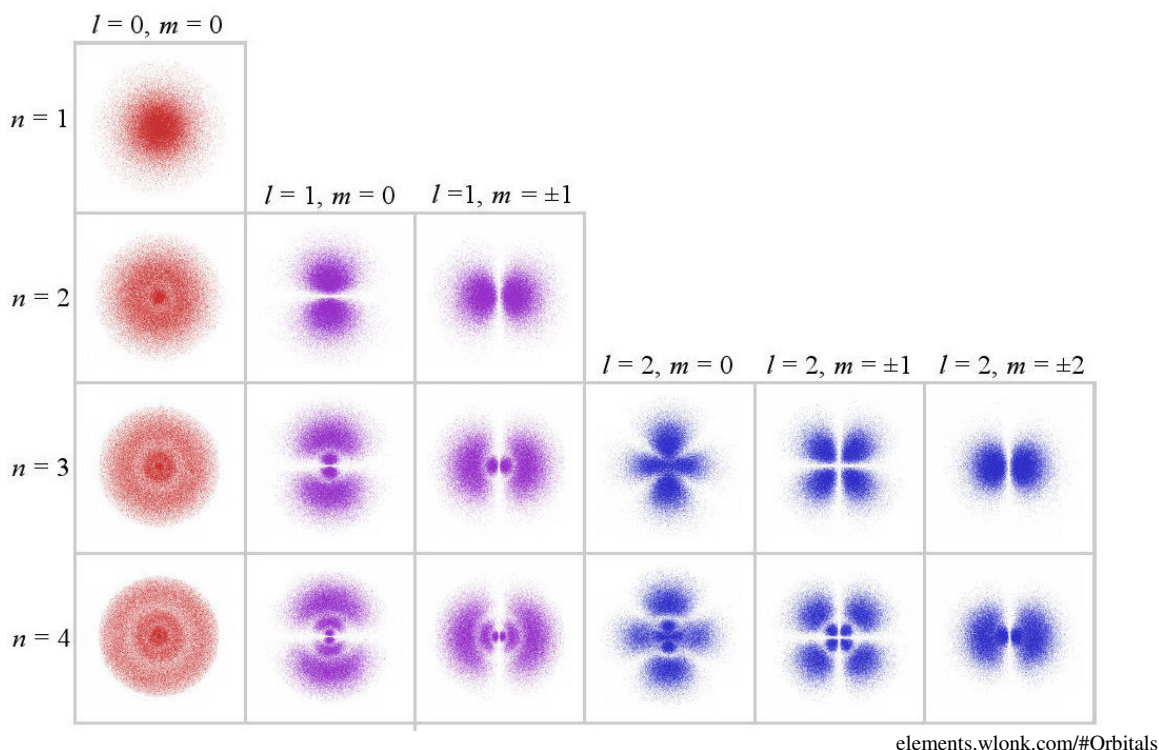
k is a constant equal to $8.9876 \times 10^9 \text{ Nm}^2/\text{C}^2$

e is the elementary electric charge $1.602 \times 10^{-19} \text{ C}$

r is the distance between the nucleus and the electron

Even though the potential energy formula is quite simple, the solution for ψ is, again, quite difficult to obtain, especially since the Schrödinger equation in 3 dimensions must be used.

This time, the solutions required the use of Bessel functions and Legendre's polynomials, which you probably don't know (unless you're a real nerd). Just as with particles in a box and particles undergoing a harmonic oscillation, there are several possible solutions. Here are diagrams showing some of these solutions. (Here, these diagrams actually show the probability densities, which are calculated with ψ^2 .)



As can be seen on the diagram, the different solutions, which are called *orbitals*, are characterized by the three integers n , l and m .

The number n can take the values 1, 2, 3, 4, 5, ...

The number l can take the values ranging from 0 up to $n - 1$. For example, if n is equal to 3, then l can take values 0, 1 and 2. Letters are also used to give the value of l . For the first 4 values of l we have s for $l = 0$, p for $l = 1$, d for $l = 2$, and f for $l = 3$. Thus, the solution with $n = 2$ and $l = 1$ corresponds to the orbital $2p$.

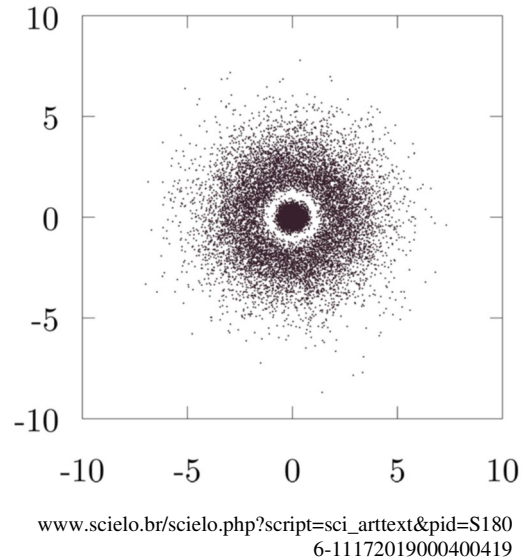
The values if m ranges between $-l$ and l . For example, if $l = 2$, then m can take the values -2, -1, 0, 1, and 2.

Let's illustrate the kind of solution obtained by taking the example of solution $n = 2$, $l = 0$, and $m = 0$ which corresponds to the orbital $2s$. In this case, the solution is

$$\psi_{200} = \frac{1}{\sqrt{32\pi r_0^2}} \left(2 - \frac{r}{r_0} \right) e^{-r/2r_0} \quad \text{where } r_0 = 5.292 \times 10^{-11} \text{ m}$$

(r_0 is called Bohr radius). From this wave, we can calculate the probability of finding the electron at a certain distance from the nucleus. The diagram to the right is then obtained (where the distances are in angstroms and 1 angstrom is worth $1 \text{ \AA} = 10^{-10} \text{ m}$).

The orbital corresponds to places where there is a high probability of finding the electron. In this model, it is not said that the electron circles around the nucleus following an orbit. All there is in quantum mechanics are orbitals and these orbitals represent only the places where there is a high chance of finding the electron. (The graph actually shows what could be obtained if the position of the electron in this orbital were measured 15 000 times.)



If the position of the electron is not measured, the electron is in a superposition of states corresponding to all possible results of the measurement of the position. This means that the electron is everywhere at the same time in the orbital. The electron is therefore in several places at the same time! If you measure the position of the electron and get a certain position, then that means that the wave function collapsed, and the electron went from being everywhere at the same time in the orbital to being at a specific location.

Energy Levels of the Electron

Again, even if the solutions of wave functions are quite complex, the possible energies of the electron are given by a very simple formula. This formula is

$$E_n = -\frac{2\pi^2 m_e k^2 e^4}{n^2 h^2} \quad \text{where } m_e \text{ is the electron mass}$$

There are a bunch of constants in this formula. The value of this combination of constants is

$$\begin{aligned} \frac{2\pi^2 m_e k^2 e^4}{h^2} &= \frac{2\pi^2 \cdot 9.1094 \times 10^{-31} \text{ kg} \cdot \left(8.9876 \times 10^9 \frac{\text{N}}{\text{C}^2 \text{ m}^2}\right)^2 \cdot (1.6022 \times 10^{-19} \text{ C})^4}{(6.6261 \times 10^{-34} \text{ Js})^2} \\ &= 2.180 \times 10^{-18} \text{ J} \\ &= 13.606 \text{ eV} \end{aligned}$$

However, the electron's wave function is not centred on the nucleus, but rather on the centre of mass of the atom. This changes the force between the electron and the nucleus

and, consequently, the energies of the levels. Taking this correction into account, the previously calculated energy value decreases to 13.598 eV. So, we have the following possible energies.

Electron Energy Levels in Hydrogen

$$E_{Hn} = -\frac{2\pi^2 m_e k^2 e^4}{n^2 h^2} = -\frac{13.598 \text{ eV}}{n^2}$$

Note that if there are orbitals with the same energy, such as the three orbitals $2p$, then the electron is everywhere at the same time in the three orbitals.

Therefore, the first 4 energy levels of the electron in the hydrogen atom are

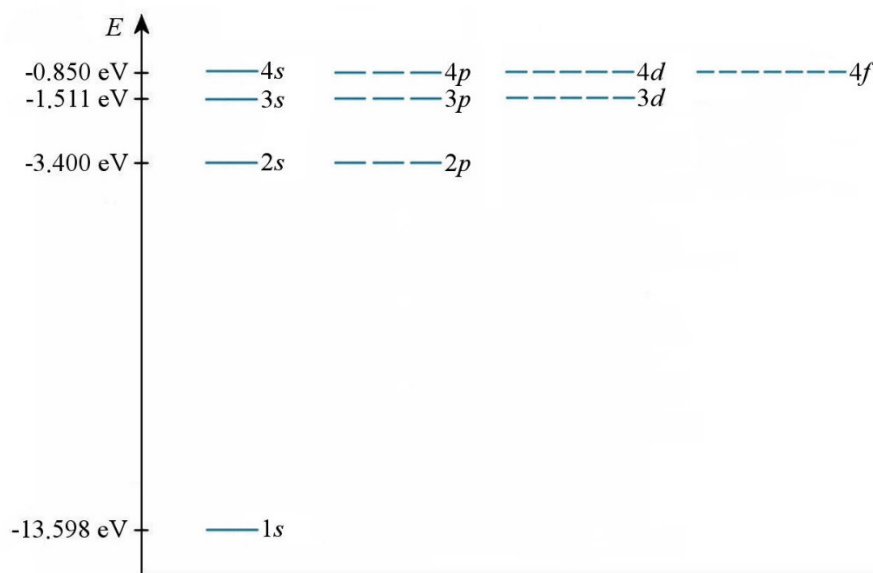
$$E_{H1} = -\frac{13.598 \text{ eV}}{1} = -13.598 \text{ eV}$$

$$E_{H2} = -\frac{13.598 \text{ eV}}{4} = -3.400 \text{ eV}$$

$$E_{H3} = -\frac{13.598 \text{ eV}}{9} = -1.511 \text{ eV}$$

$$E_{H4} = -\frac{13.598 \text{ eV}}{16} = -0.850 \text{ eV}$$

These 4 energy levels can be represented by this diagram.



(The small lines show the levels having different values of m on this diagram. For example, the three lines at level $2p$ represent the 3 levels with $m = -1$, $m = 0$, and $m = 1$.)

It can be noted that the energy of the levels increases (less and less negative) as n increases. The energy of the levels is negative because the electron is bound to the nucleus. Since the

electric energy U is zero far away from the nucleus, the electron cannot leave the nucleus because it cannot be where the energy U is greater than the mechanical energy.

Ionization Energy

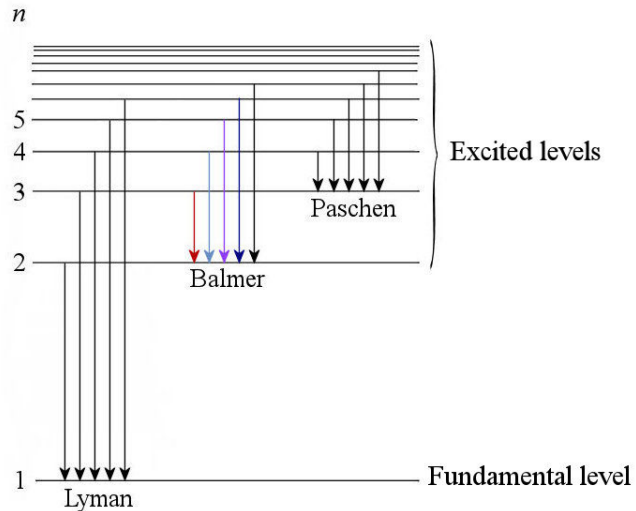
To extract an electron from the atom (thus ionizing the atom), energy must be given to the electron. The minimum energy of the electron far away from the nucleus is 0 (zero kinetic energy and $U = 0$ far away from the nucleus). If the electron's energy in its orbit is $-13,598 \text{ eV}$, then it must be given at least $13,598 \text{ eV}$ to bring its energy to 0. Thus, the absolute values of the calculated energies correspond to the energies needed to pull the electron out of the atom.

Hydrogen Emission Spectrum

When the electron in hydrogen changes level to a lower energy level, then a photon is emitted.

The level $n = 1$ is called the fundamental level. When the electron is not at the fundamental level, the atom is said to be *excited*. The level $n = 2$ is the first excited level, the level $n = 3$ is the second excited level and so on.

For hydrogen, transitions between the levels have specific names. For example, all transitions that end at the level $n = 1$ are part of Lyman's series, and all transitions that end at level $n = 2$ are part of Balmer's series.



Example 11.7.1

An electron in a hydrogen atom moves from the level $n = 4$ to the level $n = 2$. What is the wavelength of the light emitted?

The energy of the photon is (using the energies of the levels calculated previously)

$$\begin{aligned}
 E_{\gamma} &= E_4 - E_2 \\
 &= -0.850 \text{ eV} - (-3.400 \text{ eV}) \\
 &= 2.550 \text{ eV}
 \end{aligned}$$

Therefore, the wavelength of the light is

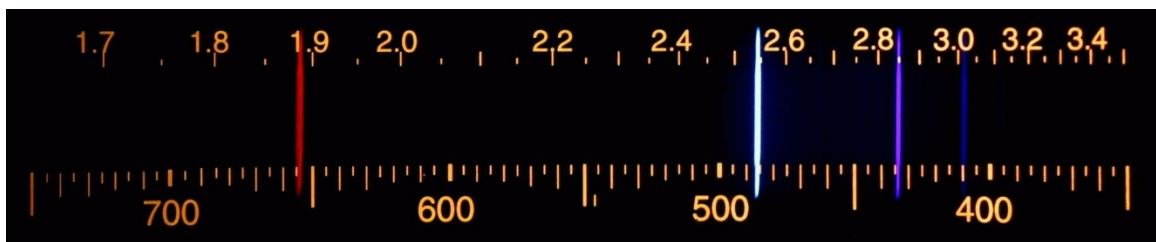
$$E_\gamma = \frac{hc}{\lambda}$$

$$2.550\text{eV} = \frac{1240\text{eVnm}}{\lambda}$$

$$\lambda = 486\text{nm}$$

This wavelength is only one possibility. Many other wavelengths could be found by taking different values of n for the initial and final levels of the electron.

This means that a hydrogen atom can only emit photons with very specific wavelengths. Of all possible wavelengths, only four are in the visible part of the spectrum (they are all in the Balmer series). These wavelengths, first measured by Anders Jona Ångström in 1853, are: 656.3 nm (red), 486.1 nm (blue), 434.1 nm (violet) and 410.2 nm (violet, very difficult to see). There are many other wavelengths, but they are outside the visible part of the spectrum. This is the spectrum of hydrogen.



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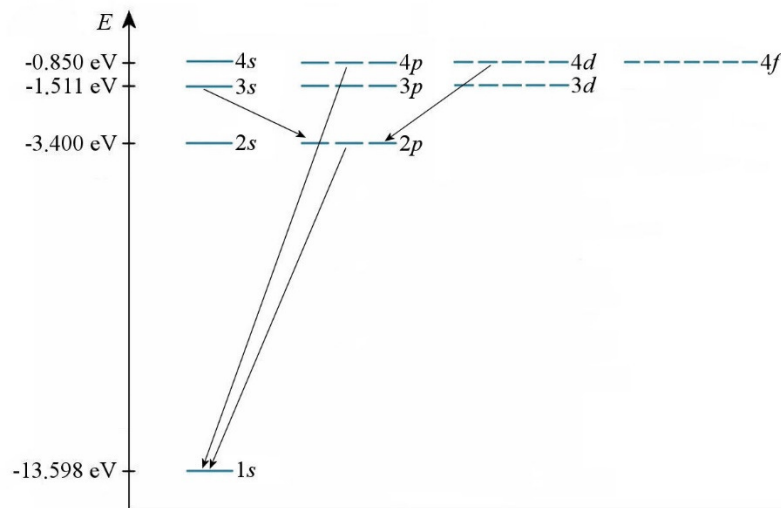
These lines are called *spectral lines*.

(The spectrum is what we see when we observe the light emitted by several hydrogen atoms. Some atoms emit red stripes, some blue, some violet and so on. One atom alone could not emit all these wavelengths at the same time.)

However, to see such a spectrum, the electrons in the hydrogen atoms must initially be on levels higher than $n = 1$ to allow the electrons to go to a lower level. The problem is that, normally, the electron is at the $n = 1$ level in all the hydrogen atoms. It is then impossible to emit photons, because the electron cannot go to a lower level. However, if the gas is heated, the situation changes. As the temperature rises, the speed of the atoms increases and the collisions between the atoms become more violent. From a certain temperature (around 3000 K), the energy of the atoms becomes large enough to sometimes cause an increase in the level of the electron during collisions. When the electron goes back to a lower level thereafter (this is done quite quickly since the electron remains, on average, only 1.6 ns at level $n = 2$ for example), a photon is emitted. Hydrogen then becomes luminous and emits its characteristic spectrum.

Selection Rules

The electron can make certain transitions more easily in a hydrogen atom (and all other atoms). As the photon emitted has a spin of 1, the angular momentum of the electron must change by 1 during a transition. This means that the value of l must go up or down by 1 during a transition. An electron cannot therefore pass from the $3p$ orbital to the orbital $2p$ since the value of l would remain the same. Here are some of these allowed transitions.



In other words, the electron must change from one column to a neighbouring column in this diagram during a transition.

In fact, transitions for which l does not change by 1 are possible, but through a more complex process that decreases the likelihood of making such a transition. Thus, an electron will remain on average only 1.6 ns on the $2p$ level before descending to $1s$ level while an electron on the $2s$ level will remain on average 0.12 s on this level before moving to the $1s$ level.

The Indeterminacy Principle and the Wavelength of the Emitted Photon

According to the indeterminacy principle $\Delta E \Delta t \approx h$, the energy of the electron on a level may have some indeterminacy if the electron does not stay for a long time on that level. If the energy of the starting level has an indeterminacy, then the energy of the photon emitted will also have an indeterminacy.

Example 11.7.2

An electron is at the $2p$ level which has an energy of $-3.399\,623\,3 \text{ eV}$. The electron stays on this level on average 1.6 ns before descending to the fundamental level which has an energy of $-13.598\,433\,8 \text{ eV}$. What is the indeterminacy on the wavelength of the light

emitted during this transition? (More precise energy level values are used because the indeterminacies are very small.)

With a lifespan of 1.6 ns, the indeterminacy on the energy of the 2*p* level is

$$\begin{aligned}\Delta E \Delta t &\approx h \\ \Delta E &\approx \frac{h}{\Delta t} \\ \Delta E &\approx \frac{6.626 \times 10^{-34} \text{ Js}}{1.6 \times 10^{-9} \text{ s}} \\ \Delta E &\approx 4.14 \times 10^{-25} \text{ J} \\ \Delta E &\approx 2.585 \times 10^{-6} \text{ eV}\end{aligned}$$

This means that the energy of the excited level can take any value between 3.399 622 0 eV and 3.399 624 6 eV (the difference between these values is 2.6×10^{-6} eV).

The energy of the emitted photon is

$$\begin{aligned}E_\gamma &= E_2 - E_1 \\ &= -3.399 623 3 \text{ eV} - (-13.598 433 8 \text{ eV}) \\ &= 10.198 810 5 \text{ eV}\end{aligned}$$

As the fundamental level has no indeterminacy (since its lifespan is very long), the indeterminacy on the energy of the photon is also 2.6×10^{-6} eV. This means that the energy of the photon can take any value between 10.198 809 2 eV and 10.198 811 8 eV (the difference between these values is 2.6×10^{-6} eV).

The wavelength of the light is

$$\begin{aligned}E_\gamma &= \frac{hc}{\lambda} \\ 10.198 810 5 \text{ eV} &= \frac{1239.841 974 \text{ eVnm}}{\lambda} \\ \lambda &= 121.567 312 \text{ nm}\end{aligned}$$

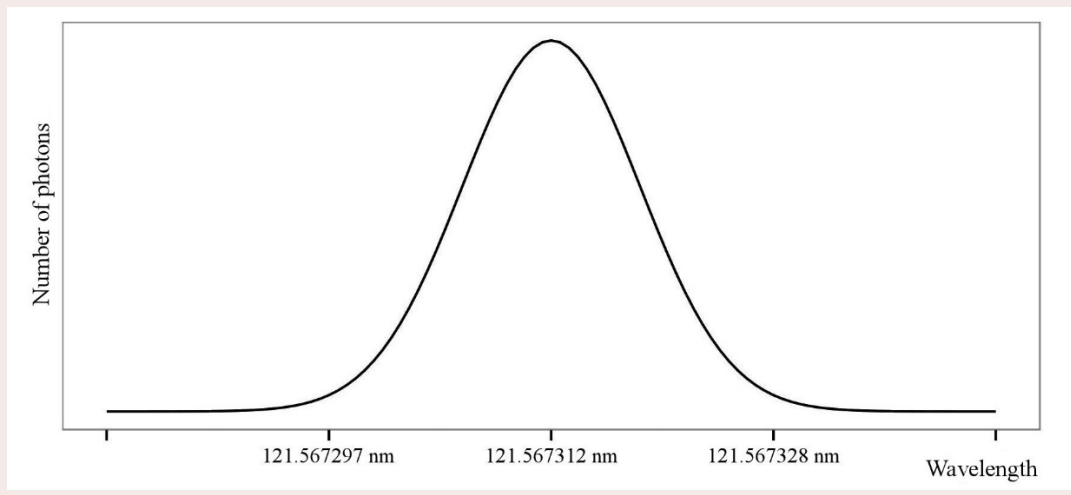
The indeterminacy on the wavelength is

$$\begin{aligned}\Delta \lambda &= \left| \frac{d \frac{hc}{E_\gamma}}{dE_\gamma} \right| \Delta E_\gamma \\ &= \frac{hc}{E_\gamma^2} \Delta E_\gamma\end{aligned}$$

$$\begin{aligned}
 &= \frac{1239.841974 \text{ eV nm}}{(10.1988105 \text{ eV})^2} \cdot 2.6 \times 10^{-6} \text{ eV} \\
 &= 3.1 \times 10^{-5} \text{ nm}
 \end{aligned}$$

This means that the wavelength of the light can take any value between 121.567 297 nm and 121.567 328 nm (the difference between these values is 3.1×10^{-5} nm).

In practice, this means that if the wavelength of the light emitted is measured for several of these atoms, you will get a distribution that looks like this.

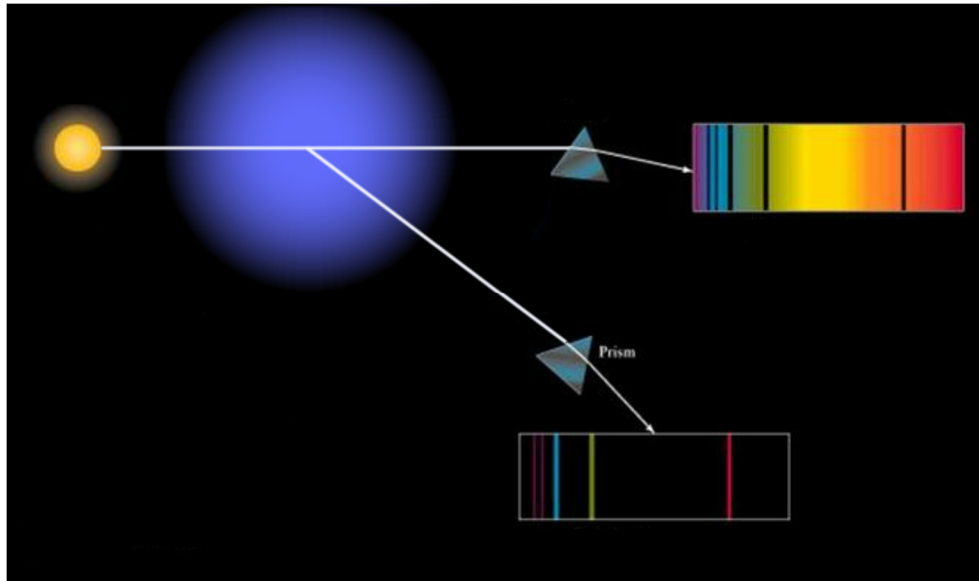


The very short lifespan of the $2p$ level means that the energy indeterminacy of the emitted photon is about 10^{-6} eV. On the other hand, the indeterminacy on the energy of the photon emitted during a transition from the $2s$ level to the $1s$ level is much smaller because the lifespan of the $2s$ level is much greater. The indeterminacy on the energy of the photon emitted in this case is only about 10^{-19} eV.

The Absorption Spectrum of Hydrogen

When white light passes through the cold gas, photons that have exactly the right energy will be absorbed by the atom. These photons have an energy that corresponds to the energy difference between two levels. For example, in hydrogen, there are 10.17 eV between the first level and the second level. If a photon has exactly this energy, it can be absorbed by an electron so that this electron goes from the first level to the second level. As photons having this energy are absorbed, they disappear from the spectrum, which creates the absorption lines. All these lines are exactly in the same place as the emission lines in the spectrum since the energies of the photons absorbed are the same as the energies of the photons emitted in the emission spectrum. In both cases, the energies are equal to the differences in energy between levels.

The electron which is at a higher level due to the absorption of a photon will eventually go back to a lower level by emitting a photon. However, this light will be, most of the time, re-emitted in a different direction. The probability that the photon is emitted in the same direction as the direction of the light passing through the gas is very low. The light passing through the gas will, therefore, be much less intense at the absorbed wavelengths, which will give the absorption spectrum. In the other directions, only the light re-emitted by the electrons going down to lower levels can be seen. An emission spectrum is thus seen.



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Balmer's Formula

Long before the development of quantum mechanics, a formula had been found that gives the wavelengths emitted by hydrogen. It was obtained through the work of Balmer (1884), Rydberg (1889) and Ritz (1908), among others. This formula is

$$\frac{1}{\lambda} = 0.01097 \text{ nm}^{-1} \cdot \left(\frac{1}{a^2} - \frac{1}{b^2} \right)$$

where a and b are integers (any integer that complies with the condition $a < b$). For example, if $a = 2$ and $b = 3$, the wavelength is 656.3 nm, and this is the red line in the hydrogen spectrum.

However, this formula was not based on any theory. It was obtained by trial and error to arrive at a formula that gives the correct values of the wavelengths obtained experimentally.

The validity of this formula can be shown from the energy levels of the electron in hydrogen.

$$\begin{aligned}
 E_\gamma &= E_i - E_f \\
 E_\gamma &= -\frac{13.598\text{eV}}{n_i^2} - \left(-\frac{13.598\text{eV}}{n_f^2}\right) \\
 hf &= \frac{13.598\text{eV}}{n_f^2} - \frac{13.598\text{eV}}{n_i^2} \\
 \frac{hc}{\lambda} &= 13.598\text{eV} \cdot \left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) \\
 \frac{1}{\lambda} &= \frac{13.598\text{eV}}{hc} \cdot \left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) \\
 \frac{1}{\lambda} &= \frac{13.598\text{eV}}{1240\text{eVnm}} \cdot \left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) \\
 \frac{1}{\lambda} &= 0.01097\text{nm}^{-1} \cdot \left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)
 \end{aligned}$$

This is the Balmer formula! The theory thus confirmed what had been found experimentally decades earlier.

Bohr Model

Bohr was the first to find, in 1913, the formula of the energy levels of the electron in the hydrogen atom. From this formula and from $E = hf$, Bohr arrives at Balmer's formula, exactly as we did before. Bohr thus gave an initial theoretical explanation for Balmer's formula, which until then was only a formula obtained from experimental results.

The explanation was quite revolutionary at that time. No one before him had found the energy levels in hydrogen and no one had talked about light emitted when the electron passes from one level to another. Moreover, it was very daring to use the constant h since this constant appeared only in the formulas of black body radiation and photoelectric effect at the time. (Note that even if Bohr uses $E = hf$, he does not think in 1913 the light emitted is in the form of a photon. Only the emission process was related to $E = hf$. Once the light was emitted, it did not have to stay in a lump to be a photon.)

However, an important question remains. How did Bohr arrive, in 1913, at the formula of the energy levels more than a decade before the development of quantum mechanics (1925)?

Bohr does this by assuming that the electron rotates around the nucleus even if this is impossible according to classical physics (since it would quickly lose its energy). For Bohr, the electron is therefore in orbit around the nucleus, like a planet around the Sun. However, the electron cannot follow any orbit according to Bohr. The permitted orbits are those for which

$$m_e v r = \frac{nh}{2\pi}$$

where n is an integer. Let's see how this assumption leads to the energy levels.

As the electron is subjected to the electrical force made by the nucleus, the force on the electron and the potential energy of the electron are given by

$$F = \frac{ke^2}{r^2} \quad U = -\frac{ke^2}{r}$$

If the electron is in a circular motion, a centripetal force acts on the electron. As the only force acting on the electron is the electric force, this force must be the centripetal force. Therefore,

$$\frac{m_e v^2}{r} = \frac{ke^2}{r^2}$$

$$m_e v^2 = \frac{ke^2}{r}$$

But the second postulate says that

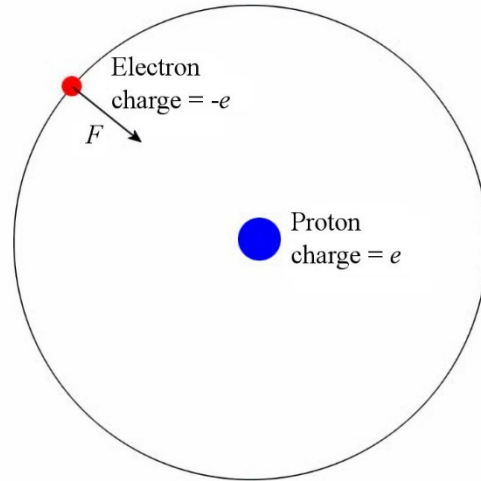
$$m_e r v = \frac{nh}{2\pi}$$

If this value of the speed is used in the equation of the centripetal force, it becomes

$$m_e v^2 = \frac{ke^2}{r}$$

$$m_e \left(\frac{nh}{2\pi m_e r} \right)^2 = \frac{ke^2}{r}$$

It can be simplified to obtain the radiuses of the orbits (according to Bohr)



$$r = \frac{n^2 h^2}{4\pi^2 m_e k e^2}$$

From that radius, the mechanical energy of the electron on its orbit can be found.

$$E = E_k + U$$

$$E = \frac{1}{2} m_e v^2 - \frac{k e^2}{r}$$

However, the equation for centripetal force

$$m_e v^2 = \frac{k e^2}{r}$$

can be used to write the kinetic energy in the following form.

$$\frac{1}{2} m_e v^2 = \frac{k e^2}{2r}$$

The energy is thus

$$E = E_k + U$$

$$= \frac{k e^2}{2r} - \frac{k e^2}{r}$$

$$= -\frac{k e^2}{2r}$$

Using the formula for the radius of the orbit, the energy can be written as

$$E = -\frac{k e^2}{2r}$$

$$= -k e^2 \frac{4\pi^2 m_e k e^2}{2n^2 h^2}$$

$$= -\frac{2\pi^2 m_e k^2 e^4}{n^2 h^2}$$

That is the same energy formula as the one previously given.

Bohr does arrive at the right formula of energy levels, but starting from the premise that $m_e v r = nh/2\pi$. This equation comes out of nowhere and has no justification in Bohr's model. He uses it just because it gives the right energy levels. Bohr just hopes that one day someone will be able to explain the origin of this equation.

This equation received its first justification in 1923 when Louis de Broglie found the formula $\lambda = h/p$. Let's see what happens to Bohr's postulate $m_e v r = nh/2\pi$ if de Broglie's formula is used.

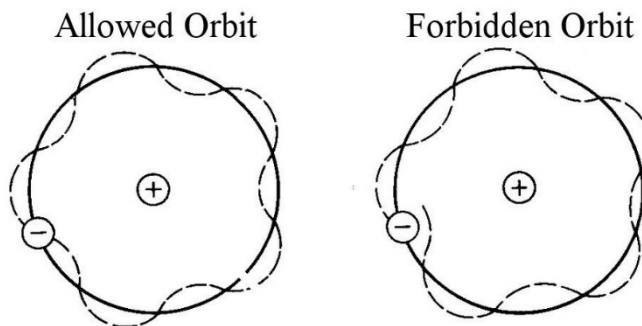
$$m_e v r = \frac{nh}{2\pi}$$

$$p r = \frac{nh}{2\pi}$$

$$\frac{h}{\lambda} r = \frac{nh}{2\pi}$$

$$n\lambda = 2\pi r$$

This result indicates that the circumference of the orbit must be an integer number of the wavelength of the electron. This could not be a coincidence. De Broglie's formula therefore seemed to provide a beginning of a justification for Bohr's postulate. De Broglie uses this result as an argument for justifying its own formula.



www.scinote.org/blog/seeking-scinote-physics-why-dont-electrons-fall-into-the-nucleus

The same condition is obtained with quantum mechanics, but with a difference. Even if there are no orbits in quantum mechanics, we find the same result as the one obtained by de Broglie since the wave function must be the same if we add 2π to the angle ϕ which gives the position around the nucleus. So, we must have

$$\psi(\phi + 2\pi) = \psi(\phi)$$

This means that the wave can only change in ϕ with $\sin(m\phi)$ and $\cos(m\phi)$ where m is an integer. The fact that m must be an integer is the equivalent of condition $n\lambda = 2\pi r$ found by de Broglie.

But there's a difference. It is m instead of n ! We remember that the solutions ψ are characterized by the values of n , l , and m . It is not the n that ends up in the condition, but m . Thus, following the logic of de Broglie and Bohr, one should obtain energy levels that depend on m rather than n , which is wrong. By accident, you get the same energy values because both n and m can only take integer values.

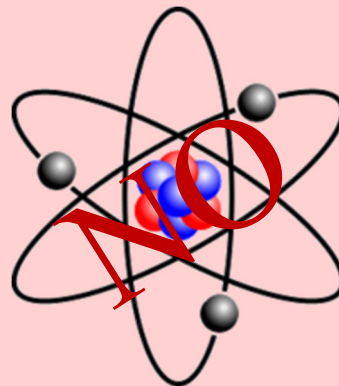
Note that if the value of m is 0 (as in the orbitals s), the condition given previously seems to give $\lambda = \infty$. This only means that there is no change in the wave when you change direction around the nucleus. There is still a wavelength because the wave varies according to the distance r .



Common Mistake: Thinking That the Electrons is Moving on an Orbit Around the Nucleus

The right energy level values are obtained with Bohr's model, but this model is not a suitable model of the atom.

The accepted model is the model of quantum mechanics. In this quantum model, there are no orbits and trajectories for the electron, there are only orbitals that represent the probability of finding the electron in a place. In the quantum model, the electron is everywhere at once in the orbital if the position of the electron is not measured.



You will certainly be surprised to learn that very few people really know the current atomic model, and that even includes students with a chemistry degree (the interviews I made to hire chemistry teachers demonstrate this pretty well!) Many people will tell you that in the hydrogen atom, there is a single electron that rotates around the nucleus following an orbit. Yet the accepted atomic model says nothing of the kind.

Corrections to the Energy Levels in Hydrogen

The model of the hydrogen atom obtained by Schrödinger does not give quite the right energy levels. Here, for example, is the difference between theoretical prediction and experimental value for the lowest energy level of hydrogen.

Schrödinger's prediction	-13.598 286 680 eV
Experimental value	-13.598 433 771 eV

However, there is a whole series of corrections that can be made to theoretical value. Here are a few.

1. **Spin-orbit interaction.** The electron in the orbitals around the nucleus generates a magnetic field. This magnetic field acts on the electron since the electron has a magnetic moment.
2. **Spin-spin interaction.** The nucleus has a magnetic moment that also generates a magnetic field that acts on the electron.
3. **Relativity.** With Dirac's equation (a relativistic version of the Schrödinger equation), orbitals and energy levels are a little different.
4. **Vacuum polarization.** In a vacuum, particles and antiparticles continually appear to disappear almost immediately. During the very brief life of these particles, they exert a force on the nucleus and the electron, and this changes the energy levels very slightly.

With all these small corrections, we get theoretical values in perfect agreement with the experimental values. In fact, quantum electrodynamics, used to make these calculations, is the most accurate scientific theory available. Theoretical predictions and experimental measurements agree with up to 10 significant figures.

11.8 OTHER ATOMS

Atoms With a Single Electron

We can find a solution in quantum mechanics for atoms that have a single electron. The nucleus then has Z protons. If $Z = 1$, it is a hydrogen atom. If $Z = 2$, it is a helium atom ionized once (He^+). If $Z = 3$, it is an atom of lithium ionized twice (Li^{2+}) and so on. In this case, the energy levels are given by

Energy of Electron Levels in an Atom With a Single Electron

$$E_n = -\frac{2\pi^2 Z^2 m_e k^2 e^4}{n^2 h^2} = -\frac{Z^2 \cdot 13.60 \text{ eV}}{n^2}$$

(Here, the value of the energy in electronvolts (13.60 eV) is a little different from the value used for hydrogen because the modification generated by the position of the center of mass is less important for these atoms.)

Example 11.8.1

An electron is in a once-ionized helium atom (He^+).

- a) What is the ionization energy if the electron is at the fundamental level?

The energy of the electron at the fundamental level is

$$\begin{aligned} E_n &= -\frac{Z^2 \cdot 13.60 \text{ eV}}{n^2} \\ E_1 &= -\frac{2^2 \cdot 13.60 \text{ eV}}{1^2} \\ &= -54.40 \text{ eV} \end{aligned}$$

So, we have to give 54.40 eV to remove this electron.

- b) What is the wavelength of the light emitted when the electron passes from the third to the second level?

The wavelength can be found with

$$E_{\gamma} = \frac{hc}{\lambda}$$

where E is the energy of the photon, which corresponds to the energy change of the electron. The first step is to find the energy variation of the electron.

The energy of the third level is

$$\begin{aligned} E_n &= -\frac{Z^2 \cdot 13.60 \text{ eV}}{n^2} \\ E_3 &= -\frac{2^2 \cdot 13.60 \text{ eV}}{3^2} \\ &= -6.04 \text{ eV} \end{aligned}$$

The energy of the second level is

$$\begin{aligned} E_n &= -\frac{Z^2 \cdot 13.60 \text{ eV}}{n^2} \\ E_2 &= -\frac{2^2 \cdot 13.60 \text{ eV}}{2^2} \\ &= -13.60 \text{ eV} \end{aligned}$$

Therefore, the energy of the photon is

$$\begin{aligned} E_{\gamma} &= E_3 - E_2 \\ &= -6.04 \text{ eV} - (-13.60 \text{ eV}) \\ &= 7.56 \text{ eV} \end{aligned}$$

Thus, the wavelength of the light is

$$\begin{aligned} E_{\gamma} &= \frac{hc}{\lambda} \\ 7.56 \text{ eV} &= \frac{1240 \text{ eVnm}}{\lambda} \\ \lambda &= 164 \text{ nm} \end{aligned}$$

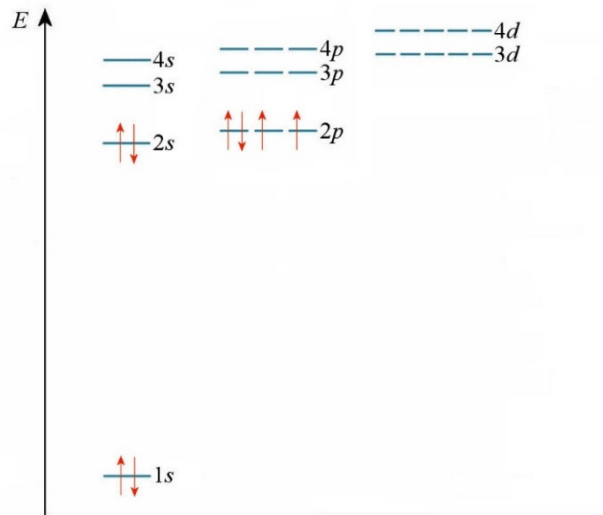
Atoms With Many Electrons

As soon as there are several electrons, there are no exact possible solutions to Schrödinger's equation. As electrons repel each other, the formula of potential energy becomes more complex. Even with only 2 electrons, we are not able to solve Schrödinger equation exactly (but interesting results can be obtained using approximations).

It is known, however, that the solutions remain characterized by the same numbers n , l , and m that were used for the hydrogen atom. The electrons must therefore be placed in the orbitals, while respecting Pauli's exclusionary principle. For an atom at its lowest energy configuration, electrons are placed in the lowest energy levels by placing a maximum of 2 electrons per level, i.e. an electron with a positive spin and an electron with a negative spin. Thus, there will be no electrons that will have the same state (same n , l , m and s).

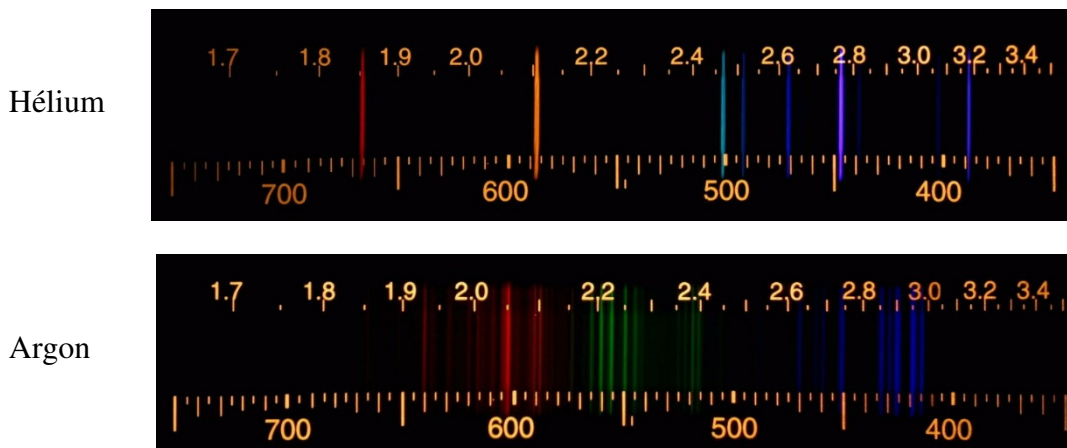
It is also known that the energies of the orbitals p are shifted upwards compared to the orbitals s , and that the energies of the d orbitals are shifted upwards even more. So, since we have to fill the orbitals by always filling the orbitals that have the least energy, we fill the orbitals in increasing order of $n + l$. In the event of a tie, the orbital with the smallest n must be filled first.

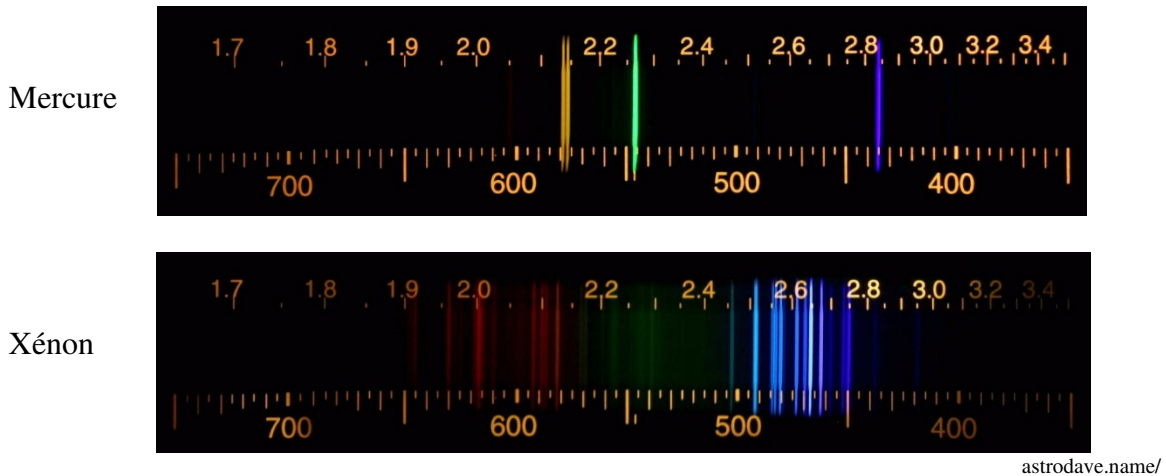
That is essentially what you did in general chemistry. For example, if the electrons are placed in the oxygen orbitals, the configuration shown to the right is obtained.



Spectrum of the Elements

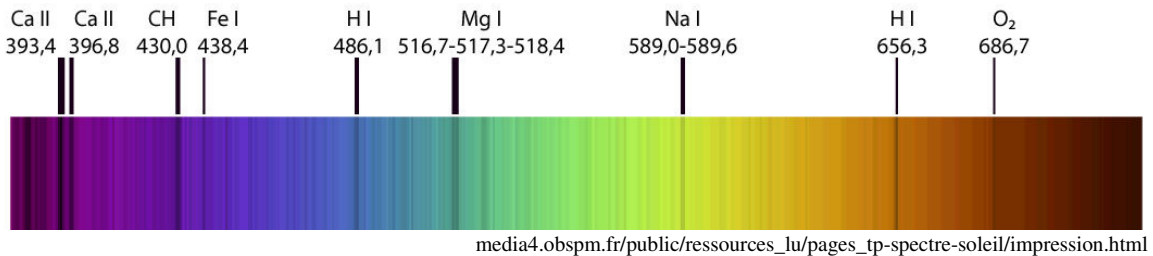
When an electron changes energy level, a photon is emitted. As the energy levels change with the number of electrons in the atom and the electrical charge of the nucleus, the energy levels are different for each atom. This means that the wavelengths emitted by each atom are different from those emitted by every other atom. So, a different spectrum is obtained for each atom. Here are a few.





It has been known since the 19th century, without knowing why at the time, that each element has a specific spectrum. Many new elements have been discovered with its spectrum. For example, new absorption lines were discovered in the solar spectrum in 1868, which match no known element. They quickly understood that they were dealing with a previously unknown element that they named helium (which comes from helios, meaning Sun in Greek). 12 new elements (cesium, rubidium, thorium, indium, gallium, scandium, germanium, helium, neon, argon, krypton and xenon) were thus first identified from their spectrum.

This is how the composition of the Sun is known. The absorption lines indicate all the elements present in the Sun. From their spectrum, the chemical composition of other stars can even be known despite their great distance. These absorption lines in the Sun's spectrum can be seen in the following image. Each of these lines is associated with an element present in the Sun (an element forms several lines).



William Wollaston was the first to observe spectral lines when he discovered absorption lines in Sun's spectrum in 1802. In 1814, Joseph Fraunhofer had catalogued 475 of these absorption lines in the solar spectrum.

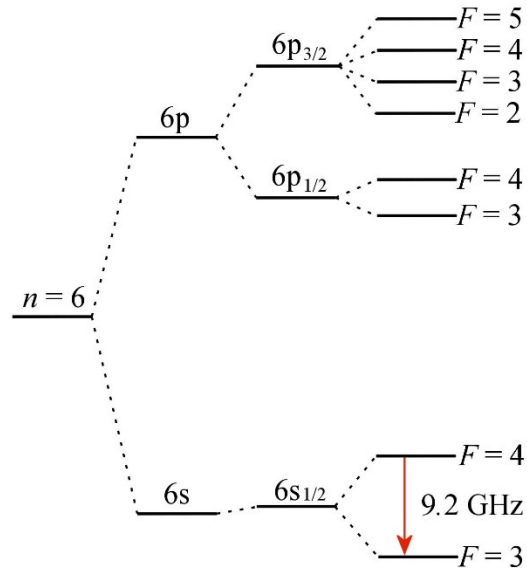
Definitions of Second, Metre and Kilogram

The definitions of the second, metre and kilogram are all related in one way or another to a particular atomic transition emitted by the cesium-133 atom, i.e. an atom with

55 electrons and a nucleus made of 55 protons and 78 neutrons. In this atom, there is only one electron on the level $n = 6$. Let's take a closer look at this 6th level.

You have seen in chemistry that the 6th level first splits into level 6s and 6p and that the energy of level 6p is greater. This can be seen in the 2nd column of the diagram on the right. However, the story does not end there, there are several other changes at these levels.

The 3rd column shows the corrections that give the *fine structure* of the atom. These corrections come from the spin-orbit interaction (i.e. the interaction between the spin of the electron and the magnetic field generated by the electron in its orbital), Einstein's relativity and certain quantum fluctuations in the atom (which gives a correction called the *Darwin correction*). In total, these corrections decrease the energy by 2 of the p levels (which are now called $6p_{1/2}$) and increase the energy by 4 p levels (which are now called $6p_{3/2}$). The level 6s (which becomes the level $6s_{1/2}$) does not split into several levels, but the energy of the level is slightly shifted by these corrections.



The following correction gives the *hyperfine structure* of the atom. It is generated by the spin-spin interaction, which is the interaction between the spin of the electron and the magnetic field generated by the atomic nucleus. This interaction splits the level $6s_{1/2}$ into 2 levels (called $F = 3$ and $F = 4$). This separation comes from the fact that the energy of the electron is a little greater when the spin of the electron is in one direction than when it is in the other direction.

When the electron passes from $F = 4$ to $F = 3$, light is emitted. It is actually the radiation emitted when the direction of the spin of the electron reverses. This light is not visible light, it is microwave radiation. They decided to use the frequency of this light to define the second.

Definition of the second

The second is defined by setting the value of the frequency of the hyperfine transition of the ground state of the unperturbed cesium-133 atom at 9 192 631 770 Hz.

In other words, it was decided that the frequency of this transition is exactly 9 192 631 770 Hz.

This definition seems quite arbitrary, but they chose this transition because it is used in atomic clocks. These clocks use the radiation from this transition to measure time.

The definition of the metre also depends on this radiation because it is based on the definition of the second.

Definition of the meter

One metre is the length of the path travelled by light in vacuum during $1/299\,792\,458$ of a second.

In other words, it was decided that the speed of light is exactly $299\,792\,458$ m/s.

To define the kilogram, it was decided to fix the value of h at $6.626\,070\,15 \times 10^{-34}$ Js. Let's see why this fixes the value of the kilogram. Since h and the frequency of the hyperfine transition are fixed, the energy of the photon emitted during the hyperfine transition is exactly

$$\begin{aligned} E_\gamma &= hf \\ &= 6.626\,070\,15 \times 10^{-34} \text{ Js} \cdot 9\,192\,631\,770 \text{ Hz} \\ &= 6.091\,102\,297\,113\,866\,55 \times 10^{-24} \text{ J} \end{aligned}$$

The equivalent mass of this photon is, according to $E = mc^2$,

$$\begin{aligned} E &= mc^2 \\ 6.091\,102\,297 \times 10^{-24} \text{ J} &= m \cdot \left(299\,792\,458 \frac{\text{m}}{\text{s}}\right)^2 \\ m &= 6.777\,265\,312\,312\,067\,610\,617 \times 10^{-41} \text{ kg} \end{aligned}$$

This means that it would take $1.475521399735279160650 \times 10^{40}$ of these photons to have 1 kg (the exact value is c^2/hf where $f = 9\,192\,631\,770$ Hz). We could therefore have the following definition.

Definition of the kilogram

One kilogram is the energy-equivalent mass of $1.475512400 \times 10^{40}$ photons coming from the hyperfine transition of the ground state of the unperturbed cesium-133 atom.

SUMMARY OF EQUATIONS

Possible Wavelengths for a Particle Trapped in a One-Dimensional Box

$$\lambda_n = \frac{2L}{n}$$

Possible Energies for a Particle Trapped to a 1-Dimensional Box

$$E_n = n^2 \frac{h^2}{8mL^2}$$

Possible Energies for a Particle Trapped in a 3-Dimensional Box

$$E_n = (n_x^2 + n_y^2 + n_z^2) \frac{h^2}{8mL^2}$$

Energy of the Photon Absorbed When a Particle Gain Energy and Passes from an Energy Level E_i to an Energy Level E_f

$$E_\gamma = E_f - E_i$$

Energy of the Photon Absorbed When a Particle Gain Energy and Passes from an Energy Level E_i to an Energy Level E_f

$$E_\gamma = E_f - E_i$$

Possible Energies for a Particle Trapped in a 1-Dimensional Box (Finite potential Well)

$$E_n = v^2 E_{1\infty}$$

where v is obtained by solving the following equations

$$v \tan\left(\frac{\pi v}{2}\right) = \sqrt{u^2 - v^2}$$

$$-v \cot\left(\frac{\pi v}{2}\right) = \sqrt{u^2 - v^2}$$

in which the value of u is given by

$$U = u^2 E_{1\infty}$$

Number of Energy Levels for a Particle Trapped in a 1-Dimensional Box (Finite potential Well)

The integer smaller than or equal to $u + 1$

Probability of Crossing a Barrier Potential

$$T = \frac{16E(U-E)}{U^2} e^{-2\alpha L} \quad \text{where } \alpha = \frac{\pi\sqrt{8m(U-E)}}{h}$$

Energy Levels for a Particle in a Harmonic Oscillation

$$E_n = \left(n + \frac{1}{2}\right) hf$$

Electron Energy Levels in Hydrogen

$$E_{Hn} = -\frac{2\pi^2 m_e k^2 e^4}{n^2 h^2} = -\frac{13.598 eV}{n^2}$$

Energy of Electron Levels in an Atom With a Single Electron

$$E_n = -\frac{2\pi^2 Z^2 m_e k^2 e^4}{n^2 h^2} = -\frac{Z^2 \cdot 13.60 eV}{n^2}$$

EXERCISES

For these exercises, use the following masses.

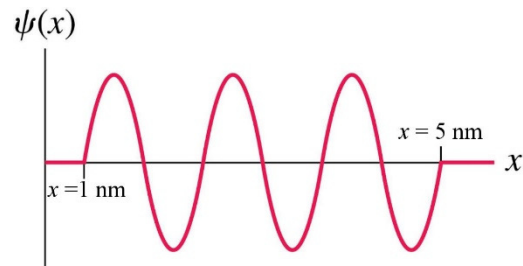
Electron	$m_e = 9.1094 \times 10^{-31} \text{ kg}$
Proton	$m_p = 1.6726 \times 10^{-27} \text{ kg}$
Neutron	$m_n = 1.6749 \times 10^{-27} \text{ kg}$

11.1 A Particle in a Box

1. A neutron is confined in a $2 \times 10^{-14} \text{ m}$ wide box.
 - a) What are the energies of the first two levels (in MeV)?
 - b) What is the wavelength of the neutron when it is at the level $n = 1$?

2. This is the wave of an electron in a one-dimensional box. What is the momentum of the electron?

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3. An electron is confined in a 1 nm wide box. What is the smallest energy that this electron can have (in eV)?
4. An electron is confined in a box. At the level $n = 4$, the energy of the electron is 10 eV. What is the width of the box?
5. The energy of the level $n = 4$ is 24 eV for a particle confined in a box. What is the energy of the level $n = 3$?
6. An electron is trapped in a 3-D box with sides 1 nm long. What is the energy of the level characterized by $n_x = 3$, $n_y = 4$ and $n_z = 2$?
7. An electron is trapped in a one-dimensional box. An energy level has an 80 eV energy and the energy level following this level has an energy of 96.8 eV.
 - a) What is the energy of the first level?
 - b) What is the width of the box?

11.2 Spin

8. There are 21 electrons in a 3-dimensional box. If these 21 electrons are on the energy levels that give the configuration having the smallest energy, on what level is the electron with the highest energy? (In other words, the last electron is on the level characterized by $n_x = ?$, $n_y = ?$ and $n_z = ?$)

11.3 Passing From One Energy Level to Another

9. A proton is confined in a 10^{-14} m wide one-dimensional box. What is the wavelength of the light emitted when the proton passes from the level $n = 2$ to the level $n = 1$?
10. An electron is at the level $n = 1$ in a 2 nm wide box. What must be the wavelength of the light that the electron must absorb to bring it up to the level $n = 4$?
11. An electron is trapped in a 3-D box with sides 0.5 nm long. What is the wavelength of the light emitted when the electron passes from the level characterized by $n_x = 2$, $n_y = 2$ and $n_z = 2$ to the level characterized by $n_x = 1$, $n_y = 1$ and $n_z = 1$?

11.4 A Particle in a Box (Finite Potential Well)

12. An electron is trapped in a box 0.6 nm wide. The potential energy outside the box is 20 eV.
- a) How many energy levels are there for the particle trapped in the box?
 - b) What are the energies of these levels?
 - c) What maximum wavelength does a photon must have to get an electron out of the box if the electron is initially at the 2nd level?

11.5 Quantum Tunnelling

13. An electron with an energy of 3 eV attempts to cross a barrier with a height of 10 eV and a width of 0.3 nm. What is the probability that the electron will cross the barrier?
14. An electron has a 5% probability of crossing a 12 eV high barrier. What is the width of the barrier if the electron has an energy of 4 eV?
15. An electron with an energy of 4 eV has a 10% probability of crossing a 8 eV barrier. What will the probability to cross be if the width of the barrier is doubled?

11.6 Harmonic Oscillator

16. An electron undergoes a harmonic oscillation with a period of 4×10^{-15} s.
- a) What is the smallest energy that this electron can have?
 - b) What is the wavelength of the light emitted if the electron goes from the level $n = 3$ to the level $n = 1$?
17. When an electron undergoing a harmonic oscillation goes from the level $n = 5$ to the level $n = 2$, a photon having a 496 nm wavelength is emitted. What is the period of the oscillations of the electron?

11.7 Hydrogen Atom

18. An electron passes from the level $n = 5$ to the level $n = 2$ in the hydrogen atom. What is the wavelength of the light emitted?
19. Hydrogen atoms are bombarded with photons to make the electrons go to higher levels. What must be the wavelength of the light to make the electrons pass from the level $n = 1$ to the level $n = 6$?
20. Hydrogen atoms are bombarded.
- a) If the hydrogen atoms are bombarded with photons with an energy of 13 eV. On what levels can the electrons rise if all the electrons were initially at the fundamental level in their atom?
 - b) If the hydrogen atoms are bombarded with electrons with an energy of 13 eV. On what levels can the electrons rise if all the electrons were initially at the fundamental level in their atom?
21. Show that the number of degenerate levels for each possible energy is equal to n^2 . (This means that there is 1 level for $n = 1$, 4 degenerate levels for $n = 2$, 9 degenerate levels for $n = 3$, and so on.)

11.8 Other Atoms

22. In a doubly ionized lithium atom (Li^{++}), calculate...
- a) the energy of the fundamental level ($n = 1$).
 - b) the ionization energy.
 - c) the wavelength of the light emitted when the electron moves from the 2nd to the 1st level.
23. Light having a 250 nm wavelength is absorbed by an atom. By absorbing the photon, the electron goes from the fundamental level up to a higher energy level. However, the electron goes down in two steps by going first to an intermediate energy level and then to the fundamental level. During the first transition, the wavelength of the emitted light is 800 nm. What will the wavelength of the light emitted during the second transition be?

Challenges

(Questions more difficult than the exam questions.)

24. It was said that the probability of finding a particle at a certain location is proportional to ψ^2 . More precisely, the probability of finding a particle between $x = a$ and $x = b$ is

$$\int_a^b \psi^2 dx$$

As the sum of all the probabilities of finding the particle at different locations must total 100%, the following equation must hold

$$\int_{\text{all possible locations}} \psi^2 dx = 1$$

Now, these ideas will be applied to a particle confined in a box (infinite potential well) at the first energy level. Calculate the probability of finding an electron between $x = 0$ nm and $x = 3$ nm if the box has a width of 10 nm.

Here's an integral that can be useful: $\int \sin^2 ax = \frac{x}{2} - \frac{1}{4a} \sin(2ax)$

25. For a harmonic oscillator, the potential energy is given by $U = \frac{1}{2}kx^2$. Show that the function

$$\psi = Ae^{-Bx^2}$$

is a solution of the Schrödinger equation if the energy of this level is $E = \frac{1}{2}hf$. (A and B are constants.)

ANSWERS

11.1 A Particle in a Box

1. a) 1st level: 0.511 MeV 2nd level: 2.045 MeV b) 4×10^{-14} m
2. 4.9696×10^{-25} kgm/s
3. 0.376 eV
4. 0.7757 nm
5. 13.5 eV
6. 10.90 eV
7. a) 0.8 eV b) 0.6856 nm

11.2 Spin

8. $n_x = 2$, $n_y = 2$ and $n_z = 2$

11.3 Passing From One Energy Level to Another

9. 2.018×10^{-4} nm

10.879 nm

11.91.60 nm

11.4 A Particle in a Box (Finite Potential Well)

12.a) 5 levels b) 0.795 eV, 3.161 eV, 7.038 eV, 12.27 eV, 18.32 eV

c) 73.64 nm

11.5 Quantum Tunnelling

13.0.0987 %

14.0.1471 nm

15.0.25%

11.6 Harmonic Oscillator

16.a) 0.517 eV b) 599.6 nm

17. 4.963×10^{-15} s

11.7 Hydrogen Atom

18.434.2 nm

19.93.8 nm

20.a) The electrons stay at the level $n = 1$ b) The electrons can pass to the levels $n = 2$, $n = 3$ and $n = 4$.

21. See the proof in the solution document.

11.8 Other Atoms

22.a) -122.4 eV b) 122.4 eV c) 13.51 eV

23.363.6 nm

Challenges

24.14.86 %