The *Schrödinger* equation in the motion of electrons

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Abstract

The *Schrödinger*equation was developed in 1925 by the Austrian physicist Erwin *Schrödinger*. This equation is of great importance in classical mechanics because it provides the main information about subatomic particles, this through the wave function, whose value describes a possible state of the electron.
In addition to this, the *Schrödinger* equation takes into account different aspects such as: the existence of an atomic nucleus, the energy levels where the electrons are distributed according to their energy, the wave-particle duality, the probability of finding the electron. The following document presents how to solve the time-dependent *Schrödinger* equation by means of analytical methods, presenting some simple examples.

1 Introduction

The *Schrödinger* equation is of vital importance in quantum mechanics, like Newton's equations in classical mechanics. These help us to predict the behavior of subatomic particles, some of which have what is called wave-particle duality, which is that a particle (such as the electron) can behave as a wave and as a particle simultaneously. Thanks to this we obtain what is called the wave function, which will give us information about the behavior of electrons in atoms.[4] It should be noted that the square of this wave function corresponds to the density function that describes the relative probability according to which said random variable will take a certain value.
But ,how is the wave function found? For this, what is known as the *Schrödinger* equation is proposed, which has the wave function as unknown, which can be determined by establishing certain values of border. Furthermore, this wave function is subject to something called the uncertainty principle, which states that it can know the position of the particle, but not its velocity, and vice versa. [3].

2 Methods and development

2.0.1 Operator

An operator is a mathematical symbol that indicates that a specific operation must be carried out on a certain number of operands (number, function, vector, etc)
Properties

- Let A be an operator and f_1, f_2 any functions.

$$A[af_1(x) + bf_2(x)] = Aaf_1 + Abf_2$$

- Let A, B be operators

$$(AB)f(x) = A(Bf(x))$$

- En general

$$AB \neq BA$$

Eigenvalues of an operator- example
Let $f(x) = e^{2x}$; $B = \frac{d}{dx}$

$$Bf(x) = \frac{df(x)}{dx} = 2e^{2x} = 2f(x)$$

The operator can be associated with the number 2, then this number is the eigenvalue of B, that is, $B \to 2$. Since if we apply the operator again on $2f(x)$, we obtain

$$B \cdot B \to 2 \cdot 2$$

In general

$$B^n \to 2^n$$

textbf Example 2
Let $\varphi(x,t) = \varphi_0 e^{i(kx-wt)}$
We define $B = \frac{\partial}{\partial x}$; $T = \frac{\partial}{\partial t}$
So

$$B\varphi = \frac{\partial \varphi}{\partial x} = ik\varphi_0 e^{i(kx-wt)}$$

$$T\varphi = \frac{\partial \varphi}{\partial t} = -iw\varphi_0 e^{i(kx-wt)}$$

Thus

$$B \to ik \tag{1}$$

$$T \to -iw \tag{2}$$

2.0.2 Variable separation method

Let $T = T(x,y)$ perform the substitution $T(x,y) = X(x)Y(y)$
Thus, for

$$\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} = 0$$

We carry out the replacement and obtain

$$\frac{\partial^2 XY}{\partial x^2} + \frac{\partial^2 XY}{\partial y^2} = 0$$

Since Y does not depend on x, nor does X depend on y, we obtain

$$Y\frac{\partial^2 X}{\partial x^2} + X\frac{\partial^2 Y}{\partial y^2} = 0$$

Dividing by XY we get

$$\frac{1}{X}\frac{\partial^2 X}{\partial x^2} + \frac{1}{Y}\frac{\partial^2 Y}{\partial y^2} = 0$$

The term on the left depends on x and the one on the right depends on y, but they must add to zero for any combination, so they must be constant or equal with opposite signs.
Let $-k^2$ be the separation constant, then:

$$\frac{1}{X}\frac{d^2 X}{dx^2} = -\frac{1}{Y}\frac{d^2 Y}{dy^2} = -k^2$$

So

$$\frac{1}{X}\frac{d^2X}{dx^2} = -k^2$$
$$\frac{1}{Y}\frac{d^2Y}{dy^2} = k^2$$

EDO

2.0.3 Dual sets

The dual $E*$ of E is the equation obtained by substituting

$$\cup \to \cap$$
$$\cap \to \cup$$
$$U \to \emptyset$$
$$\emptyset \to U$$

3 Results

The *Schrödinger* equation is defined with the following expression

$$H\varphi = i\hbar\frac{\partial}{\partial t}(\varphi)$$

Where

- $\hbar$ = constants of nature.
- H = Hamiltonian.
- φ = wave function.

The Hamiltonian changes as a function of the system. Y is equal to the mechanical energy of the system

$$H = E_m = E_c + E_p$$

Kinetic energy is that associated with motion.

$$E_c = \frac{1}{2}mv^2$$

But in the case of quantum mechanics this is of the form

$$E_c = \frac{-\hbar^2}{2m}\bigtriangledown^2$$

Where

- $\hbar$ = Planck's constant.
- m = mass of the particle.
- $\bigtriangledown^2$ = Laplacian.

Potential energy is that associated with force:

$$E_p = K\frac{q_1 q_2}{r}$$

Where K corresponds to Coulomb's constant, q_1 and q_2 are the charges and r the radius between them.
In the Hydrogen atom, only the interaction between 1 electron and 1 proton occurs, so the Hamiltonian appears as a relatively simple expression

$$H = \frac{-\hbar^2}{2m} \bigtriangledown^2 - K\frac{q_e^2}{r}$$

The existence of waves of matter postulated by Broglie suggests the existence of the equation of waves that describe it. Recalling the equation of a plane wave that moves along the x-axis. Its displacement at point x and at time t is given by the real part of the complex quantity.

$$A(x,t) = A_0 exp(i(kx - \omega t)) \tag{3}$$

Where

- ω =angular frequency
- k =wave vector

(3) is a solution of the wave equation that has the form:

$$\frac{\partial^2 A}{x^2} = \frac{1}{c^2}\frac{\partial^2 A}{t^2} \tag{4}$$

Where c is a real constant that represents the wave speed. By (3) we have

$$\frac{\partial^2 A}{\partial x^2} = i^2 k^2 A(x,t) \tag{5}$$

$$\frac{\partial^2 A}{t^2} = i^2 \omega^2 A(x,t) = -\omega^2 A(x,t) \tag{6}$$

Replacing in (4) we get

$$-k^2 A(x,t) = \frac{-\omega^2}{c^2} A(x,t) \tag{7}$$

In this way $k^2 = \frac{\omega^2}{c^2}$, this is $\omega = ck$ Taking into account that the energy and the linear momentum of a free particle can be expressed in terms of the angular frequency and the wave vector

$$E = \hbar\omega \tag{8}$$

$$E = \hbar k \tag{9}$$

So $E = \hbar ck$, this is $E = cp$. This is that the energy is directly proportional to the momentum p. Since for non-relativistic free particles, it is well known that the energy is proportional to the square of the linear momentum.

$$E = \frac{p^2}{2m} \tag{10}$$

We must look for a function whose shape is different from (4) but since we know that plane waves are associated with free particles, (3) must be a solution of the new wave function.
This equation must satisfy (8), (9) and (10), that is, the angular frequency must be proportional

to the square of the wave vector, thus $\omega = ctek^2$.
This suggests that the proper wave equation must contain the second derivative with respect to x and a single derivative with respect to t.
Consider the equation.

$$\frac{\partial^2\varphi}{\partial x^2} = \alpha\frac{\partial\varphi}{\partial t} \tag{11}$$

To find *alpha* we consider *varphi* as a plane wave, indicated in (3)

$$\varphi(x,t) = \varphi_0 exp(i(kx-\omega t))$$

Replacing in (11)

$$i^2k^2\varphi = \alpha(-i\omega)\varphi$$

$$k^2 = i\omega\alpha \tag{12}$$

By (8) and (9)

$$E = \frac{p^2}{\hbar^2};\omega = \frac{E}{\hbar}$$

This is $\frac{p^2}{\hbar^2} = i\alpha\frac{E}{hbar}$. So

$$E = \frac{p^2}{i\alpha\hbar} \tag{13}$$

Comparing (10) and (13)

$$E = \frac{p^2}{2m} = \frac{p^2}{i\alpha\hbar}$$

So

$$\frac{1}{2m} = \frac{1}{i\alpha\hbar} \tag{14}$$

Then $\alpha = \frac{2m}{i\hbar}$ Replacing in the equation proposed above

$$\frac{\partial^2\varphi(x,t)}{\partial x^2} = \frac{2m}{i\hbar}\frac{\partial\varphi}{\partial t}$$

Dividing by 2m

$$\frac{1}{2m}\frac{\partial^2\varphi(x,t)}{\partial x^2} = \frac{1}{i\hbar}\frac{\partial\varphi}{\partial t}$$

Multiplying by $(i\hbar)^2$

$$\frac{-\hbar^2}{2m}\frac{\partial^2\varphi(x,t)}{\partial x^2} = i\hbar\frac{\partial\varphi}{\partial t} \tag{15}$$

We can verify that this equation obtained fulfills the requirement that the particle is a free particle, for them we substitute the de Broglie relations in a plane wave and obtain

$$\varphi(x,t) = \varphi_0 exp\left(i\left(\frac{p}{\hbar}x - \frac{E}{\hbar}t\right)\right) \tag{16}$$

Thus, by (15) and (16)

$$\frac{-\hbar^2}{2m}\frac{\partial^2\varphi(x,t)}{\partial x^2} = \frac{-\hbar^2}{2m}\frac{(ip)^2}{\hbar^2}\varphi = \frac{p^2}{2m}\varphi$$

$$i\hbar\frac{\partial\varphi}{\partial t} = i\hbar\frac{-iE}{\hbar}\varphi(x,t) = E\varphi$$

Thus

$$\frac{p^2}{2m}\varphi = E\varphi$$

This is $E = \frac{p^2}{2m}$
As it should be in the case of the free particle
Now, we will see a more general expression for the equation moving under the influence of a potential V (x, t)

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

3.1 Probability density function

The probability distribution function $P(x)$ is always positively defined in such a way that $P(x)dx$ is the probability that the variable x takes on any real value in the interval between x and x + dx.
In this case, $P(x)$ is replaced by $\varphi(\bar{x},t)\varphi(x,t)$. Then

$$\varphi(\bar{x},t)\varphi(x,t) = |\varphi(x,t)|^2 \tag{17}$$

3.2 Vector interpretation

The equation under study is linear, homogeneous of the second order, whose solutions satisfy the superposition principle.
This indicates that the functions of this behave like vectors. The vectors that describe the quantum stationary states A, B, C ... are called Ket vectors

$$A, B.C$$

They are representations of the wave function φ_A, φ_B, φ_C, ... Since these vectors are defined in a complex vector space, it is necessary to introduce a second set of vectors called bra vectors

$$A, B, C$$

That corresponds to the conjugate complex of the Ket vectors, together the Bra and the Ket constitute a dual set.

3.3 Solution of the equation

Using the separable variables method, suppose that

$$\varphi(x,t) = \varphi(x)\varphi(t) \tag{18}$$

We rewrite the equation for *Schrödinger* as

$$i\hbar\frac{\partial\varphi(t)\varphi(x)}{\partial t} = \left(\frac{-\hbar^2}{2m}\bigtriangledown^2 + V(x)\right)\varphi(x)\varphi(t)$$

This is

$$\frac{1}{\varphi(t)}i\hbar\frac{\partial\varphi(t)}{\partial t} = \frac{1}{\varphi(x)}\left(\frac{-\hbar^2}{2m}\bigtriangledown^2 + V(x)\right)\varphi(x) \tag{19}$$

We set a constant E

- **Time dependent equation**

$$i\hbar\frac{d\varphi(t)}{dt} = E\varphi(t) \tag{20}$$

Solution

$$i\hbar\frac{d\varphi(t)}{\varphi(t)} = Edt$$
$$i\hbar ln(\varphi(t)) = Et$$
$$ln(\varphi(t)) = \frac{Et}{i\hbar}$$

By (8)

$$\varphi(t) = \varphi_0 exp\left(\frac{Et}{i\hbar}\right) = \varphi_0 exp(-i\omega t)$$

- **Space dependent equation**

$$\left(\frac{-\hbar^2}{2m}\bigtriangledown^2 + V(x)\right)\varphi(x) = E\varphi(x)$$

3.4 Examples

3.4.1 Null potential

$V(x) = 0$; $B = \frac{d}{dx}$;$H = \frac{-\hbar^2}{2m}B^2$.

We have the equation

$$\frac{-\hbar^2}{2m}B^2\varphi = E\varphi$$

Where $B^2 = -k^2$, then we have

$$\left(\frac{-\hbar^2}{2m}k^2 - E\right)\varphi = 0$$

As $\varphi \neq 0$, we have

$$\frac{-\hbar^2}{2m}k^2 - E = 0$$

Then

$$k = \pm\frac{\sqrt{2Em}}{\hbar}$$

Thus, since we know that the solution is $\varphi = \varphi_0 exp(ikx)$, we have $\varphi = \varphi_0 exp(i\pm)\frac{\sqrt{2Em}}{\hbar}x)$

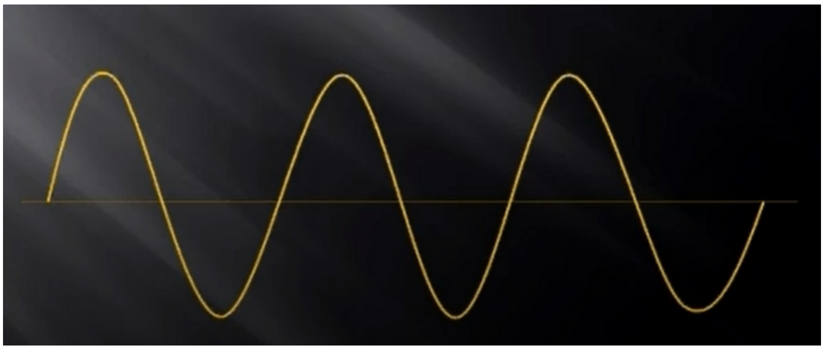

Figure 1: Solution for zero potential

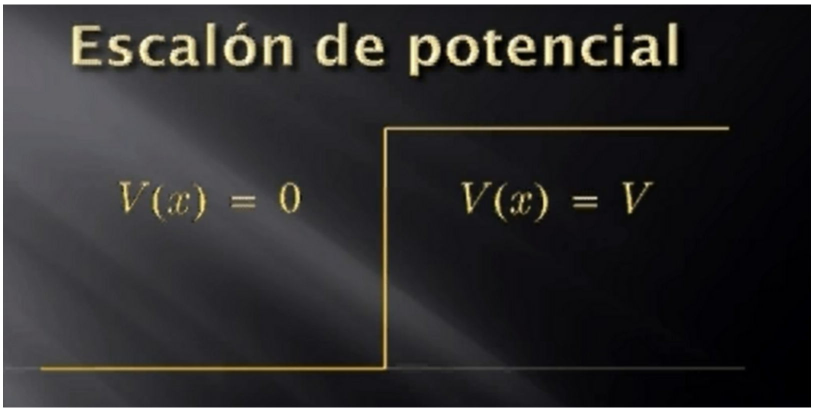

Figure 2: Step of potential

3.4.2 Step of potential

$H = \frac{-\hbar^2}{2m}B^2 + V$ We have the equation

$$\left(\frac{-\hbar^2}{2m}B^2 - (E - V)\right)\varphi = 0$$

Whose solution is $k = \pm\frac{\sqrt{2m(E-V)}}{\hbar}$
We will consider two cases

- $E > V$

$$\varphi = \varphi_0 exp\left(i\frac{\sqrt{2m(E-V)}}{\hbar}x\right)$$

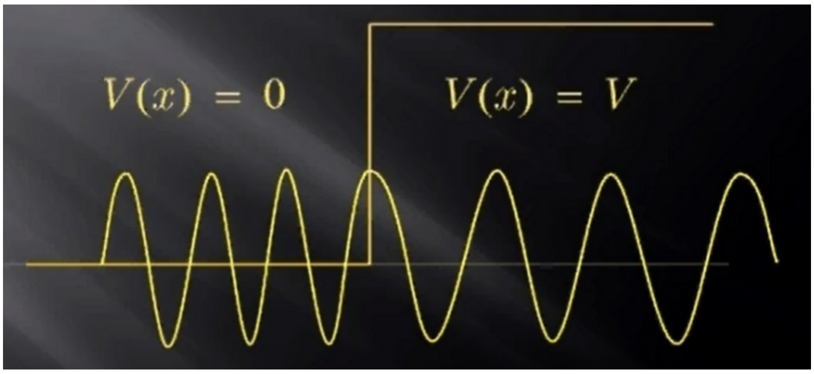

Figure 3: Solution for the potential step

- $E < V$
  We have a complex case, where

$$k = \pm\frac{i\sqrt{2m(|E-V|)}}{\hbar}$$

  Then

$$\varphi = \varphi_0 exp\left(\frac{-\sqrt{2m(E-V)}}{\hbar}x\right)$$

  Denote $\rho = \frac{-\sqrt{2m(E-V)}}{\hbar}x$

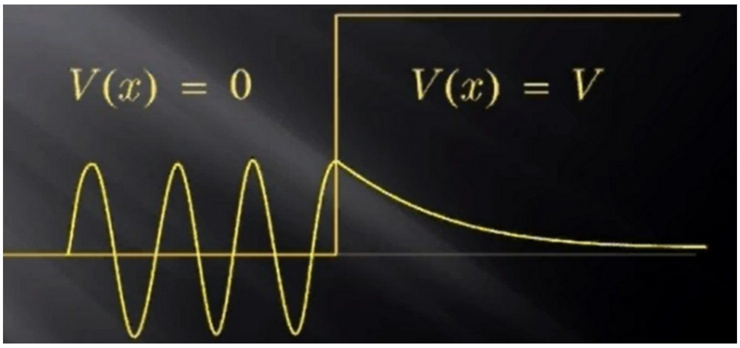

Figure 4: Solution for the potential step

3.4.3 Potential barrier-tunnel effect

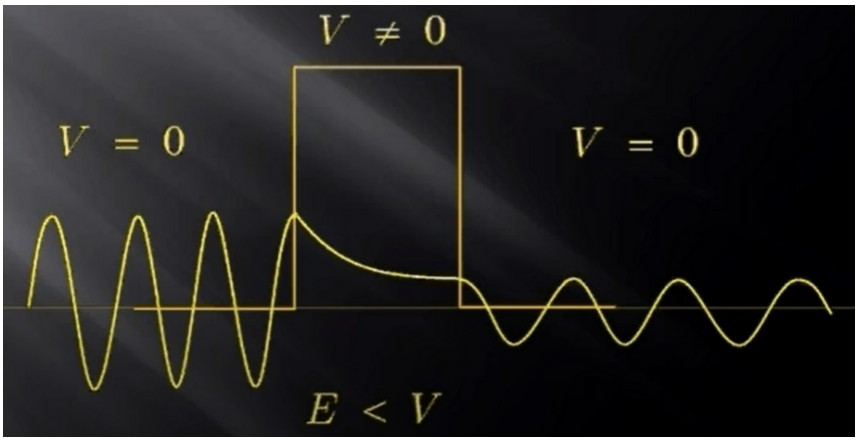

Figure 5: Solution for potential barrier

3.4.4 Potential well

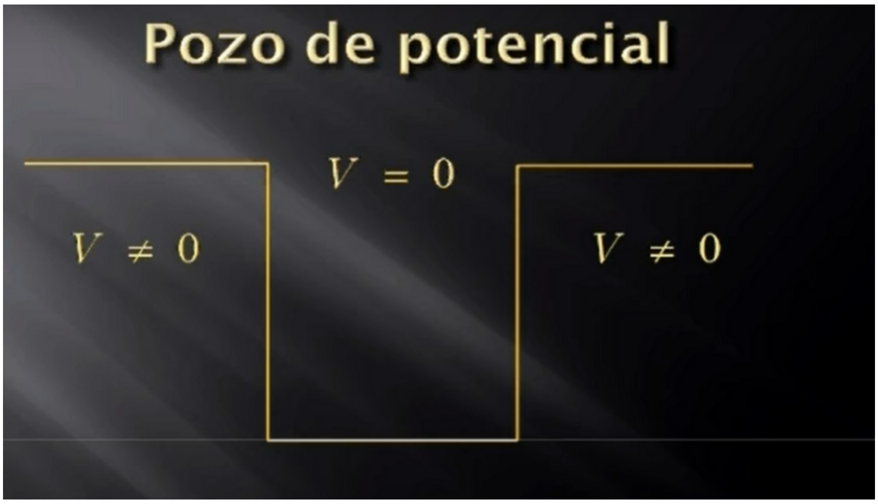

Figure 6: Potential well

$$\varphi_1 = \varphi_0 exp(\rho x); \varphi_2 = \varphi_0 exp(ikx); \varphi_3 = \varphi_0 exp(-\rho x)$$

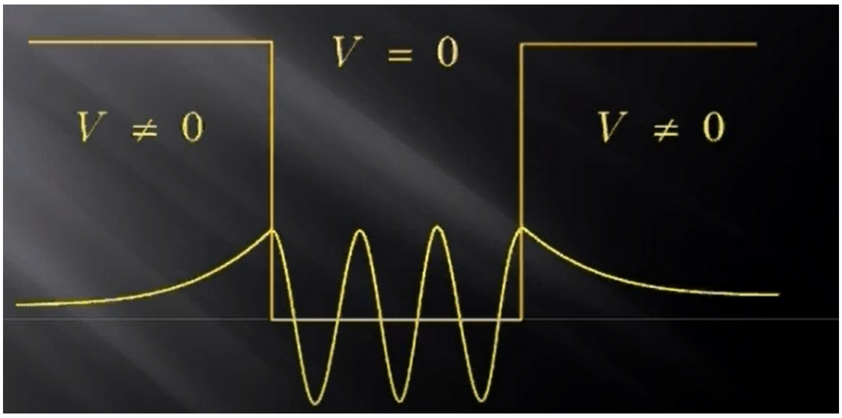

Figure 7: Solution for a potential well

3.4.5 Wall of infinite potential

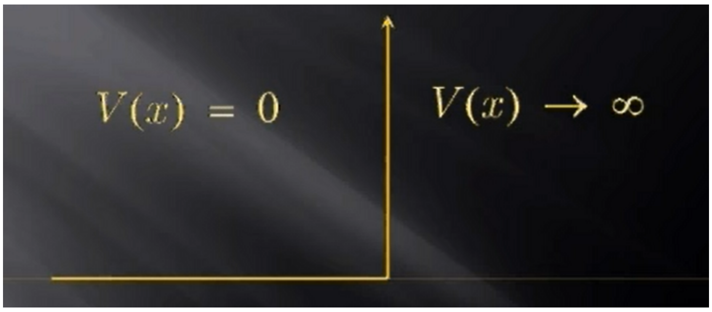

Figure 8: Wall of infinite potential

$$\rho = \frac{-\sqrt{2m(E-\infty)}}{\hbar}x = -\infty$$

So

$$\varphi = \varphi_0 exp(-\infty) = 0$$

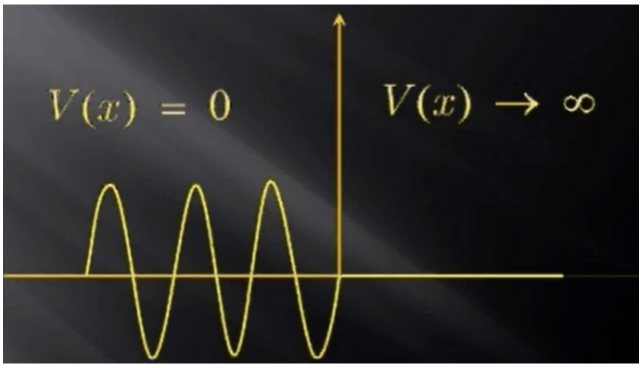

Figure 9: Infinite potential wall solution

3.4.6 Well with two walls of infinite potential

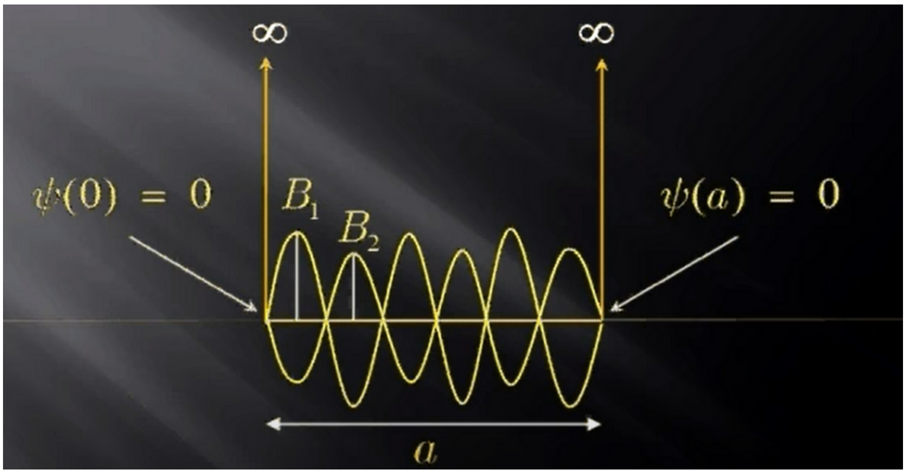

Figure 10: Solution for well with two walls of infinite potential

$$\varphi = B_1 exp(ikx) + B_2 exp(-ikx)$$

With

$$k = \frac{\sqrt{2mE}}{\hbar} \tag{21}$$

As $\varphi(0) = 0$

$$\varphi(0) = B_1 exp(ik0) + B_2 exp(-ik0) = B_1 + B_2$$

So $B_1 = -B_2$,then

$$\varphi = (exp(ikx) - exp(-ikx)) = B(cos(kx) + isen(kx) - (cos(kx) - isen(kx))$$

$$= B(2isen(kx))$$

As $\varphi(a) = 0$

$$\varphi(a) = B2isen(ka) = 0$$

Then $sen(ka) = 0$ that means $ka = n\pi$ n=0,1,2,...
We can prove that

$$\varphi = \sqrt{\frac{2}{a}} sen\left(\frac{n\pi x}{a}\right)$$

So, as $ak = n\pi$ then $k = \frac{n\pi}{a}$.

$$\frac{n\pi}{a} = k = \frac{\sqrt{2mE}}{\hbar}$$

Then

$$\frac{n^2\pi^2\hbar^2}{a^2 2m} = E$$

4 Scope

For the second installment, the development of the finite element method will be carried out in a simple example

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