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 contains a brief study on the general steps to solve the *Schrödinger* equation and its interpretation in the world of quantum mechanics, in addition, a simple example of how this is done is presented process.
We also expose the solution of the *Schrödinger* equation for the Hydrogen atom in spherical coordinates is exposed in development. This equation is separated into a polar, azimuthal and radial equation by means of the method of separation of variables, the solutions of these equations allow to obtain the 3 quantum numbers: principal quantum number, orbital quantum number and magnetic quantum number.
We finally present the relation between the azimuthal and magnetic quantum number is exposed, this is achieved by solving the problem of eigenvalues of angular momentum. Additionally, the implementation of the difference method in the solution of the *Schrödinger* equation for the particle in a one-dimensional box is exposed.

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.[2]
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. [4].
The *Schrödinger* equation for the time-independent hydrogen atom consists of a differential equation whose solution gives the probability of finding the electron in a certain region of space. Given the geometry of the hydrogen atom, it is convenient to approach this equation in spherical coordinates and arrive at its solution by means of the method of separation of variables,

which consists of separating the wave function (solution of the equation) as the multiplication of three functions, a that depends on the radius, another that depends on the polar angle and a last one that depends on the azimuth angle.[4].
The solution of the *Schrödinger* equation for the Hydrogen atom allows us to obtain the relationship between the principal, azimuthal and magnetic quantum numbers. To establish the relationship between the azimuthal and magnetic quantum numbers. It is necessary to solve the problem of eigenvalues of angular momentum, since these quantum numbers are obtained with the solution of the polar and azimuthal equation.
On the other hand, the finite difference method will allow us to obtain a numerical solution of the equation, since not all cases have an analytical solution.

2 Methods

2.1 Quantum numbers

To properly understand the statement of the *Schrödinger* equation, it was necessary to know the main operator of quantum mechanics called Hamiltonian [3].
On the other hand, basic knowledge was needed on the solution of ordinary differential equations and initial value problems, especially of homogeneous second-order differential equations. In addition to this, it was necessary to learn about quantum numbers and how it relates to the physical structure of the atom, which is summarized in the following table.

N	l	m	Orbital
1	0	0	1s
2	0	0	2s
2	1	-1,0, +1	$2p_x$,$2p_y$,$2p_z$
3	0	0	3s
3	1	-1,0, +1	$3p_x$,$3p_y$,$3p_z$
3	2	-2,-1,0, +1, +2	$3d_{x^2-y^2}$,$3d_{xy}$,$3d_{z^2}$,$3d_{yz}$,$3d_{xy}$

2.2 Method of separating variables:

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 perform 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 term 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:

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

So

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

EDO

2.2.1 Requirements to apply the method of separation of variables

- Any function defined such that when looking for solutions in the form of the product of functions of a variable, they give rise to differentiable equations for each of the variables.
  Example

  $$U_{tt} = U_{xx} + Ax$$

  Let's consider $U(x,t) = X(x)T(t)$.
  Replacing we get

  $$XT'' = X''T + Ax$$

  Divide by XT.

  $$\frac{T''}{T} = \frac{X''}{X} + \frac{Ax}{XT}$$

  Variables cannot be separated

- All second order PDEs with constant coefficients, except those with cross derivatives.

2.3 Legendre differential equation

Legendre's differential equation is of the form

$$(1-x^2)y'' - 2xy' + n(n+1)y = 0 \tag{1}$$

Whose solution can be obtained by means of series of powers, of the form

$$y = \sum_{m=0}^{\infty} C_m x^m$$

After replacing in the equation, it is possible to find a relationship between the coefficients, described as:

$$C_{m+2} = -\frac{(n-m)(n+m+1)}{(m+2)(m+1)}C_m$$

So

$$y = C_0\left(1 - \frac{n(n+1)}{2}x^2 + \frac{(n-2)(n+3)n(n+1)}{4!}x^4 + ...\right)$$
$$+C_1\left(x - \frac{(n-1)(n+2)}{3!}x^3 + \frac{(n-3)(n+4)/n-1)(n+2)}{5!}x^5\right)$$

If n is not an integer, these series converge for $-1 < x < 1$ but diverge if $x = \pm 1$. If n is a positive integer or zero, one of the series ends up becoming a polynomial, while the other converges for $-1 < x < 1$ but diverges for $x = \pm 1$.
When finding the Legendre polynomials, it is necessary to multiply by a chosen constant so that the polynomial has the value of 1 if x = 1.
Let's see some examples:

- $P_0(x) = 1$
- $P_1(x) = x$
- $P_2(x)$

$$1 - 3x^2$$
$$(1 - 3x^2)\frac{1}{2}$$
$$(3x^2 - 1)\frac{1}{2}$$

- $P_3(x)$

$$x - \frac{10}{6}x^3$$
$$x - \frac{5}{3}x^3$$
$$3x - 5x^3$$
$$(5x^3 - 3x)\frac{1}{2}$$

2.4 Finite difference method

Finite Difference Methods (FDM) are a class of numerical techniques for solving differential equations by approximating derivatives with finite differences. Both the spatial domain and the time interval (if applicable) are discretized or divided into a finite number of steps, and the value of the solution at these discrete points is approximated by solving algebraic equations containing finite differences and values of close points.
Deduction

For the deduction of the discretization of the differential of the equations, we will use the Taylor series, which corresponds to an approximation of functions through a series of powers. It should be noted that although we carry out the deduction of the equations for the first and second drift, it is It is possible to deduce the formulas for the nth derivative by reasoning analogously. To begin with, we will have to take into account the expression of the Taylor series:

$$(x + h) = f(x) + hf'(x) + \frac{h^2}{2!}f''(x) + \frac{h^3}{3!}f'''(x) + ...$$

$$f(x - h) = f(x) - hf'(x) + \frac{h^2}{2!}f''(x) - \frac{h^3}{3!}f'''(x) + ...$$

In this way, if we want to deduce the first derivative, it will only be enough to take up to the first derivative of the Taylor series, also by notation we will call $x_i = x$, $x_{i+1} = x + h$ y $x_{i-1} = xh$, thus solving the first derivative with x_{i+1} and x_{i-1} we will have:

$$f'(x_i) \simeq \frac{f(x_{i+1}) - f(x_i)}{h}$$

$$f'(x_i) \simeq \frac{f(x_i) - f(x_{i-1})}{h}$$

These approximations correspond to the forward and backward difference respectively.
Now, to obtain the formula for centered differences, we have the following Theorem:
THEOREM
Suppose that $f \in C^3[a,b]$ and that $x+h, x, x-h \in [a,b]$, then:

$$f'(x_i) \simeq \frac{f(x_{i+1}) - f(x_{i-1})}{2h}$$

Proof
Using the Taylor formula of order two of f around x_i for $f(x_{i+1})$ y $f(x_{i-1})$

$$f(x_{i+1}) = f(x_i) + hf'(x_i) + \frac{h^2}{2!}f''(x_i)$$

$$f(x_{i-1}) = f(x_i) - hf'(x_i) + \frac{h^2}{2!}f''(x_i)$$

Subtracting these two equations we obtain:

$$f'(x_i) \simeq \frac{f(x_{i+1}) - f(x_{i-1})}{2h}$$

Similarly, to deduce the second derivative, we will take the Taylor series up to the second derivatives and solve for:

$$f''(x_i) \simeq \frac{2f(x_{i+1}) - 2f(x_i) - 2hf'(x_i)}{h^2}$$

$$f''(x_i) \simeq \frac{2f(x_{i-1}) - 2f(x_i) + 2hf'(x_i)}{h^2}$$

These approximations correspond to the forward and backward difference respectively
Now adding them we will obtain a centered approximation that would be:

$$f''(x_i) \simeq \frac{f(x_{i+1}) - 2f(x_i) + f(x_{i-1})}{h^2}$$

2.5 Angular momentum

It is a set of 3 operators for which there is a set of linearly independent states $|\alpha, \beta\rangle$ that satisfy

- $$\hat{J}^2|\alpha,\beta\rangle = \hbar^2\alpha(\alpha+1)|\alpha,\beta\rangle$$

  Where
  $\hat{J}^2 = \hat{J}_x^2 + \hat{J}_y^2 + \hat{J}_z^2$

- $$\hat{J}_3|\alpha,\beta\rangle = \hat{\beta}|\alpha,\beta\rangle$$

They also satisfy

$$\left[\hat{J}_i, \hat{J}_j\right] = \hbar\epsilon_{ijk}\hat{J}_k \tag{2}$$

$$\left[\hat{J}_i, \hat{J}^2\right] = 0 \tag{3}$$

Where ϵ_{ijk} is the Levi-civita symbol which depends on the indices
Properties

$$\epsilon_{ijk} = \epsilon_{kij} = \epsilon_{jki}$$

$$\epsilon_{ijk} = -\epsilon_{jik}$$

2.5.1 Commutation of quantum operators

It is said that two quantum operators commute when they fulfill

$$\left[\hat{A}, \hat{B}\right] = \hat{A}\hat{B} - \hat{B}\hat{A} = 0$$

Two operators switch if and only if they have a set of eigenfunctions in common.

3 Results

3.1 General concepts

The *Schrödinger* equation is defined with the following expression

$$H\varphi = ih'\frac{\partial}{\partial t}(\varphi)$$

Where

- ih = 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

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

Where

- h = 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

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

Schrödinger equation for the Hydrogen atom.

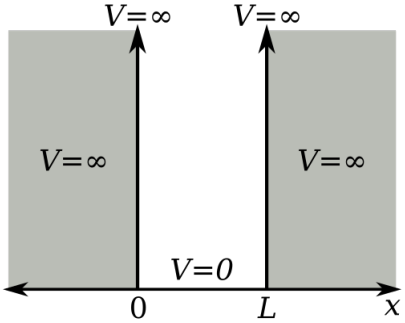
$$\left(\frac{-h^2}{2m} \bigtriangledown^2 - K\frac{q_e^2}{r}\right)\varphi = ih'\frac{\partial}{\partial t}\varphi$$

In the case of having an atom with more electrons, the *Schrödinger* equation becomes more complicated, since the Hamiltonian corresponds to the repulsion between electrons, the attraction between protons and electrons, and the repulsion between electrons that is mitigated by protons. In these cases, the *Schrödinger* equation does not have an analytical solution and it is necessary to resort to numerical methods for its solution.
It should be noted that the solution obtained from these equations corresponds to what we call the wave function, this squared function corresponds to the probability density function describing the probability of finding the electron in a certain region of the atom.
On the other hand, certain boundary conditions must be established for the solution of the equation, these boundary values are established by means of the quantum numbers [4] that establish an atomic orbital that encloses 90 % of the probability of finding an electron in that area. This atomic orbital is established thanks to the first 3 quantum numbers n, l, m

- n = principal quantum number, represents the energy level, n = 1,2, ...
- l = angular momentum quantum number, set the orbit type (s, p, d, f); l = 0,1, ..., n-1.
- m = magnetic quantum number, sets the orientation of the orbital; m = -l, ..., 0, ..., l
- s = spin quantum number $s\ pm\ frac12$, the latter represents the state of rotation of the electron, which can only take two values.

3.2 Example 1- Particle in a one-dimensional box

The particle in a box is defined as a point particle, enclosed in a box where it does not experience any type of force, that is, its potential energy is constant, although without loss of generality we can assume that it is zero. On the walls of the box the potential increases to infinity. [5]



$V(x) = 0$ for $0 \leq x \leq L$

$V(x) = \infty$ for $x < 0$ y $x > L$
1)For this case, we consider the equation *Schr ddotodinger* of independent of time:

$$\frac{-h^2}{2m}\frac{d^2\varphi(x)}{dx^2} = E\varphi(x)$$

Where

- h = planck's constant.

- m = mass of the particle.
- φ = time independent wave function.
- E = particle energy

2) Since the wave function vanishes out of the box, we set the following boundary conditions:

$$\varphi(0) = 0 \tag{4}$$

$$\varphi(L) = 0 \tag{5}$$

3)Solve the differential equation, using an auxiliary equation

$$\frac{-h^2}{2m}\varphi'' - E\varphi = 0$$

$$\varphi = \frac{\pm\sqrt{0 - 4\left(\frac{-h^2}{2m}\right)(-E)}}{\frac{-2h^2}{2m}} = \frac{\pm\sqrt{\left(\frac{-2h^2E}{m}\right)}}{\frac{-h^2}{m}} = \frac{(\sqrt{2Em}h)i}{-\sqrt{m}h^2} = \frac{-(\sqrt{2Em})i}{h}$$

General solution

$$\varphi(x) = \epsilon^0(Asen(kx) + Bcos(kx)) \tag{6}$$

Where $k^2 = \frac{2mE}{h^2}$ and A and B are complex numbers Considering the boundary condition and replacing in the general solution

$$0 = Asen(0) + Bcos(0) = B$$

Luego

$$\varphi(x) = Asen(kx) \tag{7}$$

Replacing condition (1) and (2)

$$\varphi(L) = Asen(kL) = 0$$

This is

$$sen(kL) = 0 \rightarrow k = \frac{n\pi}{L} \tag{8}$$

With $n \in \mathbf{Z}^+$. Note that this consideration does not take into account negative values of n, since these only represent a change of sign, and do not suggest new states. Likewise, in the calculation of E, it will be squared, so it is not necessary to consider its negative value.

4)Get A

$$1 = \int_{-\infty}^{\infty} |\varphi(x)|^2 dx = |A|^2 \int_0^L sen^2(kx)dx = |A|^2 \int_0^L \frac{1 - cos(2kx)}{2}dx \tag{9}$$

$$= \frac{|A|^2}{2}\left(L - \frac{sen(2kL)}{2k}\right) = \frac{|A|^2 L}{2}$$

then

$$1 = \frac{|A|^2 L}{2}$$

then

$$|A| = \sqrt{\frac{2}{L}} \tag{10}$$

Note that the value of A is initially complex, but in this particular case, the imaginary value that meets (7) is taken, which corresponds precisely to this real value. Replacing in (3)

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

5)Find the eigenvalues
We know that $kL = n\pi$ for $n \in \mathbf{Z}^+$, then

$$\frac{\sqrt{2mE}L}{h} = n\pi$$

Solving for E we obtain that for n = 1,2,3, ...

$$E = n^2 \frac{\pi^2 h^2}{2mL^2} \tag{11}$$

This establishes conditions on E for the solutions of the *Schr ddotodinger* equation of the particle in a one-dimensional box. The possible values of E are the eigenvalues or energy levels.
Conclusions
Self-functions and energies for the problem of the particle in a one-dimensional box

$$\varphi_n(x) = \sqrt{\frac{2}{L}} sen\left(\frac{n\pi x}{L}\right); \tag{12}$$

$$E_n = n^2 \frac{\pi^2 h^2}{2mL^2} \tag{13}$$

Where n characterizes φ_n and E_n is the quantum number for the system considered.

3.3 Equation of *Schrödinger* in spherical coordinates

Let's remember:
In the hydrogen atom:

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

Where:

- h = Planck's constant.
- m = mass of the particle.
- $bigtriangledown^2$ = Laplacian.
- K is the Coulomb constants
- r is the distance between the particles

So the equation for *Schr ddotodinger* is of the form:

$$H\varphi = E\varphi \tag{14}$$

Laplacian in spherical coordinates We know that, in rectangular coordinates

$$\bigtriangledown^2\varphi = \frac{\partial^2\varphi}{\partial x^2} + \frac{\partial^2\varphi}{\partial y^2} + \frac{\partial^2\varphi}{\partial z^2}$$

Transformation of rectangular coordinates to spherical coordinates:

$$r = \sqrt{x^2 + y^2 + z^2}$$

$$\theta = cos^{-1}\left(\frac{z}{\sqrt{x^2 + y^2 + z^2}}\right)$$

$$\phi = tan^{-1}\left(\frac{y}{x}\right)$$

Making use of the chain rule. For $\varphi(r, \theta, \phi)$

$$\frac{\partial \varphi}{\partial x} = \frac{\partial \varphi}{\partial r}\frac{\partial r}{\partial x} + \frac{\partial \varphi}{\partial \theta}\frac{\partial \theta}{\partial x} + \frac{\partial \varphi}{\partial \phi}\frac{\partial \phi}{\partial x}$$

$$\frac{\partial \varphi}{\partial y} = \frac{\partial \varphi}{\partial r}\frac{\partial r}{\partial y} + \frac{\partial \varphi}{\partial \theta}\frac{\partial \theta}{\partial y} + \frac{\partial \varphi}{\partial \phi}\frac{\partial \phi}{\partial y}$$

$$\frac{\partial \varphi}{\partial z} = \frac{\partial \varphi}{\partial r}\frac{\partial r}{\partial z} + \frac{\partial \varphi}{\partial \theta}\frac{\partial \theta}{\partial z} + \frac{\partial \varphi}{\partial \phi}\frac{\partial \phi}{\partial z}$$

Taking into account that:

$$x = rsen(\theta)cos(\phi)$$

$$y = rsen(\theta)sen(\phi)$$

$$x = rcos(\theta)$$

We obtain

$$\frac{\partial r}{\partial x} = \frac{\partial}{\partial x}\left(\sqrt{x^2 + y^2 + z^2}\right) = \frac{2x}{2\sqrt{x^2 + y^2 + z^2}} = \frac{x}{r}$$

$$\frac{\partial r}{\partial y} = \frac{\partial}{\partial y}\left(\sqrt{x^2 + y^2 + z^2}\right) = \frac{2y}{2\sqrt{x^2 + y^2 + z^2}} = \frac{y}{r}$$

$$\frac{\partial r}{\partial z} = \frac{\partial}{\partial z}\left(\sqrt{x^2 + y^2 + z^2}\right) = \frac{2z}{2\sqrt{x^2 + y^2 + z^2}} = \frac{z}{r}$$

$$\frac{\partial \theta}{\partial z} = \frac{-(z/r)'}{\sqrt{1 - (z/r)^2}} = \frac{-1}{sen(\theta)}\frac{\partial}{\partial z}\left(\frac{z}{r}\right) = \frac{-1}{sen(\theta)}\frac{r - z(\partial r/\partial z)}{r^2}$$

$$= \frac{-1}{sen(\theta)}\frac{r - (r^2 cos^2(\theta)/r)}{r^2} = \frac{-1}{sen(\theta)}\frac{sen^2(\theta)}{r} = \frac{-sen(\theta)}{r}$$

$$\frac{\partial \theta}{\partial x} = \frac{cos(\theta)cos(\phi)}{r}$$

$$\frac{\partial \theta}{\partial y} = \frac{cos(\theta)cos(\phi)}{r}$$

Thus:

$$\frac{\partial \varphi}{\partial x} = sen(\theta)cos(\phi)\frac{\partial \varphi}{\partial r} + \frac{1}{r}cos(\theta)cos(\phi)\frac{\partial \varphi}{\partial \theta} - \frac{1}{r}\frac{sen(\phi)}{sen(\theta)}\frac{\partial \varphi}{\partial \phi}$$

We define $\frac{\partial}{\partial x}$ as an operator that acts on φ. Then

$$\frac{\partial}{\partial x} = sen(\theta)cos(\phi)\frac{\partial}{\partial r} + \frac{1}{r}cos(\theta)cos(\phi)\frac{\partial}{\partial \theta} - \frac{1}{r}\frac{sen(\phi)}{sen(\theta)}\frac{\partial}{\partial \phi}$$

So

$$\frac{\partial^2}{\partial x^2} = \left(sen(\theta)cos(\phi)\frac{\partial}{\partial r} + \frac{1}{r}cos(\theta)cos(\phi)\frac{\partial}{\partial \theta} - \frac{1}{r}\frac{sen(\phi)}{sen(\theta)}\frac{\partial}{\partial \phi} \right)$$
$$\left(sen(\theta)cos(\phi)\frac{\partial}{\partial r} + \frac{1}{r}cos(\theta)cos(\phi)\frac{\partial}{\partial \theta} - \frac{1}{r}\frac{sen(\phi)}{sen(\theta)}\frac{\partial}{\partial \phi} \right)$$

Using the product rule

$$\frac{\partial^2}{\partial x^2} = sen^2(\theta)cos^2(\phi)\frac{\partial}{\partial r^2} + sen(\theta)cos(\phi)\left(\frac{-1}{r^2}cos(\theta)cos(\phi)\frac{\partial}{\partial \theta} + \frac{1}{r}cos(\theta)cos(\phi)\frac{\partial^2}{\partial r \partial \theta} \right)$$
$$-cos(\phi)sen(\phi)\left(-r^2\frac{\partial}{\partial \phi} + \frac{1}{r}\frac{\partial^2}{\partial r \partial \theta} \right) + \frac{1}{r}cos(\theta)cos^2(\phi)\left(cos(\theta)\frac{\partial}{\partial r} + sen(\theta)\frac{\partial^2}{\partial r \partial \theta} \right)$$
$$+\frac{1}{r^2}cos(\theta)cos^2(\phi)\left(-sen(\theta)\frac{\partial}{\partial \theta} + cos(\theta)\frac{\partial^2}{\partial \theta^2} \right) - \frac{1}{r^2}cos(\theta)cos(\phi)sen(\phi)\left(-sen^2(\theta)cos(\theta)\frac{\partial}{\partial \phi} \right)$$
$$-\frac{1}{r}\frac{sen(\phi)}{sen(\theta)}\left(-sen(\phi)\frac{\partial}{\partial r}\Delta + cos(\theta)\frac{\partial^2}{\partial \phi \partial \theta} \right)$$

Thus

$$\bigtriangledown^2\varphi(r,\theta,\phi) = \frac{\partial^2\varphi}{\partial r^2} + \frac{2}{r}\frac{\partial\varphi}{\partial r} + \frac{cos(\theta)}{r^2 sen(\theta)}\frac{\partial\varphi}{\partial\theta} + \frac{1}{r^2}\frac{\partial^2\varphi}{\partial\theta^2} + \frac{1}{r^2 sen^2(\theta)}\frac{\partial^2\varphi}{\partial\phi^2}$$

This is

$$\bigtriangledown^2\varphi(r,\theta,\phi) = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\varphi}{\partial r} \right) + \frac{1}{r^2 sen(\theta)}\frac{\partial}{\partial\theta}\left(sen(\theta)\frac{\partial\varphi}{\partial\theta} \right) + \frac{1}{r^2 sen^2(\theta)}\frac{\partial^2\varphi}{\partial\phi^2}$$

Rewriting equation (2) we obtain

$$\frac{-h^2}{2m}\left(\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\varphi}{\partial r} \right) + \frac{1}{r^2 sen(\theta)}\frac{\partial}{\partial\theta}\left(sen(\theta)\frac{\partial\varphi}{\partial\theta} \right) + \frac{1}{r^2 sen^2(\theta)}\frac{\partial^2\varphi}{\partial\phi^2} \right) - \frac{kq_e^2}{r}\varphi = E\varphi$$

This is

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\varphi}{\partial r} \right) + \frac{1}{r^2 sen(\theta)}\frac{\partial}{\partial\theta}\left(sen(\theta)\frac{\partial\varphi}{\partial\theta} \right) + \frac{1}{r^2 sen^2(\theta)}\frac{\partial^2\varphi}{\partial\phi^2} + \frac{2m}{h^2}\left(E + \frac{Kq_e^2}{r} \right)\varphi = 0 \quad (15)$$

3.4 Variable separation method for the *Schrödinger* equation

Now, using the variable separation method:

$$\varphi(r,\theta,\phi) = R(r)Y(\theta,\phi)$$

Since Y does not depend on r and R does not depend on θ or phi, we get

$$\frac{\partial\varphi}{\partial r} = \frac{\partial}{\partial r}RY = Y\frac{dR}{dr}$$
$$\frac{\partial\varphi}{\partial\theta} = \frac{\partial}{\partial\theta}RY = R\frac{\partial Y}{\partial\theta}$$
$$\frac{\partial\varphi}{\partial\phi} = \frac{\partial}{\partial\phi}RY = R\frac{\partial Y}{\partial\phi}$$

Replacing in (3)

$$\frac{Y}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{R}{r^2 sen(\theta)}\frac{\partial}{\partial\theta}\left(sen(\theta)\frac{\partial Y}{\partial\theta}\right)+\frac{R}{r^2 sen^2(\theta)}\frac{\partial^2 Y}{\partial\phi^2}+\frac{2m}{h^2}\left(E+\frac{Kq_e^2}{r}\right)RY=0$$

Multiplying by r^2 and dividing by RY, we get

$$\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{1}{Y sen(\theta)}\frac{\partial}{\partial\theta}\left(sen(\theta)\frac{\partial Y}{\partial\theta}\right)+\frac{1}{Y sen^2(\theta)}\frac{\partial^2 Y}{\partial\phi^2}+\frac{2m}{h^2}\left(E+\frac{Kq_e^2}{r}\right)=0$$

Separating the radial part and the angular part of the equations and taking into account that a separation constant must be used (see methods section - separation of variables), we obtain the following radial and angular equations

Radial equation

$$\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{2m}{h^2}\left(E+\frac{Kq_e^2}{r}\right)R-AR=0 \tag{16}$$

Angular equation

$$\frac{1}{sen(\theta)}\frac{\partial}{\partial\theta}\left(sen(\theta)\frac{\partial Y}{\partial\theta}\right)+\frac{1}{sen^2(\theta)}\frac{\partial^2 Y}{\partial\phi^2}+AY=0$$

Where A is the separation constant.
Note that Y still depends on two variables, so for this function we will also proceed to perform the method of separation of variables.
Suppose that

$$Y(\theta,\phi)=\Theta(\theta)\Phi(\phi)$$

So

$$\frac{\partial Y}{\partial\theta}=\frac{\partial}{\partial\theta}\Theta\Phi=\Phi\frac{d\Theta}{d\theta}$$
$$\frac{\partial Y}{\partial\phi}=\frac{\partial}{\partial\phi}\Theta\Phi=\Theta\frac{d\Phi}{d\phi}$$

Replacing in the angular equation we obtain:

$$\frac{\Phi}{sen(\theta)}\frac{d}{d\theta}\left(sen(\theta)\frac{d\Theta}{d\theta}\right)+\frac{\Theta}{sen^2(\theta)}\frac{d^2\Phi}{d\phi^2}+A\Phi\Theta=0$$

Multiplying by $sin^2(\theta)$ and dividing by $\Phi\Theta$

$$\frac{sen(\theta)}{\Theta}\frac{d}{d\theta}\left(sen(\theta)\frac{d\Theta}{d\theta}\right)+\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2}+Asen^2(\theta)=0$$

We separate the polar part (θ) and the azimuthal part (ϕ), obtaining

Polar part

$$\frac{sen(\theta)}{\Theta}\frac{d}{d\theta}\left(sen(\theta)\frac{d\Theta}{d\theta}\right)+Asen^2(\theta)-B=0 \tag{17}$$

Azimuth part

$$\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2}+B=0 \tag{18}$$

Now we will proceed with the solution of equations (16), (17) and (18), taking into account the following restrictions for the wave function

- The squared wave function is absolutely integrable.
- φ must take a single value at each point in space.
- φ must be continuous.

In addition to this, as previously mentioned, each of the equations to solve provides a quantum number, as we will see below:

- The solution of the radial equation is restricted to integer values. This gives the **principal quantum number** n.
- The solution of the polar equation gives the **orbital quantum number** l
- The solution of the azimuthal equation gives the **magnetic quantum number** m. This given that m represents the dependence with the azimuth angle.

3.5 Solution of the azimuthal equation

$$\frac{d^2\Phi}{d\phi^2} + B\Phi = 0$$

$$\phi(0) = 0\phi(2\pi) = 0$$

ODE of constant coefficients.
Auxiliary equation

$$r^2 + B = 0$$

- if $B < 0$, then $B = -\alpha$, with $\alpha > 0$ then

  $$r^2 - \alpha = 0$$

  $$r = \pm\sqrt{\alpha}$$

  So

  $$\Phi(\phi) = C_1 e^{-\sqrt{\alpha}\phi} + C_2 e^{\sqrt{\alpha}\phi}$$

  Since $\phi(0) = 0$, $C_1 = -C_2$. Later

  $$\Phi = C_2\left(-e^{-\sqrt{\alpha}\phi} + e^{\sqrt{\alpha}\phi}\right)$$

  Since $\phi(2\pi) = 0$. $C_2 = 0$ (trivial solution) or $-e^{-\sqrt{\alpha}2\pi} + e^{\sqrt{\alpha}2\pi} = 0$
  So

  $$2\sqrt{\alpha}2\pi = 0$$

  $$\alpha = 0$$

- If B = 0, then

  $$\Phi'' = 0$$

  $$\Phi' = C$$

  $$\Phi = C\phi + D$$

  Since $\phi(0) = 0$, D = 0 and since $\phi(2\pi) = 0$, then $C_2\pi = 0$, then C = 0. Trivial solution

It must happen that $B > 0$, like this

$$r^2 + B = 0$$

$$r = \pm\sqrt{B}i$$

Let $m^2 = B$, we have

$$\Phi(\phi) = C_1 e^{im\phi} + C_2 e^{-im\pi}$$

Since the angle ϕ is the azimuth, we are going to define this angle by measuring itself in the opposite direction to the hands of the clock, from a given angle, thus doing $C_2 = 0$. Then

$$\Phi(\phi) = C_1 e^{im\phi}$$

3.6 Solution of the polar equation

$$\frac{sen(\theta)}{\Theta}\frac{d}{d\theta}\left(sen(\theta)\frac{d\Theta}{d\theta}\right) + Asen^2(\theta) - B = 0$$

Since $B = m^2$, we have

$$\frac{sen(\theta)}{\Theta}\frac{d}{d\theta}\left(sen(\theta)\frac{d\Theta}{d\theta}\right) + Asen^2(\theta) - m^2 = 0$$

Dividing by $sin^2(\theta)$ and multiplying by Θ

$$\frac{1}{sen(\theta)}\frac{d}{d\theta}\left(sen(\theta)\frac{d\Theta}{d\theta}\right) + \left(A - \frac{m^2}{sen^{2(\theta)}}\right)\Theta = 0 \tag{19}$$

We carry out the replacement

$$P(cos(\theta)) = \Theta(\theta); x = cos(\theta)$$

$$\frac{d}{d\theta} = \frac{dx}{d\theta}\frac{d}{dx} = -sen(\theta)\frac{d}{dx}; \frac{d\Theta}{d\theta} = \frac{dP}{dx}\frac{dx}{d\theta} = -sen(\theta)\frac{dP}{dx}$$

Replacing in (19)

$$\frac{1}{sen(\theta)}\frac{d}{dx}\left(sen(\theta)(-sen(\theta))\frac{dP}{dx}\right) + \left(A - \frac{m^2}{sen^{2(\theta)}}\right)P = 0$$

$$\frac{d}{dx}\left(1 - x^2\frac{dP}{dx}\right) + \left(A - \frac{m^2}{sen^{2(\theta)}}\right)P = 0$$

Applying the product rule for the first term

$$(1 - x^2)\frac{d^2P}{dx} - 2x\frac{dP}{dx} + + \left(A - \frac{m^2}{1 - x^2}\right)P = 0$$

Similar to **Legendre equation**
Power series solution
Let's suppose

$$P = \sum_{n=0}^{\infty} a_n x^n$$

$$P' = \sum_{n=1}^{\infty} n a_n x^{n-1}$$

$$P'' = \sum_{n=2}^{\infty} n(n-1)a_n x^{n-2}$$

Note that these derivatives are well defined, by the linearity of the derivative.
Replacing

$$(1-x^2)\sum_{n=2}^{\infty} n(n-1)a_n x^{n-2} - 2x\sum_{n=1}^{\infty} n a_n x^{n-1} + (A-m^2)\sum_{n=0}^{\infty} a_n x^n = 0$$

Applying the distributive law

$$\sum_{n=2}^{\infty} n(n-1)a_n x^{n-2} - \sum_{n=2}^{\infty} n(n-1)a_n x^n - 2\sum_{n=1}^{\infty} n a_n x^n + A\sum_{n=0}^{\infty} a_n x^n - m^2\sum_{n=0}^{\infty} a_n x^n = 0$$

$$\sum_{n=0}^{\infty}(n+2)(n+1)a_{n+2}x^n - \sum_{n=2}^{\infty} n(n-1)a_n x^n - 2\sum_{n=1}^{\infty} n a_n x^n + A\sum_{n=0}^{\infty} a_n x^n - m^2\sum_{n=0}^{\infty} a_n x^n = 0$$

$$\sum_{n=2}^{\infty}[(n+2)(n+1)a_{n+2} + ((-n(n-1) - 2n + A - m^2)a_n]x^n = 0$$

We add the terms

$$2a_2 + 6a_3 x - 2a_1 x + Aa_0 + Aa_1 x - m^2 a_0 - m^2 a_1 x = 0$$

Given the linearity of each x^n, we have that these values must be different from zero, then, it must happen that

$$2a_2 + Aa_0 - m^2 a_0 = 0$$
$$6a_3 - 2a_1 + Aa_1 - m^2 a_1 = 0$$
$$(n+2)(n+1)a_{n+2} + ((-n(n-1) - 2n + A - m^2)a_n = 0 \tag{20}$$

Based on (20) we obtain

$$a_{n+2} = \frac{(n+m)(n+m+1-A)}{(n+2)(n+1)}a_n$$

So

$$P = a_0 + a_1 x + \frac{m(m+1)-A}{2}a_0 x^2 + \frac{(m+1)(m+3)}{3!}a_1 x^3$$
$$+\frac{[((2+m)(3+m)-A)(m(m+1)-A}{4!}a_0 x^4 + ...$$

Thus

$$P = a_0(1 + \frac{m(m+1)-A}{2}x^2 + \frac{[((2+m)(3+m)-A)(m(m+1)-A}{4!}x^4 + ...)$$
$$+a_1\left(x + \frac{(m+1)(m+3)}{3!}a_1 x^3 + ...\right)$$

Taking this into account, we have that the solution of the equation is of the form

$$P_l^m = (1-x^2)^{m/2}\left(a_0\sum_{n=0}^{\infty}\frac{a_{2n}}{a_0}x^{2n} + a_1\sum_{n=1}^{\infty}\frac{a_{2n+1}}{a_1}x^{2n+1}\right)$$

With coefficients

$$a_{n+2} = \frac{(n+m)(n+m+1-A)}{(n+2)(n+1)}a_n$$

A series solution is useful if the series converges so that from a certain value it can be truncated.This particular series converges if $A = l(l+1)$.
The values of the coefficients a_0 and a_1 are chosen depending on the values of l, to ensure that only the convergent series survives.

3.7 Radial equation solution

Before proceeding with the solution of the equation, it is necessary to emphasize the concepts of particle in bound and unbound state.

- **Particle in a bound state**
  Given a small particle, whose presence is confined to a fairly localized region, such as an atom, its quantum state can be adequately represented by a wave function. The function will only take on significantly nonzero values in a region roughly the size of the atom.

$$Pr(V) = \int_V |\phi(x)|^2 dx$$

- **Particle in an unbound state**
  Their collision states represent particles that can move through an infinite region of space and whose wave function does not decay exponentially toward zero. A particle without spin with a completely defined moment $p = (p_x, p_y, p_z)$ has a state that can be represented by the function:

$$\phi(x, y, z) = e^{i(p_x x + p_y y, p_z z)/h}$$

  Non-normalizable function

Remembering the radial equation

$$\frac{d}{dr}\left(r^2 \frac{dR}{dr}\right) + \frac{2mr^2}{h^2}\left(E + \frac{KZq_e^2}{r}\right) R - AR = 0$$

Since $A = l(l+1)$

$$\frac{d}{dr}\left(r^2 \frac{dR}{dr}\right) + \frac{2mr^2}{h^2}\left(E + \frac{KZq_e^2}{r}\right) R - l(l+1)R = 0$$

Terms

- $R \to 0$ if $r \to \infty$ for all l
- $R \to 0$ if $r \to 0$ for $l \neq 0$

For the chain rule

$$\left[r^2 \frac{d^2}{dr^2} + 2r\frac{d}{dr} + \frac{2mr^2 E}{h^2} + \frac{2mr^2 KZq_e^2}{h^2} - l(l+1)\right] R(r) = 0 \tag{21}$$

It makes sense to use the energy of the free electron as the zero point of the potential energy, that is, in the case $E \to 0$ for the electron away from the nucleus, since it is practically free. Since the presence of positive charge stabilizes the atom. We must consider solutions in which E becomes negative as it approaches the nucleus.
What's more

- If $E > 0$, unbound state, ϕ not normalizable.
- If $E < 0$, bound state, region confined particle, ϕ normalizable.

Let $\alpha^2 = \frac{-2mE}{h^2}$;$\rho = 2\alpha r$. We have

$$\frac{d}{dr} = \frac{d\rho}{dr}\frac{d}{d\rho} = 2\alpha\frac{d}{d\rho}$$

$$\frac{d^2}{dr^2} = 4\alpha^2\frac{d^2}{d\rho^2}$$

substituting in (21) we obtain

$$\left[\rho^2\frac{d^2}{d\rho^2} + 2\rho\frac{d}{d\rho} - \frac{\rho^2}{4} + \frac{2mKq_e^2\rho}{2\alpha h^2} - l(l+1)\right]R(\rho) = 0$$

If we denote $\beta = \frac{mKZq_e^2}{\alpha h^2}$ and divide by ρ^2 we obtain

$$\left[\frac{d^2}{d\rho^2} + \frac{2}{\rho}\frac{d}{d\rho} - \frac{1}{4} + \frac{\beta}{\rho} - \frac{l(l+1)}{\rho^2}\right]R(\rho) = 0 \tag{22}$$

When $\rho \to \infty$ we obtain:

$$\frac{d^2R}{d\rho^2} - \frac{R}{4} = 0$$

ODE of constant coefficients.
Auxiliary equation

$$r^2 - \frac{1}{4} = 0$$

$$r^2 = \frac{1}{4}$$

$$r = \pm\frac{1}{2}$$

$$R(\rho)_{\rho\to\infty} = e^{\pm\frac{\rho}{2}}$$

Taking into account the conditions previously established for the radial equation, we will only consider the solution with a negative exponent. This is:

$$R(\rho) = e^{-\rho/2}$$

We propose solutions of the form

$$R(\rho) = G(\rho)e^{-\rho/2}$$

So

$$\frac{dR}{d\rho} = \frac{d}{d\rho}e^{-\rho/2} = e^{-\rho/2}\left[\frac{dG}{d\rho} - \frac{G}{2}\right]$$

$$\frac{d^2R}{d\rho^2} = \frac{d^2}{d\rho^2}Ge^{-\rho/2} = \frac{d}{d\rho}e^{-\rho/2}\left[\frac{dG}{d\rho} - \frac{G}{2}\right] = e^{-\rho/2}\left[\frac{d^2G}{d\rho^2} - \frac{dG}{d\rho} + \frac{G}{4}\right]$$

Substituting in (22) we obtain

$$\left[\frac{d^2}{d\rho^2} - \frac{d}{d\rho} + \frac{1}{4} + \frac{2}{\rho}\left(\frac{d}{d\rho} - \frac{1}{2}\right) - \frac{1}{4} + \frac{\beta}{\rho} - \frac{l(l+1)}{\rho^2}\right]G = 0$$

Reordering and multiplying by ρ^2

$$\left[\rho^2\frac{d^2}{d\rho^2} + \rho(2-\rho)\frac{d}{d\rho} + \rho(\beta-1) - l(l+1)\right]G = 0 \tag{23}$$

Power series solution

$$G(\rho) = \rho^s \sum_{j=0}^{\infty} b_j \rho^j$$

Thus

$$\rho(2-\rho)\frac{dG}{d\rho} = \rho(2-\rho)\frac{d}{d\rho}\sum_{j=0}^{\infty} b_j\rho^{j+s} = \rho(2-\rho)\sum_{j=0}^{\infty}(j+s)b_j\rho^{j+s-1} = 2\rho\sum_{j=0}^{\infty}(j+s)b_j\rho^{j+s-1} - \rho^2\sum_{j=0}^{\infty}(j+s)b_j\rho^{j+s-1}$$

$$= 2\rho^s\sum_{j=0}^{\infty} b_j(j-s)\rho^j - \rho^{s+1}\sum_{j=0}^{\infty} b_j(j-s)\rho^j$$

$$\rho^2\frac{d^2G}{d\rho^2} = \rho^2\frac{d^2}{d\rho^2}\sum_{j=0}^{\infty} b_j\rho^{j+s} = \rho^2\sum_{j=0}^{\infty}(j+s)(j+s-1)b_j\rho^{j+s-2} = \rho^s\sum_{j=0}^{\infty}(j+s)(j+s-1)b_j\rho^j$$

Substituting in (23)

$$\rho^s\sum_{j=0}^{\infty}(j+s)(j+s-1)b_j\rho^j + 2\rho^s\sum_{j=0}^{\infty}(j+s)(j+s-1)b_j\rho^j - \rho^{s+1}\sum_{j=0}^{\infty}(j+s)b_j\rho^j$$

$$+(\beta-1)\rho^{s+1}\sum_{j=0}^{\infty} b_j\rho^j - l(l+1)\rho^s\sum_{j=0}^{\infty} b_j\rho^j = 0$$

Dividing by ρ^s

$$\sum_{j=0}^{\infty} b_j\rho^j[(j+s)(j+s-1) + 2(j+s) - l(l+1)] = \sum_{j=0}^{\infty} b_j\rho^j[j+1-\beta+1] \tag{24}$$

The summation on the left can be written as

$$\sum_{j=0}^{\infty} b_j\rho^j[(j+s)(j+s-1) + 2(j+s) - l(l+1)] = b_0[s(s-1) + 2s - l(l+1)]$$

$$+\sum_{j=0}^{\infty} b_{j+1}\rho^{j+1}[(j+1+s)(j+s) + 2(j+s+1) - l(l+1)]$$

We can rewrite (24) as

$$b_0[s(s-1) + 2s - l(l+1)] + \sum_{j=0}^{\infty}\rho^{j+1}\{b_{j+1}((j+1+s)(j+1) + 2(j+s+1) - l(l+1))$$

$$-b_j(j+s-\beta+1)\} = 0$$

Then since ρ^j are linearly independent, it happens that

$$b_0[s(s-1) + 2s - l(l+1)] = 0$$

So $s = l$ y for all j

$$b_{j+1} = \frac{j+l+1-\beta}{(j+1)(j+2l+2}b_j$$

For R not to be divergent, it must truncate at some point, that is, from a certain value it must be zero, there exists j = k such that

$$b_{k+1} = \frac{k+l+1-\beta}{(k+1)(k+2l+2}b_k = 0$$

So

$$k+l+1-\beta = 0$$

This is

$$\beta = k+l+1$$

We going to call $n = k+l+1$ **principal quantum number** which is an integer and $n = 1, 2, 3, ...$
Remembering the definition of β and α

$$\beta^2 = n^2 = \frac{m^2Z^2q_e^4}{\alpha^2h^4} = \frac{-h^2}{2mE}\frac{m^2Z^2q_e^4}{h^4} = \frac{-mZ^2q_e^4}{2Eh^4}$$

So

$$E_n = \frac{-Z^2q_e^2}{2n^2a_0}$$

Where $a_0 = \frac{h^2}{mq_e^2}$ is called the Bohr radius

3.8 Eigenvectors or eigenstates of angular moments

Previously we have seen the solution of the polar and azimuthal equations, whose multiplication forms the angular function. Now, let's find the relationship between the magnetic quantum number and the azimuthal quantum number. (l, m)
Let $\{|a,b\rangle\}$the set of eigen-states of angular momentum such that:

$$\hat{J}^2|a,b\rangle = a\hbar^2|a,b\rangle$$

$$\hat{J}_z|a,b\rangle = b\hbar|a,b\rangle$$

We must describe the eigenvalues a and b.
We define

$$\hat{J}_\pm = \hat{J}_x \pm i\hat{J}_y$$

$$\hat{J}_\pm{}^+ = \hat{J}_\mp$$

That satisfy

1. $$\left[\hat{J}^2, \hat{J}_\pm\right] = 0$$

2. $$\left[\hat{J}_z, \hat{J}_\pm\right] = \left[\hat{J}_z, \hat{J}_x\right] \pm \imath\left[\hat{J}_z, \hat{J}_y\right] = \imath\hbar\epsilon_{zxy}\hat{J}_y \mp \imath(\imath\hbar\epsilon_{zxy}\hat{J}_x)$$
$$= \imath\hbar\epsilon_{zxy}\hat{J}_y \pm \hbar\epsilon_{zxy}\hat{J}_x = \imath\hbar\epsilon_{xyz}\hat{J}_y \pm \hbar\epsilon_{xyz}\hat{J}_x = \pm\hbar\hat{J}_\pm$$

3. $$\left[\hat{J}_+, \hat{J}_-\right] = \left[\hat{J}_x + \imath\hat{J}_y, \hat{J}_x - \imath\hat{J}_y\right] = \left[\hat{J}_x, \hat{J}_x\right] - \imath\left[\hat{J}_x, \hat{J}_y\right] + \imath\left[\hat{J}_y, \hat{J}_x\right] - \imath^2\left[\hat{J}_y, \hat{J}_y\right]$$
$$= -\imath\left[\hat{J}_x, \hat{J}_y\right] + \imath\left[\hat{J}_y, \hat{J}_x\right] = -\imath(\imath\hbar\epsilon_{xyz}\hat{J}_z) + \imath(\imath\hbar\epsilon_{yxz}\hat{J}_z)$$
$$= \hbar\epsilon_{xyz}\hat{J}_z + \hbar\epsilon_{xyz}\hat{J}_z = 2\hbar\hat{J}_z$$

They involve in particular

- **a)**

$$\hat{J}^2\left(\hat{J}_\pm|a,b\rangle\right) = \hat{J}_\pm\left(\hat{J}^2|a,b\rangle\right) = \hat{J}_\pm(a\hbar^2|a,b\rangle)$$

$$a\hbar^2\left(\hat{J}_\pm|a,b\rangle\right) \sim |a\rangle$$

  In this way $\hat{J}_\pm(|a,b\rangle)$ corresponds to an eigenvalue of $\hat{J}_\pm$ with eigenvalue $a\hbar^2$, therefore it must be proportional to the eigenvector that corresponds to that eigenvalue.

- **b)**

$$\hat{J}_z\left(\hat{J}_\pm|a,b\rangle\right) = (\hat{J}_\pm\hat{J}_z \pm \hat{J}_\pm|a,b\rangle$$

$$= \left(\hat{J}_z \pm 1\right)\hat{J}_\pm|a,b\rangle$$

$$= \hbar(b\pm 1)\left(\hat{J}_\pm|a,b\rangle\right) \sim |b\pm 1\rangle$$

  It means that $\hat{J}_\pm$ is a eigenvector with eigenvalue $b \pm 1$

So $\{\hat{J}^2, \hat{J}_z\}$ is a full set of supported observables, that is, if I have an eigenvalue, only a single eigenvector corresponds to it $|a,b\rangle$.
Then , by a) and b)

$$\hat{J}_\pm|a,b\rangle = C_\pm|a,b\pm 1\rangle$$

We have

$$\hat{J_x}^2 + \hat{J_y}^2 = \frac{1}{2}\left(\hat{J_x}^2 - \imath\hat{J}_x\hat{J}_y + \imath\hat{J}_y\hat{J}_x + \hat{J_y}^2 + \hat{J_x}^2 + \imath\hat{J}_x\hat{J}_y - \imath\hat{J}_x\hat{J}_y + \hat{J_y}^2\right)$$

$$= \frac{1}{2}\left(\hat{J}_x + \imath\hat{J}_y\right)\left(\hat{J}_x - \imath\hat{J}_y\right) + \left(\hat{J}_x - \imath\hat{J}_y\right)\left(\hat{J}_x + \imath\hat{J}_y\right)$$

$$= \frac{1}{2}\left(\hat{J_-^+}\hat{J}_- + \hat{J_+^+}\hat{J}_+\right) \tag{25}$$

On the other hand

$$< a,b|\hat{J^2} - \hat{J_z}^2|a,b >= \hbar(a-b^2) \tag{26}$$

As $\hat{J^2} = \hat{J_x}^2 + \hat{J_y}^2 + \hat{J_z}^2$ entonces $\hat{J^2} - \hat{J_z}^2 = \hat{J_x}^2 + \hat{J_y}^2$.
So , by (25)

$$< a,b|\hat{J^2} - \hat{J_z}^2|a,b >=< a,b|\hat{J_-^+}\hat{J}_-|a,b > + \frac{1}{2} < a,b|\hat{J_+^+}\hat{J}_+|a,b >$$

This corresponds to the sum of the squared norms of two proper spaces that are greater than or equal to zero, then by (26)

$$a - b^2 \geq 0$$

So

$$b^2 \geq a$$

Given a exist b_{min} y b_{max} such that $b_{min} < b < b_{max}$
So

$$\hat{J}_+|a,b_{max}\rangle = |\rangle \tag{27}$$

$$\hat{J}_-|a,b_{min}\rangle = |\rangle \tag{28}$$

Note that this occurs because the ladder operator decreases or increases one unit, as we are working with the minimum and the maximum this value must be zero.
Using that $[\hat{J}_+, \hat{J}_-] = 2\hbar\hat{J}_z$, we get

$$\hat{J}_\mp \hat{J}_\pm = \hat{J}^2 - \hat{J}_z{}^2 \mp \hbar\hat{J}_z$$

Working with $\hat{J}_+$ by (27)

$$|\rangle = (\hat{J}^2 - \hat{J}_z{}^2 - \hbar\hat{J}_z|a, b_{max}\rangle$$
$$= \hbar(a - b_{max}^2 - b_{max})|a, b_{max}\rangle$$

Must happen

$$a - b_{max}^2 - b_{max} = 0$$

Then

$$a = b_{max}^2 + b_{max} = b_{max}(b_{max} + 1)$$

Now working with $\hat{J}_-$ by (28)

$$|\rangle = (\hat{J}^2 - \hat{J}_z{}^2 + \hbar\hat{J}_z|a, b_{min}\rangle$$

$$= \hbar^2(a - b_{min}^2 + b_{min})|a, b_{min}\rangle$$

Must happen

$$a - b_{min}^2 + b_{min} = 0$$

Then

$$a = b_{min}^2 - b_{min} = b_{min}(b_{min} - 1)$$

Thus

$$b_{max}(b_{max} + 1) = b_{min}(b_{min} - 1)$$

Must happen that $b_{min} = -b_{max}$,since

$$b_{min}(b_{min} - 1) = -b_{max}(-b_{max} - 1) = b_{max}^2 + b_{max} = b_{max}(b_{max} + 1)$$

So

$$-b_{max} \leq b \leq b_{max}$$

As b) define a ladder operator, exists $N \in \mathbb{N}$ such that

$$\hat{J}_\pm{}^N |a, -b_{max}\rangle = c|a, b_{max}\rangle$$

This is

$$-b_{max} + N = b_{max}$$

Then

$$b_{max} = \frac{1}{2}N$$

So

$$a = \frac{1}{2}N\left(\frac{1}{2}N + 1\right)$$

Taking $l \in \frac{1}{2}\mathbb{N}; m \in \frac{1}{2}\mathbb{N}$

$$a = l(l + 1)$$
$$b = m$$

Then

$$-l \leq m \leq l \tag{29}$$

Also

$$\hat{J}^2|j,m\rangle = \hbar^2 l(l+1)|j,m\rangle$$
$$\hat{J}_z|j,m\rangle = \hbar m|j,m\rangle$$

Conclusions

- Given l there are 2l + 1 values of m, giving integer jumps by the ladder operator. What's more
$$dim(E_i) = 2l+1$$
The total space of angular momentum states can be divided into subspaces for different l

- E_i they are invariant under rotation
. Since l is the quantum number associated with $\hat{J}_z$ and $\hat{J}^2$ it commutes with the components of angular momentum, which are the generators of rotations. Then when a rotation is applied to a state of angular momentum, its eigenvalue does not change.
If I take a state in E_l and apply a rotation, I fall back into the same subspace.

About an arbitrary state

$$< l,m|\hat{J}^2 - \hat{J_z}^2 - \hbar\hat{J}_z|l,m >=< l,m|\hat{J_+^+}\hat{J}_+|l,m >$$
$$\hbar^2[l(l+1) - m(m+1)] = |C_+^{lm}|^2$$

So

$$\hat{J}_\pm|l,m >= \hbar\sqrt{l(l+1) - m(m+1)}|l,m \pm 1 >$$

On the other hand, for a particle without spin.

$$\hat{J} = \hat{L} = \hat{r}x\hat{p}$$

Where

- $\hat{p}$ is the orbital angular momentum
- $\hat{r}$ is the position.

With representation in position

$$< \hat{r}|\hat{L}|\hat{r}' = \imath\hbar(\hat{r}x\bigtriangledown)\delta(\hat{r} - \hat{r}')$$

As an operator acting on the wave function

$$\hat{L}|\varphi\rangle = -\imath\hbar(\hat{r}x \bigtriangledown \varphi(\hat{r})) = \mathcal{L}(\varphi(\hat{r})$$

Where $\mathcal{L}$ is the angular momentum differential operator.
Since we work in spherical coordinates, this differential operator is of the form

$$\mathcal{L}_x = -\imath\hbar\left(-sen(\phi)\frac{\partial}{\partial\theta} - cot(\theta)\frac{\partial}{\partial\theta}\right)$$
$$\mathcal{L}_y = -\imath\hbar\left(cos(\phi)\frac{\partial}{\partial\theta} - cot(\theta)sen(\phi)\frac{\partial}{\partial\phi}\right)$$
$$\mathcal{L}_z = -\imath\hbar\frac{\partial}{\partial\phi}$$

Also

- $$\mathcal{L}^2 = \mathcal{L}_x^2 + \mathcal{L}_y^2 + \mathcal{L}_z^2 = i^2\hbar^2\left(sen^2(\phi)\frac{\partial^2}{\partial\theta^2} - 2sen(\phi)cot(\theta)\frac{\partial}{\partial\theta}\frac{\partial}{\partial\phi} + cot^2(\theta)\frac{\partial}{\partial\phi^2}\right)$$
$$+i^2\hbar^2\left(cos^2(\phi)\frac{\partial^2}{\partial\theta^2} - 2cos(\phi)sen(\phi)cot(\theta)\frac{\partial}{\partial\theta}\frac{\partial}{\partial\phi} + cot^2(\theta)sen^2(\phi)\frac{\partial}{\partial\phi^2}\right) + i^2\hbar^2\frac{\partial}{\partial\phi^2}$$
$$= \hbar^2\left(-sen^2(\phi)\frac{\partial^2}{\partial\theta^2} + 2sen(\phi)cot(\theta)\frac{\partial}{\partial\theta}\frac{\partial}{\partial\phi} - cot^2(\theta)\frac{\partial}{\partial\phi^2} - cos^2(\phi)\frac{\partial^2}{\partial\theta^2} + 2cos(\phi)sencot(\theta)\frac{\partial}{\partial\theta}\frac{\partial}{\partial\phi}\right)$$
$$-cot^2(\theta)sen^2(\phi)\frac{\partial}{\partial\phi^2} - \frac{\partial}{\partial\phi^2} = -\hbar^2\frac{1}{sen(\theta)}\left[\frac{\partial}{\partial\theta}\left(sen(\phi)\frac{\partial}{\partial\theta}\right) + \frac{1}{sen(\theta)}\frac{\partial^2}{\partial\phi^2}\right]$$
- $$\mathcal{L}_\pm = \hbar e^{\pm\imath\phi}\left(\frac{\partial}{\partial\theta} + cot(\theta)\frac{\partial}{\partial\theta}\right)$$
- $$\mathcal{L}_\pm = \mathcal{L}_x \pm i\mathcal{L}_y = -i\hbar\left(-sen(\phi)\frac{\partial}{\partial\theta} - cos(\theta)cos(\phi)\frac{\partial}{\partial\phi}\right) = -i\hbar\left(cos(\phi)\frac{\partial}{\partial\theta} - cot(\theta)sen(\phi)\frac{\partial}{\partial\phi}\right)$$
$$= -i\hbar\left(-sen(\phi)\frac{\partial}{\partial\theta} - cos(\theta)cos(\phi)\frac{\partial}{\partial\phi}\right) \pm \hbar\left(cos(\phi)\frac{\partial}{\partial\theta} - cot(\theta)sen(\phi)\frac{\partial}{\partial\phi}\right)$$
$$\hbar\left(isen(\phi)\frac{\partial}{\partial\theta} + icot(\theta)cos(\phi)\frac{\partial}{\partial\phi}\right) \pm \hbar cos(\phi)frac\partial\partial\theta - cot(\theta)sen(\phi)\frac{\partial}{\partial\phi}$$
$$= \hbar\left(\frac{\partial}{\partial\theta}\left(isen(\phi) \pm cos(\phi)\right) + \frac{\partial}{\partial\phi}\left(icot(\theta)cos(\phi) - cot(\theta)sen(\phi)\right)\right)$$
$$\hbar\left(\frac{\partial}{\partial\theta}e^{\pm i\phi} + \frac{\partial}{\partial\phi}e^{\pm i\phi}cot(\phi)\right) = \hbar e^{\pm i\phi}\left(\frac{\partial}{\partial\theta} + cot(\theta)\frac{\partial}{\partial\phi}\right)$$
$$= \hbar e^{\pm\imath\phi}\left(\frac{\partial}{\partial\theta} + cot(\theta)\frac{\partial}{\partial\theta}\right)$$

From what was done before

$$\mathcal{L}^2|l,m> = \hbar^2 l(l+1)|l,m>$$
$$\mathcal{L}_z|l,m> = \hbar m|l,m>$$

Con $-l \leq m \leq l$ And we previously obtained that

$$Y_{lm}(\theta,\phi) = e^{\imath m\phi}P_l^m(\theta)$$

Boundary conditions

$$Y_{lm}(\theta,\phi) = Y_{lm}(\theta,\phi+2\pi)$$
$$e^{im\phi} = e^{im(\phi+2\pi)}$$
$$1 = e^{im2\pi}$$
$$cos(2\pi m) + \imath sen(2\pi m) = 1$$

This occurs if and only if $m \in \mathbb{Z}$, then $l \in \mathbb{N}$
For m=l

$$\mathcal{L}_+|l,l> = |>$$

Then

$$\mathcal{L}_+ Y_{ll}(\theta,\phi) = \hbar e^{\imath l\phi}\left(\frac{\partial}{\partial\theta} + cot(\theta)\frac{\partial}{\partial\theta}\right) Y_{ll}(\theta,\phi)$$

With solution

$$Y_{ll}(\theta,\phi) = C_l e^{\imath l\phi} sen^l(\theta)$$

This because the eigenfunctions of the equation are called spherical harmonics.
We can find C_l normalizing the function, doing the substitution $x = cos(\theta)$

$$1 = \int |Y_{ll}|^2 d\Omega = \int_0^\pi sen(\theta)d\theta \int_0^{2\pi} |C_l|^2 sen^{2l}(\theta)d\phi$$

$$= \int_0^\pi sen^{2l+1}(\theta)d\theta \int_0^{2\pi} |C_l|^2 d\phi$$

$$= 2\pi|C_l|^2 \int_0^\pi sen^{2l+1}(\theta)d\theta$$

$$= 2\pi|C_l|^2 \int_{-1}^1 (1-x^2)^l dx$$

So

$$|C_l|^2 = \frac{(-1)^l}{2^l l!}\sqrt{\frac{(2l+1)(2l)}{4\pi}}$$

In general

$$Y_{lm}(\theta,\phi) = \sqrt{\frac{(2l+1)(l-m)!}{4\pi(l+m)!}} e^{im\phi} P_l^m(cos(\theta))$$

We are going to have eigenstates that have associated eigenfunctions which are the spherical harmonics and the eigenvalues are related to the quantum numbers.

3.9 Normalization of the radial equation

The radial funtion satifies the Laguerre equation- In such a way that the radial equation is a type of Laguerre polynomial.

$$F(\rho) = \mathcal{L}_{n-l-1}^{2l+1}(\rho)$$

Of standarization

$$\int_0^\infty \rho^2 \left(e^{-\rho/2}\rho^l \mathcal{L}_{n-l-1}^{2l+1}(\rho)\right) d\rho = \frac{2n(n+l)!}{(n-l-1)!}$$

Finally

$$\varphi_{nlm} = \sqrt{\left(\frac{2z}{na_0}\right)\frac{(n-l-1)!}{2n(n+l)!}} e^{-\alpha r}(2\alpha r)\mathcal{L}_{n-l-1}^{2l+1}(2\alpha r) Y_{lm}$$

Degeneration

- $$E = \frac{1}{2}\varepsilon_0 \frac{Z^2}{n^2}$$

  It doesn't depend on l or m, so for the same n, m and l can vary without changing the value of the energy. That is, I can obtain differents differents states that have the same energy value.

- Given n, there are n values of l.

- Given l, there are 2l+1 possibles values of m
- In total

$$deg = \sum_{l=0}^{n}(2l+1) = \frac{2n(n-1)}{2} + n = n^2$$

Thath is, even higher is the n, then higuer the level of degeneracy, so the are more possibles states.

3.9.1 Energy autofunctions

Taking into account what has been seen above, we can know the shape of the energy cloud around the atomic nucleus.
If we want to know the probability of finding the the particle in a volume differential

$$dV = r^2 sen(\theta) dr d\theta d\phi$$

$$P_{dV(r,\theta,\phi)} = |\varphi_{nlm}(r,\theta,\phi)|^2 r^2 sen(\theta) dr d\theta d\phi$$

Solid angle probability density
As

$$|\varphi_{nlm}(r,\theta,\phi)|^2 = |Y_{lm}(\theta,\phi)|^2 |R_{nl}(r)|^2$$

We obtain

$$\frac{dP_{dV}}{d\Omega} = \int_0^\infty \frac{P_{dV(r,\theta,\phi)}}{d\Omega} dr = |Y_{lm}(\theta,\phi)|^2$$

It means thta if I add all the radii, in such a way thta if I look in one direction. I get the probability of finding the electron in that direction.
Thus, this result give us spherical harmonics, with indicates thta the atom tas axial symmetry. The axial symmetry refers to symmetry around an axil.
Radial probability density
Integrating over the solid angle

$$\frac{dP_{dV}}{dr} = \int \frac{P_{dV(r,\theta,\phi)}}{dr} d\Omega = r^2 \left|R_{nl(r)}\right|^2$$

It means that I take a fixed distance from the nucleos and evaluate the probibilty that by atom, it will find the electron. Then we add that probability

3.10 Numerical solution of *Schrödinger* equation for the particle in a box

The approach to solving the *Schrödinger* equation in the one dimensional box is to view the wave function as an vector and solve the eigenvalue problem.

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

$$E\begin{bmatrix}\varphi_1\\ \varphi_2\\ \vdots\\ \varphi_N\end{bmatrix} = \begin{bmatrix} \\ H \\ NxN \\ \\ \end{bmatrix}\begin{bmatrix}\varphi_1\\ \varphi_2\\ \vdots\\ \varphi_N\end{bmatrix} \tag{30}$$

Once we have the orevious equation we have an equation of eigenvalues. The eigenvalues of the matrix H can be obtained, So there will be N eigenvalues and N eigenvector.

$$E\varphi = \left[\frac{-\hbar}{2m}\frac{d^2}{dx^2} + U(r)\right]\varphi$$

Firt we write the matrix for $u(x)$ and then for $\frac{-\hbar^2}{2m}\frac{d^2}{dx^2}$
The Hamiltonian must be the sum of these two, for now we will concentrate on $u(x)$ Consider

$$E\varphi = \left[U(x)\right]\varphi$$

Since $u(x)$ is a potential function in a discrete lattice , u will give us the potential at each point o the lattice. That is, if there were no kinetic energy in the system, we expect the value in each component of the matrix to be equal to the potential energy, so the matrix u must to be diagonal.
Then Then

$$E\varphi_n = U(x_n)\varphi_n$$

So

$$E\begin{bmatrix}\varphi_1\\ \varphi_2\\ \vdots\\ \varphi_N\end{bmatrix} = \begin{bmatrix} H = U(x) \end{bmatrix}\begin{bmatrix}\varphi_1\\ \varphi_2\\ \vdots\\ \varphi_N\end{bmatrix}$$

With

$$U(x) = \begin{bmatrix} U(x_1) & 0 & 0\cdots & 0 & \\ 0 & U(x_2) & 0\cdots & 0 & \\ 0 & 0 & U(x_3)\cdots & 0 & \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & 0\cdots & U(x_N) & \end{bmatrix} \tag{31}$$

Now as we write the second derivate of a particular point

$$E\varphi_n = \frac{\hbar^2}{2m}\left(\frac{d^2\varphi}{dx^2}\right)_n$$

Takign into account the discretization

$$\frac{d\varphi}{dx} \approx \frac{\varphi(x+h) - \varphi(x)}{h}$$

$$\frac{d\varphi}{dx} \approx \frac{\varphi(x) - \varphi(x-h)}{h}$$

We have

$$\left[\frac{d\varphi}{dx}\right]_{forward} = \frac{\varphi_{N+1} - \varphi_N}{a}$$

$$\left[\frac{d\varphi}{dx}\right]_{backward} = \frac{\varphi_N - \varphi_{N-1}}{a}$$

Then

$$\left[\frac{d^2\varphi}{dx^2}\right] = \frac{\left[\frac{d\varphi}{dx}\right]_{forward} - \left[\frac{d\varphi}{dx}\right]_{backward}}{a} = \frac{\varphi_{N+1} - 2\varphi_N + \varphi_{N-1}}{a^2}$$

So

$$E\varphi_N = -t_0[2\varphi_N - \varphi_{N-1} - \varphi_{N+1}]$$

With

$$t_0 = \frac{-\hbar^2}{2ma^2}$$

We obtain the system of equations

$$\begin{aligned}
-t_0\varphi_0 + (2t_0 + U(x_1))\varphi_1 - t_0\varphi_2 &= E\varphi_1 \\
-t_0\varphi_1 + (2t_0 + U(x_2))\varphi_2 - t_0\varphi_3 &= E\varphi_2 \\
-t_0\varphi_2 + (2t_0 + U(x_3))\varphi_3 - t_0\varphi_4 &= E\varphi_3 \\
&\vdots \\
-t_0\varphi_{N-1} + (2t_0 + U(x_N))\varphi_N - t_0\varphi_{N+1} &= E\varphi_N
\end{aligned}$$

This system is equivalent to the following matrix eigenvalue problem

$$E\begin{bmatrix}\varphi_1\\ \varphi_2\\ \vdots\\ \varphi_N\end{bmatrix} = \begin{bmatrix} 2t_0 + U(x_1) & -t_0 & 0 & \cdots & 0 \\ -t_0 & 2t_0 + U(x_2) & 0 & \cdots & 0 \\ 0 & -t_0 & 2t_0 + U(x_3) & \cdots & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & 0 & \cdots & 2t_0 + U(x_N) \end{bmatrix}\begin{bmatrix}\varphi_1\\ \varphi_2\\ \vdots\\ \varphi_N\end{bmatrix}$$

In a one-dimensional box with zero potential
We obtain that the hamiltonian is of the form

$$\begin{bmatrix} 2t_0 & -t_0 & 0 & \cdots & 0 \\ -t_0 & 2t_0 & 0 & \cdots & 0 \\ 0 & -t_0 & 2t_0 & \cdots & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & 0 & \cdots & 2t_0 \end{bmatrix}$$

Wich corresponds to the system of equations

$$\begin{aligned}
-t_0\varphi_0 + 2t_0\varphi_1 - t_0\varphi_2 &= E\varphi_1 \\
-t_0\varphi_1 + 2t_0\varphi_2 - t_0\varphi_3 &= E\varphi_2 \\
-t_0\varphi_2 + 2t_0\varphi_3 - t_0\varphi_4 &= E\varphi_3 \\
&\vdots \\
-t_0\varphi_{N-1} + 2t_0\varphi_N - t_0\varphi_{N+1} &= E\varphi_N
\end{aligned}$$

3.10.1 Code

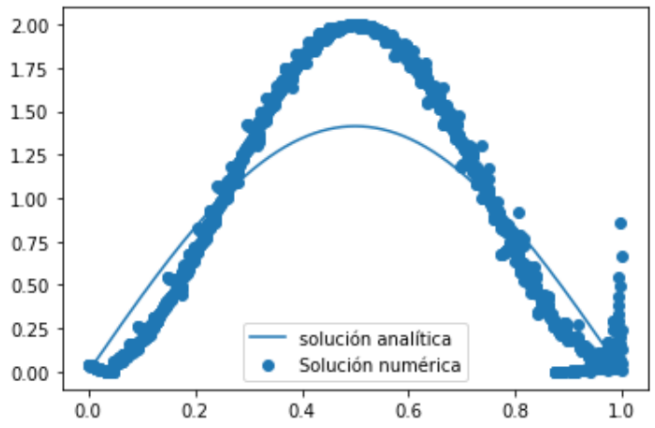
The previously described procedure is used in the following code, which graphs the analytical solution for n = 1 and its corresponding numerical solution

```python
import numpy as np
import matplotlib.pyplot as plt

steps = 2000
hbar=6.63e-34
m=9.109e-28
h= 1/ float(steps - 1)
t0=(hbar**2)/(2*m*(h**2))
delta=1/steps

hamiltoniano = np.zeros((steps, steps))

for i in range(steps):
    for j in range(steps):
        if i == j:
            hamiltoniano[i, j] = 2 * t0
        elif i == j + 1 or j == i + 1:
            hamiltoniano[i, j] = -t0
valores, vectores = np.linalg.eig(hamiltoniano)
x=np.linspace(0,1,steps)
s=np.sqrt(2)*np.sin(np.pi*x)
v=(vectores[0])**2
a=delta*v
suma=sum(a)
vector1=(1/suma)*v
plt.scatter(x,vector1,label="Solución numérica")
plt.plot(x,s,label="solución analítica")
plt.legend()
```



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