FINAL DEGREE PROJECT IN CHEMISTRY

# How is the Schrödinguer equation actually solved? Three different methods to address the Quantum Harmonic Oscillator problem



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# Motivation

Quantum chemistry is a central subject in Chemistry degree because it provides ultimate answers to explain reactivity, structural, stability and spectroscopy of atoms molecules and solids. However, to derive practical conclusions, one need to be familiar with several specific mathematical concepts and techniques. Undergraduate courses on Quantum Chemistry often omit much of this mathematical background in order to highlight the physical concepts, as doing otherwise would likely confuse the majority of students. Who would "not see the forest because of the leaves". As a result, the solutions of the Schrödinguer equation are usually provided right after presenting the Hamiltonian. Obviously, a student with interest in the matter realizes he is missing an important step, for he is then unable to obtain solutions autonomously.

The goal of this work is to provide an introductory view on some of the mathematical tools used in Quantum Chemistry to obtain eigenvalues and eigenstates of the time-independent Schrödinguer equation. Namely, we study polynomial method, the factorization method and the method of finite differences. All three techniques are applied to solve the Quantum Harmonic oscillator problem. We purpose fully fully choose this problem because it is pervasive in most areas of Physical Chemistry, and susceptible of being solved through any of the techniques, which will allow us to draw comparisons and conclusions in the end

# 1. Introduction

**On the importance of the harmonic oscillator model**

A harmonic oscillator (hereafter HO) [1] is a system which returns to the position of equilibrium describing sine waves when displaced out of it.

This system has a great value in Physics and Chemistry. The reason is that any system weakly shifted from a stable point can be modeled as a harmonic oscillator. We can apply it to a myriad of cases. Typical instances at the a macroscopic level are pendulums and springs. At a microscopic level, we can apply quantum harmonic oscillator in order to study vibration modes, electronic states in semiconductor nanostructures or photon modes in radiation, to name a few.

**Classical explanation and systems**

As we said before, any system able to return to the position of equilibrium once it's released out of this, will be a HO. A clear example of harmonic oscillator can be an item, with mass "m", bound to a spring. When we apply a force in axis x, we will move the item to the balance position and, if we release in any point, the spring speed up the item to the balance position. The value of this acceleration will be proportional to the distance to the item balance position, multiplied by a spring elasticity constant (Hooke's Law)

**Equations**

We can calculate the acceleration through Newton's second law and Hooke's law, as we can see in the equations 1 and 2.

$$F = -kx = ma = m\frac{d^2x}{dt^2} \quad (1)$$

Where:

- $k$ is the elasticity constant of the spring
- $x$ is the distance between the mass and the balance position
- $a$ is the acceleration of the item
- $m$ is the mass of the item

Now, we can replace acceleration with the second derivative of the movement respect to the time, according to his definition. After that, we will clear the acceleration.

$$a = \frac{d^2 x}{dt^2} = -\frac{k}{m}x \ \ (2)$$

We define the angular frequency, in radian/second (rad/s):

$$\omega^2 = \frac{k}{m} \ \ (3)$$

And determine the position of the mass as a function of time solving Eq.(2). The following result is obtained:

$$x(t) = A\cos(\omega t + \delta) \ \ (4)$$

Where:

- *A* is a constant called range of motion and it's the maximum movement of the mass respecting the balance position
- *(ωt+δ)* is the phase
- *δ* is the constant of the phase and it is set by the initial conditions of the problem.

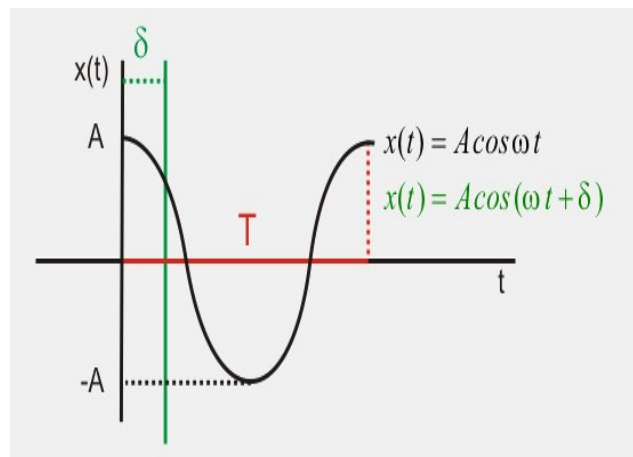A graphical interpretation of Eq.(4) is given in Fig.1:



Figure 1. Time-evaluation of the position in a classical HO [2]

One can determine the time it takes for the mass to carry out a complete oscillation by means of the Period (T). The period is related to the angular frequency by the following equation:

$$T = \frac{2\pi}{\omega} \quad (5)$$

**Energy**

From Hooke's law and the fact that $F = \frac{-dE}{dx}$, it is straightforward to express the potential energy of HO as:

$$E_p = \frac{1}{2}kx^2 \quad (6)$$

The energy is conserved as long as there is no friction in the system, switching to kinetic energy cyclically.

In figure 2, we can see the total energy, the kinetic energy and the elastic energy for different positions of a particle that describes a simple harmonic movement
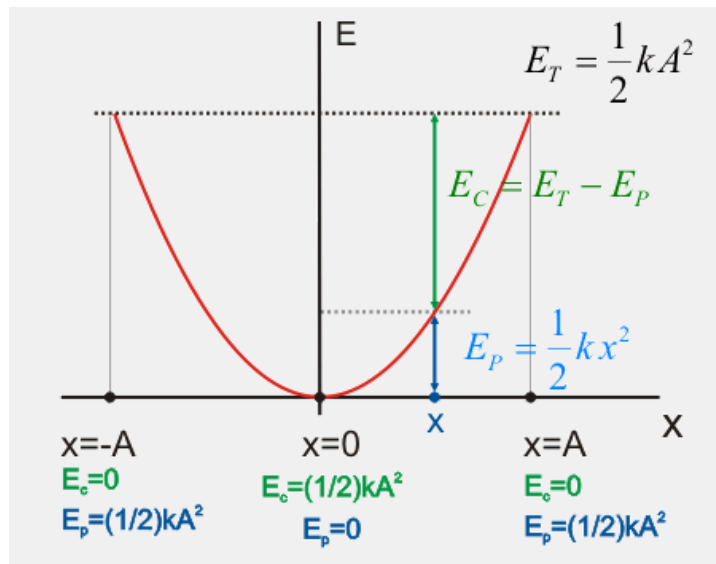


Figure 2. Energy for different particle positions  [2]

Since the mechanical energy is conserved, the total energy, which is the sum of kinetic energy and potential, can be calculated by equation 7:

$$E_t = \frac{1}{2}kA^2 = \frac{1}{2}m\omega^2 A^2 \ (7)$$

## Origin of the parabolic confinement

The problem of the harmonic oscillator is common and of great relevance in physics, since any mass in equilibrium subjected to a conservative force, behaves like a simple harmonic oscillator.

A force is conservative if the total work done on a particle that maintains a closed trajectory is zero. In this case, the conservative force is associated with the potential energy. Consider an arbitrary potential function $V(x)$, which we take one-dimensional for simplicity. [3]

Then, using a Taylor series, you can approximate this function to a specific point. In this way, the function is approximated to the point of minimum energy, where $x = x_0$, so we know the behavior of the particle at the point of equilibrium against small perturbations. Applying this, the function remains as follows:

$$V(x) = V(x_0) + V'(x)(x - x_0) + \frac{1}{2}V''(x_0)(x - x_0)^2 + ... \ (8)$$

Where the higher-order terms are safely neglected if the displacement $(x - x_0)$ is small.

Because $x_0$ is a minimum, the first derivative of the potential $V'(x) = 0$, so the term V' disappears. Also, $V(x_0)$ can be taken as the reference energy, $V(x_0) = 0$, so the first term can be discarded from the equation. Equation 9 shows what the function looks like after applying these adjustments:

$$V(x) = \frac{1}{2}V^2(x_0)(x - x_0)^2 \ (9)$$

If we define the equilibrium position as $x_0 = 0$ (origin of coordinates), and V² is a constant, which will be called K, we obtain:

$$V(x) = \frac{1}{2}V^2(0)(x - 0)^2 = \frac{1}{2}V^2 x^2 = \frac{1}{2}kx^2 \ (10)$$

It is worth to remarking the generality of the parabolic potential in Eq.(10). It holds for any system weakly displaces $(\Delta x = (x - x_0))$ from its equilibrium position, as long as the force is conservative

# Quantum Harmonic Oscillator

The Quantum Harmonic Oscillator (QHO) [4] is the quantum mechanical analogue of the classical HO. It is one of the most important models in quantum mechanics, because the electrostatic and electrodynamics interactions that determine the behavior of atoms and molecules are of conservative nature. It is also one of the few systems in quantum mechanics for which exact analytical solution is known.

**Hamiltonian, energy and eigenfunctions**

As we have studied above, the potential of a system describing simple harmonic motion can be calculated through equation 10, where a particle of mass "m" is subjected to a quadratic potential.

At the quantum level, the Hamiltonian must be defined for the particle. This is an operator whose eigenvalues gives the observable "energy". Thus, the Hamiltonian of the particle will be:

$$\frac{1}{2}k\hat{x}^2 = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2 x^2 \ (13)$$

Where we have used to relationship between $k$ and $w$ in Eq.(3). Notice that the Hamiltonian is composed of kinetic and potential energy terms. Also:

$x$ corresponds to the operator position $(x = \hat{x})$
$p$ is the linear moment operator, defined as:

$$\hat{p} = -i\hbar\frac{d}{dx} \ (12)$$

The time independent Schrödinguer equation is:

$$\hat{H} \parallel \psi \parallel = E \parallel \psi \parallel (13)$$

For the HO becomes in equation 14:

$$-\frac{\hbar}{2m}\frac{d^2\psi(x)}{dx^2} + \frac{1}{2}mw^2x^2\psi(x) - E\psi(x) = 0 \ (14)$$

It is convenient use non-dimensionalization in order to simplify the above equation. To do this, we avail of the fact that the harmonic oscillator has natural scales of energy, expressed in hω and of length, expressed in $\sqrt{\dfrac{h}{m\omega}}$

Furthermore, $|\psi(x)|^2$ represents the probability density, which is dimensionless when integrated over x, therefore, $|\psi(x)|^2$ has inverse length units. Therefore, the equation must be rewritten as a function of a non-dimensional variable, where the following relationship is established:

$$\bar{x} \equiv \frac{x}{x_c} \ (15)$$

Where $x_c$ which will be set afterwards corresponds to a natural system length. This gives the dimensionless wave function:

$$\psi(x) = \psi(\bar{x}x_c) = \psi(x(x_c)) = \bar{\psi}(\bar{x}) \ (16)$$

Then the differential equation is as follows:

$$\left(-\frac{-\hbar^2}{2m}\frac{1}{x_c^2}\frac{d^2}{d\bar{x}^2} + \frac{1}{2}m\omega^2 x_c^2\bar{x}^2\right)\bar{\psi}(\bar{x}) = E\bar{\psi}(\bar{x}) \ (17)$$

This equation is readjusted in order to further simplify the equation:

$$\left(-\frac{d^2}{d\bar{x}^2} + \frac{m^2\omega^2 x_c^4}{\bar{h}^2}\bar{x}^2\right)\bar{\psi}(\bar{x}) = \frac{2mx_c^2 E}{h^2}\bar{\psi}(\bar{x}) \ (18)$$

The coefficient of $x^2$ in the potential term can be simplified by imposing:

$$\frac{m^2\omega^2 \bar{x}_c^4}{\bar{h}^2} = 1 \ (19)$$

Which gives the natural length scales of the system:

$$x_c = \sqrt{\frac{\hbar}{m\omega}} \ (20)$$

Finally, the non-dimensional equation is as follows:

$$(-\frac{d^2}{d\bar{x}^2} + \bar{x}^2)\bar{\psi}(\bar{x}) = \bar{E}\bar{\psi}(\bar{x}) \text{ (21)}$$

Where it is established:

$$E \equiv \frac{\hbar\omega}{2}\bar{E} \text{ (22)}$$

If we look at equation 21, we can see that the term in front of $\bar{E}$ corresponds to the energy of the harmonic oscillator. The equation can then be rearranged:

$$\frac{\hbar\omega}{2}(-\frac{d^2}{d\bar{x}^2} + \bar{x}^2)\bar{\psi}(\bar{x}) = E\bar{\psi}(\bar{x}) \text{ (23)}$$

The Hamiltonian of equation 24 corresponds to:

$$H = -\frac{1}{2}\frac{d^2}{dx^2} + \frac{1}{2}x^2 \text{ (24)}$$

To solve equation 24, the allowed energies and their respective wave functions must be found. These functions need to be normalized and symmetrical with respect to x=0. This ensures that the probability density will be finite within the range of $-\infty$ y $\infty$.

The allowed energies as shown elementary Quantum Chemistry textbooks [5]:

$$E_n = (n + \frac{1}{2}) \text{ (25)}$$

$$n = 0, 1, 2, 3, ...$$

In turn, the corresponding wave functions for the energies described in equation 26 are shown below:

$$\psi_n(x) = \frac{1}{\sqrt{2^n n!}}\pi^{\frac{-1}{4}}exp(\frac{-x^2}{2})H_n(x) \text{ (26)}$$

$$n = 0, 1, 2, 3, ...$$

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Where:

  - The value of β is $\dfrac{1}{x_c}$

  - $N_n$ corresponds to the normalization constant

  - $H_n$ is a grade-n polynomial called the Hermite polynomial

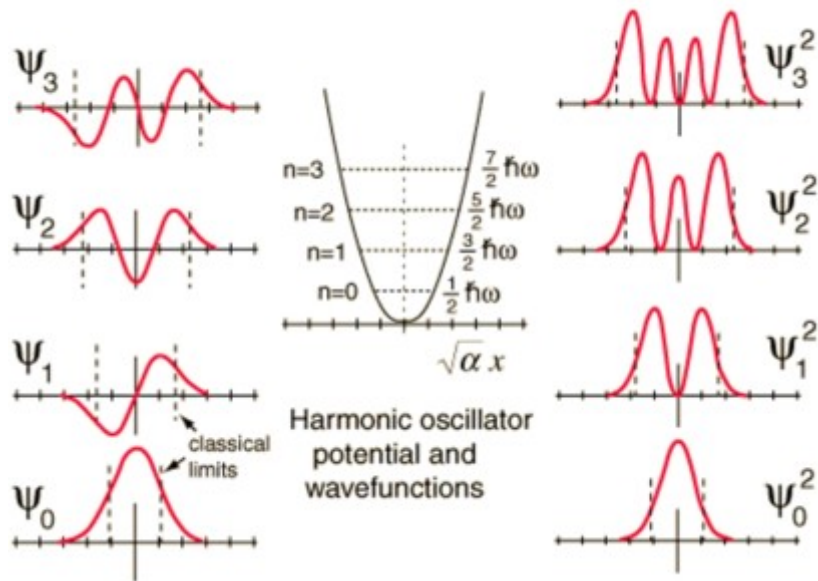Finally, figure 3 shows the first four wave functions of the Quantum Harmonic Oscillator [6]:



Figure 3. First four wave functions of the Quantum Harmonic Oscillator

# Difference between classical and quantum harmonic oscillator

The solutions of Eq.(7) and (21) reveal significant differences, which evidence the different behavior of classical and quantum regimen.

The first difference that must be treated is the energy. In the case of the classical harmonic oscillator, there are no forbidden energies, all the energies within the range described above are allowed. On the other hand, in the case of the Quantum Harmonic Oscillator, the energy levels are quantized, so there are allowed and forbidden energies.

The second difference to be dealt with is where the particle can be found. At the classical level, the particle will be in the range described above, between the limit being the length of the spring. At a quantum level, however, the particle is capable of exceeding the amplitude $A$ by means of the tunnel effect, allowing it to be found outside the range of the spring length.

Finally, we have discussed where the particle can be found, so the next step is to argue where it is most likely to be found. In both cases, the system can be solved by a purely statistical study. The mass to oscillate from to must pass through the point of equilibrium, which is at x=0. It is the same in the opposite direction, so the particle is twice as likely to be at the point of equilibrium as at the ends. At the quantum level, as shown in figure 3, at the ground state level, the particle has a correlation with the classical level and is at the point of equilibrium. However, we have different energy levels in QHO, being the probability of find the particle different in every energy level, in contrast to HO.

# 2. The Polynomial Method

As we said before, we would like to solve Schrödinguer equation for the quantum harmonic oscillator. For that, we must calculate the eigenstates with their respective eigenvalues. So, we can get this purpose through many ways. The first method we are going to apply is an algebraic method, called Polynomial method. [7]

From Eq.(23), the non-dimensional Schrödinguer equation of the QHO is:

$$\frac{-1}{2}\psi'' + \frac{1}{2}x^2\psi = E\psi \quad (27)$$

$$\psi'' + (2E - x^2)\psi = 0 \quad (28)$$

The associated boundary conditions are $\psi(\infty) = \psi(-\infty) = 0$. The wave function is integrable.

The idea behind the Polynomial method is that we can express any $\psi$ as a infinite length polynomial. This is in principle unpractical because we cannot handly infinite series, but under certain conditions it becomes viable to consider a finite expansion. (Because we can't solve an equation composed for infinite terms of x. Therefore, we must to deal with the equation and find out a finite length polynomial, which will be our problem solution.) So, as we mentioned before, we are going to express $\psi$ as a infinite length polynomial and the goal is to determine de coefficients $a_1$, $a_2$ ... that make $\psi$ fulfill Eq.(28). We calculate its respective first and second derivatives:

$$\psi = a_0 + a_1 x + a_2 x^2 + a_3 x^3 + a_4 x^4 + a_5 x^5 + a_6 x^6 + ... \,(29)$$

$$\psi' = a_1 + 2a_2 x + 3a_3 x^2 + 4a_4 x^3 + 5a_5 x^4 + 6a_6 x^5 + ... \,(30)$$

$$\psi'' = 2a_2 + 6a_3 x + 12a_4 x^2 + 20a_5 x^3 + 30a_6 x^4 + ... \,(31)$$

After that, we can substitute in the equation 28, and we have:

$$2a_2 + 6a_3 x + 12a_4 x^2 + 20a_5 x^3 + 30a_6 x^4 + ...$$
$$+(2E - x^2)a_0 + (2E - x^2)a_1 x + (2E - x^2)a_2 x^2 + (2E - x^2)a_3 x^3 + (2E - x^2)a_4 x^4 \quad (32)$$
$$+(2E - x^2)a_5 x^5 + a_6 x^6 + ... = 0$$

There are a lot of terms and it may be quite hard to find out any way to solve the equation. Therefore, we are going to group equation 32 according to the power of x:

$$(2Ea_0 + 2a_2) + (2Ea_1 + 6a_3)x + (2Ea_2 + 12a_4 - a_0)x^2 + (2Ea_3 + 20a_5 - a_1)x^3 + \quad (33)$$
$$(2Ea_4 + 32a_5 - a_2)x^4 + ... = 0$$

At this moment, we have infinite terms and for the equations 33 to hold for any value of x each of them must individually equal zero. Then:

$$2Ea_0 + 2a_2 = 0 \quad (34)$$
$$2Ea_1 + 6a_3 = 0 \quad (35)$$
$$2Ea_2 + 12a_4 - a_0 = 0 \quad (36)$$
$$2Ea_3 + 20a_5 - a_1 = 0 \quad (37)$$
$$2Ea_4 + 30a_6 - a_2 = 0 \quad (38)$$
$$\vdots$$

If we look at the our proposed solution, one may feel that there isn't a practical solution. The reason of that is because all the even $a$ depends of $a_0$ and, obviously, all the odd $a$ depends of $a_1$. We must make a choice of the values of $E, a_0, a_1$ and expect that the polynomial will be finite at some $x$ power. Unfortunately, there is no chance to get that, because any of the values that we attribute, the polynomial will tend to an infinite series.

As we said before, we can't find a direct solution for equation 28. However, if we analyze the equation and the method to solve it, we will notice that we can succeed if we rewrite the guess function $\psi$ as the product of the polynomial and a Gaussian function:

$$\psi = exp(\frac{-x^2}{2})f(x) \quad (39)$$

Then: the derivatives become:

$$\psi' = (-x)exp(\frac{-x^2}{2})f(x) + exp(\frac{-x^2}{2})f'(x) \quad (40)$$

$$\psi'' = (x^2 - 1)exp(\frac{-x^2}{2})f(x) + (-2x)exp(\frac{-x^2}{2})f'(x) + exp(\frac{-x^2}{2})f''(x) \quad (41)$$

We apply common factor in order to simplify 41 equation:

$$\psi'' = [exp(\frac{-x^2}{2})](f''(x) + (-2x)f'(x) + (x^2 - 1)f(x)) = 0 \quad (42)$$

After substituting 39, 40 and 42 in 28, we will obtain:

$$[exp(\frac{-x^2}{2})](f''(x) + (-2x)f'(x) + (2E - 1)f(x)) = 0 \quad (43)$$

To find the roots of Eq.(43), we focus on the polynomial, because an exponential function can never equal zero. Therefore:

$$f''(x) + (-2x)f'(x) + (2E - 1)f(x) = 0 \quad (44)$$

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In order to simplify, we are going to define $2n = 2E - 1$. Then, Eq.(44) becomes:

$$f''(x) + (-2x)f'(x) + (2n)f(x) = 0 \quad (45)$$

Eq.(45) is Hermitte's differential equation, which is known to be susceptible of being solved through the polynomial method, so, we are going to follow exactly the same steps as before.

$$f(x) = a_0 + a_1 x + a_2 x^2 + a_3 x^3 + a_4 x^4 + a_5 x^5 + a_6 x^6 + ... \quad (46)$$

$$f(x)' = a_1 + 2a_2 x + 3a_3 x^2 + 4a_4 x^3 + 5a_5 x^4 + 6a_6 x^5 + ... \quad (47)$$

$$f(x)'' = 2a_2 + 6a_3 x + 12a_4 x^2 + 20a_5 x^3 + 30a_6 x^4 + ... \quad (48)$$

Then, we can substitute equation 34, 34.1 and 34.2 in the equation 33.2, and we will have:

$$
\begin{aligned}
2a_2 + 6a_3 x + 12a_4 x^2 + 20a_5 x^3 + 30a_6 x^4 + ... \\
-2xa_1 - 4a_2 x^2 - 6a_3 x^3 - 8a_4 x^4 - 10a_5 x^5 - 12a_6 x^6 + ... \\
2na_0 + 2na_1 x + 2na_2 x^2 + 2na_3 x^3 + 2na_4 x^4 + 2na_5 x^5 + 2na_6 x^6 + ... = 0 \quad (49)
\end{aligned}
$$

After that, we are going to group equation 35 according to the power of x:

$$
\begin{aligned}
(2a_2 + 2na_0) + (6a_3 + 2(n-1)a_1)x + (12a_4 + 2(n-2)a_2)x^2 \\
+(20a_5 + 2(n-3)a_3)x^3 + (30a_6 + 2(n-4)a_4)x^4 + ... = 0 \quad (50)
\end{aligned}
$$

We equal all of the terms to zero in order to find out a solution for the coefficients:

$$
\begin{aligned}
2na_0 + 2a_2 = 0 \quad (51) \\
6a_3 + 2(n-1)a_1 = 0 \quad (52) \\
12a_4 + 2(n-2)a_2 = 0 \quad (53) \\
20a_5 + 2(n-3)a_3 = 0 \quad (54) \\
30a_6 + 2(n-4)a_4 = 0 \quad (55) \\
\vdots
\end{aligned}
$$

If we clear the coefficients, we will obtain:

$$a_2 = -na_0 \quad (56)$$
$$a_3 = \frac{(1-n)a_1}{3} \quad (57)$$
$$a_4 = \frac{(2-n)a_2}{6} \quad (58)$$
$$a_5 = \frac{(3-n)a_3}{10} \quad (59)$$
$$a_6 = \frac{(4-n)a_4}{15} \quad (60)$$
$$\vdots$$

Ultimately, all coefficients depends on n, $a_0$ and $a_1$. Basically, the idea is to set values that we can obtain a finite polynomial. For this to occur, on the one hand, we set increasing integer values for $n$, from 0 to the value we would like to get. On the other hand, we set $a_0 = 1$ and $a_1 = 0$ for even $n$ and vice versa for the odd $n$. The reason of the solution is because all even and odd $a$ coefficients are directly related with his previous, so, once a coefficient vanishes, all his relatives will vanish as well.

In the next table, we show the first five $n$ values with his respective $a_0, a_1$.

Table 1. First six energies and Hermite polynomials

| n | $a_0$ | $a_1$ | E | f |
|---|---|---|---|---|
| 0 | 1 | 0 | $\frac{1}{2}$ | 1 |
| 1 | 0 | 1 | $\frac{3}{2}$ | $x$ |
| 2 | 1 | 0 | $\frac{5}{2}$ | $1 - 2x^2$ |
| 3 | 0 | 1 | $\frac{7}{2}$ | $x - \frac{2}{3}x^3$ |
| 4 | 1 | 0 | $\frac{9}{2}$ | $1 - 4x^2 + \frac{4}{3}x^4$ |
| 5 | 0 | 1 | $\frac{11}{2}$ | $x - \frac{4}{3}x^3 + \frac{4}{15}x^5$ |

Where we have used the relationship:

$$2n = 2E - 1 \longrightarrow E = n + \frac{1}{2} \quad (61)$$

And:

$$f = a_0 + a_1 x + a_2 x^2 + a_3 x^3 + a_4 x^4 + a_5 x^5 + a_6 x^6 + ... \quad (62)$$

The polynomial in table 1 are known as Hermite polynomials

Once we have obtained the functions, we can readily obtain HO eigenfunctions, $\psi$, through equation 39 and the associated eigenvalues.

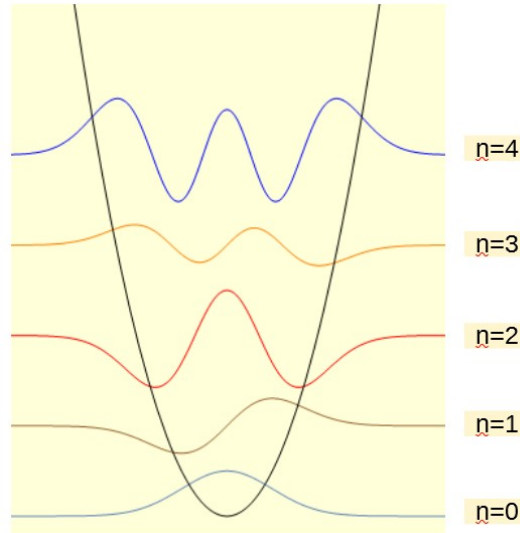We can represent the first five solutions:



Figure 4. First five wave functions of the Quantum Harmonic Oscillator through polynomial method.

One can see that the figure we have obtained matches perfectly the textbook solution depicted in Chapter 1, figure 3.

Finally, we must check if our proposed resolution fulfills boundary conditions. In this case, the particle is located in a potential where the limits are 0 and L. Both sides of the potential tend to $\infty$ and the probability to find the particle in these limits must equal zero, so the wave function must be zero. The wave function can be expressed as:

$$\psi(x) = \frac{H}{exp(\frac{x^2}{2})} \quad (64)$$

It is evident that both numerator and denominator tend to infinity if $x \to \infty$. To solve this undetermination apply L'Hopital's rule. It is defined as: [8]

$$\lim_{x \to c} = \frac{f(x)}{g(x)} = \lim_{x \to c} \frac{f'(x)}{g'(x)} \quad (65)$$

From Eqs. (29) and (39), we calculate the derivatives

$$f'(x) = a_1 x + 2a_2 x + 3a_3 x^2 + ... + na_n x^{n-1} \quad (66)$$
$$g'(x) = xe^{\frac{x^2}{2}} \quad (67)$$

Again, we realize $\dfrac{f'}{g'}$ is undetermined at $x \to \infty$, because both functions continue depending of $x$. However, In equation 39 the power of $x$ decreases one grade while in equation 39 keeps constant in the first derivatives. So, we can continue applying L'Hopital's rule in order to study how the equation 39 changes:

$$f''(x) = 2a_2 + 6a_3 x + n(n-1)a_n x^{n-2} \quad (68)$$
$$f'''(x) = 6a_3 + 24a_4 x + 60a_5 x^3 + n(n-1)(n-2)a_n x^{n-3} \quad (69)$$

To further analysis, we are going to focus only on the polynomial of the highest degree, because tt is the most restrictive term to solve the undetermination. From Eq.(66), (68), and (69), one can infer the general expression of the derivative:

$$f^n(x) = \prod_{i=0}^{k-1} (n-i)x^{n-k} \quad (70)$$

Clearly, when $n = k$ the polynomial derivative becomes constant. So:

$$\lim_{x \to \infty} f^k(x) = \prod_{i=0}^{k-1} (k-i) \quad (71)$$

Once we have studied the equation 29, we are going to study equation 39. First derivative has been calculated, equation 67, so, we must calculate second and third derivatives:

$$g''(x) = (x^2 + 1)e^{\frac{x^2}{2}} \quad (72)$$
$$g'''(x) = (x^3 + 3x)e^{\frac{x^2}{2}} \quad (73)$$

As we can see, the power of x is increasing when we calculate second and third derivative, so, that means $g^k(x)$ tend to $\infty$.

$$\lim_{x \to \infty} g^k(x) = \infty \quad (74)$$

After studying equation 37, we can conclude that:

$$\lim_{x \to \infty} \psi(x) = \lim_{x \to \infty} \frac{f}{exp(\frac{x^2}{2})} = \lim_{x \to \infty} \frac{\prod_{i=0}^{k-1}(k-i)}{g^k(x)} = \frac{cte}{\infty} = 0 \quad (75)$$

This means that our proposed resolution accomplish boundary conditions and the polynomial method is a practicable way to solve Schrödinguer equation for the quantum harmonic oscillator.

# 3. The Factorization Method

Another way to solve Schrödinguer equation for the quantum harmonic oscillator is the factorization method [9]. This is an algebraic method which let us solve Schrödinguer equation through ladder operators. First, we must define the energy operator, Hamiltonian:

$$\hat{H} = \frac{1}{2}(x^2 - \frac{d^2}{dx^2}) \quad (76)$$

The Hamiltonian is reminiscent of the difference of two squares. This is just an idea, because we are working with operators, no with numbers, so we must to study their rule commutations in order to establish how far we can arrive.

$$(x - \frac{d}{dx})(x + \frac{d}{dx}) = (x^2 + x\frac{d}{dx} - x\frac{d}{dx} - \frac{d^2}{dx^2} - 1) = (x^2 - \frac{d^2}{dx^2} - 1) \quad (77)$$

As we can see, our idea can work properly because we obtain a similar expression of the equation 76. So, according to the above expression, the following step will be to define ladder operators, where $b^+$ is the raising operator and $b$ is the lowering operator. In addition to that, we are going to introduce a constant, $\frac{1}{\sqrt{2}}$ ,with the aim to simplify the equation 77.

$$b^+ = \frac{1}{\sqrt{2}}(x - \frac{d}{dx}) \quad (78)$$

$$b = \frac{1}{\sqrt{2}}(x + \frac{d}{dx}) \quad (79)$$

Once ladder operators are defined, we are going to multiply them and try to find a new Hamiltonian expression in function of them.

$$b^+b = [\frac{1}{\sqrt{2}}(x - \frac{d}{dx})][\frac{1}{\sqrt{2}}(x + \frac{d}{dx})] \quad (80)$$

$$b^+b = \frac{1}{2}(x^2 + x\frac{d}{dx} - x\frac{d}{dx} - \frac{d^2}{dx^2} - 1) \quad (81)$$

$$b^+b = \frac{1}{2}(x^2 - \frac{d^2}{dx^2} - 1) \quad (82)$$

$$\frac{1}{2}(x^2 - \frac{d^2}{dx^2}) = b^+b + \frac{1}{2} \quad (83)$$

It could be interesting to solve $bb^+$ as well, in order to ease our future work:

$$bb^+ = [\frac{1}{\sqrt{2}}(x + \frac{d}{dx})][\frac{1}{\sqrt{2}}(x - \frac{d}{dx})] \quad (84)$$

$$bb^+ = \frac{1}{2}(x^2 + x\frac{d}{dx} - x\frac{d}{dx} - \frac{d^2}{dx^2} + 1) \quad (85)$$

$$bb^+ = \frac{1}{2}(x^2 - \frac{d^2}{dx^2} + 1) \quad (86)$$

From Eq.(83), it is clear we can rewrite the Hamiltonian as:

$$\hat{H} = b^+b + \frac{1}{2} \quad (87)$$

Now, it's time to understand how these operators commute. First, we will study commutation between $b^+$ and $b$:

$$[b, b^+] = bb^+ - b^+b \quad (88)$$

$$bb^+ = \frac{1}{2}(x^2 - \frac{d^2}{dx^2} + 1) \quad (89)$$

Collecting equation 88 and 89:

$$[b, b^+] = \frac{1}{2}(x^2 - \frac{d^2}{dx^2} + 1) - \frac{1}{2}(x^2 - \frac{d^2}{dx^2} - 1) = \frac{1}{2} + \frac{1}{2} = 1 \quad (90)$$

$$[b, b^+] = 1 \quad (91)$$

It could be interesting define equation 93

$$bb^+ - b^+b = 1 \quad (92)$$

$$bb^+ = 1 + b^+b \quad (93)$$

Now, we are going to study commutation between $\hat{H}$ and $b$:

$$[\hat{H}.b] = \hat{H}b - b\hat{H} \quad (94)$$

$$[\hat{H}.b] = (bb^+ + \frac{1}{2})b - b(bb^+ + \frac{1}{2}) \quad (95)$$

$$[\hat{H}.b] = (bb^+b + \frac{1}{2}b) - (bbb^+ + \frac{1}{2}b) \quad (96)$$

$$[\hat{H}.b] = (bb^+b) - (bbb^+) \quad (97)$$

$$[\hat{H}.b] = bb^+b - b(1 + b^+b) \quad (98)$$

$$[\hat{H}.b] = (bb^+b) - (b + bb^+b) \quad (99)$$

$$[\hat{H}.b] = -b \quad (100)$$

Finally, $\hat{H}$ and $b^+$ will commutate as:

$$[\hat{H}.b^+] = \hat{H}b^+ - b^+\hat{H} \quad (101)$$

$$[\hat{H}.b^+] = (bb^+ + \frac{1}{2})b^+ - b^+(bb^+ + \frac{1}{2}) \quad (102)$$

$$[\hat{H}.b^+] = (bb^+b^+ + \frac{1}{2}b^+) - (b^+bb^+ + \frac{1}{2}b^+) \quad (103)$$

$$[\hat{H}.b^+] = (bb^+b^+) - (b^+bb^+) \quad (104)$$

$$[\hat{H}.b^+] = (1 + b^+b)b^+ - (b^+bb^+) \quad (105)$$

$$[\hat{H}.b^+] = (b^+ + b^+bb^+) - (b^+bb^+) \quad (106)$$

$$[\hat{H}.b^+] = b^+ \quad (107)$$

Here below we sum up the three commutations:

$$[b, b^+] = 1 \quad (108)$$

$$[\hat{H}.b] = -b \quad (109)$$

$$[\hat{H}.b^+] = b^+ \quad (110)$$

Now, it's time to study how will influence our operators on the Schrödinguer equation. We shall realize when we apply raising operator to $\psi_v$, we will obtain $\psi_{v+1}$, with a quantum number of one greater unity. On the other hand, the application of the lowering operator to $\psi_v$ would lead us to $\psi_{v-1}$, with a quantum number of one lower unity. This can be seen by letting the Hamiltonian set upon the wave functions $b\psi$ and $b^+\psi$.

$$\hat{H}(b\psi) = (\hat{H}b)\psi \quad (111)$$

$$\hat{H}(b\psi) = ([\hat{H}, b] - b\hat{H})\psi \quad (112)$$

$$\hat{H}(b\psi) = (\hat{H}b - b)\psi \quad (113)$$

$$\hat{H}(b\psi) = (E_n b - b)\psi \quad (114)$$

$$\hat{H}(b\psi) = (E_n - 1)(b\psi) \quad (115)$$

And with the raising operator will be:

$$\hat{H}(b^+\psi) = (\hat{H}b^+)\psi \quad (116)$$

$$\hat{H}(b^+\psi) = ([\hat{H}, b^+] - b^+\hat{H})\psi \quad (117)$$

$$\hat{H}(b^+\psi) = (\hat{H}b^+ + b^+)\psi \quad (118)$$

$$\hat{H}(b^+\psi) = (E_n b^+ + b^+)\psi \quad (119)$$

$$\hat{H}(b^+\psi) = (E_n + 1)(b^+\psi) \quad (120)$$

This confirms that the application of the ladder operators to oscillator eigenfunctions lead us to obtain $\psi_{v+1}$ and $\psi_{v-1}$, according to the operator that we apply.

By correspondence with the HO solutions, see the table 1, we infer:

$$b\psi \approx \psi_{v-1} \quad (121)$$

$$b^+\psi \approx \psi_{v+1} \quad (122)$$

We wish to determine the constant of proportionality:

$$b\psi = k\psi_{v-1} \quad (123)$$

$$b^+\psi = k^+\psi_{v+1} \quad (124)$$

Once we propose equations 123 and 124, we must think a way to calculate the $k$ and $k^+$ value. This looks like pretty hard but we can get these values through calculating expectations values of the ladder operators. The procedure will be as:

$$< \psi_v \mid b^+ b \mid \psi_v >=< \psi_v \mid \hat{H} - \frac{1}{2} \mid \psi_v >=< \psi_v \mid \hat{E}_v - \frac{1}{2} \mid \psi_v > \quad (125)$$

As $E_v = v + \frac{1}{2}$:

$$< \psi_v \mid v + \frac{1}{2} - \frac{1}{2} \mid \psi_v >=< \psi_v \mid v \mid \psi_v = v > \quad (126)$$

Therefore:

$$< \psi_v \mid b^+ b \mid \psi_v >= v \quad (127)$$

As $b^+ b$ are Hermitian adjoints, we can apply some commutation rules in order to estimate $k$ value:

$$< \psi_v \mid b^+ b \mid \psi_v > \quad (128)$$

$$< [\psi_v b^+] \mid [b \psi_v] > \quad (129)$$

$$< [b^+ \psi_v^*] \mid [b \psi_v] > \quad (130)$$

Collecting with equation 123:

$$< [k \psi_{v-1}^*] \mid [k \psi_{v-1}] > \quad (131)$$

$$k^2 < (\psi_{v-1}^* \mid \psi_{v-1}) > \quad (132)$$

$$< \psi_v \mid b^+ b \mid \psi_v >= k^2 \quad (133)$$

So, after calculating expectation value of $b^+ b$, we find a mathematical relation between $k$ and the quantum number, $v$. Now, we can express k in function of the quantum number, $v$.

$$< \psi_v \mid b^+ b \mid \psi_v >= v = k^2 \quad (134)$$

$$k = \sqrt{v} \quad (135)$$

Then, collecting equation 123 and 135, we will obtain equation 136:

$$b\psi = \sqrt{v}\psi_{v-1} \quad (136)$$

Now, it's time to repeat the above process in order to estimate $k^+$ value. Once again, we take advantage of the expectation value to get this constant.

$$< \psi_v \mid bb^+ \mid \psi_v > \quad (137)$$

$$< \psi_v \mid \hat{H} + \frac{1}{2} \mid \psi_v > \quad (138)$$

$$< \psi_v \mid \hat{E}_v + \frac{1}{2} \mid \psi_v > \quad (139)$$

As $E_v = v + \dfrac{1}{2}$

$$< \psi_v \mid v + 1 \mid \psi_v > \quad (140)$$

$$< \psi \mid v + 1 \mid \psi_v >= v + 1 \quad (141)$$

$$< \psi_v \mid bb^+ \mid \psi_v >= v + 1 \quad (142)$$

As $bb^+$ are Hermitian adjoints, we can apply some commutation rules in order to estimate $k^+$ value:

$$< \psi_v \mid bb^+ \mid \psi_v > \quad (143)$$

$$< [\psi_v b][b^+ \psi_v] > \quad (144)$$

$$< [b^+ \psi_v^*][b^+ \psi_v] > \quad (145)$$

Collecting with equation 124:

$$< [(k^+)^2 \psi_{v+1}^*][(k^+)^2 \psi_{v+1}] > \quad (146)$$

$$(k^+)^2 < (\psi_{v+1}^* \psi_{v+1}) > \quad (147)$$

$$< \psi_v \mid bb^+ \mid \psi_v >= (k^+)^2 \quad (148)$$

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After calculating expectation value of $bb^+$, as the same way we did in $b^+b$, we find a mathematical relation to express $k^+$ in function of the quantum number, $v$:

$$< \psi_v \mid bb^+ \mid \psi_v >= v + 1 = (k^+)^2 \quad (149)$$

$$k^+ = \sqrt{v + 1} \quad (150)$$

Collecting equations 124 and 150, we will obtain:

$$b^+ \psi_v = \sqrt{v + 1}\psi_{v+1} \quad (151)$$

After getting equation 151, we can easily obtain a general expression fot the HO wave functions. To begin, we must clear $\psi_{v+1}$

$$\psi_{v+1} = \frac{1}{\sqrt{v + 1}}b^+\psi_v \quad (152)$$

The following step will be assign value numbers to $v$. We must remember that energy is quantized, so, $v$ will raise only in positive enter numbers, from 0 to $\infty$ . The procedure would be as for $v = 0$:

$$\psi_{0+1} = \frac{1}{\sqrt{0 + 1}}b^+\psi_0 \quad (153)$$

$$\psi_1 = \frac{1}{\sqrt{1}}b^+\psi_0 \quad (154)$$

The eigenfunction for $v = 1$ would be:

$$\psi_{1+1} = \frac{1}{\sqrt{1 + 1}}b^+\psi_1 \quad (155)$$

$$\psi_2 = \frac{1}{\sqrt{2}}b^+\psi_1 \quad (156)$$

$$\psi_2 = \frac{1}{\sqrt{2}}b^+[\frac{1}{\sqrt{1}}b^+\psi_0] \quad (157)$$

$$\psi_2 = \frac{1}{\sqrt{2}}\frac{1}{\sqrt{1}}(b^+)^2\psi_0 \quad (158)$$

And for $v = 2$ would be:

$$\psi_{2+1} = \frac{1}{\sqrt{2+1}} b^+ \psi_2 \quad (159)$$

$$\psi_3 = \frac{1}{\sqrt{3}} b^+ \psi_2 \quad (160)$$

$$\psi_3 = \frac{1}{\sqrt{3}} b^+ [\frac{1}{\sqrt{2}} \frac{1}{\sqrt{1}} (b^+)^2 \psi_0] \quad (161)$$

$$\psi_3 = \frac{1}{\sqrt{3}} \frac{1}{\sqrt{2}} \frac{1}{\sqrt{1}} (b^+)^3 \psi_0 \quad (162)$$

The first three eigenfunction resolution suggest us the equation 163, where we express any eigenfunction in function of the quantum number, $v$. The value of $\psi_0$ will be estimate in the following step, in equation 168. In addition to that, we know $b^+$ value, which is the raising operator, expressed in equation 78.

$$\psi_v = \frac{1}{\sqrt{v!}} (b^+)^v \psi_0 \quad (163)$$

As we said before, the following step will be to calculate the ground state formula, $\psi_0$, through applying it lowering operator. The reason of that is we can't reduce the quantum number of the ground state, because this is zero. So, we are going to try to develop this idea:

$$b\psi_0 = 0 \quad (164)$$

$$(x + \frac{d}{dx})\psi_0 = 0 \quad (165)$$

$$x\psi_0 + \frac{d}{dx}\psi_0 = 0 \quad (166)$$

$$\frac{d\psi_0}{\psi_0} = dx * (-x) \quad (167)$$

$$\psi_0 = exp(\frac{-x^2}{2}) \quad (168)$$

To follow our research, we are going to estimate ground state energy. We can get it through equation 71 and the procedure is explained below. Basically, as we tell before, when we apply lowering operator to the ground state eigenfunction, the result will be $0$, because we can get a quantum number lower than $0$. So, we are going to take advantatge of this:

$$\hat{H}\psi_0 = E_0\psi_0 \quad (169)$$

$$\hat{H}\psi_0 = (b^+b + \frac{1}{2})\psi_0 \quad (170)$$

$$\hat{H}\psi_0 = b^+b\psi_0 + \frac{1}{2}\psi_0 \quad (171)$$

As $b\psi_0 = 0$

$$\hat{H}\psi_0 = \frac{1}{2}\psi_0 \quad (172)$$

$$E_0 = \frac{1}{2} \quad (173)$$

Well, the final step in our research, obviously, will be find the eigenfunctions and the eigenvalues associated, which are the energies for a given state. For this, we know when we apply raising operator to a eigenfunction, we will obtain the function with a quantum number with a greater unity. So, we are to apply it to the equation 174 and we will obtain the energy of the following eingenfunction, $E_1$.

$$\hat{H}(b^+\psi_v) = (E_v + 1)(b^+\psi_v) \quad (174)$$

Collecting equation 173 and 174, we obtain the following expression:

$$\hat{H}(b^+\psi_0) = (E_0 + 1)(b^+\psi_0) \quad (175)$$

$$\hat{H}(b^+\psi_0) = (\frac{1}{2} + 1)(b^+\psi_0) \quad (176)$$

$$\hat{H}(b^+\psi_0) = \frac{3}{2}(b^+\psi_0) \quad (177)$$

$$E_1 = \frac{3}{2} \quad (178)$$

We repeat the above procedure to calculate $E_2$, $E_3$ and $E_4$:

$$E_2 = \frac{5}{2} \quad (179)$$

$$E_3 = \frac{7}{2} \quad (180)$$

$$E_4 = \frac{9}{2} \quad (181)$$

As we can see, the application of the raising operator time and again let us obtain the energy that we wish. Of course, this energies quantized.

On the other hand, we notice that the above procedure let us estimate the value of the energy in function of quantum number as well. Generally, we can express the results obtained as:

$$\hat{H}(b^+\psi_v) = ((\frac{1}{2} + v) + 1)(b^+\psi_v) \quad (182)$$

The, the value of the energy for the quantum harmonic oscillator will be:

$$E_v = \frac{1}{2} + v \quad (183)$$

Now, it's time to calculate the eigenfunctions. The procedure will be the same to calculate the energies, we are going to apply the raising operator time and again to a eigenfunction in order to obtain the eigenfunction with a quantum number one unity greater. We need the following equations:

$$\psi_v = (b^+)^v \psi_0 \quad (184)$$

$$\psi_0 = C exp(\frac{-x^2}{2}) \quad (185)$$

$$b^+ = (x - \frac{d}{dx}) \quad (186)$$

Collecting equation 184, 185 and 186:

$$\psi_v = (x - \frac{d}{dx})^v C exp(\frac{-x^2}{2}) \quad (187)$$

First, we calculate $\psi_1$:

$$\psi_0(b^+) = \psi_1 = (x - \frac{d}{dx}) C exp(\frac{-x^2}{2}) \quad (188)$$

$$\psi_1 = (2x) C exp(\frac{-x^2}{2}) \quad (189)$$

Now, time to calculate $\psi_2$:

$$\psi_1(b^+) = \psi_2 = (x - \frac{d}{dx})(2x) C exp(\frac{-x^2}{2}) \quad (190)$$

$$\psi_2 = (4x^2 - 2) C exp(\frac{-x^2}{2}) \quad (191)$$

And to calculate $\psi_3$:

$$\psi_2(b^+) = \psi_3 = (x - \frac{d}{dx})(4x^2 - 2) C exp(\frac{-x^2}{2}) \quad (192)$$

$$\psi_3 = (8x^3 - 12x) C exp(\frac{-x^2}{2}) \quad (193)$$

Finally, we estimate $\psi_4$:

$$\psi_3(b^+) = \psi_4 = (x - \frac{d}{dx})(4x^2 - 2) C exp(\frac{-x^2}{2}) \quad (194)$$

$$\psi_4 = (16x^4 - 48x^2 + 12) C exp(\frac{-x^2}{2}) \quad (195)$$

In equation 196, we can see the general expression for the eigenfunctions calculated, where $H_v$ are the Hermite polynomials, which take a different value in functions of the quantum number:

$$\psi_v = H_v C exp(\frac{-x^2}{2}) \quad (196)$$

We can sum up the results obtained in the following table:

Table 2. First five energies and Hermite polynomials

| $v$ | $E_v$ | $H_v$ |
|---|---|---|
| 0 | $\frac{1}{2}$ | $1$ |
| 1 | $\frac{3}{2}$ | $x$ |
| 2 | $\frac{5}{2}$ | $1 - 2x^2$ |
| 3 | $\frac{7}{2}$ | $x - \frac{2}{3}x^3$ |
| 4 | $\frac{9}{2}$ | $1 - 4x^2 + \frac{4}{3}x^4$ |

The energies and functions obtained by the factorization method correspond to the results obtained by the polynomial method, table 1.

# 4. The finite differences

## Method explication

The difference finite approximation [10] is a simple and versatile numerical method used to solve differential equations. This method is able to replace the integration of the differential equation by the resolution of a system composed by some linear equations. We can do this substituting the continuous space to a discrete space with finite points. In addition to that, it has got many applications in different fields, such as chemical engineering, mathematics, physics and, of course, quantum chemistry.

In order to begin to study our method, we will define $f(x)$ as a function which only depends of $x$, and we can express its derivative centered on one point of as:

$$f'(x) = \lim_{x \to \infty} \frac{f(x+\delta) - f(x-\delta)}{2\delta} \quad (197)$$

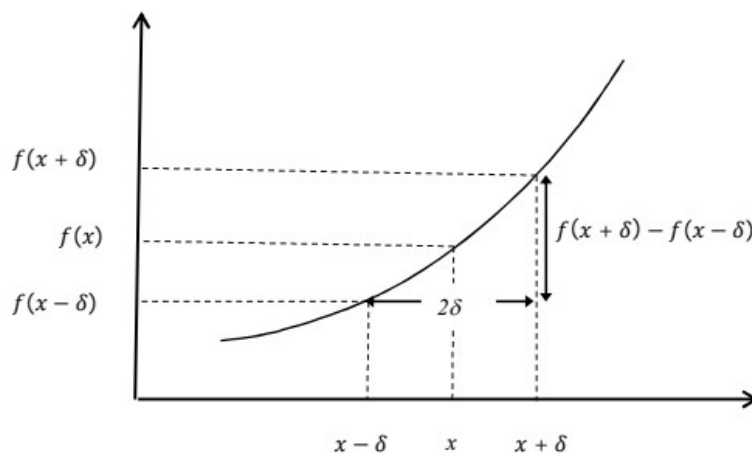Graphically, we can visualize equation 197 as shown in the figure 5:



Figure 5. Geometrical interpretation of a point centered 3-point derivative

Where $\delta$ is an infinitesimally small change

Nevertheless, we are going to approach $\delta$ as a finite (yet small) distance. Therefore, the first derivative will take the following value:

$$f'(x) \simeq \frac{f(x+\delta) - f(x-\delta)}{2\delta} \quad (198)$$

In order to find out the value of the second derivative, we are going to develop the functions through Taylor series. The mathematical procedure will be the following:

$$f(x+\delta) = f(x) + \delta f'(x) + \frac{\delta^2 f''(x)}{2} \quad (199)$$

$$f(x-\delta) = f(x) - \delta f'(x) + \frac{\delta^2 f''(x)}{2} \quad (200)$$

Once we know the definitions, we can sum both Taylor series and will obtain the following result:

$$f(x+\delta) + f(x-\delta) = 2f(x) + \frac{2\delta^2 f''(x)}{2} \quad (201)$$

And finally, clearing the second derivative:

$$f''(x) = \frac{f(x+\delta) + f(x-\delta) - 2f(x)}{\delta^2} \quad (202)$$

In order to sum up, the first and second derivatives will be:

$$f'(x) = \frac{f(x+\delta) - f(x-\delta)}{2\delta} \quad (203) \qquad f''(x) = \frac{f(x+\delta) + f(x-\delta) - 2f(x)}{\delta^2} \quad (204)$$

To finalize the theory of the method, we are going to split *x* axis in such a way that the difference between two point is $\delta$. This will be as the following picture:
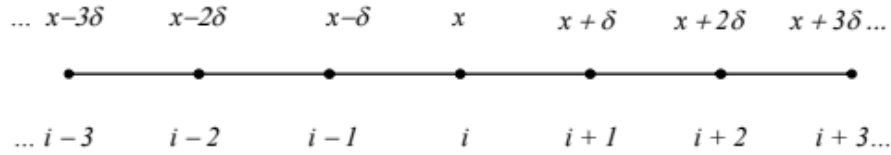


Figure 6. Discretization of the *x* space

Then, we can express the first and second derivative as:

$$f'(i) = \frac{f(i+1) - f(i-1)}{2\delta} \quad (205) \qquad f''(i) = \frac{f(i+1) + f(i-1) - 2f(i)}{\delta^2} \quad (206)$$

Where:

- $f(i)$ is the value of the function on the point $i$ of the split
- $f(i+1)$ is the value of the function on the next point
- $f(i-1)$ is the value of the function on the before point

## Discretization of the differential harmonic oscillator equation

Expressions 205 and 206 allow us to solve numerically any differential equation up to 2nd order. We shall illustrate how it can be used for the HO case.

The starting point is the non-dimensionalizated HO Schrodinguer equation, recall Eq. (24):

$$\frac{1}{2}(x^2 - \frac{d^2}{dx^2})\psi = E\psi \quad (207)$$

Now, to solve equation 207 through the difference finite method, we can combine it with equation 206 and we will obtain the following expression:

$$\frac{1}{2}(x^2\psi(i) - \frac{\psi(i+1) + \psi(i-1) - 2\psi(i)}{\delta^2}) = E\psi(i) \ (208)$$

We can develop equation 208 as the following way:

$$\frac{1}{2}x^2\psi(i) - \frac{1}{2\delta^2}\psi(i+1) - \frac{1}{2\delta^2}\psi(i-1) + \frac{2}{\delta^2}\psi(i) = E\psi(i) \ (209)$$

And collect all terms corresponding to the wave function, $\psi(i)$, at different points:

$$-\frac{1}{2\delta^2}\psi(i+1) - \frac{1}{2\delta^2}\psi(i-1) + \frac{x^2\delta^2 + 2}{2\delta^2}\psi(i) = E\psi(i) \ (210)$$

In order to simplify, we define the following coefficients:

$$A = \frac{1}{2\delta^2} \ (211) \qquad\qquad B(i) = \frac{x^2\delta^2 + 2}{2\delta^2} \ (212)$$

Then, equation 210 takes the form:

$$-A\psi(i+1) - A\psi(i-1) + B(i)\psi(i) = E\psi(i) \ \ (213)$$

Once we have obtained our discretizated equation, equation 213, we must convert it in a linear equation system and, finally, in a matrix structure. To get this goal, it's necessary to define some parameters.

For instance, the potential is defined in a range between x=$-\infty$ to x=$+\infty$ (we will explain in the following section how to deal with this range when we program with Mathematica). In addition to that, according to the theory above, we are going to split this range in $n$ points and $\delta$ will be the separation between two consecutive points. Then, we can define $\delta$ according to the above definitions:

$$\delta = \frac{L}{n} \ (214)$$

Where:

- L is the integration length
- n is the number of points which we are going to take

As we said before, we establish the potential is defined in a range of $x = -\infty$ to $x = \infty$. As L express the length of the potential, $-L = -\infty$ and $L = \infty$ will be definitions, but, we can't program this, because we would need infinite loop $(n = \infty)$. Then, the solution will be to define $L$ as a big number that represent this infinite. If we establish $L$ as a number not large enough, the wave length can't be represented properly, because we have established a border in a place where the wave functions should be non-zero

In addition to that, B is a function of $(i)$ and it has got the variable $x$, which is the position of the particle. This variable with determine the value of B and takes a specific value for every $i$. So, we must establish the link between $x$ and $i$. Well, in the first point, $i = 0$ and $x = -L$, according to the above paragraph, where we establish $L$ as the frontier. If we continue analyzing points, the difference between two consecutive $i$ is $\delta$, so, in the second point $(i = 1)$, $x$ will be $(-L) + \delta$. In the third $(i = 2)$, $(-L) + 2\delta$. Then, we can define $x_i = -L + (i * \delta)$.

Now, the following step will be to particularize some points of the equation 91. We must mention that we can't particularize the function in the extremes $(i = 0$ and $i = N)$. The reason of that is because we need the previous and the next points to particularize a specific point. In these cases, the points $\psi(-1)$ and $\psi(n+1)$ won't be in the range of $L$, respectively. We must remember that we define $L$ as a large number, creating a huge space that represent the $-\infty$ to $\infty$.

$$\text{i=1} \longrightarrow -A\psi(0) + B(1)\psi(1) - A\psi(2) = E\psi(1) \quad (215)$$

$$\text{i=2} \longrightarrow -A\psi(1) + B(2)\psi(2) - A\psi(3) = E\psi(2) \quad (216)$$

$$\text{i=3} \longrightarrow -A\psi(2) + B(3)\psi(3) - A\psi(4) = E\psi(3) \quad (217)$$

$$\text{i=4} \longrightarrow -A\psi(3) + B(4)\psi(4) - A\psi(5) = E\psi(4) \quad (218)$$

$$\text{i=n-2} \longrightarrow -A\psi(n-3) + B(n-2)\psi(n-2) - A\psi(n-1) = E\psi(n-2) \quad (219)$$

$$\text{i=n-1} \longrightarrow -A\psi(n-2) + B(n-1)\psi(n-1) - A\psi(n) = E\psi(n-1) \quad (220)$$

$$\text{i=n} \longrightarrow -A\psi(n-1) + B(n)\psi(n) - A\psi(n+1) = E\psi(n) \quad (221)$$

We can write this system as the following matrix, according to the Schrodinguer equation, $H\psi = E\psi$:

$$
\begin{pmatrix}
B(1) & -A & 0 & ... & & & & & 0 \\
-A & B(2) & -A & 0 & ... & & & & 0 \\
0 & -A & B(3) & -A & 0 & ... & & & 0 \\
0 & 0 & -A & B(4) & -A & 0 & & ... & 0 \\
& & & & & & & & \\
0 & & & ... & 0 & -A & B(n-2) & & -A \\
0 & & & & ... & 0 & -A & & B(n-1)
\end{pmatrix}
\begin{pmatrix}
\psi(1) \\
\psi(2) \\
\psi(3) \\
\psi(4) \\
... \\
\psi(n-2) \\
\psi(n-1)
\end{pmatrix}
= E
\begin{pmatrix}
\psi(1) \\
\psi(2) \\
\psi(3) \\
\psi(4) \\
... \\
\psi(n-2) \\
\psi(n-1)
\end{pmatrix}
$$

Through the diagonalization of the matrix H, we can obtain the eigenvalues, which correspond to the energies and their respective eigenvectors. The graphical representation of the eigenvectors let us obtain the wave function:

$$\psi_i = [\psi_i(1), \psi_i(2), \psi_i(3).\psi_i(4), ..., \psi_i(n-1)] \quad (222)$$

For the first four energies, the wave function will be:

$$E_1 \longrightarrow \psi_1 = [\psi_1(1), \psi_1(2), \psi_1(3).\psi_1(4), ..., \psi_1(n-1)] \qquad \text{Ground state}$$

$$E_2 \longrightarrow \psi_2 = [\psi_2(1), \psi_2(2), \psi_2(3).\psi_2(4), ..., \psi_2(n-1)] \qquad \text{First excited state}$$

$$E_3 \longrightarrow \psi_3 = [\psi_3(1), \psi_3(2), \psi_3(3).\psi_3(4), ..., \psi_3(n-1)] \qquad \text{Second excited state}$$

$$E_4 \longrightarrow \psi_4 = [\psi_4(1), \psi_4(2), \psi_4(3).\psi_4(4), ..., \psi_4(n-1)] \qquad \text{Third excited state}$$

We establish L=10 atomic units of space and n=1000 to calculate the energies. In table 3, we can see the values of the energy obtained and the analytical value of the energy as obtained in previous chapters, for every state.

Table 3. Comparative between analytical values and real energies

| State | Finite difference | Real energies |
| --- | --- | --- |
| $E_1$ | 0, 4999 | 0, 5 |
| $E_2$ | 1, 499 | 1, 5 |
| $E_3$ | 2, 499 | 2, 5 |
| $E_4$ | 3, 499 | 3, 5 |

As we can see, there is hardly no difference between the energy values obtained and the real energies. Then, finite difference method is a good way to solve harmonic oscillator Schrödinguer equation. Now, we will represent these states in the following picture:
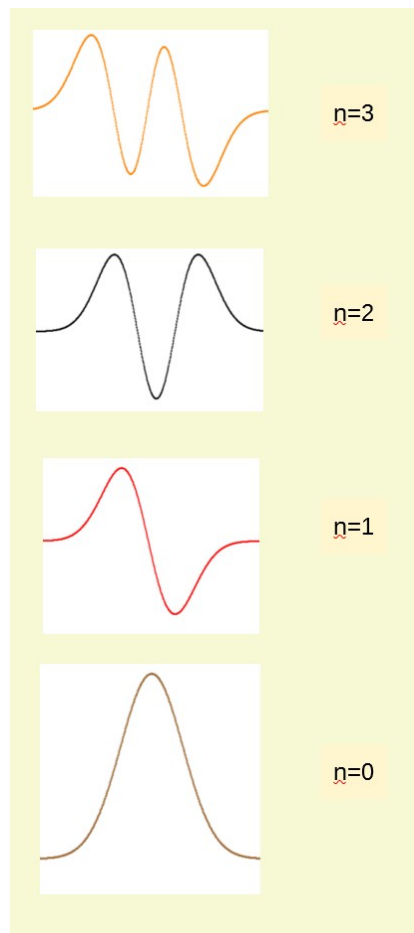


Figure 7. First four wave functions of the Quantum Harmonic Oscillator through finite differences method

Then, to conclude, we would just like to underscore that we have obtained numerical results practically identical to the other methods. Moreover, unlike the other methods, where we follow an analytical procedure to obtain the energies and wave lengths, we have obtained the results though a numerical procedure.

Mathematica codes employed to calculate eigenvalues, eigenvectors and plot figure 8 are provided in Appendix 1

# 5. Critical comparison of the three methods

**Introduction**

In this paper, the Schrödinguer equation of the quantum harmonic oscillator has been solved using three different methods, obtaining the same wave energies and functions for each level.

Each of the methods contains well-defined features, leading to similarities and differences between the three methods. Some of these features may be either the nature of the method or the versatility of each. All of this will be discussed below, naming their advantages and disadvantages over the other methods.

**Polynomial method**

The polynomial method presents a solution to the Schrödinguer equation by a series of finite length polynomials. To do this, one must master mathematical knowledge in order to apply techniques that allow transforming a polynomial of infinite length into a polynomial of finite length, which contains a meaningful solution that physically reflects the solution to the Schrödinguer equation.

In addition, the method is analytical in nature, since the solution will be obtained by developing the polynomials, so it does not require any knowledge of programming, as well as only a basic knowledge of differential calculus. Furthermore, the method requires basic knowledge of algebra. The method is capable of providing us with a solution from a simple mathematical point of view, without using physical terms.

Regarding the required knowledge of quantum chemistry, basic knowledge will be required to identify the solutions with physical meaning, as well as to discard the trivial solutions.

**Factorization method**

The factorization method is characterized by solving the Schrödinguer equation using a series of operators, called ladder operators. These operators will allow us to obtain the energies and wave functions of the quantum harmonic oscillator through a complex set of mathematical operations. The understanding and development of these operations will allow us to apply the operators to obtain the energies of the next or previous quantum level, depending on the operator applied.

The method can be defined as analytical, and, like the polynomial method, it does not require any programming knowledge. However, this method teaches us to put into practice quantum chemistry concepts to obtain the solution of the Schrödinguer equation. Therefore, we must master these in order to apply them properly. As for the algebraic difficulty, it requires only a basic level.

**Finite difference method**

Finite difference method presents a solution to the QHO by means of discretization of the continuum space, where the initial differential equation becomes a discretized differential equation. This discretized equation is then transformed into a linear system of equations and then a matrix equation. This method is based on approximations, so the greater the discretization of the potential, the greater its accuracy.

In addition, the method has a numerical character, so for its resolution, programming knowledge is required, as well as a basic knowledge of quantum chemistry that allows us the appropriate approach to the problem to be solved.

With respect to the required knowledge of differential calculation, these go into the background, since the basis of the method is to propose an alternative to solving differential equations in the classical way.

Finally, the method requires some basic knowledge of mathematical development in order to correctly complete each of the stages mentioned in the first paragraph

**Conclusion**

In the table 4, we can see the summary described above:

Table 4. Comparative of the three methods.

| Method | Nature | Differential calculation knowledge | Mathematical development knowledge | Quantum Chemistry knowledge | Programming knowledge | Versatility |
|---|---|---|---|---|---|---|
| Polynomial | Analytical | Basic | Average | Basic | Low | Basic |
| Factorization | Analytical | Basic | Average | High | Low | High |
| Difference finite | Numerical | Low | High | Basic | High | High |

The numerical method is characterized by requiring a high mathematical development, since this is the basis of this method. This characteristic can easily be dispensed with if we opt for an analytical method, which its requirements of mathematical development are lower.

Furthermore, if we want to choose to learn the basics of quantum chemistry along with its application, it would be better to choose an intuitive method, such as the factorization method

Finally, knowledge of programming stands out in a numerical method, such as the finite difference method, being a feature more than dispensable in analytical methods.

**Adequacy of the methods**

After analyzing the characteristics of the different methods with which the Schrödinguer equation of the quantum harmonic oscillator has been solved throughout this paper, it would be convenient to discuss their properties from the point of view of learning.

In introductory courses to quantum chemistry it is usual to present the solutions of the different models of quantum mechanics without the explanation of the procedure carried out to acquire these solutions. Therefore, the analysis of the methods made in table 4 can help us if we decide to choose a method to explain the reasoning behind the derivation of Hamiltonian solutions.

A priori, all three methods have well-defined characteristics. From an introductory point of view to quantum chemistry, the polynomial method presents at the same time a greater mathematical simplicity in determining how the solutions of the quantum harmonic oscillator are obtained. This feature will allow the student to easily understand the Hamiltonian solution of the QHO with a simple mathematical development. Furthermore, the method has different applications, such as its application to obtain the solutions of the radial part of the hydrogen atom or the spherical harmonics. [7]

On the other hand, methods such as factorization require the application of mathematical operators, whose treatment can be complex if you are not familiar with them. The application of this method for resolution is determined by a number of requirements, described in the article by Hull and Infeld [11]. As a clarification, quantum mechanical models such as the rigid rotor meet these conditions, so their resolution by the factorization method is perfectly feasible.

A similar case occurs with numerical methods such as the finite difference method. The method can be really useful if our knowledge of quantum chemistry and programming is remarkable. In that case, the method is presented as a very good alternative, since it allows us to settle the previous knowledge acquired. Furthermore, this method has different applications, which can be either other models of quantum mechanics, such as the particle in the box or the resolution of a system in three dimensions to which we add a potential. This last application may involve a series of difficulties. For example, the Schrödinguer equation is always a second order differential equation in space, but sometimes spin-orbit interactions or other terms of the equation can add derivatives of different order, making the resolution of the equation difficult.

All this analysis can be altered according to the context in which we find ourselves. For example, if we are in a course where introductory knowledge of programming and quantum mechanics is taught, the finite difference method acquires a great potential, since its difficulty in demanding programming knowledge is valued.

Another example could be an introductory course to the different methods of quantum mechanics. In this case, it is necessary to find a method applicable to several quantum models, in order to facilitate the understanding of the process carried out for the resolution of quantum models. In this case, the factorization method plays a fundamental role. It leads us to obtain directly the eigenvalues and to a manufacturing process of the eigenfunctions, without a difficult mathematical procedure. We can reproduce the procedure carried out to solve the harmonic oscillator with the equations of other quantum models, such as that of the hydrogen atom. With this we will achieve a simple and standard procedure with which we will demonstrate the solution of the different models of quantum mechanics

# 6. Appendix 1: Mathematica codes employed to calculate eigenvalues and eigenvectors

Clear["Global`*"]

**\*Matrix build**

matriu=Table[0,{fil,1,n-1},{col,1,n-1}];

**\*Definitions**

(* L is a large number that represent the lenght of discretizated space,
n represents in how many points we have discretizated the space
delta is the separation between two consecutives points, Eq.(214) *)

n=1000;
L=10;
delta=L/n;
x[i_]:=(-L/2)+(i*delta); a=-1/(2*delta$^2$);

**\*Diagonals build**

For[i=1,i<=n-1,i=i+1,matriu[[i,i]]=(x[i])^2/2+1/delta$^2$];
For[i=1,i<= n-2,i=i+1,matriu[[i,i+1]]=a];
For[i=2,i<= n-1,i=i+1,matriu[[i,i-1]]=a];

**\*Obtaining eigenvalues (energies)**

eners=Eigenvalues[matriu //N] ;

eners

{...,9.53598,8.51101,7.50257,6.50034,5.49991,4.49988,3.49992,2.49996,1.49998,0.499997}
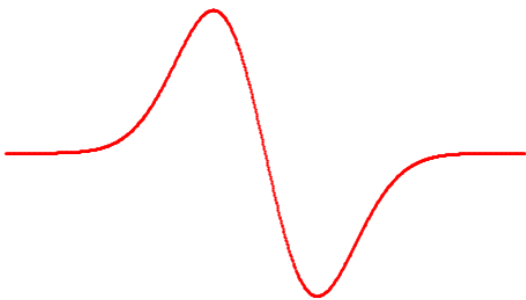
**\*Obtaining eigenvectors (wave function)**

funs=Eigenvectors[matriu//N];

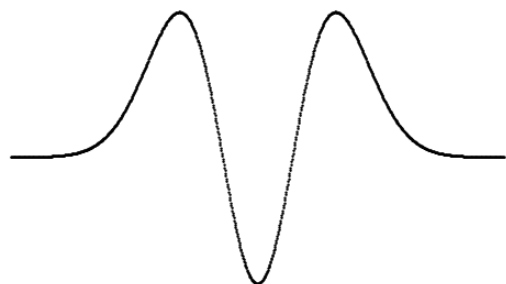**\*Plot of the first four wave function**

ListPlot[funs[[n-1]],Axes-> False,PlotStyle → Brown]
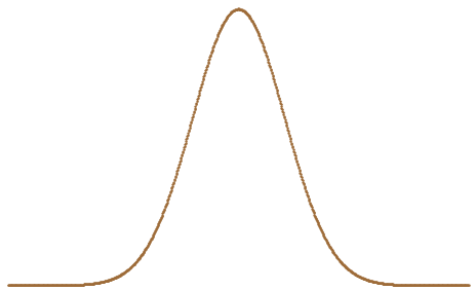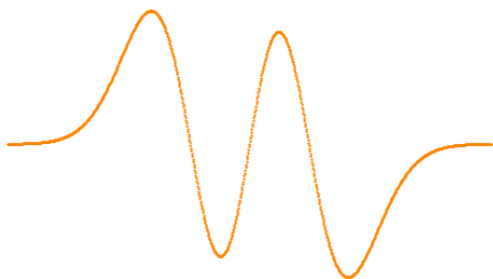


ListPlot[funs[[n-2]]+5,Axes-> False,PlotStyle → Red]



ListPlot[funs[[n-3]]+10,Axes-> False,PlotStyle → Black]



ListPlot[funs[[n-4]]+15,Axes-> False,PlotStyle → Orange]

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