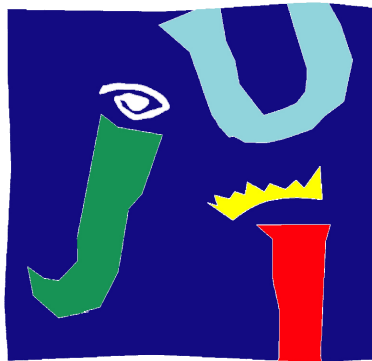


DEGREE FINAL PROJECT

“HOME-MADE GAUSSIAN “



**UNIVERSITAT
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“Sometimes one can improve theories in the sense of discovering a quicker, more efficient way of doing a given calculation.”

John Pople.

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1.INTRODUCTION

1.1.0 Motivation

What is the reason for doing this final degree dissertation?

Quantum Mechanics is one of the most important theories in the last century. Nowadays, this theory is behind many discoveries in different fields of science. When studying Quantum Chemistry, you can discover the most fundamental part of nature and intimate with it. In the Quantum Chemistry one can prove that the concept of beauty is linked to that of chaos on many occasions [6].

This work has started with a quote about other ways to improve science. Scientific theory can many times be improved step by step and, after the quantum revolution, this area of science has been improved with smalls steps. Small steps which together have performed a great advance.

To finish this section, I would like to talk about the main question which will largely be addressed in this work. Which is the influence of the mathematical methods in modern quantum chemistry?

Obviously, Mathematics is the language of science and therefore it is behind all the theoretical frameworks and, what is more, they nowadays have a special importance thanks to the development of computers and the growing calculation capability they have.

Thus, in order to simulate and understand complex quantum system, new methods are becoming increasingly relevant. In this final degree dissertation, the reader will be introduced into a mathematical method of approximation which is pivotal in modern quantum chemistry: the theory of linear variations built on a basis of Gaussian functions.

1.1.1 Objective

This project consists in a exploration about some aspects in quantum chemistry and how it can use an approximated method to give solution to some quantum models without analytical solution.

To begin with, the reader will be able to know the basis and the background of a Gaussian-software quantum resolution method in this project The reader will also be able to deepen in one of the methods of algebraic resolution with most elegant mono electronic systems used in quantum mechanics, called factorization method.

Therefore, one of the main objectives in this project is also to get acquainted with some of the basic research methods in chemistry as well as to learn to have a critical view. In general, this project consist in creating a computer programme based on Gaussians and variational principle in order to give solution to some quantum systems.

1.2.1 Historic context

Quantum mechanics was born in 1850 with the statement of the black-body radiation problem by Gustav Kirchhoff (1824-1887). Yet it was not until 1900 when the German physicist Max Planck (1858-1947) introduced a revolutionary hypothesis which consists in the fact that any energy-radiating atomic system can theoretically be divided into a number of "energy elements" .

Albert Einstein (1879-1955) in 1905, needed to take Max Planck's hypothesis in order to explain the photoelectric effect. Definitely, a new concept was born, a concept which would settle the basis of the modern physics and chemistry and this concepts was called quantum mechanics.

Therefore, a new subatomic world was discovered thanks to this theory. There have been a lot of advances from those days until now, and great scientists have contributed with their genius in this field. It is the case of wave mechanics by Schrödinger, the uncertainty principle by Heisenberg and the relativistic mechanics and delta notation by Dirac among many others.

At that time, as along XX century, the theoretical studies advanced. However, its implementation in chemistry problems so as to resolve complex systems like polyelectronic atoms or in order to follow the energy mechanism in one reaction had several problems due to the great amount of calculations, as well as the time spent.

Thus, a new challenge was born, and to get a solution to this problem a new era started for the computational quantum chemistry in 1970 by some quantum programs such as Gaussian, Gamess...

This project is focused in Gaussian software. Thus, the next question that it can be solved are the following:

Who created Gaussian? What is Gaussian?

Gaussian was invented by John Pople [1].

John Pople (31 October 1925 – 15 March 2004) was born in Burnham-on-Sea, Somerset, At the age of twelve he became interested in mathematics. He joined a scholarship at the University of Cambridge in 1943, where he graduated in mathematics in 1946 and received his doctorate in chemistry in 1951.

He moved to the United States in the decade of 1960 when for there he lives rest of his life. In 1961 he was appointed to the Royal Society of London and in 2003 he was appointed sir by the Queen Elizabeth II of the United Kingdom. Finally, John died on March 15, 2004 at his residence in Sarasota, located in the US state of Florida.

His first contribution was a theory of approximate calculations of molecular orbitals on pi bonding systems in 1953. This theory was identical to that developed by Rudolph Pariser and Robert Parr in the same year, which is why it was called Pariser-Parr Pople.

Interested in quantum chemistry, he developed quantum computing methods, on which he based the Gaussian computer programme. Through this type of methods the so-called computational chemistry was developed, which allows to investigate the properties of molecules in chemical processes.

In 1998, he was awarded with half of the Nobel Prize in Chemistry for the development of computational methods of quantum chemistry. The other half of the prize went to the American physicist Walter Kohn for the development of the functional theory of density.

1.2.2 Gaussian program.

A fundamental and characteristic feature of Gaussian is that it provides computationally orbitals by resorting to the description of complex molecular orbitals by means of the use of STO-nG basis functions [5]. The underlying idea is to replace Slater orbitals - which are the natural solution of hydrogenoid atoms- by a linear combination of Gaussian orbitals providing the closest possible solution. For example, a STo-3G basis set:

$$\Psi(STO - 3G) = C_1 \phi_1 + C_2 \phi_2 + C_3 \phi_3 \quad (1.1)$$

Where:

$$- \phi_1 = N e^{-\alpha_1 r^2} \quad (1.2)$$

$$- \phi_2 = N e^{-\alpha_2 r^2} \quad (1.3)$$

$$- \phi_3 = N e^{-\alpha_3 r^2} \quad (1.4)$$

Where “ C_1, C_2, C_3 ” are coefficient to be optimized variationally.

The choice of Gaussian functions, instead of Slater ones, is motivated by the availability of analytical integrals, in many of the Hamiltonian matrix elements, as we show in the section 2.2.1 This renders calculations very efficient.

Gaussian is a commercial software used in theoretical chemistry. The programme solves the molecular Schrödinger equation based on the theory of molecular orbitals (TOM) from some initial parameters, such as the ab initio method type (Hartree-Fock, Möller-Plesset, etc.), Functional of Density (DFT) or semi-empirical, (AM1, PM3, CNDO ...), base functions (STO-3G, 6-31G, 6-311 + G * ...).

The programme works in cartesian coordinates (indicating the position x, y, z of the atoms of the molecule) or in internal coordinates (z-matrix) (distances, angles and dihedrals), and the charge and multiplicity calculates the function of the molecular wave and from there a series of atomic and molecular properties are obtained (energy of the molecule, optimization of the coordinates, electronic density, dipolar moments, quadrupoles, etc.)

2. BACKGROUND

2.1.1 Linear variational principle

In this section the reader will be able to know the background behind the method which is going to be used.

The importance of the variational principle is because of only in very few cases the Schrodinger equation (2.1) has analytical solution [7]

$$\hat{H} \phi = E \phi \quad (2.1)$$

Where, " \hat{H} " is a Hermitian operator called Hamiltonian, " ϕ " is the wavefunction and "E" is the eigenvalue.

This method is based on the variational method [4]. The basis of this method can be written with one theorem.

Theorem: *The average value of the Hamiltonian calculated with an arbitrary function " Ψ " that meets the boundary conditions, is continuous and derivable and is greater than the lower eigenvalue of the cited Hamiltonian.*

The mathematical expression of the previous theorem is detailed in the following equation:

$$W = \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} \geq E_0 \quad (2.2)$$

Furthermore, this method consist in applying the variation method [4] with the guess function. The property of the guess function which makes it useful is that it can be approached as a linear combination of linearly independent functions.

$$\Phi = \sum_i c_i f_i \quad (2.3)$$

Where Φ is the most approximated function that we can build with the " f_i " basis functions. And " c_i " the variational coefficient which is going to be minimized in order to obtain the solution and " f_i " is the basis function which has to satisfy the boundary conditions. For a more general solution, it is going to be assumed that the basis functions are not orthonormals ($\langle f_i/f_j \rangle \neq 1$).

Example:

First of all we are develop to obtain the following expression (2.2). For a simple case in which the function is spanned in a basis of two functions.

Next, it is necessary to define the following expressions:

Overlap integral: This concept is the scalar product between two functions. The mathematical expression "overlap" is detailed in expression (2.4)

$$S_{jk} = \langle f_j/f_k \rangle = \int f_i^* f_k d\sigma \quad (2.4)$$

and we assume that the functions " f_i " are real ($S_{jk} = S_{jk}$)

To prove this method we going to take two basis functions: $\{f_1, f_2\}$

So, the arbitrary function can be expressed into the following expression:

$$\Phi = c_1 f_1 + c_2 f_2 \quad (2.5)$$

Once it has the expression of the arbitrary function, the overlap integral will result:

$$\langle \Phi/\Phi \rangle = \langle c_1 f_1 + c_2 f_2 / c_1 f_1 + c_2 f_2 \rangle = c_1^2 S_{11} + 2c_1 c_2 S_{12} + c_2^2 S_{22} \quad (2.6)$$

On the other hand, the integral of the Hamiltonian average value will result:

$$\langle \Phi | \hat{H} | \Phi \rangle = \langle c_1 f_1 + c_2 f_2 | \hat{H} | c_1 f_1 + c_2 f_2 \rangle = c_1^2 H_{11} + 2c_1 c_2 H_{12} + c_2^2 H_{22} \quad (2.7)$$

Where, because of the Hamiltonian is an hermitian operator.

$$H_{jk} = \langle f_j | \hat{H} | f_k \rangle = \langle f_k | \hat{H} | f_j \rangle = H_{kj} \quad (2.8)$$

Thus, the energy has the next expression,

$$E = \frac{c_1^2 H_{11} + 2c_1 c_2 H_{12} + c_2^2 H_{22}}{c_1^2 S_{11} + 2c_1 c_2 S_{12} + c_2^2 S_{22}} \quad (2.9)$$

Energy will be a function of a coefficients of the basis ($E = E(c_1, c_2)$).

Thus, since this method consists in finding the best function and the energy that is closer to the real, the next step is applying the minimum condition ($\partial E / \partial c_i = 0$) in order to find the best coefficients of the basis functions. So the following equations are the result of deriving expression (2.9) with respect to the coefficients c_1 and c_2 .

$$\text{- Respect to } c_1: c_1 H_{11} + c_2 H_{12} = E (c_1 S_{11} + c_2 S_{12}) \quad (2.10)$$

$$\text{- Respect to } c_2: c_1 H_{12} + c_2 H_{22} = E (c_1 S_{12} + c_2 S_{22}) \quad (2.11)$$

Furthermore, the equations (2.12) and (2.13) can be expressed as a homogenous system:

$$c_1 (H_{11} - E S_{11}) + c_2 (H_{12} - E S_{12}) = 0 \quad (2.12)$$

$$c_1 (H_{21} - E S_{21}) + c_2 (H_{22} - E S_{22}) = 0 \quad (2.13)$$

And the solutions of this system are E_0 and E_1 . If we agrupate this energy from the lowest to the highest the result is:

$$E_0 < E_1 \quad (2.14)$$

Where “ E_0 ” is the approximate energy to the fundamental state and “ E_1 ” is the approximate energy to the first excited state.

The method of linear variations can be solved in an alternative way. To do this, we will write in a matrix form the system of equations (2.12) and (2.13):

$$\begin{pmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{pmatrix} \begin{pmatrix} C_1 \\ C_2 \end{pmatrix} = \begin{pmatrix} E_1 \\ E_2 \end{pmatrix} \begin{pmatrix} S_{11} & S_{12} \\ S_{21} & S_{22} \end{pmatrix} \begin{pmatrix} C_1 \\ C_2 \end{pmatrix} \quad (2.15)$$

An the expression (2.15) can be written as:

$$HC = ESC \quad (2.16)$$

The expression (2.16) is the matrix representation of the variational linear principle. Then, if you multiply on the left the expression (2.16) by the inverse of the matrix "S" you obtain:

$$S^{-1}HC = S^{-1}SEC \quad (2.17)$$

$$S^{-1}HC = EC \quad (2.18)$$

Therefore, we get a matrix equation of eigenvalues. In order to get the solution, we diagonalize the matrix “ $S^{-1}H$ ”.

When we diagonalize the previous matrix, we get the eigenvalues and the eigenvectors.

Thus, the wavefunction for a state “i” is:

$$\Phi_i = c_1^{(i)} f_1 + c_2^{(i)} f_2 \quad (2.19)$$

2.1.2 Useful Properties of Gaussian functions.

The background of useful properties of Gaussian functions [3] consists principally in one mathematical function which has many useful properties such a product rule. In this section, we are going to demonstrate the product rule.

As an observation, it should be noted that throughout the following mathematical treatment the normalization constant has been omitted to facilitate calculations.

The gaussian function has the following expression:

$$g(r - Ra) = e^{-\alpha(r-Ra)^2} \quad (2.20)$$

Where “Ra” is the position in which the gaussian is situated. “ α ” is the envelope of the function.

Product rule:

The product rule is one of the most useful properties. It states that the product of two Gaussians functions, is yet another function displaced with respect to the original ones.

$$g(r - Ra) g(r - Rb) = K g(r - Rp) = K e^{-p(r-Rp)^2} \quad (2.21)$$

Where:

$$- K = e^{[-\alpha \beta / (\alpha + \beta) * (Ra - Rb)^2]} \quad (2.22)$$

$$- Rp = \frac{\alpha Ra + \beta Rb}{\alpha + \beta} \quad (2.23)$$

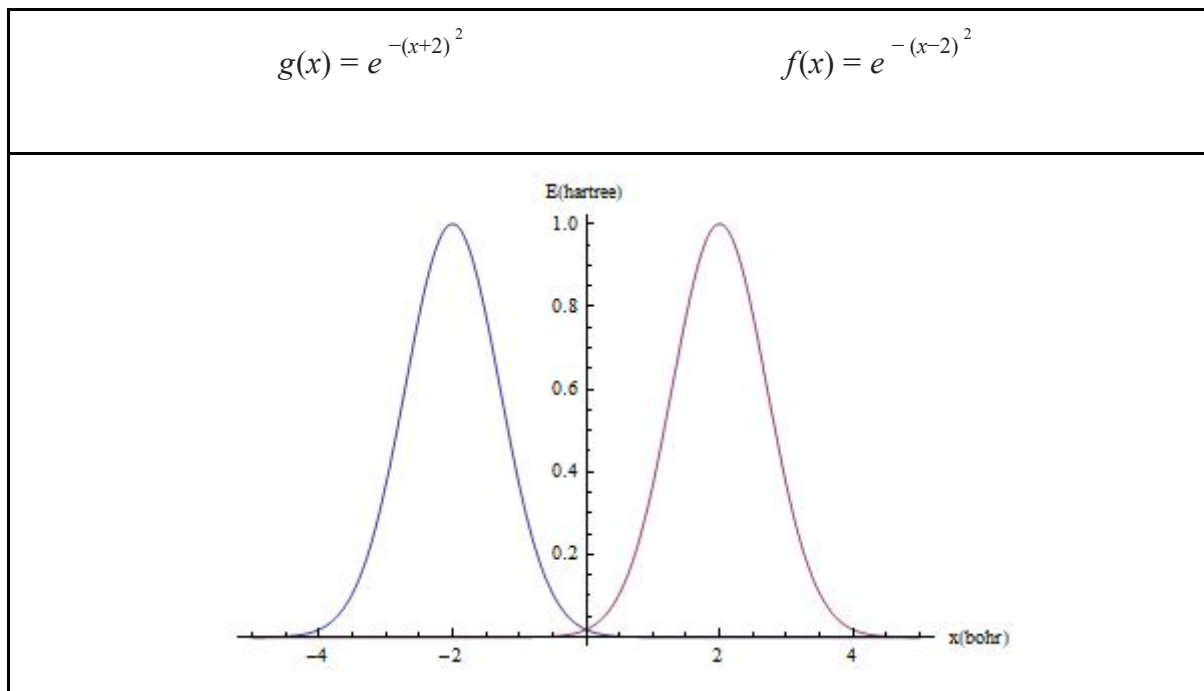
$$- p = \alpha + \beta \quad (2.24)$$

Graphic demonstration

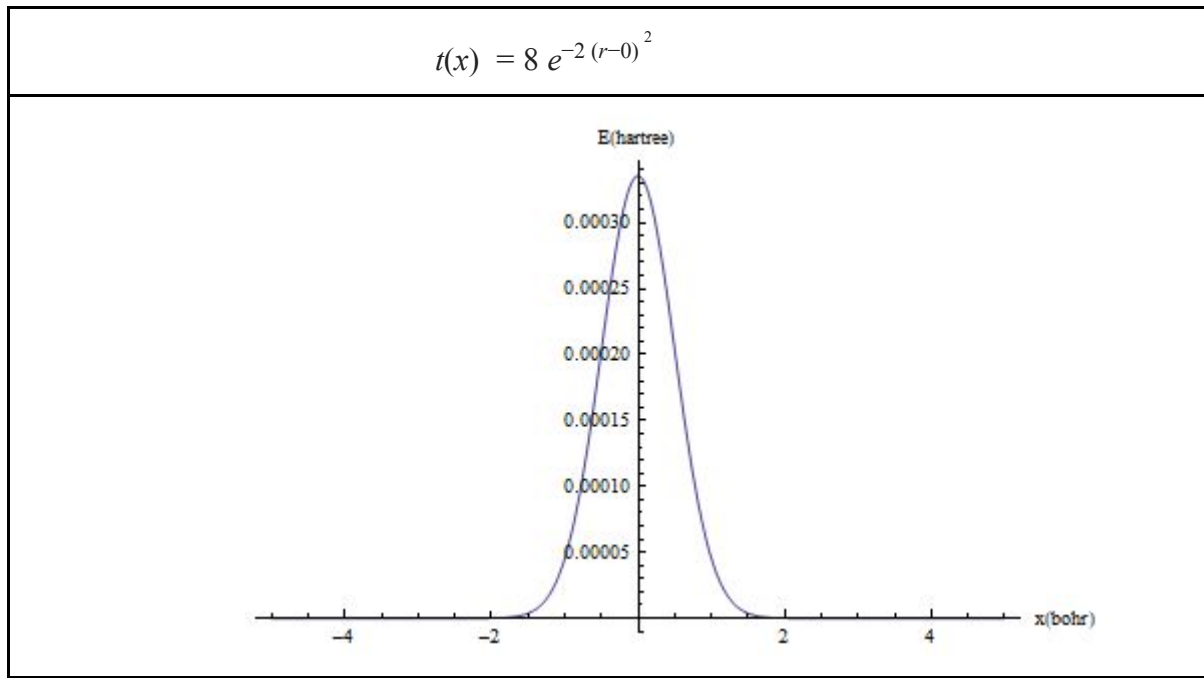
Once the product rule is known, in this section it this rule is going to be demonstrated with one simple graph:

In figure 2.1 the two gaussian functions and their graphics are detailed:

Figure 2.1: Two gaussian functions and their graphics



and then, the product of these two functions is detailed in the figure 2.2

Figure 2.2:Result of gaussian $f(x)$ and $g(x)$ product

This rule is used in solving analytically the following quantum concepts. It should be noted that the following demonstration are based on that of Szabo [3], but considering a 1D system instead of a 3D one, and providing more explicit analysis.

Analytical demonstration

First, it has two Gaussian functions,

$$f(r) = e^{-\alpha(r-Ra)^2} \quad (2.25)$$

$$g(r) = e^{-\beta(r-Rb)^2} \quad (2.26)$$

Then, it makes the product of the previous functions.

$$k(r) = f(r) g(r) = e^{-\alpha(r-Ra)^2} e^{-\beta(r-Rb)^2} \quad (2.27)$$

$$k(r) = e^{-\alpha(r-Ra)^2 - \beta(r-Rb)^2} \quad (2.28)$$

$$k(r) = e^{-\alpha(r^2 - 2rRa + Ra^2) - \beta(r^2 - 2rRb + Rb^2)} \quad (2.29)$$

$$k(r) = e^{-\alpha r^2 + 2\alpha rRa - \alpha Ra^2 - \beta r^2 + 2\beta rRb - \beta Rb^2} \quad (2.30)$$

$$k(r) = e^{-(\alpha+\beta)r^2 + 2r(\alpha Ra + \beta Rb) - (\alpha Ra^2 + \beta Rb^2)} \quad (2.31)$$

Thus, it takes into account the exponential part in the expression (2.32)

$$-(\alpha + \beta)r^2 + 2r(\alpha Ra + \beta Rb) - (\alpha Ra^2 + \beta Rb^2) \quad (2.32)$$

We can do some algebraic transformations:

$$-(\alpha + \beta)r^2 + 2r(\alpha Ra + \beta Rb) - (\alpha Ra^2 + \beta Rb^2) \quad (2.33)$$

$$\frac{1}{-(\alpha+\beta)} [-(\alpha + \beta)r^2 + 2r(\alpha Ra + \beta Rb)] - \frac{1}{-(\alpha+\beta)} [\alpha Ra^2 + \beta Rb^2] \quad (2.34)$$

$$r^2 - \frac{1}{(\alpha+\beta)} [2r(\alpha Ra + \beta Rb)] + \frac{1}{(\alpha+\beta)} [\alpha Ra^2 + \beta Rb^2] \quad (2.35)$$

$$r^2 - \frac{1}{(\alpha+\beta)} [2r(\alpha Ra + \beta Rb)] + \left(\frac{\alpha Ra + \beta Rb}{\alpha+\beta}\right)^2 + \frac{1}{(\alpha+\beta)} [\alpha Ra^2 + \beta Rb^2] - \left(\frac{\alpha Ra + \beta Rb}{\alpha+\beta}\right)^2 \quad (2.36)$$

By identifying the first term as the square, we obtain:

$$- \left[r^2 - \left(\frac{\alpha Ra + \beta Rb}{\alpha+\beta}\right)^2 \right] - \frac{1}{(\alpha+\beta)} [\alpha Ra^2 + \beta Rb^2] + \left(\frac{\alpha Ra + \beta Rb}{\alpha+\beta}\right)^2 \quad (2.37)$$

Thus, we can rewrite the exponent of the gaussian function as:

$$k(r) = e^{-[r^2 - (\frac{\alpha Ra + \beta Rb}{\alpha + \beta})]^2} e^{-\frac{1}{(\alpha + \beta)} [Ra^2 \alpha + \beta Rb^2] + (\frac{\alpha Ra + \beta Rb}{\alpha + \beta})^2} \quad (2.38)$$

Where the first exponential is a function of "r" and the second exponential is a constant then,

$$k(r) = K e^{-[r^2 - (\frac{\alpha Ra + \beta Rb}{\alpha + \beta})]^2} \quad (2.39)$$

$$k(r) = K e^{-(r - Rp)^2} \quad (2.40)$$

With:

$$K = e^{-\frac{1}{(\alpha + \beta)} [Ra^2 \alpha + \beta Rb^2] + (\frac{\alpha Ra + \beta Rb}{\alpha + \beta})^2} \quad (2.41)$$

Application of product rule

This rule is used in solving analytically the following quantum concepts. It should be noted that in the following demonstrations it has considered a 1D system.

- **Overlap integral.** As we already know from the previous section, the overlap mathematical expression between two centers is $\langle A/B \rangle$.

Hence, in this section we are going to resolve these overlap integrals with the gaussian product rule:

$$\langle A/B \rangle = \int_{-\infty}^{\infty} C g(r_1 - Ra) * C g(r_1 - Rb) dV \quad (2.42)$$

$$\langle A/B \rangle = C^2 \int_{-\infty}^{\infty} g(r_1 - Ra) * g(r_1 - Rb) r^2 dr_1 \quad (2.43)$$

$$\langle A/B \rangle = C^2 K \int_{-\infty}^{\infty} g(r_1 - Rp) r^2 dr_1 \quad (2.44)$$

$$\langle A/B \rangle = C^2 K \int_{-\infty}^{\infty} e^{-p(r_1 - Rp)^2} r^2 dr_1 \quad (2.45)$$

And if we know let $r = r_1 - Rp$ and $dr_1 = dr$, then

$$\langle A/B \rangle = C^2 K \int_{-\infty}^{\infty} e^{-p r^2} r^2 dr \quad (2.46)$$

The last integral is just $(\frac{\pi}{p})^{3/2} / 4\pi$, so that

$$\langle A/B \rangle = \left(\frac{\pi}{\alpha+\beta}\right)^{1/2} e^{(-\alpha\beta/(\alpha+\beta) |Ra-Rb|^2)} \quad (2.47)$$

$$\langle A/B \rangle = \left(\frac{\pi}{\alpha+\beta}\right)^{1/2} e^{(-\alpha\beta/(\alpha+\beta) |Ra-Rb|^2)} \quad (2.48)$$

There are other concepts which are important for a quantum system such as the hamiltonian of the system. So, we are going to evaluate the hamiltonian. Thus, we are going to evaluate the kinetic energy. The treatment of the potential energy is shown in [3].

- **Kinetic energy:** The mathematical expression of the kinetic energy integral is (in atomic units)

$$\langle A / -\frac{1}{2} \nabla_1^2 / B \rangle = \int_{-\infty}^{\infty} C g(r_1 - Ra)^* \left(-\frac{1}{2} \nabla_1^2\right) C g(r_1 - Rb) dV \quad (2.49)$$

$$\text{Where } \vec{\nabla} = \left(\frac{\partial}{\partial x} i + \frac{\partial}{\partial y} j + \frac{\partial}{\partial z} k\right) \quad (2.50)$$

The kinetic energy can be evaluated in a similar way after applying the operator. Thus, the final expression is:

$$\langle A / -\frac{1}{2} \nabla_1^2 / B \rangle = \alpha\beta/(\alpha + \beta) \left[3 - \frac{2\alpha\beta}{\alpha+\beta} |Ra - Rb|^2\right] \left[\pi/(\alpha + \beta)\right]^{3/2} e^{[-\alpha\beta/(\alpha+\beta) |Ra-Rb|^2]} \quad (2.51)$$

$$\langle A / -\frac{1}{2} \nabla_1^2 / B \rangle = \alpha\beta/(\alpha + \beta) \left[3 - \frac{2\alpha\beta}{\alpha+\beta} |Ra - Rb|^2\right] \left[\pi/(\alpha + \beta)\right]^{1/2} e^{[-\alpha\beta/(\alpha+\beta) |Ra-Rb|^2]} \quad (2.52)$$

3.COMPUTATIONAL METHODS.

3.1.0 Single harmonic oscillator 1D

Single harmonic oscillator is a quantum vibration system which has an analytical solution. In the figure (3.1) the form of the potential of the system are detailed [2].

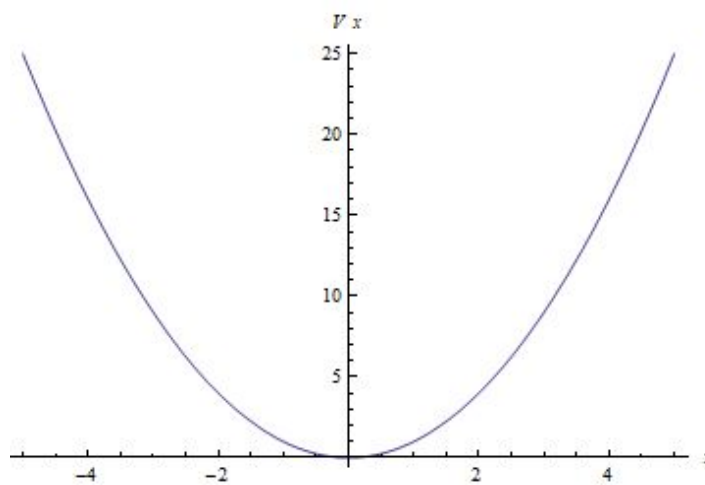


Figure 3.1 Form of one single harmonic oscillator potential

In this section, we will obtain the analytical solution of the fundamental state of the single harmonic oscillator in 1D.

First of all, we introduce the classical hamiltonian for our system.

$$\hat{H} = \frac{p^2}{2m} + \frac{1}{2} k x^2 \quad (3.1)$$

Where the first term refers to kinetic energy and the second term refers to potential energy. In order to change into a quantum point of view, we introduced the following operators:

$$\hat{p} = -i\hbar \frac{\partial}{\partial x} \quad (3.2)$$

$$\hat{x} = x \quad (3.3)$$

Thus, the hamiltonian is:

$$\hat{H} = \frac{-\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + \frac{1}{2} k x^2 \quad (3.4)$$

Once we obtain the hamiltonian of the system, the problem is resolved with the Shrödinger stationary equation.

$$\hat{H} \varphi = E \varphi \quad (3.5)$$

Then, we obtain the differential equation,

$$\left[\frac{-\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + \frac{1}{2} k x^2 \right] \varphi = E \varphi \quad (3.6)$$

In order to resolve the previous differential equation, we are going to proceed with one elegant method called factoring method.

This method is valid for equations that has the structure like:

$$\frac{\partial^2 \varphi}{\partial x^2} + f(x, m) \varphi + C \varphi = 0 \quad (3.7)$$

Note that the equation (3.6) can be written such as:

$$\frac{\partial^2 \varphi}{\partial x^2} + \left(\frac{-m k x^2}{\hbar^2} \right) \varphi + \left(\frac{2m E}{\hbar^2} \right) \varphi = 0 \quad (3.8)$$

To get started with the factoring demonstration, the equation (3.6) is rewritten like a:

$$\frac{\hbar}{2} \left(\frac{k}{m} \right)^{1/2} \left[- \left(\frac{\hbar}{k^{1/2} m^{1/2}} \right) \left(\frac{\partial^2}{\partial x^2} \right) + \frac{m^{1/2} k^{1/2}}{\hbar} x^2 \right] \varphi = E \varphi \quad (3.9)$$

Next, we are going to make a change of variables in order to eliminate the constants that accompany the variable x. This change will be:

$$\mathcal{E} = \left(\frac{m^{1/2} k^{1/2}}{\hbar} \right)^{1/2} x \quad (3.10)$$

Where “ \mathcal{E} ” is adimensional constant.

Then,

$$\frac{\partial}{\partial x} = \frac{\partial}{\partial \mathcal{E}} \frac{\partial \mathcal{E}}{\partial x} \quad (3.11)$$

$$\frac{\partial \mathcal{E}}{\partial x} = \left(\frac{m^{1/2} k^{1/2}}{\hbar} \right)^{1/2} \quad (3.12)$$

So, if we take the derivative (3.12) and we substitute it into the equation (3.11):

$$\frac{\partial}{\partial x} = \frac{\partial}{\partial \mathcal{E}} \left(\frac{m^{1/2} k^{1/2}}{\hbar} \right)^{1/2} \quad (3.13)$$

And then,

$$\frac{\partial^2}{\partial x^2} = \left(\frac{m^{1/2} k^{1/2}}{\hbar} \right)^{1/2} \frac{\partial^2}{\partial \mathcal{E}^2} \frac{\partial \mathcal{E}}{\partial x} \quad (3.14)$$

If we take into account the equation (3.12), the expression results:

$$\frac{\partial^2}{\partial x^2} = \left(\frac{m^{1/2} k^{1/2}}{\hbar} \right) \frac{\partial^2}{\partial \mathcal{E}^2} \quad (3.15)$$

Once we have the expression (3.15), the Schrödinger equations results:

$$\frac{\hbar}{2} \left(\frac{k}{m} \right)^{1/2} \left[\mathcal{E}^2 - \frac{\partial^2}{\partial \mathcal{E}^2} \right] \varphi = E \varphi \quad (3.16)$$

The element inside square bracket can be expressed in the following way:

$$\mathcal{E}^2 - \frac{\partial^2}{\partial \mathcal{E}^2} = (\mathcal{E} - d/\mathcal{E}) (\mathcal{E} + d/\mathcal{E}) + 1 \quad (3.17)$$

Thus, if we take the equation (3.16) and (3.17) we obtain the following expression:

$$\hbar \left(\frac{k}{m} \right)^{1/2} \left[\frac{1}{\sqrt{2}} (\mathcal{E} - d/\mathcal{E}) \frac{1}{\sqrt{2}} (\mathcal{E} + d/\mathcal{E}) + 1/2 \right] \varphi = E \varphi \quad (3.18)$$

Now, we are going to define two new operators:

- Creation operator: $b^+ = \frac{1}{\sqrt{2}} (\mathcal{E} - d/\mathcal{E})$
- Annihilation operator: $b = \frac{1}{\sqrt{2}} (\mathcal{E} + d/\mathcal{E})$

And we are going to apply the following relation:

$$w = \left(\frac{k}{m} \right)^{1/2} \quad (3.19)$$

So, the expression (3.18) changes to:

$$\hbar w \left[b^+ b + \frac{1}{2} \right] \varphi = E \varphi \quad (3.20)$$

$$\hbar w b^+ b \varphi = \left(E - \frac{\hbar w}{2} \right) \varphi \quad (3.21)$$

$$\hbar w b^+ b \varphi = E' \varphi \quad (3.22)$$

Where $E' = E - \frac{\hbar w}{2}$

Once we obtain the Schrödinger equation with the factorial method and with the new creator and annihilation operators, we can solve this equation for the fundamental state with the lower eigenvalue:

$$\hbar \omega b^+ b \varphi_0 = E_0' \varphi_0 \quad (3.23)$$

Then, we multiply to the left by the operator “b”:

$$\hbar \omega b b^+ b \varphi_0 = E_0' b \varphi_0 \quad (3.24)$$

To start with the demonstration, it is necessary to know the next commutation rule:

$$[b, b^+] = 1 \quad (3.25)$$

This commutation rule implies that:

$$b b^+ - b^+ b = 1 \quad (3.26)$$

$$b b^+ = 1 + b^+ b \quad (3.27)$$

If we carry the expression (3.27) to the expression (3.24):

$$\hbar \omega (1 + b^+ b) b \varphi_0 = E_0' b \varphi_0 \quad (3.28)$$

$$\hbar \omega b^+ b (b \varphi_0) = (E_0' - \hbar \omega) (b \varphi_0) \quad (3.29)$$

The equation (3.29) presents one paradox if we take into account that “ $\hbar \omega$ ” has a positive value. We have found one state which has less energy than the fundamental state (E_0')

The only way that the expression (3.29) is correct and the fact that “ E_0' ” corresponds to the fundamental state, is that $b \varphi_0 = 0$. This conclusion allows us to obtain “ φ_0 ”, Indeed,

$$b \varphi_0 = \frac{1}{\sqrt{2}} (\mathcal{E} + d/\mathcal{E}) \varphi_0 = 0 \quad (3.30)$$

$$\mathcal{E} \varphi_0 + d(\varphi_0)/d\mathcal{E} = 0 \quad (3.31)$$

$$d(\varphi_0)/\varphi_0 = -\mathcal{E} d\mathcal{E} \quad (3.32)$$

The differential equation (3.32) has an analytical solution (separable variables), so the fundamental state wavefunction results:

$$\varphi_0 = C e^{(-\mathcal{E}^2/2)} \quad (3.33)$$

Where “ C ” is the normalization constant.

This results remark the wavefunction for the fundamental state. It should be noted that the form of the wavefunction is the same as a gaussian function. This similarity will allow us to obtain solutions in systems that cannot have an analytical solution.

In order to obtain the energy “ Eo' ”, we take the expression (3.33) and we introduce it in the equation (3.28):

$$\hbar\omega b^+ b C e^{(-\varepsilon^2/2)} = Eo' C e^{(-\varepsilon^2/2)} \quad (3.34)$$

$$\hbar\omega \left(\frac{C}{\sqrt{2}}\right) b^+ (\varepsilon + d/d\varepsilon) e^{(-\varepsilon^2/2)} = Eo' C e^{(-\varepsilon^2/2)} \quad (3.35)$$

$$\left(\frac{\hbar\omega}{\sqrt{2}}\right) b^+ [\varepsilon e^{(-\varepsilon^2/2)} - \varepsilon e^{(-\varepsilon^2/2)}] = Eo' e^{(-\varepsilon^2/2)} \quad (3.36)$$

$$\left(\frac{\hbar\omega}{\sqrt{2}}\right) b^+ 0 = Eo' e^{(-\varepsilon^2/2)} \quad (3.37)$$

$$Eo' = 0 \quad (3.38)$$

Finally, if we introduce the previous result ($Eo' = 0$) and we introduce it in the expression (xx) we obtained the energy of the fundamental state:

$$Eo = \hbar\omega/2 \quad (3.39)$$

This result marks the energy of the fundamental state for a single harmonic oscillator.

3.1.1 Coupled 1D harmonic oscillators (H.O)

For a higher number of harmonic oscillator, an algebraic solution like the one in the previous section is no longer available.

At this point, it is worth resorting to approximate methods such as the method of linear variation described in section 2.2.2. In what follows, we apply the linear variations method built on a basis of Gaussian functions to study the low lying energy levels of two and three harmonics oscillators coupled.

To this end, we take advantage of the product rule properties described in the section 2.1.2. The comparison between single and coupled harmonic oscillator with rearing distance between oscillators, will in turn provide basic insight into the formation and dissociation of “single-electron” molecules, revealing some of the fundamental concepts that are often introduced in Introductory Chemistry textbooks.

These include the formation of bonding and antibonding molecules states, the presence of an equilibrium interatomic distance, and the different behaviour of homonuclear and heteronuclear molecules..

The mathematical programme which is used in order to get the energies and the wavefunctions is detailed in the Annex I.

3.1.1.1 Two coupled H.O.s : homo and heteronuclear molecules

First of all, we consider a quantum system that represents a homonuclear diatomic molecule.

The hamiltonian of this system has the form:

$$\hat{H} = \frac{p^2}{2m} + \frac{1}{2} m \text{Min}[wa^2(x-xa)^2, (x-xb)^2] \quad (3.40)$$

Where:

- The first term corresponds to kinetic energy and the second term is the potential function of the quantum system.
- “ wa ” and “ wb ” are the quantum confinement of the two atoms and it is represented by the frequency of the oscillator.
- “ xa ” and “ xb ” are the position where the oscillators are on the axis.

Let me remark that in these examples we are going to work with the atomic units ($\hbar = 1, m_e = 1$).

Homonuclear molecule

Thus, the potential of this system is detailed in the figure (3.2)

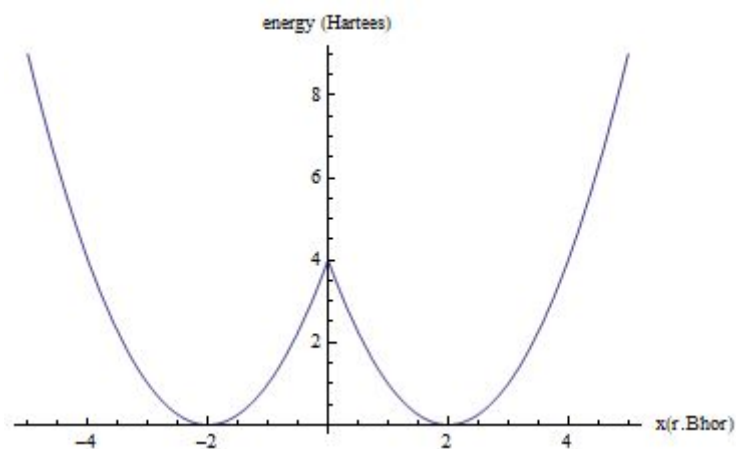


Figure 3.2: Potential of two coupled harmonic oscillators.

Where:

- We choose “ wa ” and “ wb ” equal to 1 a.u.
- “ xa ” and “ xb ” have the value of 2 and -2 respectively.

This potential cannot resolve with the analytical form because the differential equation formed by function “Min” can’t be resolved by analytical methods. Thus, in order to find the energy and the wavefunction of the system we have used the linear variation principle which is explained in section (2.1.2).

First, the guess wavefunction that we have taken is a linear combination between the following functions:

$$\phi_1 = N e^{-\alpha(x-xa)^2} \quad (3.41)$$

$$\phi_2 = N e^{-\beta(x-xb)^2} \quad (3.42)$$

Where:

- “N” is the normalized constant that, for the fundamental state, has the value of:

$$N = 1/\pi^{1/4} \quad (3.43)$$

- α has the value of:

$$\alpha = 1/(2\sqrt{\hbar/(m wa)}) \quad (3.44)$$

- β has the value of:

$$\beta = 1/(2\sqrt{\hbar/(m wb)}) \quad (3.45)$$

We choose this functions because they provide exact solutions in the limit of distant (decoupled) oscillators.

So, the guess wavefunction that we take is:

$$\Psi = C_1 \phi_1 + C_2 \phi_2 \quad (3.43)$$

Once it has the guess function we apply the linear variational principle in matrix form. Therefore, we apply the following matrix equation which is explained in section 2.2.2:

$$S^{-1}HC = EC \quad (3.44)$$

Furthermore, if we diagonalize the matrix $(S^{-1}H)$, we obtain the coefficients of the wavefunctions (C) and the energy (E) of the system.

Results.

First, we describe the change of behavior in the system when we change the separation between the oscillators. In order to get the solution, we take into account that the energy of the fundamental state in one single harmonic oscillator is 0.5 u.a. (expression 3.39) for $\hbar = 1, w = 1$.

Thus, if we perform a representation of the energy according to the separation between the two oscillators, this energy has to get the result of 0.5 for a wide separation (high values on x axis).

This fact is because when the oscillators are widely separated from each other, they have a behaviour such as one single harmonic oscillator.

This concept is demonstrated in figure 3.3

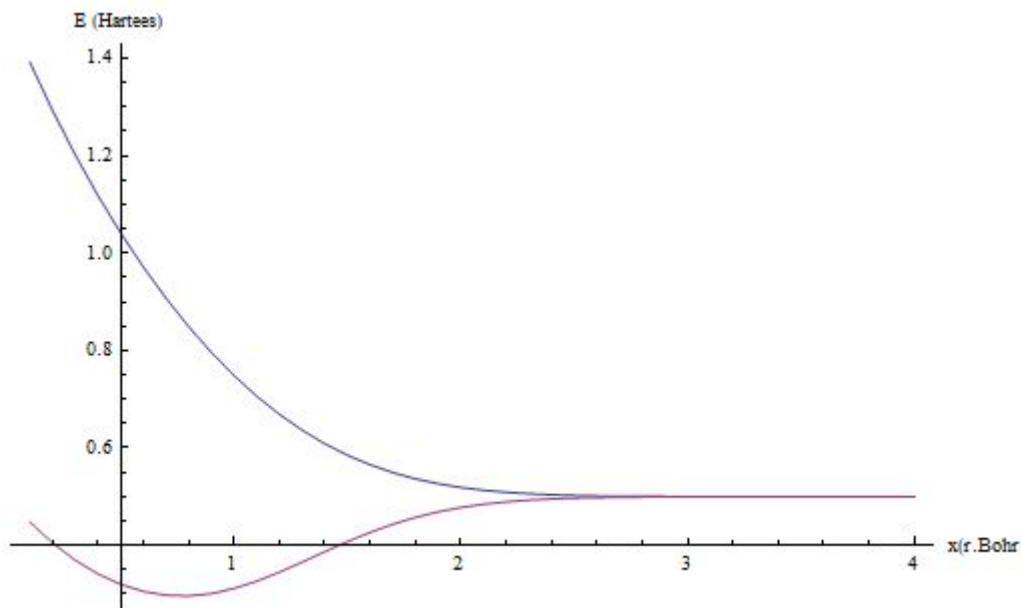


Figure 3.3 Dissociation diagram of diatomic homonuclear molecule formed by harmonic oscillators

Where the blue function represents the behavior of the excited state and the pink functions represents the behavior of the fundamental state.

Figure 3.4 has the expected behaviour of a diatomic molecule dissociation diagram. In the limit of long inter-oscillator distance, both states tend towards the energy of two independent degenerate state. As the oscillators approach to each other, the ground and excited states split energetically.

An equilibrium distance is found around 0.8 bohr radii, where the ground state energy reaches 0.296414 hartree, well below the energy of the single harmonic oscillator. For small distances the ground state energy increases again because quantum confinement increases. Eventually, when the two parabolic overlap, the energy of the ground state should be 0.5 hartree because that of an independent harmonic oscillator. However, our method cannot reach such a limit because the overlap matrix becomes singular.

First case.

The first case consists in the fact that when the Gaussian functions are focused in 10 bohr. the representation of the Gaussian functions are shown in figure 3.4.

Thus, the reader can prove the results of the fundamental state and the excited state as well as the wavefunctions of the system in the table 3.1, and the representation of the fundamental state and excited state are detailed in figure 3.4.

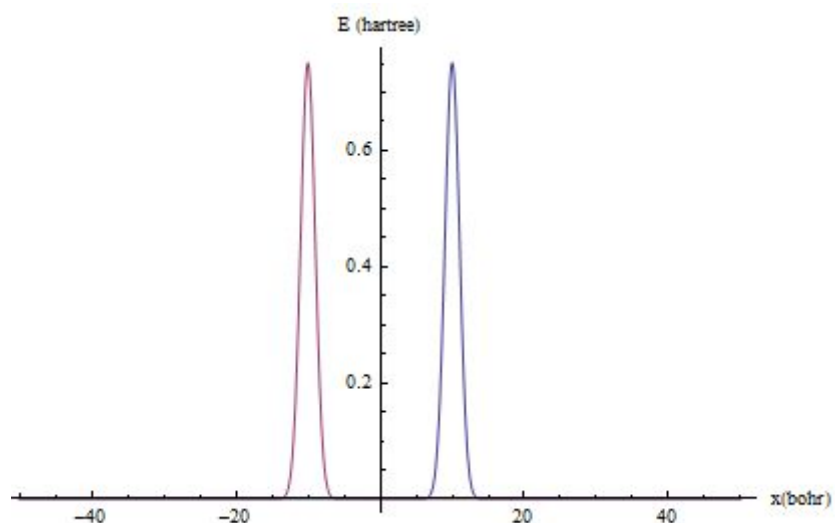


Figure 3.4: Gaussian functions centred in 10 and -10 bohr radio

Table 3.1: Results of the homonuclear coupled harmonic oscillators for a large distance.

Ground state	
Energy (u.a)	0.5
Wavefunction	$\Psi = 1 \phi_1$
Excited state	
Energy(u.a)	0.5
Wavefunction	$\Psi = 1 \phi_2$

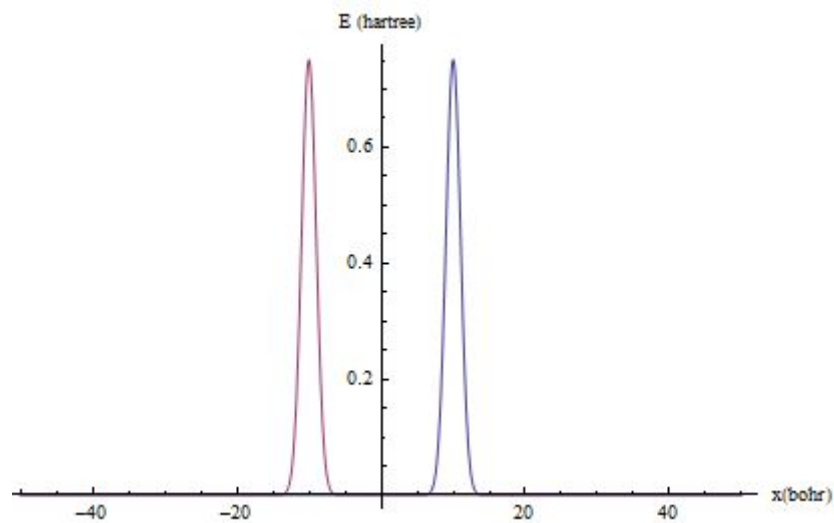


Figure 3.5: Wavefunction for a ground state (blue) and excited state (pink).

Remark that this results indicate that for this position, our systems change into a one simple harmonic oscillator whose energy is degenerated located either in a Gaussian function or in the other with a value of 0.5 hartree.

The wavefunctions in this case are converted into a one Gaussian function.

Second case.

In this case, we going to consider that the position of our system is focused around the equilibrium point.

The Gaussian functions which are focused in 0.8 and -0.8 bohr are detailed in figure 3.6.

The results are detailed in table 3.2 and the wavefunctions are detailed in figure 3.7

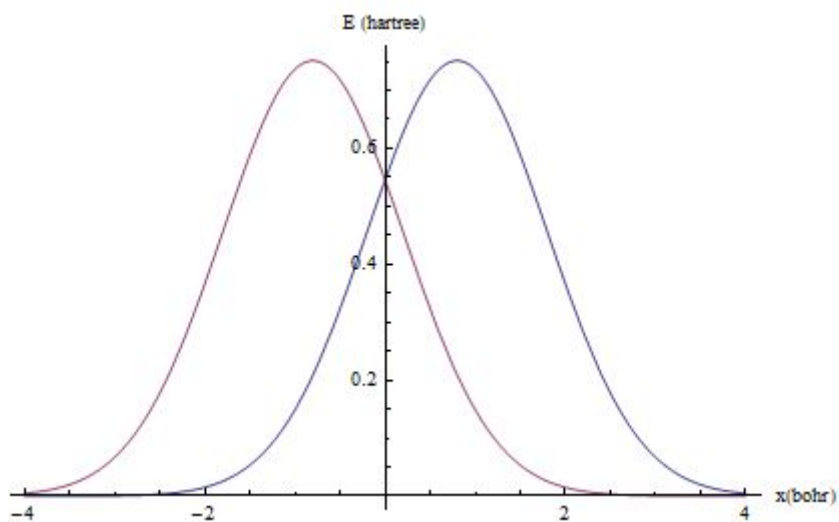


Figure 3.6: Gaussian functions focused in 0.8 Å and -0.8 Å.

Table 3.2: Results of the homonuclear coupled harmonic oscillators for an equilibrium point.

Ground state	
Energy (u.a)	0.296414
Wavefunction	$\Psi_0 = 1/\sqrt{2} \phi_1 + 1/\sqrt{2} \phi_2$
Excited state	
Energy(u.a)	0.849167
Wavefunction	$\Psi_1 = 1/\sqrt{2} \phi_1 - 1/\sqrt{2} \phi_2$

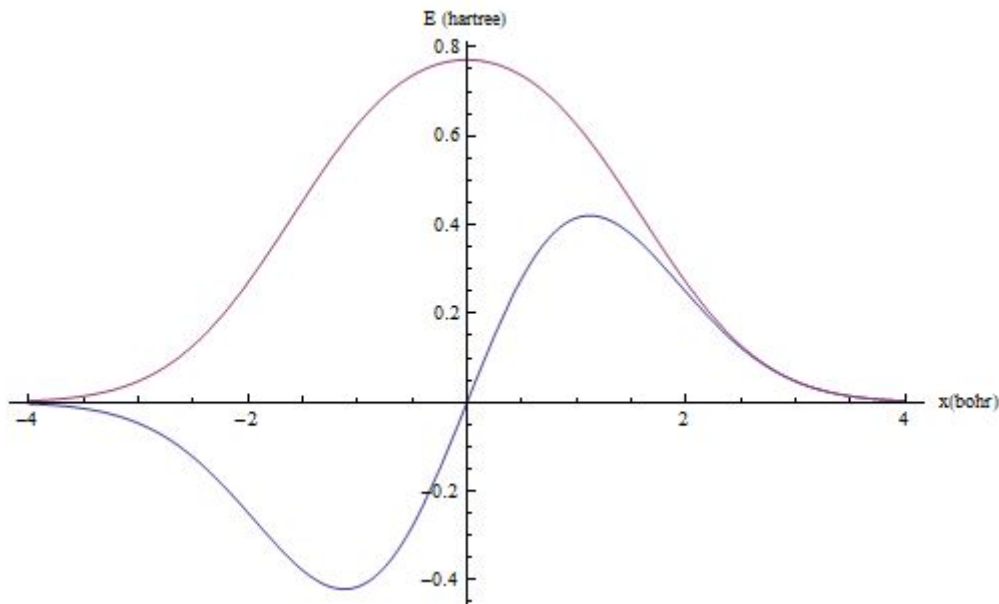


Figure 3.7:Representation of ground state (pink) and excited state (blue).

Remark that this results indicate that for this position, our systems change and the eigenvalues stop being degenerate. It obtains two different energies, the lower corresponds to the fundamental state and the higher corresponds to the excited state.

The wavefunctions in this case are converted into two different linear combination Gaussian function. The function which represents the ground state has not any node whereas the wavefunction of excited state has one in " $x = 0$ ". The nodes mean that the probability to find the particle in this position can't exist. Another conclusion is that the excited state present symmetry as long as the Hamiltonian does.

Optimized of frequency

Now, we are going to study how the system behaves when the frequency parameter is optimized. For each separation, we will optimize the frequency of the oscillator and then, we represent one curve such a figure 3.4 in order to prove the changes that there are when we optimized the parameter and when we don't do it (3.8)

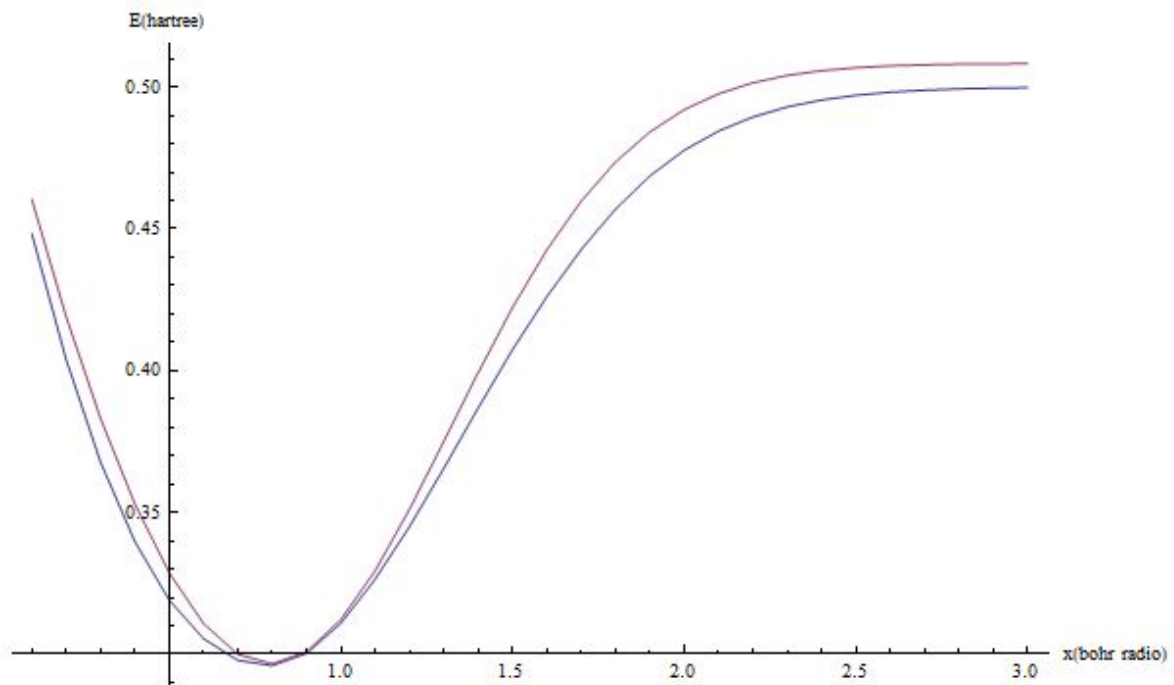


Figure 3.8: Dissociation diagram of diatomic homonuclear molecule formed by harmonic oscillators with the frequency optimization (blue) and with $w=1$ (pink).

As can be seen in figure 3.8, the behaviour of the curve is almost the same for a “ w ” and for the best “ w ” but, in the case of frequency optimization, the

Therefore, in figure 3.9 can be observed that the best value of the frequency is around 1 with little changes near to equilibrium point.

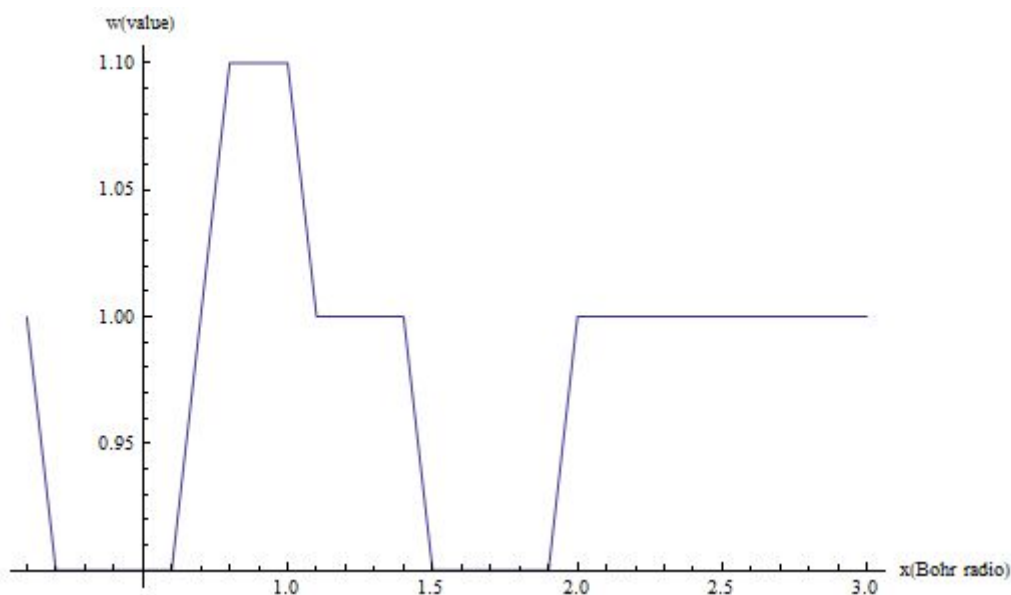


Figure 3.9: Value of optimization frequency depending on the distance.

Figure 3.9 has the expected the optimization value of “w” depending on the distance. Can be conclude that the value of the best “w” changing near to the equilibrium point because of the harmonic oscillators start to overlap, whereas for a huge separation, the best “w” is 1 due to the harmonic oscillators are separated and they adopt the energy of the one single harmonic oscillator.

Heteronuclear molecule:

In this system we take into account that the molecule is heteronuclear.

The difference between the heteronuclear and homonuclear molecule is that in the heteronuclear molecule the frequencies (“ w_a ” and “ w_b ”) which marks the curvature of the potential, and therefore the quantum confinement for each particle is different.

The mathematical treatment to show this relation is the following:

$$wa(hetero) = n wa(homo) \quad (3.45)$$

Where "n" is a positive scalar number.

$$w = \sqrt{\frac{k}{m}} \quad (3.46)$$

$$k = w^2 m \quad (3.47)$$

$$ka(homo) = wa(homo)^2 m \quad (3.48)$$

$$ka(hetero) = (n wa(homo))^2 m \quad (3.49)$$

$$\frac{ka(homo)}{ka(hetero)} = \frac{wa(homo)^2}{(n wa(homo))^2} \quad (3.50)$$

$$\frac{ka(homo)}{ka(hetero)} = \frac{1}{n^2} \quad (3.51)$$

$$ka(homo) = \frac{1}{n^2} ka(hetero) \quad (3.52)$$

Thus, with the expression (3.52) it has been demonstrated that when you change the frequency, the force constant and therefore the curvature of potential changes as well.

The conclusion that we can get is that when the frequency is higher, the force constant and the quantum confinement is also higher.

In this example it has considered that " w_a " = 2 , " w_b " = 1 u.a.

In this case, it takes into account that the normalization constant of the gaussian is different.

Thus, in this case the constant of the gaussian wavefunctions are:

$$N_1 = \left(\frac{2\alpha}{\pi}\right)^{1/4} \quad (3.53)$$

$$N_2 = \left(\frac{2\beta}{\pi}\right)^{1/4} \quad (3.54)$$

Thus, the representation of potential in this case is detailed in figure 3.10

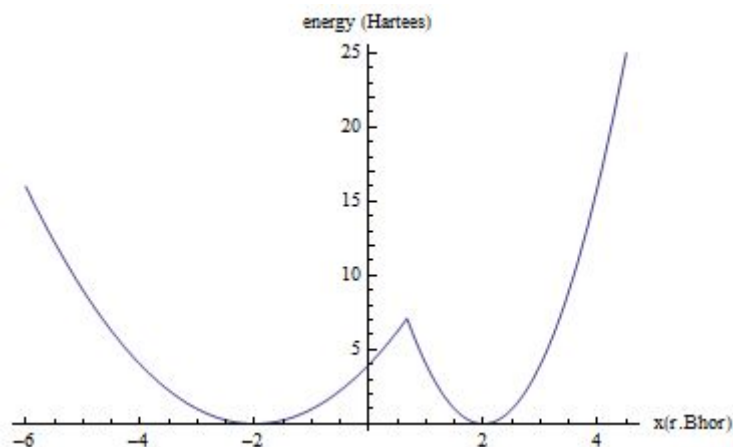


Figure 3.10 : Potential heteronuclear molecule

Remark that the Gaussian functions are equal to functions (3.41) and (3.42) but with different value of frequencies.

Therefore, in heteronuclear molecule we also considered two cases, when the oscillators are separate with a huge distance and near to equilibrium point. In the figure 3.11 the behaviour of the system is detailed.

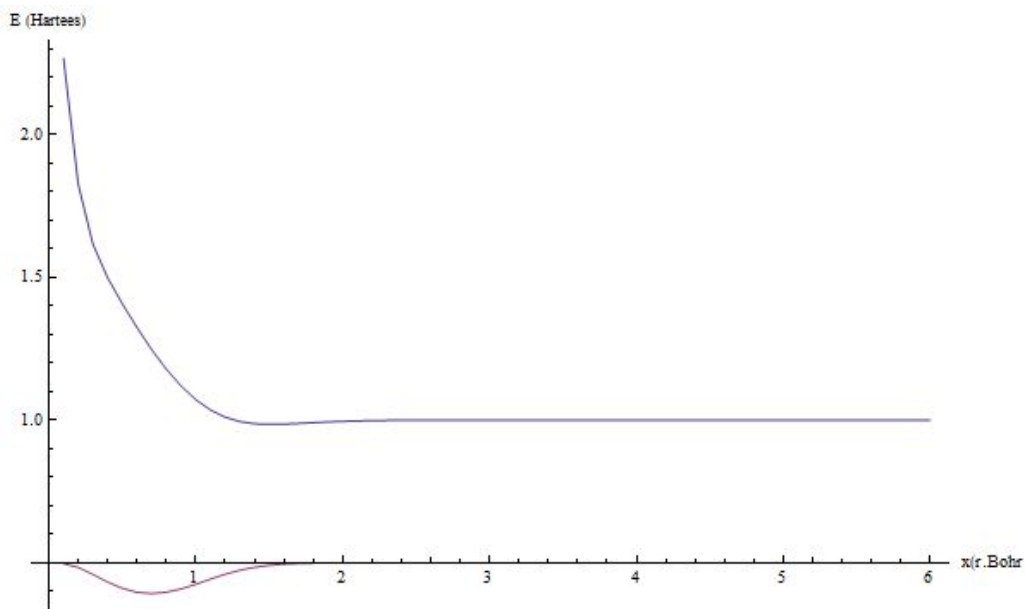


Figure 3.11: Dissociation diagram of diatomic heteronuclear molecule formed by harmonic oscillators

Figure 3.11 has the expected behaviour of a heteronuclear diatomic molecule dissociation diagram. The difference between homonuclear and heteronuclear dissociation is that in the limit of long inter-oscillator distance, the heteronuclear system is not degenerate.

An equilibrium distance is found in the same radii, but the ground state is less stabilized than the homonuclear molecule (0.491225 hartree) because the quantum confinement increases.

Thus, we study the system for a large distance and for an equilibrium point.

The guess Gaussian functions which are centred in 10 and -10 are detailed in figure 3.12.

The results are detailed in table 3.3 and the wavefunctions in figure 3.13.

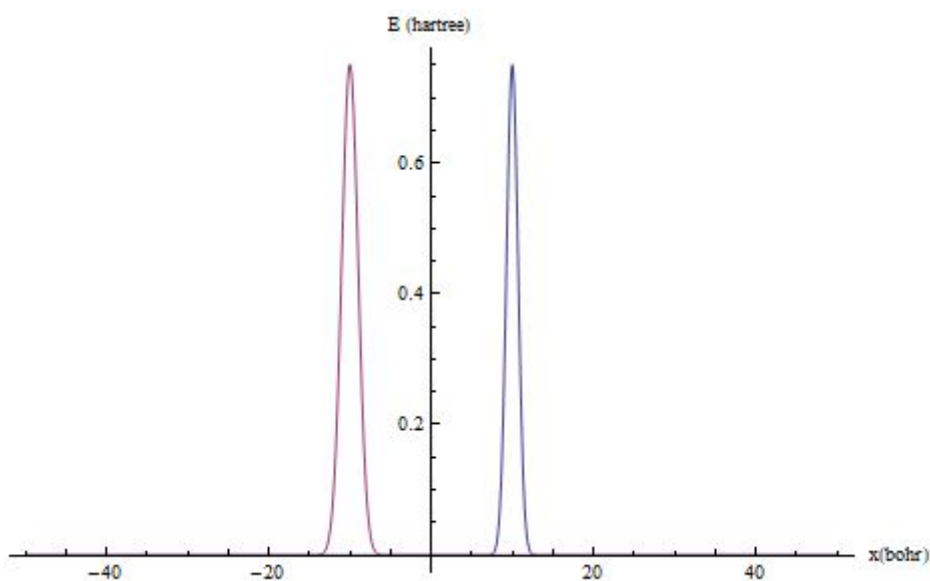


Figure 3.12: Gaussians functions for a 10 bohr.

Table 3.3: Results of the heteronuclear coupled harmonic oscillators for a large distant.

Ground state	
Energy (u.a)	0.5
Wavefunction	$\Psi_0 = \phi_2$
Excited state	
Energy(u.a)	1
Wavefunction	$\Psi_1 = \phi_1$

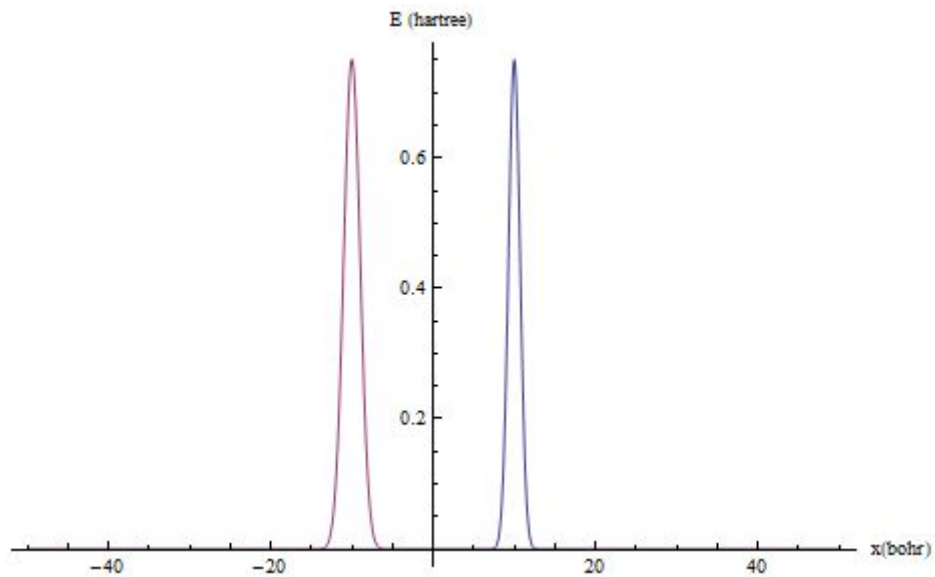


Figure 3.13: Wavefunction of ground state (pink) and excited state (blue) for a 10 bohr.

So the linear combination is the own function focused in “xa” and “xb” . The energy of the fundamental state is 0.5 hartree whereas the energy of the excited state is 1 hartree.

Second case

In this case, we going to consider that the position of our system is focused around the equilibrium point.

The gaussian functions which are focused in 1.5 and -1.5 (bohr) are detailed in figure 3.14
The results are detailed in table 3.4 and the wavefunctions are detailed in figures 3.15.

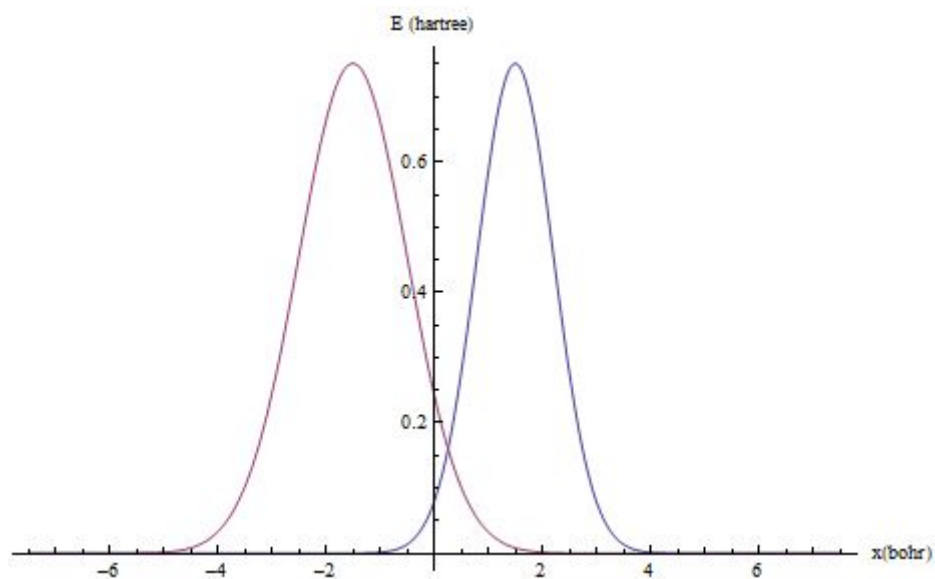


Figure 3.14: Gaussians functions near to the equilibrium point

Table 3.4: Results of the heteronuclear coupled harmonic oscillators for an equilibrium point.

Ground state	
Energy (u.a)	0.491225
Wavefunction	$\Psi_0 = 0.993692 \phi_1 + 0.112142 \phi_2$
Excited state	
Energy(u.a)	0.984896
Wavefunction	$\Psi_1 = 0.987391 \phi_1 - 0.1583 \phi_2$

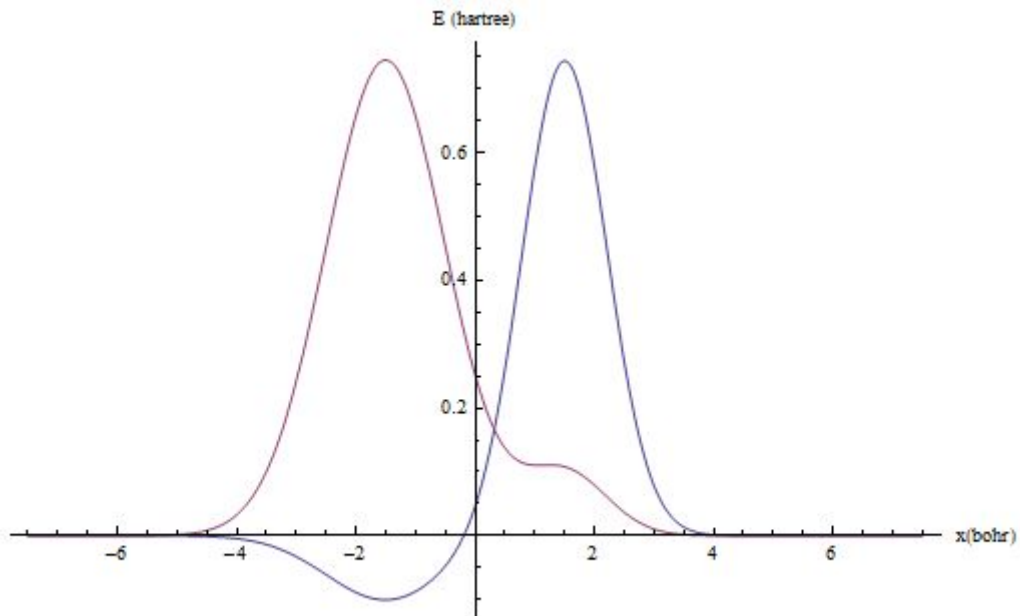


Figure 3.15: Representation of wavefunction for a ground state (blue) and excited state (pink) around the equilibrium point.

As we can see, the node persists but the symmetry about the antisymmetric plane has been broken.

3.1.1.2 Three coupled H.O. : Trinuclear molecules.

In this section another quantum system is going to be explored. This quantum system represents a trinuclear molecule. Thus, in this case the quantum confinement, the hamiltonian of the system and the potential are different.

First, the study of the hamiltonian is this one:

It has another harmonic oscillator in order to describe the third atom. Therefore, the hamiltonian of the system is the following:

$$\hat{H} = \frac{p^2}{2m} + \frac{1}{2} m \text{Min}[wa^2(x-xa)^2, wb^2(x-xb)^2, wc^2(x-xc)^2] \quad (3.55)$$

Where:

- "wc" are the quantum confinement of the third atom and it represents by the frequency of the oscillator.
- "xc" are the position where the third harmonic oscillator are on the axis.

In this case it is going to be considered that the frequency of the three harmonic oscillators are the same and equal to 1.

Then, the potential of the quantum system can be represented by the figure 3.16

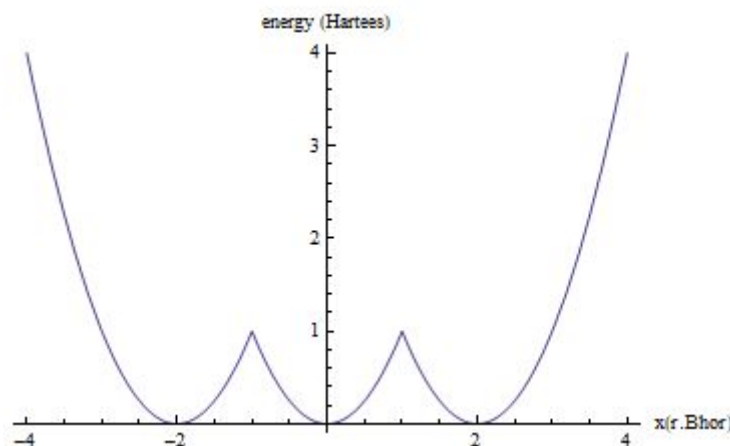


Figure 3.16: Three harmonic oscillator coupled

Then, in this quantum system the arbitrary gaussians wavefunctions are:

$$\phi_1 = N_1 e^{-\alpha(x-xa)^2} \quad (3.56)$$

$$\phi_2 = N_2 e^{-\beta(x-xb)^2} \quad (3.57)$$

$$\phi_3 = N_3 e^{-\gamma(x-xc)^2} \quad (3.58)$$

Where:

- “ N_1 ”, “ N_2 ” is the normalized constant that for the fundamental state and their value is shown in the expressions (3.53) and (3.54)
- “ α ” and “ β ” are detailed in expressions (3.44) and (3.45).
- “ γ ” has the value of:

$$\gamma = \frac{1}{2\sqrt{h/(m\omega c)}} \quad (3.58)$$

and,

$$N_3 = \left(\frac{2\gamma}{\pi}\right)^{1/4} \quad (3.59)$$

Furthermore, the next step is to follow the behaviour of the quantum system depending on the separation of the harmonic oscillators.

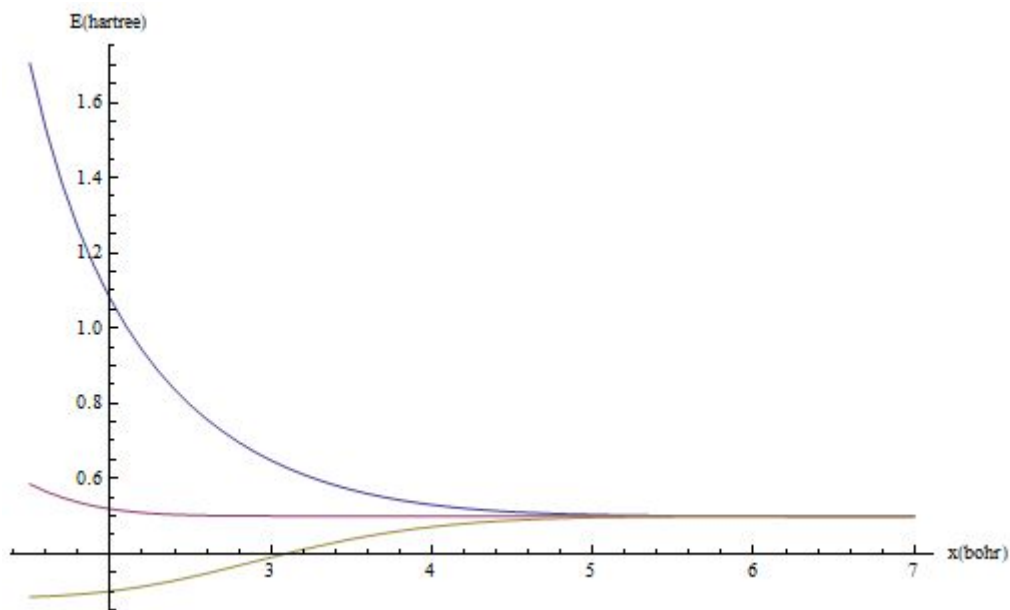


Figure 3.17:Representation of the three harmonic oscillators behaviour.

Thus, on the one hand, in the figure 3.17 it can be observed that for a large distance the system obtains the value of the fundamental state for one single harmonic oscillator (0.5 hartree) and that the three states are degenerate.

On the other hand, when the harmonic oscillators approach one to each others the quantum confinement and the potential affect the system and the degenerate changes into a one bonding state, one nonbonding state and one antibonding state with different energies.

In order to study the three harmonic oscillators coupled, they can be studied when the degeneracy has been broken. Thus, the energy and the wavefunctions of the different states are shown in the table 3.5 and in the figure 3.18 respectively.

Table 3.5: Results of the three harmonic oscillators coupled

Bonding state	
Energy (u.a)	0.390129
Wavefunction	$\Psi_0 = 0.500232 \phi_1 + 0.706776 \phi_2 + 0.500236 \phi_3$
Non bonding state	
Energy(u.a)	0.500199
Wavefunction	$\Psi_1 = 0.707109 \phi_1 - 0.707105 \phi_3$
Antibonding state	
Energy (u.a)	0.648102
Wavefunction	$\Psi_2 = 0.499801 \phi_1 + 0.70739 \phi_2 - 0.499799 \phi_3$

The wavefunctions of the bonding state, non bonding state and antibonding state are detailed in the figures 3.18.

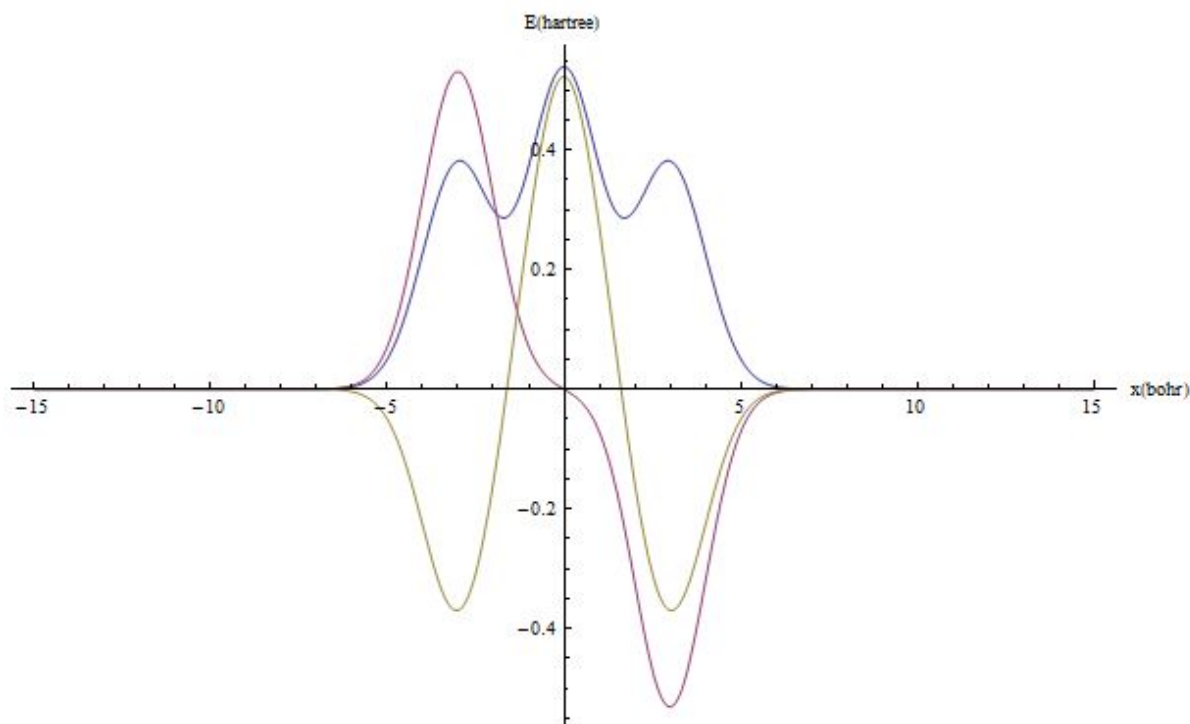


Figure 3.18: Wavefunction of bonding state (blue), non bonding state (pink) and antibonding state (brown).

Therefore, it can be seen that the bonding state has not any node, in the non bonding state there is one node and in the antibonding state there are two nodes. The increasing number of nodes with energy is consistent with the properties of one-dimensional systems in Quantum Mechanics [2]

To sum up, it can be concluded that when one oscillator is added, the quantum system is perturbed and the behaviour of the molecule is different. It can be concluded also that for two H.O.s there are two states (ground state and excited state) while for three H.O.s there are three states (bonding, non bonding and antibonding).

4.CLOSING REMARKS

Once the background, the computational programme and the results have been exposed, it can be concluded that the project aimed at:

- Knowing the importance and the historical context of the Gaussian method, as well as the history of its creator Jhon People and his research group.
- Understanding the mathematical foundation used in many computational quantum systems. This background consist in a quantum method called linear variational, which is used in order to resolve systems that can't be solved by analytical methods, as well as in the property of the Gaussian functions and how it can be applied in modern Quantum Chemistry.
- Knowing the behaviour of the diatomic and triatomic molecule with harmonic oscillator couples.
- Knowing the basis of the mathematical programming as well as convert the theoretical foundations into an operational programme.
- Improving my knowledge in quantum chemistry as well as learning new concepts such as the factoring method.

Therefore, I can conclude that after these months learning and focusing on some aspects of quantum chemistry, I expose that this science is brilliant, and also that the theoretical chemistry and the scientific challenges of today are very close to each other.

5.ACKNOWLEDGMENTS

Firstly, I would like to thank my tutor Juan Ignacio Climente Plasencia for giving me the opportunity to delve into quantum chemistry as well as for helping me start to understand the world of programming.

I would also like to thank the University Jaume I for giving me the opportunity of studying Chemistry in Castelló.

To finish with my final degree project, I am very grateful to the teachers who, with their effort, have instilled me the curiosity to investigate as well as having taught us to think critically.

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7 ANNEX

Annex I. Mathematica codes.

A.1.1 Three H.O.s coupled 1D

```

Clear["Global`*"];
(* Definim parametres del sistema: {{xa,wa},{xb,wb}}. x i w en unitats atomiques *)
wa = 1; wb = 1; wc = 1; xmin = 1.5; xmax = 3; pas = 0.1;

(* Definicions internes i constants *)

(* Massa *)
m = 1;
(* Constant de Planck barrada *)
h = 1;
(* Punt de no retorn *)
a =  $\sqrt{h / (m * wa)}$ ;
b =  $\sqrt{h / (m * wb)}$ ;
c =  $\sqrt{h / (m * wc)}$ ;
(* Exponent gaussiana *)
 $\alpha = 1 / (2 * a^2)$ ;
 $\beta = 1 / (2 * b^2)$ ;
 $\gamma = 1 / (2 * c^2)$ ;
(* Nombre elements a calcular. Llista per a desar resultats *)
nelems = (xmax - xmin) / pas + 1;
llistaeners = Table[{0, 0}, {i, nelems}];
llistaeners2 = Table[{0, 0}, {i, nelems}];
llistaeners3 = Table[{0, 0}, {i, nelems}];

(* Funció gaussiana ls *)
f[x_, xa_, alpha_] := ((1/Pi)^0.25) * Exp[-alpha * (x - xa)^2];

(* Representem la funcio per a xmax i visualment determinem un valor segur del limit
d'integracio. Per aquests valors d'omega, queda clar que xmax*5 es suficient *)
Plot[{f[x, xmax,  $\alpha$ ], f[x, 0,  $\beta$ ], f[x, -xmax,  $\gamma$ ]}, {x, -5 * xmax, 5 * xmax}, PlotRange -> All]

(* Integral de solapament *)
intS[xa_, xb_, alpha_, beta_] :=
  Integrate[f[x, xa, alpha] * f[x, xb, beta], {x, -5 * xmax, 5 * xmax}];
intS
(* Integral d'energia cinetica *)
intT[xa_, xb_, alpha_, beta_] := Integrate[
  f[x, xa, alpha] * (-1 / (2 * m)) * D[f[x, xb, beta], {x, 2}], {x, -5 * xmax, 5 * xmax}];
(* Integral d'energia potencial *)
intV[xa_, xb_, alpha_, beta_] :=
  NIntegrate[f[x, xa, alpha] * (1/2) * m * Min[wc^2 * (x - Abs[xa])^2, wb^2 * (x + Abs[xb])^2,
  wa^2 * (x + Abs[xa])^2] * f[x, xb, beta], {x, -5 * xmax, 5 * xmax}];

```

```

For[k = 1, k ≤ nelems, k++,
  x0 = xmin + (k - 1) * pas;
  xa = x0;
  xb = 0;
  xc = -x0;

  llista = {{xa, wa}, {xb, wb}, {xc, wc}};
  dim = Length[llista];

  (* Quin calcul fem ara? *)

  (* Comprova norma -vist una vegada que funcione be, es pot omitir-
  Print["Comprovacio norma: <f|f>=", Integrate[f[xt, xa, a]^2, {xt, -Infinity, Infinity}]];
  Print["Ara amb fórmula: <f|f>=", intS[xa, xa, a, a]]; *)

  (* Ompli matrius *)
  matS = Table[0, {i, 1, dim}, {j, 1, dim}];
  matT = Table[0, {i, 1, dim}, {j, 1, dim}];
  matV = Table[0, {i, 1, dim}, {j, 1, dim}];

  For[i = 1, i ≤ dim, i++,
    For[j = i, j ≤ dim, j++,

      (* Coordenades *)
      x1 = llista[[i, 1]];
      x2 = llista[[j, 1]];

      (* Freqüència *)
      w1 = llista[[i, 2]];
      w2 = llista[[j, 2]];
      (* Punt de no retorn *)
      a =  $\sqrt{h / (m * w1)}$ ;
      b =  $\sqrt{h / (m * w2)}$ ;
      (* Exponent *)
      a1 =  $1 / (2 * a^2)$ ;
      a2 =  $1 / (2 * b^2)$ ;

      matS[[i, j]] = intS[x1, x2, a1, a2];
      matT[[i, j]] = intT[x1, x2, a1, a2];
      matV[[i, j]] = intV[x1, x2, a1, a2];

      matS[[j, i]] = matS[[i, j]];
      matT[[j, i]] = matT[[i, j]];
      matV[[j, i]] = matV[[i, j]];

    ]
  ];

```

```

];

iS = Inverse[matS];
(* Print["matriu identitat=", iS.matS];
(* test, una vegada comprovat es pot omitir *) *)

mH = matV * matT;
mE = iS.mH;

eners = Eigenvalues[mE];

ener1 = eners[[1]];
ener2 = eners[[2]];
ener3 = eners[[3]];

vectors = Eigenvectors[mE];

llistaeners[[k]] = {x0, ener1};
llistaeners2[[k]] = {x0, ener2};
llistaeners3[[k]] = {x0, ener3};
];

eners
vectors // MatrixForm
{0.648102, 0.500199, 0.390129}


$$\begin{pmatrix} -0.499801 & 0.70739 & -0.499799 \\ 0.707105 & 9.84342 \times 10^{-9} & -0.707109 \\ 0.500236 & 0.706776 & 0.500232 \end{pmatrix}$$


ListPlot[{llistaeners, llistaeners2, llistaeners3},
  Joined -> True, PlotRange -> All, AxesLabel -> {"x(bohr)", "E(hartree)"}]

```

```

vectors

{{-0.499801, 0.70739, -0.499799},
 {0.707105, 9.84342×10-9, -0.707109}, {0.500236, 0.706776, 0.500232}}

c1=vectors[[1, 1]];
c2=vectors[[1, 2]];
c3=vectors[[1, 3]];
c4=vectors[[2, 1]];
c5=vectors[[2, 2]];
c6=vectors[[2, 3]];
c7=vectors[[3, 1]];
c8=vectors[[3, 2]];
c9=vectors[[3, 3]];
funciofonamental[x_]:=c9*f[x, xmax, a]+c8*f[x, xb, b]+c7*f[x, -xmax, y];
funcioexcitat[x_]:=c6*f[x, xmax, a]+c5*f[x, 0, b]+c4*f[x, -xmax, y];
funcioexcitat2[x_]:=c3*f[x, xmax, a]+c2*f[x, 0, b]+c1*f[x, -xmax, y];

fexci=Plot[{c9*f[x, xmax, a]+c8*f[x, xb, b]+c7*f[x, -xmax, y],
 c6*f[x, xmax, a]+c5*f[x, 0, b]+c4*f[x, -xmax, y],
 c3*f[x, xmax, a]+c2*f[x, 0, b]+c1*f[x, -xmax, y]},
 {x, -5*xmax, 5*xmax}, PlotRange->All, AxesLabel->{"x", "energy (a.u.)"}]

fexci=Plot[funcioexcitat2[x], {x, -5*xmax, 5*xmax},
 PlotRange->All, AxesLabel->{"x", "energy (a.u.)"}]

fexi2=Plot[funcioexcitat[x], {x, -5*xmax, 5*xmax},
 PlotRange->All, AxesLabel->{"x", "energy (a.u.)"}]

```

A.1.2 Two H.O.s coupled

```

Clear["Global`*"];
(* Definim parametres del sistema: {{xa,wa},{xb,wb}}. x i w en unitats atomiques *)
wa = 2; wb = 1; xmin = 0.1; xmax = 10; pas = 0.1;

(* Definicions internes i constants *)

(* Massa *)
m = 1;
(* Constant de Planck barrada *)
h = 1;
(* Punt de no retorn *)
a =  $\sqrt{h / (m * wa)}$ ;
b =  $\sqrt{h / (m * wb)}$ ;
(* Exponent gaussiana *)
 $\alpha = 1 / (2 * a^2)$ ;
 $\beta = 1 / (2 * b^2)$ ;

(* Nombre elements a calcular. Llista per a desar resultats *)
nelems = (xmax - xmin) / pas + 1;
llistaeners = Table[{0, 0}, {i, nelems}];
llistaeners2 = Table[{0, 0}, {i, nelems}];

(* Funció gaussiana 1s *)
norm = 1 / (Pi^0.25);
f[x_, xa_, alpha_] := norm * Exp[-alpha * (x - xa)^2];

(* Representem la funcio per a xmax i visualment determinem un valor segur del limit
d'integracio. Per aquests valors d'omega, queda clar que xmax*5 es suficient *)
Plot[{f[x, xmax,  $\alpha$ ], f[x, -xmax,  $\beta$ ]}, {x, -5 * xmax, 5 * xmax},
PlotRange -> All, AxesLabel -> {"x(bohr)", "E (hartree)"}

```

```

(* Integral de solapament *)
intS[xa_, xb_, alpha_, beta_] :=
  norm^2 * (Pi / (alpha + beta)) ^ 0.5 * Exp[-alpha * beta / (alpha + beta) * (xa - xb) ^ 2];
(* Integral d'energia cinetica *)
intT[xa_, xb_, alpha_, beta_] := Integrate[
  f[x, xa, alpha] * (-1 / (2 * m) * D[f[x, xb, beta], {x, 2}]), {x, -5 * xmax, 5 * xmax}];
(* Integral d'energia potencial *)
intV[xa_, xb_, alpha_, beta_] :=
  NIntegrate[f[x, xa, alpha] * (1 / 2) * m * Min[wa^2 * (x - Abs[xa]) ^ 2, wb^2 * (x + Abs[xa]) ^ 2] *
  f[x, xb, beta], {x, -5 * xmax, 5 * xmax}];

For[k = 1, k <= nelems, k++,
  x0 = xmin + (k - 1) * pas;
  xa = x0;
  xb = -x0;

  llista = {{xa, wa}, {xb, wb}};
  dim = Length[llista];

  (* Quin calcul fem ara? *)

  (* Comprova norma -vist una vegada que funcione be, es pot omitir-
  Print["Comprovacio norma: <f|f>=", Integrate[f[xt, xa, alpha]^2, {xt, -Infinity, Infinity}]];
  Print["Ara amb fórmula: <f|f>=", intS[xa, xa, alpha, alpha]]; *)

  (* Ompli matrius *)
  matS = Table[0, {i, 1, dim}, {j, 1, dim}];
  matT = Table[0, {i, 1, dim}, {j, 1, dim}];
  matV = Table[0, {i, 1, dim}, {j, 1, dim}];

  For[i = 1, i <= dim, i++,
    For[j = i, j <= dim, j++,

      (* Coordenades *)
      x1 = llista[[i, 1]];
      x2 = llista[[j, 1]];

```

```

(* Freqüència *)
w1 = llista[[i, 2]];
w2 = llista[[j, 2]];
(* Punt de no retorn *)
a =  $\sqrt{h / (m \cdot w1)}$ ;
b =  $\sqrt{h / (m \cdot w2)}$ ;
(* Exponent *)
a1 = 1 / (2 * a^2);
a2 = 1 / (2 * b^2);

matS[[i, j]] = intS[x1, x2, a1, a2];
matT[[i, j]] = intT[x1, x2, a1, a2];
matV[[i, j]] = intV[x1, x2, a1, a2];

matS[[j, i]] = matS[[i, j]];
matT[[j, i]] = matT[[i, j]];
matV[[j, i]] = matV[[i, j]];

];
];

iS = Inverse[matS];
(* Print["matriu identitat=", iS.matS];
(* test, una vegada comprovat es pot omitir *) *)

mH = matV + matT;
mE = iS.mH;

enerS = Eigenvalues[mE];
ener1 = enerS[[1]];
ener2 = enerS[[2]];

vectors = Eigenvectors[mE];

llistaeners[[k]] = {x0, ener1};
llistaeners2[[k]] = {x0, ener2};

];

ListPlot[{llistaeners, llistaeners2}, Joined -> True,
PlotRange -> All, AxesLabel -> {"x (r.Bohr)", "E (Hartees)"}]

```

```
c1 = vectors[[1, 1]];
c2 = vectors[[1, 2]];
c3 = vectors[[2, 1]];
c4 = vectors[[2, 2]];
f1 = c1*f[x, xmax, alpha] + c2*f[x, -xmax, beta];
f2 = c3*f[x, xmax, alpha] + c4*f[x, -xmax, beta];

c2
{{Null}, {Null}}
0.

Plot[{c1*f[x, xmax, alpha] + c2*f[x, -xmax, beta], c3*f[x, xmax, alpha] + c4*f[x, -xmax, beta]},
{x, -5*xmax, 5*xmax}, PlotRange -> All, AxesLabel -> {"x(bohr)", "E (hartree)"}]
```


A.1.3 Frequency optimization

```

Clear["Global`*"];
(* Definim parametres del sistema: {{xa,wa},{xb,wb}}. x i w en unitats atomiques *)
xmin = 0.1; xmax = 3; pas = 0.1; wa = 1; wb = 1;
wmin = 0.80; wpas = 0.1;
(* Definicions internes i constants *)

(* Massa *)
m = 1;
(* Constant de Planck barrada *)
h = 1;
(* Punt de no retorn *)
a =  $\sqrt{h / (m * wa)}$ ;
b =  $\sqrt{h / (m * wb)}$ ;
(* Exponent gaussiana *)
 $\alpha = 1 / (2 * a^2)$ ;
 $\beta = 1 / (2 * b^2)$ ;

(* Nombre elements a calcular. Llista per a desar resultats *)
nelems = (xmax - xmin) / pas + 1;
llistaeners = Table[{0, 0}, {i, nelems}];
llistaeners2 = Table[{0, 0}, {i, nelems}];
llistalpha = Table[{0, 0}, {i, nelems}];
llistabestw = Table[{0, 0}, {i, nelems}];

f[x_, xa_, alpha_] := (((2 * alpha / Pi)) ^ 0.25) * Exp[-alpha * (x - xa) ^ 2];

(* Integral de solapament *)
intS[xa_, xb_, alpha_, beta_] :=
  Integrate[f[x, xa, alpha] * f[x, xb, beta], {x, -5 * xmax, 5 * xmax}];
(* Integral d'energia cinetica *)
intT[xa_, xb_, alpha_, beta_] := Integrate[
  f[x, xa, alpha] * (-1 / (2 * m) * D[f[x, xb, beta], {x, 2}]), {x, -5 * xmax, 5 * xmax}];
(* Integral d'energia potencial *)
intV[xa_, xb_, alpha_, beta_] :=
  NIntegrate[f[x, xa, alpha] * (1 / 2) * m * Min[wa ^ 2 * (x - Abs[xa]) ^ 2, wb ^ 2 * (x + Abs[xa]) ^ 2] *
  f[x, xb, beta], {x, -5 * xmax, 5 * xmax}];

```

```
For[k = 1, k ≤ nelems, k++,
  millorener = 10;
  millorw = 2;

  For[w = 1, w ≤ 5, w++,

    w0 = wmin + (w - 1) * wpas;
    x0 = xmin + (k - 1) * pas;
    xa = x0;
    xb = -x0;
    llista = {{xa, wa}, {xb, wb}};
    lista = {{xa, w0}, {xb, w0}};

    dim = Length[llista];

    (* Quin calcul fem ara? *)

    (* Comprova norma -vist una vegada que funcione be, es pot omitir-
    Print["Comprovacio norma: <f|f>=", Integrate[f[xt, xa, α]^2, {xt, -Infinity, Infinity}]];
    Print["Ara amb fórmula: <f|f>=", intS[xa, xa, α, α]]; *)

    (* Ompli matrius *)
    matS = Table[0, {i, 1, dim}, {j, 1, dim}];
    matT = Table[0, {i, 1, dim}, {j, 1, dim}];
    matV = Table[0, {i, 1, dim}, {j, 1, dim}];

    For[i = 1, i ≤ dim, i++,
      For[j = i, j ≤ dim, j++,
```

```

(* Coordenades *)
x1 = lista[[i, 1]];
x2 = lista[[j, 1]];
(* Freqüència *)
w1 = lista[[i, 2]];
w2 = lista[[j, 2]];
(* Punt de no retorn *)
a =  $\sqrt{h / (m * w1)}$  ;
b =  $\sqrt{h / (m * w2)}$  ;
(* Exponent *)
a1 = 1 / (2 * a^2);
a2 = 1 / (2 * b^2);

matS[[i, j]] = intS[x1, x2, a1, a2];
matT[[i, j]] = intT[x1, x2, a1, a2];
matV[[i, j]] = intV[x1, x2, a1, a2];

matS[[j, i]] = matS[[i, j]];
matT[[j, i]] = matT[[i, j]];
matV[[j, i]] = matV[[i, j]];

; ]
; ] ;

iS = Inverse[matS];

mH = matV + matT;
mE = iS.mH;

eners = Eigenvalues[mE];

```

```
ener1 = eners[[1]];
ener2 = eners[[2]];
energia = eners[[2]];

vectors = Eigenvectors[mE];
If[energia < millorener, millorener = energia; millorw = w0]
];

llistaeners[[k]] = {x0, ener1};
llistaeners2[[k]] = {x0, ener2};
llistalpha[[k]] = {x0, millorener};
llistabestw[[k]] = {x0, millorw};

];

ListPlot[{llistalpha, llistaeners2},
PlotRange -> All, AxesLabel -> {"x(bohr radio)", "E(hartree)"}]

ListPlot[llistabestw, Joined -> True,
PlotRange -> All, AxesLabel -> {"x(Bohr radio)", "w(value)"}]
```