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Particle in a Box Revisited

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1. Abstract

Some important concepts will be introduced on quantum chemistry such as symmetry labels of molecular states by dwelling on the "particle in a box" model. The mathematical models introduced allow understanding orthogonality relationships, expansion of an orbital in a complete set of basis functions, perturbation theory of nondegenerate energy levels, and transition probabilities with some attention to selection rules. This project is developed by means of Mathematica and COMSOL codes in an experimental laboratory.

2. Introduction

In the present work we will evaluate the particle in a one-dimensional and two-dimensional box. For both situations we will study the addition of a potential whose effect, on the energy and wave functions, will analyzed by two approximation methods: 1) *Linear variation method* and 2) *Perturbation theory time-independent*. The results obtained will be contrasted with an "exact" numerical method. This method will carried out through COMSOL code in finite elements. We will also make reference, succinctly, to the time-independent perturbation theory meaning to introduce the transition dipole moment to pay attention to radiation-matter interaction evaluating the probabilities transitions between energy levels of particle in a box. With aim to simplify the algebra of formula used, we will use u.a.(atomic units).

2.1 Particle in a Box without Potential

The stationary-state wave functions and energy levels of a one-particle are found by solving the ***time-independent*** Schrödinger equation. The model of the particle in a box has a perfect extension to one, two or three dimensions.

2.1.1 Particle in a One-Dimensional Box

This is a simple system model where a particle is subjected to a potential-energy function that is infinite everywhere along the x axis except for a line segment of length a, where the potential energy is zero. In this case, the box is centered at the origin of coordinates.
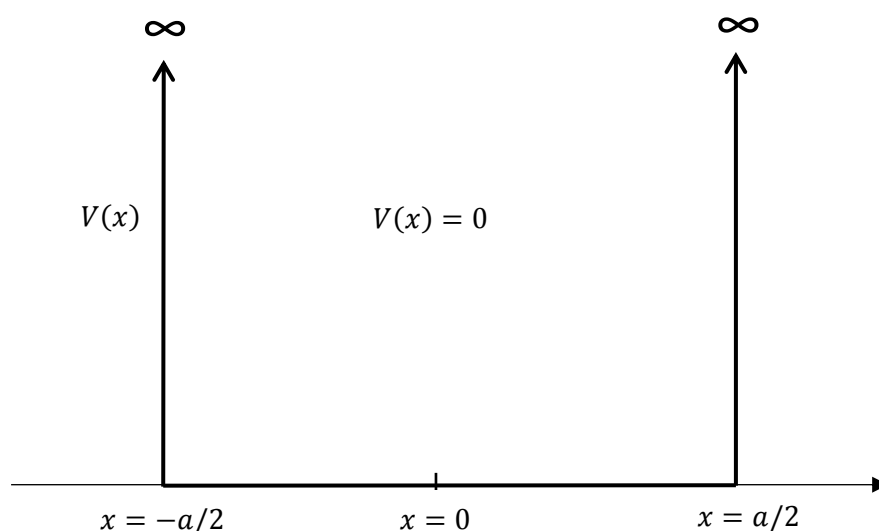

Figure 1. Particle in a one-dimensional box $-a/2 \leq x \leq a/2$.

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It has assumed throughout this work that the particle has a mass, m, 1 u.a. The length of the box is from $x = -a/2$ to $x = a/2$, where $a = 1$ u.a. As usual, an infinite potential is invoked on the two extremities of the box. Thus, the set of normalized eigenfunctions satisfying the basic axioms of quantum theory are

$$\Psi_n = \sqrt{\frac{2}{a}} \cos \frac{n \pi x}{a} \quad n = odd \tag{1}$$

$$\Psi_n = \sqrt{\frac{2}{a}} \sin \frac{n \pi x}{a} \quad n = pair \tag{2}$$

where $n = 1,2,3…$

This means that the hamiltonian inside the box is exactly known. Besides, the only contribution to the Hamiltonian will, at this stage, be assumed to be the kinetic energy and is therefore given by

$$\hat{H} = -\frac{1}{2} \frac{d^2}{dx^2} \tag{3}$$

being the Schrödinger equation for the system

$$\hat{H} \Psi_n(x) = E_n \Psi_n(x) \tag{4}$$

The energy that represents the exact energy of the nth level will be

$$E_n = \frac{\hat{H} \Psi_n}{\Psi_n} \tag{5}$$

The eigenfunctions of the Schrödinger equation form a complete set of orthonormal basis functions. Therefore,

$$< \Psi_i | \Psi_j > = \delta_{ij} \begin{cases} 0 & i \neq j \\ 1 & i = j \end{cases} \tag{6}$$

The Figure 2 shows the graphic representation of functions with their respective values and exact energies of the states. We can observe that the number of nodes (place inside the box where the wave functions dies) is equal to (n-1) where i is the quantum number of the state under study.

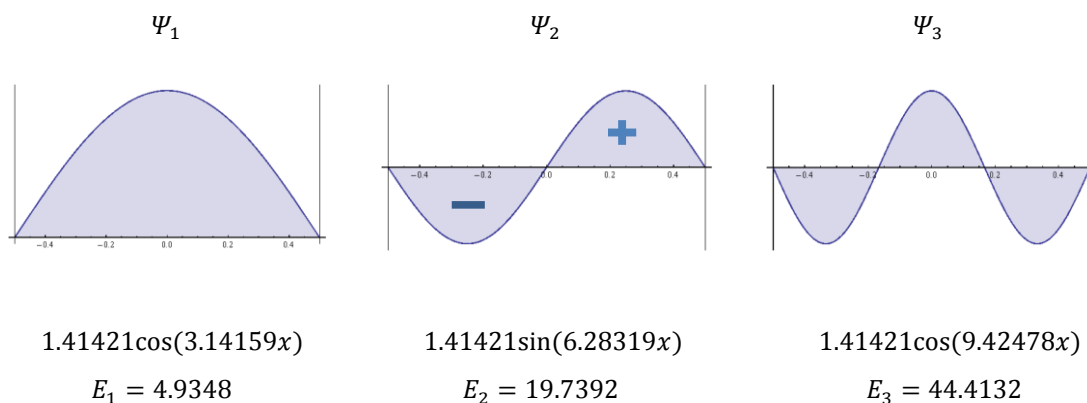| Ψ_1	Ψ_2	Ψ_3
$1.41421\cos(3.14159x)$	$1.41421\sin(6.28319x)$	$1.41421\cos(9.42478x)$
$E_1 = 4.9348$	$E_2 = 19.7392$	$E_3 = 44.4132$

Figure 2. The shapes of the first three exact eigenfunctions of the particle in a one-dimensional box model by Mathematica.

Thus, for example, the number of nodes in the function corresponding to the third state is equal to 2. The energies presents in the Figure 2 correspond, in a.u., to the exact equation of the energy for a particle in a one-dimensional box that is

$$E_n = \frac{\pi^2 n^2}{2a^2}$$

(7)

Now, we will verify the orthogonality by elemental integration techniques. However, orthogonality can be easily established by studying graphical plots of the functions $\Psi_i \Psi_j$

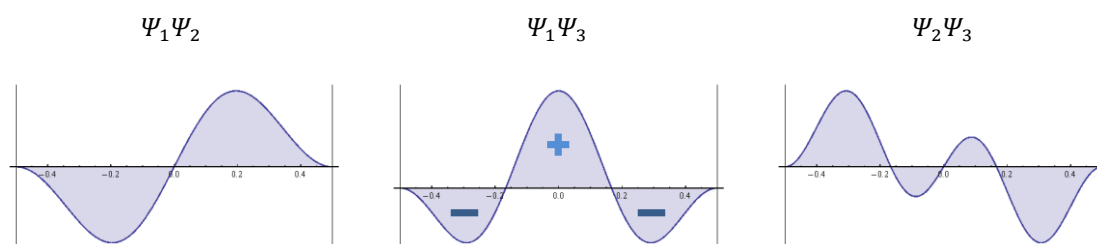The Figure 3 shows the shapes of the orthogonality basis functions

$\Psi_1 \Psi_2$ $\quad\quad\quad\quad\quad\quad\quad$ $\Psi_1 \Psi_3$ $\quad\quad\quad\quad\quad\quad\quad$ $\Psi_2 \Psi_3$

Figure 3. The shape of the functions $\boldsymbol{\Psi_i \Psi_j}$.

The most relevant we can see in the Figure 3 is that the shapes of the functions, in the graphic plots, are symmetric and present the same areas dimension. The orthogonality of the functions is graphically demonstrated.

These functions satisfy the $< \Psi_i | \Psi_j > = \delta_{ij}$ condition showed above in Eq. (6). Therefore, is demonstrated, at the same time, that the overlap matrix is the unit matrix $\mathbb{S} = 1$.

If each of these functions is normalized, then set of functions Ψ_i is said to form a complete orthonormal set. Any function that satisfies the boundary conditions of the system can be written as a linear combination of this orthonormal basis set.

2.1.2 Particle in a Two-Dimensional Box

For the two-dimensional system and following the Eqs. (3) and (4) the Schrödinger equation satisfies

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}\right)\Psi_n(x,y)=E_n\Psi_n(x,y) \tag{8}$$

The position in the coordinates is $-a/2 \le x \le a/2$ and $-b/2 \le y \le b/2$ assumed a rectangular box in the case that $a \ne b$ and a square box if $a = b$.
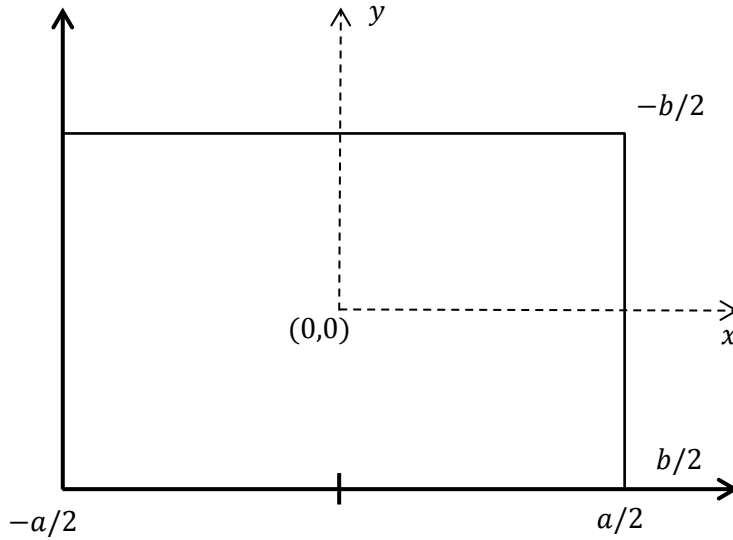

Figure 4. Particle in a two-dimensional box $-a/2 \le x \le a/2$ and $-b/2 \le y \le b/2$.

Based on the Eq. (8) can be considered $\hat{H}_x + \hat{H}_y$ (independent operators). Thus, applying the same methodology as in one-dimension, the functions used will be

$$\left.\begin{aligned}\Psi_{n_x}(x) &= \sqrt{\frac{2}{a}}\cos\left(\frac{n_x\pi x}{a}\right)\\ \Psi_{n_y}(y) &= \sqrt{\frac{2}{b}}\cos\left(\frac{n_y\pi y}{b}\right)\end{aligned}\right\} \quad n = odd \quad (9) \qquad \left.\begin{aligned}\Psi_{n_x}(x) &= \sqrt{\frac{2}{a}}\sin\left(\frac{n_x\pi x}{a}\right)\\ \Psi_{n_y}(y) &= \sqrt{\frac{2}{b}}\sin\left(\frac{n_y\pi y}{b}\right)\end{aligned}\right\} \quad n = pair \quad (10)$$

So, a complete set of functions used will be

$$\Psi_{n_x n_y}(x,y)=\Psi_{n_x}(x)\Psi_{n_y}(y) \tag{11}$$

and the energy

$$E = E_x + E_y \tag{12}$$

The values of the exact energy, in a 2D box, are given by

$$E_{n_x n_y}=\frac{\pi^2}{2}\left(\frac{n_x^2}{a^2}+\frac{n_y^2}{b^2}\right) \tag{13}$$

The Figure 5 represents the functions of three states, with the values of exact energies and symmetrical functions (remember Eq. (11)), for a particle in a rectangular box ($a \neq b$), that is to say, both dimensions of the box must not be equal, to avoid degeneracies [3] as would happen in a square box.
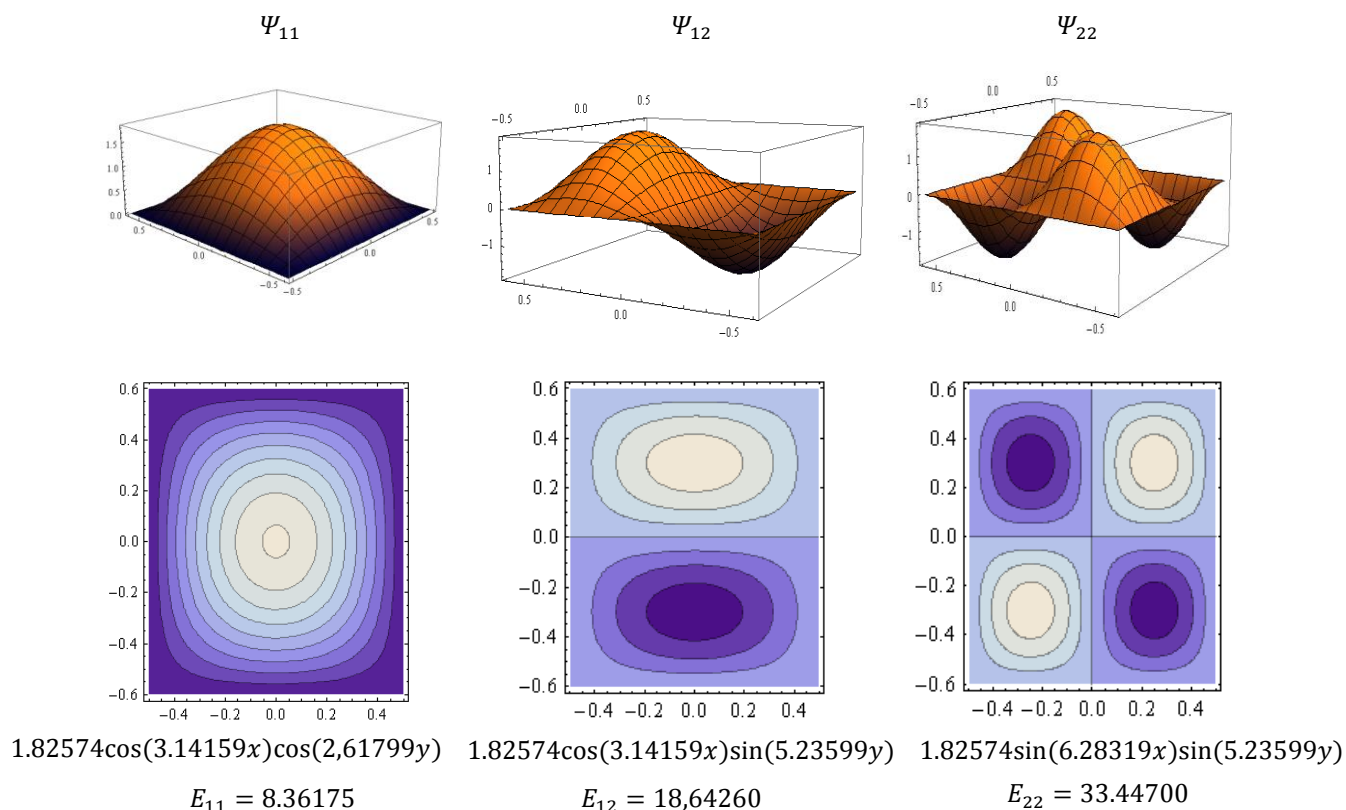
$$\Psi_{11} \qquad\qquad \Psi_{12} \qquad\qquad \Psi_{22}$$

$$1.82574\cos(3.14159x)\cos(2{,}61799y) \quad 1.82574\cos(3.14159x)\sin(5.23599y) \quad 1.82574\sin(6.28319x)\sin(5.23599y)$$

$$E_{11} = 8.36175 \qquad\qquad E_{12} = 18{,}64260 \qquad\qquad E_{22} = 33.44700$$

Figure 5. The shape of the three exact eigenfunctions for a particle in a rectangular box.

As we can see in Figure 5, for a 2D box, the nodes are represented by lines where state 12 has one node and state 22 has two nodes.

Contrasting Figure 5 and 6 we can see, as $a \neq b$, the states ($n_x = 1, n_y = 2$) and ($n_x = 2, n_y = 1$) are not degenerated. Thus, the absence of degeneracy is demonstrated for a rectangular box.

$$\Psi_{21}$$

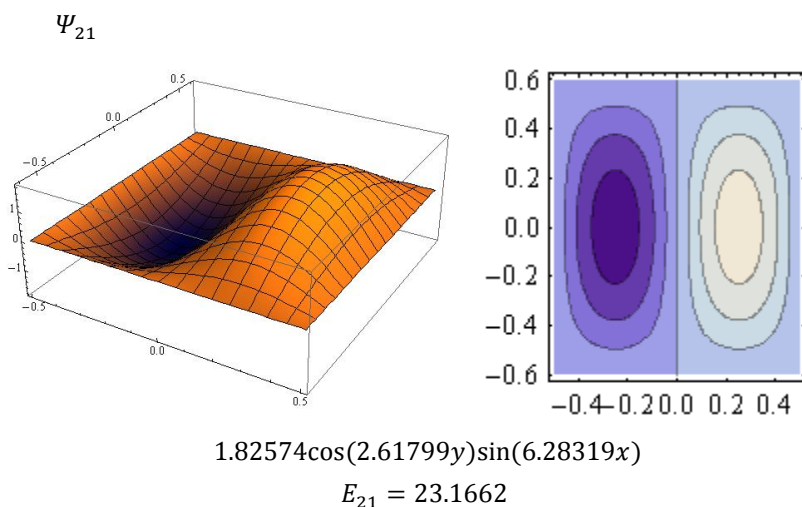
$$1.82574\cos(2.61799y)\sin(6.28319x)$$

$$E_{21} = 23.1662$$

Figure 6. The shape of the function Ψ_{21} and exact energy of the corresponding state. Respect to Ψ_{12} it can only observe difference in the position of the function.

If the particle was in a square box ($a = b$) the states Ψ_{12} and Ψ_{21} will be degenerate ($E_{12} = E_{21}$) as Figure 7 shows
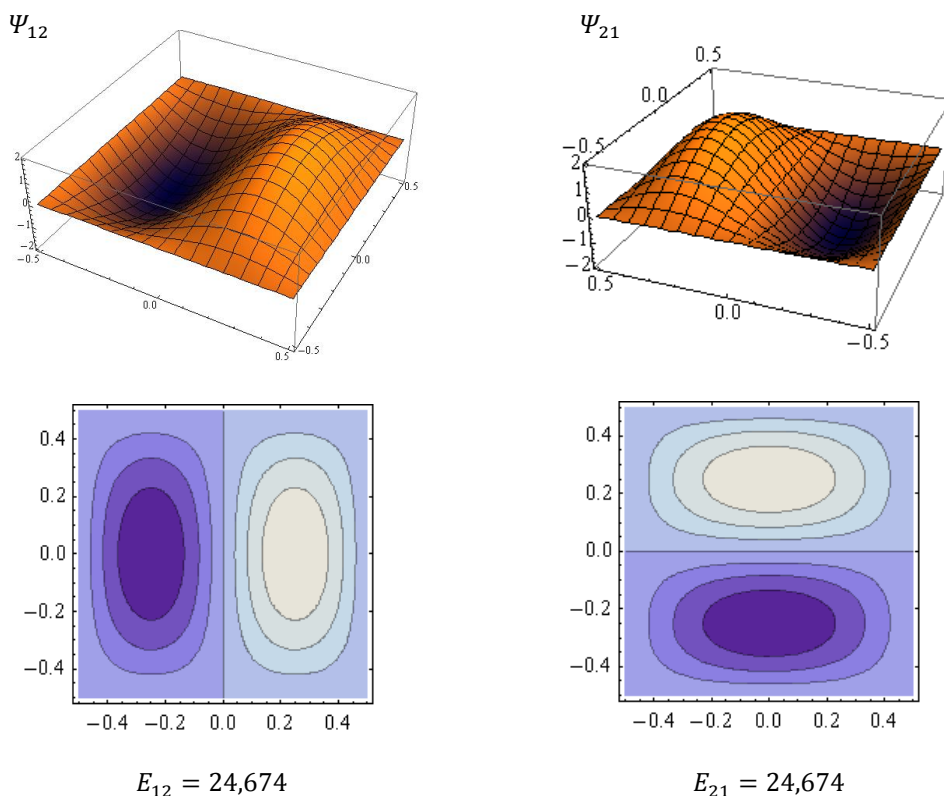

$$E_{12} = 24{,}674 \qquad\qquad E_{21} = 24{,}674$$

Figure 7. Shapes of functions $\boldsymbol{\Psi_{12}}$ and $\boldsymbol{\Psi_{21}}$ and degeneracy formed in states 12 and 21 in a square box.

As we can observe, comparing Figure 5 with Figure 6, the energy of the state 12 and 21 do not seem similar, meaning that there is not degeneracy [3]. So, we can conclude that, in a rectangular box, unless at least two of the values a or b are integers, would has not degeneracy[1].

Figure 7 shows Ψ_{12} and Ψ_{21} functions represented in a square box, with the intention of seeing, clearly, the difference between one and other states variating the box.

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[1] Accidental degeneracies are possible in a rectangular box ($a \neq b$). Sometimes, parameters of 2D box are not equal, the "exact" energies of the levels could be to coincide.

2.2 Particle in a Box with Potential

Now, we shall throughout $V \neq 0$ in the system. For an arbitrary potential, the Schrödinger equation has not analytical solution (exact solution) and its must be solved by approximated methods such as linear variation theory.

2.2.1 Linear Variations Method

A linear variation method [1] is a variation process which allows approximating to the exact solution of a quantum system as a lineal combination of n linearly independent functions. The functions ϕ are real; therefore, all coefficients c_i and functions Ψ_i (which are called **basis functions**) are real. Due to coefficients c_i of expansion are unknown, the function ϕ is normalized. Thus, the variational integral is

$$\varepsilon = \frac{<\phi_i|\hat{H}|\phi_j>}{<\phi_i|\phi_j>} \tag{14}$$

where

$$\phi = c_1\Psi_1^\circ + c_2\Psi_2^\circ + \cdots + c_n\Psi_n^\circ = \sum_{i=1}^{n} c_i\Psi_i^\circ \tag{15}$$

The coefficients c_i are parameters to be determined by minimizing the variational integral, and the basis functions Ψ_i must satisfy the boundary conditions of the problem. As a set of basis functions we will use the exact functions of the particle in a box.

Then, through a little bit of algebra, we will get

$$\mathbf{H}\,\mathbf{C} = \boldsymbol{\varepsilon}\,\mathbb{S}\,\mathbf{C} \tag{16}$$

where $\mathbf{H}$ is the matrix

$$H_{ij} = \int \Psi_i^\circ \hat{H}\,\Psi_j^\circ\,d\tau \tag{17}$$

and

$$\hat{H} = -\frac{1}{2}\nabla^2 + V \tag{18}$$

$\mathbb{S}$ is the overlap matrix

$$S_{ij} = <\Psi_i^\circ|\Psi_j^\circ> = S_{ji} \tag{19}$$

Due to set of functions $\{\Psi_i^\circ\}$ is orthonormal, $S_{ij} = S_{ij}$ and, therefore, Eq. (16) is reduced[2] to

$$\mathbf{H}\,\mathbf{C} = \boldsymbol{\varepsilon}\,\mathbf{C} \tag{20}$$

the matrix $\mathbf{H}$ diagonalization, provides the coefficients of expansion (15) (eigenvectors) and the approximate energies (eigenvalues).

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[2] As the functions are normalized, $\mathbb{S}$ is the identity matrix ($\mathbb{S} = 1$).

2.2.2 Nondegenerate Perturbation Theory

I shall now study perturbation theory [2] for a particle in a one-dimensional box and two-dimensional box. The idea is to introduce an additional term to the exact Hamiltonian through a potential *V*. This term will be assumed to be ***time-independent*** and is identified as the perturbation $\widehat{H}'$. But, the perturbation treatments of degenerate and nondegenerate energy levels differ.

$\widehat{H}^{\circ}$ will be the hamiltonian operator of the ***unperturbed system*** and Ψ_i° will be a complete set of eigenfunctions of $\widehat{H}^{\circ}$.

Nondegenerate perturbation theory let Ψ_i° be the wave function of some particular unperturbed nondegenerate level with energy E_i°.that appoints the complete set of eigenvalues and represents the exact energy of the state's levels. Therefore

$$\widehat{H}^{\circ}\Psi_i^{\circ} = E_i^{\circ}\Psi_i^{\circ} \tag{21}$$

so

$$E_i^{\circ} = \frac{\widehat{H}^{\circ}\Psi_i^{\circ}}{\Psi_i^{\circ}} \tag{22}$$

The Hamiltonian of ***perturbed*** system is represented by

$$\widehat{H} = \widehat{H}^{\circ} + \widehat{H}' \tag{23}$$

where $\widehat{H}'$ is the perturbation, commented before, and the superscript $^{\circ}$ denotes the unpertubed system.

Due to aim is to get the relationship of the unknown eigenfunctions and eigenvalues of the perturbed system with those known of the unpertubed system, it is introduced a parameter[3] λ in the hamiltonian. This parameter provides a gradually application, giving a continuous change from the unperturbed to the perturbed system, so that

$$\widehat{H} = \widehat{H}^{\circ} + \lambda\widehat{H}' \tag{24}$$

where Ψ_i is the perturbed wave function into which Ψ_i° will be become when the potential or perturbation is applied. From Eqs. (4) and (23), the Schrödinger equation for ith perturbed state satisfying

$$\widehat{H}\,\Psi_i = \left(\widehat{H}^{\circ} + \lambda\widehat{H}'\right)\Psi_i = E_i\Psi_i \tag{25}$$

It is important that Ψ_i satisfy

$$< \Psi_i^{\circ}|\Psi_i >= 1 \tag{26}$$

Thus, all corrections $\Psi_i^{(k)}$ meet the orthogonality condition with Ψ_i°

$$< \Psi_i^{\circ}|\Psi_i^{(k)} > = \delta_{0k} \tag{27}$$

By a little bit of algebra, we will get the general term for λ^n

$$\left(\widehat{H}^{\circ} - E_i^{\circ}\right)\Psi_i^{(n)} + \widehat{H}'\Psi_i^{(n-1)} - \sum_{k=0}^{n-1} E_i^{(n-k)}\,\Psi_i^{(k)} = 0 \tag{28}$$

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[3] When λ is zero the system is unpertubed. If λ grow up, the perturbation increase and $\lambda=1$ the perturbation is fully apply. As Eq. (25) depends on the parameter λ, both the eigenfunction Ψ_i and the eigenvalue E_i depend on λ: $\Psi_i = \Psi_i(\lambda, q)$ and $E_i = E_i(\lambda)$ where $q = (x, y, z)$ if is Cartesian coordinates system.

The First-Order Energy Correction

$E_i^{(n)}$ is the **nth-order correction** to the energy. By the Eq. (28), for $n = 1$, we have

$$\left(\hat{H}^{\circ} - E_i^{\circ}\right)\Psi_i^{(1)} + \hat{H}'\Psi_i^{\circ} - E_i^{(1)}\Psi_i^{\circ} = 0 \tag{29}$$

multiplying by $(\Psi_i^{\circ})^*$ and integrating all space we have

$$E_i^{(1)} = <\Psi_i^{\circ}|\hat{H}^{\circ} - E_i^{\circ}|\Psi_i^{(1)}> + <\Psi_i^{\circ}|\hat{H}'|\Psi_i^{\circ}> \tag{30}$$

Then

$$\boxed{E_i^{(1)} = <\Psi_i^{\circ}|\hat{H}'|\Psi_i^{\circ}> = \int \Psi_i^{\circ*}\hat{H}'\Psi_i^{\circ}\, d\tau} \tag{31}$$

Eq. (31)[4] gives the first order energy correction. Thus, the energy for ith state will be

$$E_i \approx E_i^{\circ} + E_i^{(1)}\ (\lambda = 1) \tag{32}$$

The First-Order Wave-Function Correction

The k-order perturbation correction for the wave function can be expanding in terms of the complete, orthonormal set of unperturbed eigenfunctions of the Hermitian operator $\hat{H}^{\circ}$. For k=1:

$$\Psi_i^{(1)} = \sum_k c_{ki}^{(1)}\Psi_k^{\circ} \tag{33}$$

where

$$c_{ki}^{(1)} = \frac{<\Psi_k^{\circ}|\hat{H}'|\Psi_i^{\circ}>}{E_i^{\circ} - E_k^{\circ}}\quad (k \neq i) \tag{34}$$

Setting $\lambda = 1$ and using just the first-order wave-function correction, we have as the approximation to the perturbed wave function

$$\boxed{\Psi_i = \Psi_i^{\circ} + \Psi_i^{(1)} = \Psi_i^{\circ} + \sum_{k \neq i}\frac{\hat{H}'_{ki}}{E_i^{\circ} - E_k^{\circ}}\Psi_k^{\circ}} \tag{35}$$

being

$$\hat{H}'_{ki} = <\Psi_k^{\circ}|\hat{H}'|\Psi_i^{\circ}> = \int \Psi_k^{\circ}\hat{H}'\Psi_i^{\circ}\, d\tau \tag{36}$$

---

[4] As $<\Psi_i^{\circ}|\Psi_i^{\circ}> = 1$ and $\hat{H}^{\circ} - E_i^{\circ}$ is hermitic, so $<\Psi_i^{\circ}|\hat{H}^{\circ} - E_i^{\circ}|\Psi_i^{(1)}> = <\left(\hat{H}^{\circ} - E_i^{\circ}\right)\Psi_i^{\circ}|\Psi_i^{(1)}> = 0$. This result to Eq. (30) gives Eq. (31).

The Second-Order Energy Correction

As the first-order wave-function correction is already known, it is possible to calculate the second-order energy correction. Through analogous procedure we used in $E_i^{(1)}$, by Eq. (28), we can obtain the next general term for the n-th correction of the energy of the i-th state

$$E_i^{(n)} = <\Psi_i^\circ|\widehat{H}'|\Psi_i^{(n-1)}>$$

(37)

Thus, for the second energy correction, when $n = 2$, we get $E_i^{(2)} = <\Psi_i^\circ|\widehat{H}'|\Psi_i^{(1)}>$ and $\Psi_i^{(1)}$ is the first correction obtained before: $\Psi_i^{(1)} = c_{ki}^{(1)}\Psi_k^\circ = \frac{<\Psi_k^\circ|\widehat{H}'|\Psi_i^\circ>}{E_i^\circ - E_k^\circ}\Psi_k^\circ$. Therefore, through a laborious process, we will have

$$E_i^{(2)} = \sum_{k \neq i} \frac{|\widehat{H}'_{ki}|^2}{E_i^\circ - E_k^\circ}$$

(38)

2.3 Radiation/matter interaction

We are now ready to consider the time-dependent Schrödinger equation [5, 6]. If appropriate amounts of energy are supplied to molecule, it would be possible to bring about transition between any two levels. However, it is found experimentally that the atomic and molecular spectra contain far fewer lines than predicted by the resonance condition, that is, $\Delta E = h\nu$. This must mean that only certain transitions are "allowed" or "preferred".

Consider the transition between the m and n stationary states, †[5] described by the state functions Ψ_m and Ψ_n. Since both Ψ_m and Ψ_n are solutions of time-dependent Schrödinger equation, it follows that their linear combination Ψ must also be a solution of the same equation. We write

$$\Psi = c_m\Psi_m(q,t) + c_n\Psi_n(q,t)$$

(39)

where c_m and c_n are constants. Eq. (39), at the same time, must be rewritten as

$$\Psi = c_m(t)\Psi_m(q,t) + c_n(t)\Psi_n(q,t)$$

(40)

since transition can now occur between the m and n states. When the radiation field is applied, the initial rate of transition is given by

$$\frac{dc_n(t)}{dt} = \frac{dc_m(t)}{i\hbar}\int \Psi_n^*(q,t) JC' \, \Psi_m(q,t) \, dq$$

(41)

The hamiltonian JC' represents the electric field electric dipole moment interaction that is given by

$$JC' = \boldsymbol{\varepsilon} \cdot \boldsymbol{\mu}$$

(42)

where μ_{nm}, the transition dipole moment, is given by

$$\mu_{nm} = \int \Psi_n^*(x)\mu\Psi_m(x) \, dx$$

(43)

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[5] By stationary state it is meant that the state remains unchanged in the absence of external perturbations.

3. Results

Having done all procedure of mathematical model on concepts explained above, developed by means of Mathematica and COMSOL, the results obtained will be shown applying atomic units (u.a.) for all quantum.

Potentials Applied

Now, if the particle of the system is subjected to a potential, we will be able to observe some variations.

It will be use two types of potential from which we will observe changes in the system and whose approximations to the lowest ground state and some excited states will be carried out through <u>linear variations method</u> and the <u>perturbation theory</u>:

	Asymmetric potential	Symmetric potential
1D	$c_1 e^{-c_2 x}$	$R - \sqrt{R^2 - x^2}$
2D	$D_1 e^{-D_2(x+c)^2 + y}$	$R - \sqrt{R^2 - x^2} \; \forall y$

Table 1. Types of potential applied where $R = (V_0\text{^}2 + a\text{^}2/4)/(2 * V_0)$.
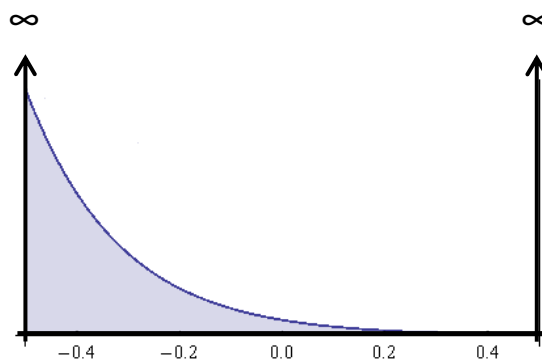
The shape of the asymmetric potentials is:

Figure 8. The shape of the _asymmetric potential_ $V(x) = 4.5 e^{-5.5x}$ in a one-dimensional box.
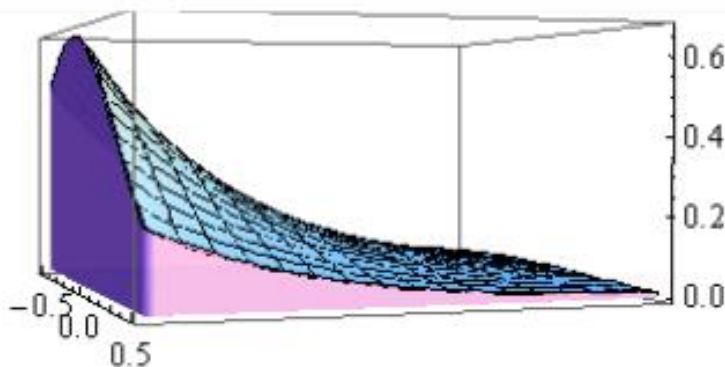

Figure 9. The shape of the _asymmetric potential_ $V(x, y) = 4.15 * e^{-2.5*((x+0.2)^2 + y)}$ in a two-dimensional box.

where the potential applied is an exponential potential, for example, $c_1 e^{-c_2 x}$. The shape of the potential in the graphic plot, shows, clearly, that the potential is a falling exponential curve $(-x)$ and, for this reason, completely asymmetric.

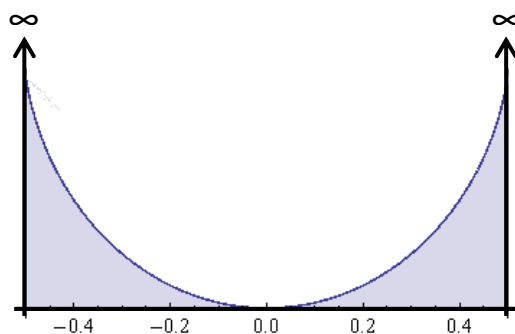The shape of the symmetric potentials is:

Figure 10. The shape of the *symmetric potential* $V(x) = R - \sqrt{R^2 - x^2}$ in a one-dimensional box.
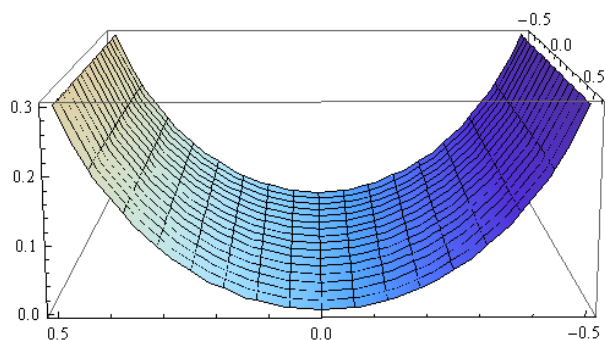

Figure 11. The shape of the *symmetric potential* $V(x, y) = R - \sqrt{R^2 - x^2}$ $(\forall y)$ in a two-dimensional box.

From graphic plots represented above, we can already observe the clear difference in respect of the symmetry of both potentials.

3.1 Approximation by Linear Variation Method

Now, asymmetric and symmetric potential is applied on a particle in a one and two-dimensional box, providing some changes in the system that will be treated to make the corresponding approximations. Firstly, the approximations will be realized by linear variation method chosen 12 basis functions.

3.1.1 Particle in a 1D System with $V \neq 0$ inside the Box

A big exponential and symmetric potential were applied. So, the variational functions obtained and the probability densities are showed by Figure 12
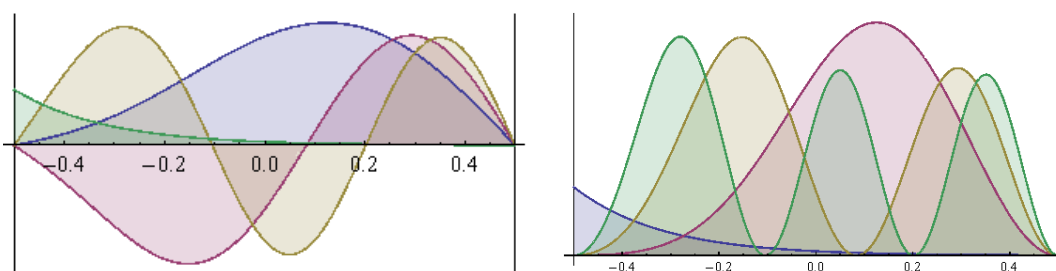

Figure 12. The shape of the first three Ψ_i and $|\Psi_i|^2$ with the *asymmetric potential* $V(x) = 4.5e^{-5.5x}$ applied in a one-dimensional box.
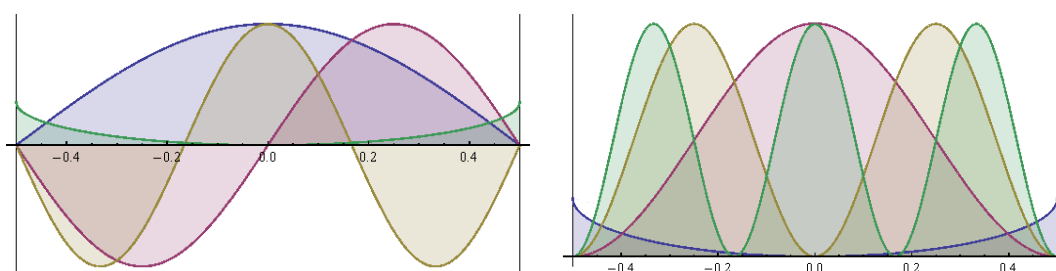

Figure 13. The shape of the first three Ψ_i and $|\Psi_i|^2$ with the *symmetric potential* $V(x) = 0.5 - \sqrt{0.25 - x^2}$ applied in a one-dimensional box.

Through the Figure 12 and 13, we can observe different effects in the functions, depending on the potential applied. In Figure 12 it is shown the tendency of the functions is go places to the right as consequence of the asymmetric potential applied. However, in Figure 13 the functions do not experiment any distortion due to the symmetric potential distributes the charge density as equal form in both parts of the box.

It should be noted that if the asymmetric potential is small, we would not have a clear vision of the distorted functions by plots, because the effect of the potential in the functions is minimal. Now, we will do a numerical comparative through the values of the approximation energies obtained after the potentials. Thus, the energies of the system are:

State i	$E_i^{s.asym.}$	$E_i^{b.asym.}$	$E_i^{sym.}$
1	5.08028	10.1026	4.96578
2	19.9168	29.4086	19.80780
3	44.5983	56.1776	44.49080
4	79.1446	91.4510	79.03790

Table 2. The energy values for the first four states provided by $E_i^{s.asym.}$ corresponding to a small *asymmetric potential* $V(x) = 0.12e^{-3.5x}$, $E_i^{b.asym.}$ corresponding to a big *asymmetric potential* $V(x) = 4.5e^{-5.5x}$ and $E_i^{sym.}$ corresponding to a *symmetric potential* $V(x) = 0.5 - \sqrt{0.25 - x^2}$.

As well as the verification of the asymmetric or symmetric distribution of charge density[6] [4] in the momentum space of the variational functions is showed by Table 3

	$\rho_i^{s.asym.}$		$\rho_i^{b.asym.}$		$\rho_i^{sym.}$	
State i	$-a/2 \leq x \leq 0$	$0 < x \leq a/2$	$-a/2 \leq x \leq 0$	$0 < x \leq a/2$	$-a/2 \leq x \leq 0$	$0 < x \leq a/2$
1	0.495039	0.504961	0.265678	0.734322	0.5	0.5
2	0.502920	0.497080	0.579364	0.420636	0.5	0.5
3	0.499902	0.500098	0.490089	0.509911	0.5	0.5
4	0.50082	0.499180	0.554533	0.445467	0.5	0.5

Table 3. Charge density distribution of variational functions in a 1D box with the same potentials applied above where the simplifications in superscript of ρ_i have the same meaning as in Table 2.

From the most part of the box subject to a potential charge to the least subject to this potential (since the shape of the potential in Figure 8 implies such a distribution). In this case, logically, the charge density is displaced to the right of the box, as we can observe by the graphic plot in Figure 12. This numeric difference in the Table 3, provides a clear idea about the distorted or displacement that the perturbed functions experience subject to a perturbation.

Judging Table 3, if we compare the distributions of charge density in small asymmetric potential case we can observe that the effect in the functions is almost symmetric. However, in the big asymmetric potential case and observing state 1, for example, we have already a clear vision of the charge density distribution to the right which confirms the asymmetric distribution of the functions. For another part, in the symmetric potential case the values of the charge density confirm that the function do not experiment any distortion as we have already commented above.

---

[6] Determining the probability distribution for the particle in state Ψ_i. As just the probability density to find the particle located within the infinitesimal range: $\rho_i = |\Psi_i|^2$.

3.1.2 Particle in a 2D System with $V \neq 0$ inside the Box

The functions obtained and the corresponding density probabilities for a symmetric and asymmetric potential applied in a rectangular box ($a = 1$, $b = 1.2$), to avoid degeneracies, are:

Figure 14. The shapes of the first four Ψ_i and $|\Psi_i|^2$ with the *asymmetric potential* $V(x, y) = 4.15 * e^{-2.5*((x+0.2)^2+y)}$ applied in a two-dimensional box.

Other shapes to obtain a clear vision of distorted functions in a two-dimensional box as consequence of asymmetric potential applied are showed in Figure 15
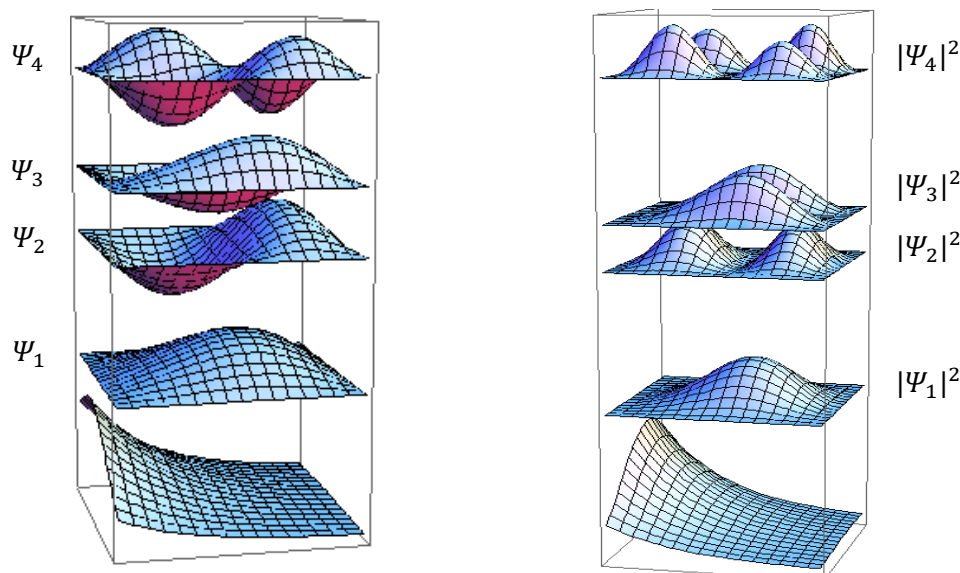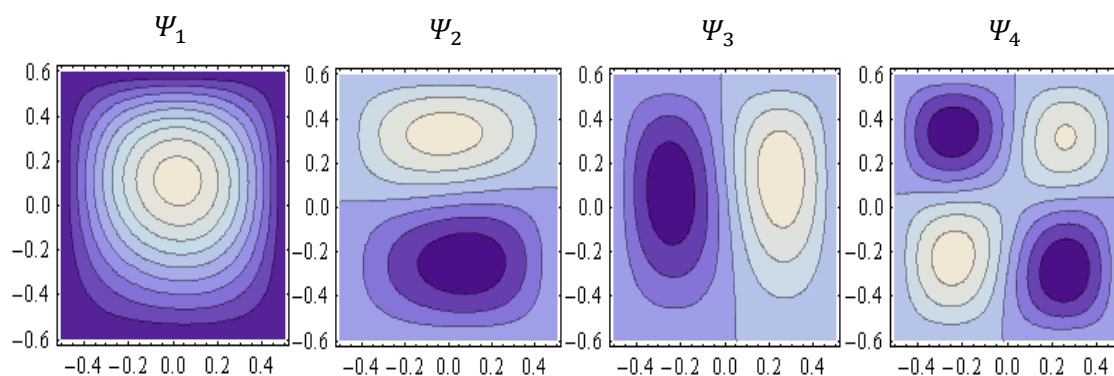

Figure 15. The contour plot of the first four Ψ_i with the *asymmetric potential* $V(x, y) = 4.15 * e^{-2.5*((x+0.2)^2+y)}$ applied in a two-dimensional box.

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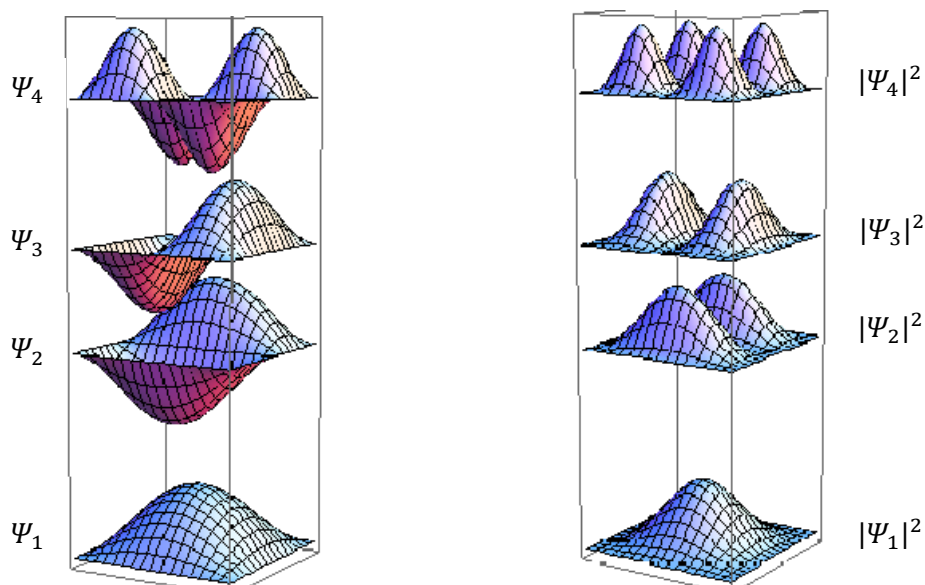Applying the symmetric potential, the shape of functions obtained were:

Figure 16. The shapes of the first four Ψ_i and $|\Psi_i|^2$ with the *asymmetric potential* $V(x,y) = 0.5 - \sqrt{0.25 - x^2}$ ($\forall y$).

Analyzing the variations in the energies of the different energetic levels of the two-dimensional system by Table 4

State i	$E_i^{s.asym.}$	$E_i^{b.asym.}$	$E_i^{sym.}$
1	8.50847	12.0119	8.39785
2	18.8138	23.3302	18.6787
3	23.3024	26.635	23.2469
4	33.9543	37.827	33.5277

Table 4. The energy values for the first four states provided by $E_i^{s.asym.}$ corresponding to a small *asymmetric potential* $V(x,y) = 0.15e^{-2.5((x+0.2)^2+y)}$, $E_i^{b.asym.}$ corresponding to a big *asymmetric potential* $V(x,y) = 4.15 * e^{-2.5*((x+0.2)^2+y)}$ and $E_i^{sym.}$ corresponding to a *symmetric potential* $V(x,y) = 0.5 - \sqrt{0.25 - x^2}$ ($\forall y$).

And the values of charge density

State i	$\rho_i^{s.asym.}$		$\rho_i^{b.asym.}$		$\rho_i^{sym.}$	
	$-a/2 \leq x \leq 0$	$0 < x \leq a/2$	$-a/2 \leq x \leq 0$	$0 < x \leq a/2$	$-a/2 \leq x \leq 0$	$0 < x \leq a/2$
1	0.493674	0.506326	0.3499070	0.650093	0.5	0.5
2	0.503698	0.496302	0.5760040	0.423996	0.5	0.5
3	0.494124	0.505876	0.356809	0.643191	0.5	0.5
4	0.503433	0.496567	0.573510	0.426569	0.5	0.5

Table 5. Charge density distribution of variational functions in a 2D box with the potentials used in Table 4.

Through the results showed in Table 4 we can observe the great effect that big asymmetric potential exercises on functions and energies providing energy values very little approximated to the "exact" energies . However, the effect of the small asymmetric potential is less than the big potential due to the energies are more similar to the "exact" energies of the system. But, realizing the comparative between three potentials, we can say that the most approximated is when symmetric potential is applied, the same for a particle in a one dimensional box..

Table 5 shows the verification of the asymmetric and symmetric charge density distribution of the functions depending of the potential applied. For a small asymmetric potential the probabilities are practically similar in both parts of the box and symmetric potential case the probabilities are equal in two parts. The most clear difference resides in big asymmetric potential where the distribution, numerically and visually, it is demonstrated the distortion to the right of the box as consequence of the asymmetry.

3.2   Approximation by Perturbation Theory Time-Independent

In this section, the particle will be evaluated by perturbation theory time-independent, where the perturbation $\hat{H}'$ is chosen to be the same potentials applied for a particle studied by linear variation method. We will have a certain number of perturbed states for which other certain number of states will be used to calculate the perturbation. In this case, the number of perturbed states will be 4 and the number of states to calculate this perturbation will be 20.

3.2.1   Particle in a 1D System with Perturbation inside the Box

Now, chosen a big and small asymmetric and symmetric potential as perturbation $\hat{H}'$ the energies and probabilities density are:

i	E_i°	$E_i^{(1)}$	$E_i^{(2)}$	E_{tot}
1	4.9348	0.146030	-0.0005511590	5.08028
2	19.7392	0.177568	0.0000624632	19.9168
3	44.4132	0.184966	0.0000934723	44.5983
4	78.9568	0.187702	0.0000707229	79.1446

Table 6. Values of the Exact Energy of the Unperturbed Box E_n°, the First Order Perturbation Energy $E_n^{(1)}$, the Second Order Perturbation Energy $E_n^{(2)}$ and the Total Energy E_{tot} for the *ith* Level of the Particle in a 1D Box with $V(x) = 0.12e^{-3.5x}$.

i	E_i°	$E_i^{(1)}$	$E_i^{(2)}$	E_{tot}
1	4.9348	7.21657	-3.15484	8.99654
2	19.7392	10.6971	-0.421295	30.0150
3	44.4132	11.7462	0.389597	56.5490
4	78.9568	12.1637	0.446217	91.5667

Table 7. Values of the Exact Energy of the Unperturbed Box E_n°, the First Order Perturbation Energy $E_n^{(1)}$, the Second Order Perturbation Energy $E_n^{(2)}$ and the Total Energy E_{tot} for the *ith* Level of the Particle in a 1D Box with $V(x) = 4.5e^{-5.5x}$.

i	E_i°	$E_i^{(1)}$	$E_i^{(2)}$	E_{tot}
1	4.9348	0.0361471	0.0000517133	4.9709
2	19.7392	0.0807531	-0.0000558346	19.8199
3	44.4132	0.0925738	2.31083×10^{-7}	44.5058
4	78.9568	0.0976427	9.74261×10^{-6}	79.0545

Table 8. Values of the Exact Energy of the Unperturbed Box E_n°, the First Order Perturbation Energy $E_n^{(1)}$, the Second Order Perturbation Energy $E_n^{(2)}$ and the Total Energy E_{tot} for the ith Level of the Particle in a 1D Box with $V(x) = 0.5 - \sqrt{0.25 - x^2}$.

State i	$\rho_i^{s.asym.}$		$\rho_i^{b.asym.}$		$\rho_i^{sym.}$	
	$-a/2 \leq x \leq 0$	$0 < x \leq a/2$	$-a/2 \leq x \leq 0$	$0 < x \leq a/2$	$-a/2 \leq x \leq 0$	$0 < x \leq a/2$
1	0.495025	0.504975	0.216085	0.783915	0.5	0.5
2	0.502941	0.497059	0.675636	0.324364	0.5	0.5
3	0.499906	0.500094	0.527671	0.472329	0.5	0.5
4	0.500823	0.499177	0.579755	0.420245	0.5	0.5

Table 9. Charge density distribution of perturbed functions in a 1D box with the same potentials used in Table 2.

Comparing Table 2 and 6 we can observe the same energy approximation for a small asymmetric potential. But, when the potential is big, though was the same potential applied in linear variation method, the energy are not the same. This fact demonstrate that the linear variation method and perturbation theory do not exercise the same effect in the system for a big asymmetric potentials. In the symmetric potential case, as it is not very big, the perturbed method provides good results (synchronized with linear variation method).

By Table 9, perturbed functions, as consequence of the potential applied, undergo a displacement to the right for an asymmetric case. The reason that the perturbed functions are distorted to the right is due to the fact that exponential potential decreases with x.

3.2.2 Particle in a 2D System with Perturbation inside the Box

Applying nondegenerate perturbation theory time-independent for a rectangular box, the energies and probabilities density were:

i	E_i°	$E_i^{(1)}$	$E_i^{(2)}$	E_{tot}
1	8.36175	0.147369	-0.000645558	8.50847
2	18.6426	0.171208	0.0000223647	18.8138
3	23.1662	0.176495	0.0005036600	23.3024
4	33.447	0.136717	-0.0004683430	33.6059

Table 10. Values of the Exact Energy of the Unperturbed Box E_n°, the First Order Perturbation Energy $E_n^{(1)}$, the Second Order Perturbation Energy $E_n^{(2)}$ and the Total Energy E_{tot} for the ith Level of the Particle in a 2D Box with $V(x, y) = 0.15 * e^{-2.5*((x+0.2)^2 + y)}$.

i	E_i°	$E_i^{(1)}$	$E_i^{(2)}$	E_{tot}
1	8.36175	4.77210	-0.4941390	11.9448
2	18.6426	4.73674	0.0171189	23.3964
3	23.1662	4.88302	0.3855240	26.5902
4	33.447	3.78249	-0.358490	37.8642

Table 11. Values of the Exact Energy of the Unperturbed Box E_n°, the First Order Perturbation Energy $E_n^{(1)}$, the Second Order Perturbation Energy $E_n^{(2)}$ and the Total Energy E_{tot} for the ith Level of the Particle in a 2D Box with $V(x, y) = 4.15 * e^{-2.5*((x+0.2)^2+y)}$.

i	E_i°	$E_i^{(1)}$	$E_i^{(2)}$	E_{tot}
1	8.36175	0.0361471	-0.0000503996	8.39784
2	18.6426	0.0361471	-0.0000503996	18.6787
3	23.1662	0.0361471	-0.0000503996	23.2469
4	33.447	0.0807532	0	33.5277

Table 12. Values of the Exact Energy of the Unperturbed Box E_n°, the First Order Perturbation Energy $E_n^{(1)}$, the Second Order Perturbation Energy $E_n^{(2)}$ and the Total Energy E_{tot} for the ith Level of the Particle in a 2D Box with $V(x, y) = 0.5 - \sqrt{0.25 - x^2}\ (\forall y)$.

	$\rho_i^{s.asym.}$		$\rho_i^{b.asym.}$		$\rho_i^{sym.}$	
State i	$-a/2 \le x \le 0$	$0 < x \le a/2$	$-a/2 \le x \le 0$	$0 < x \le a/2$	$-a/2 \le x \le 0$	$0 < x \le a/2$
1	0.493650	0.506350	0.334844	0.665156	0.5	0.5
2	0.503734	0.496266	0.599735	0.400265	0.5	0.5
3	0.502624	0.497376	0.568570	0.431430	0.5	0.5
4	0.494112	0.505888	0.348837	0.651163	0.5	0.5

Table 13. Verification of the asymmetric and symmetric distributions of the charge density of the first four perturbed states. The superscripts in ρ refer to the same potentials $V(x, y)$ used in Table 4.

As we can observe, in Tables 10, 11 and 12, the order is aleatory due to the perturbed functions are dispersed in the all range.

Using perturbed theory and by Table 12 we have demonstrated that the corrections are, practically, equals between them and, the energies approximated are the same for both method applied except in big asymmetric potential case where the first order correction of energy is very high which thing does not make any sense.

3.3   Selection Rules of Transitions

Now, we are going to study the possible transitions of a system from one quantum state to another. So, for the "exact" model of particle in a one-dimensional box the values of the integral are:

$n \to m$	$|\mu_{nm}|$	$(\mu_{nm})^2/(\mu_{1,2})^2$
$1 \to 2$	0.377256	1
$1 \to 3$	0	0
$1 \to 4$	0.0301805	0.0064
$1 \to 5$	0	0
$1 \to 6$	0.00831503	0.000485798

Table 14. The values of the $|\frac{2\pi}{3} < \Psi_n^* x \Psi_m >|$ and $(\frac{2\pi}{3} < \Psi_n^* x \Psi_m >)^2/(\frac{2\pi}{3} < \Psi_1^* x \Psi_2 >)^2$ when the transition go from $n = 1$ to $m = 2, 3, 4, 5, 6$.

As we can observe the integral is zero if the function $\Psi_n^*(x)x\Psi_m(x)$ is odd and nonzero if the function is even. When $\Psi_n(x)$ and $\Psi_m(x)$ have the same parity, dipole radiation cannot occur, in which case, we are in a forbidden transition. This provides the selection rules where the parity of the state must be change so there is electric dipole radiation. Table 14 shows that the biggest μ_{nm} value is for transition $1 \to 2$ due to from fundamental state to excited state we have the greatest energy transition. This is the reason to do a division of the transition dipole moment between of $1 \to 2$ transition's dipole moment.

So, the selection rules establish the useful results:

$$\Psi_{odd} \to \Psi_{even} \quad \longrightarrow \quad allowed$$

$$\Psi_{odd} \to \Psi_{odd} \quad \longrightarrow \quad forbidden$$

3.4 Comparative Results between approximated Methods and COMSOL

With the intention to compare the approximate results obtained by linear variation method and perturbation theory, we require a pattern with which compare. For this reason we have used a numerical integration method based on the finite elements theory. This method is implemented in the COMSOL, and as we can use an excellent discretization, due to the small dimensionality of the problem, it makes these calculations provide quasi-exact results. Thus, the energies obtained in a 1D and 2D box, applying big and small asymmetric potential, through COMSOL were:

State	E (Linear Variation M.)	E (Perturbation T.)	COMSOL
1	10.1026	8.99654	10.102552
2	29.4086	30.015	29.408563
3	56.1776	56.549	56.177549
4	91.451	91.5667	91.450811
5	136.085	136.112	136.084322

Table 15. The energy values of particle in a **One-dimensional** box by Linear Variation Method, Nondegenerate Perturbation Theory and COMSOL using $V(x) = 4.5e^{-5.5x}$.

State	E (Linear Variation M.)	E (Perturbation T.)	COMSOL
1	5.08028	5.08028	5.080283
2	19.9168	19.9168	19.916837
3	44.5983	44.5983	44.598279
4	79.1446	79.1446	79.144608
5	123.559	123.559	123.559103

Table 16. The energy values of particle in a **One-dimensional** box by Linear Variation Method, Nondegenerate Perturbation Theory and COMSOL using $V(x) = 0.12e^{-3.5x}$.

State	E (Linear Variation M.)	E (Perturbation T.)	COMSOL
1	12.0119	11.9448	12.011446
2	23.3302	23.3964	23.323711
3	26.6350	26.5902	26.632627
4	37.8270	37.8642	37.815004
5	41.0245	41.0459	40.7339

Table 17. The energy values of particle in a **Two-dimensional** box by Linear Variation Method, Nondegenerate Perturbation Theory and COMSOL using $V(x, y) = 4.15 * e^{-2.5*((x+0.2)^2+y)}$.

State	E (Linear Variation M.)	E (Perturbation T.)	COMSOL
1	8.50847	8.50847	8.508472
2	18.8138	18.8138	18.813789
3	23.3024	23.3024	23.3024
4	33.6059	33.6059	33.605828
5	35.9543	35.9543	35.953937

Table 18. The energy values of particle in a **Two-dimensional** box by Linear Variation Method, Nondegenerate Perturbation Theory and COMSOL using $V(x, y) = 0.15 * e^{-2.5*((x+0.2)^2+y)}$.

As we can observe COMSOL provides quasi-successful results with a wider range of decimals. Between results obtained by linear variation method and perturbation theory the most approximated to the COMSOL's energies are those provided by linear variation method. This indicates that linear variation method works very well for a big potentials and perturbation theory is not a good method because it works bad in a systems subject to a big potential, except in cases of small asymmetric potential where both methods actuate from the same way due to the perturbation theory works well for a systems subject to perturbations which involve small potentials and changes.

4. Discussion

The Schrödinger equation for real systems becomes difficult to handle, and analytical solutions are only available for very simple systems, which we described as fundamental systems in this module. Numerical approaches can deal with more complex problems and are necessary to deal with real systems.

Using linear combination of solutions of the fundamental systems to build something similar to the real system. Strictly speaking, linear combinations must be solutions of the same differential equation to provide an accurate result. Thus, applying the two mathematical techniques, perturbation and variation theory, that provided a good approximation along with an estimate of their accuracy, we have observed, through the results obtained, that both approximation method for an equal potentials provides similarly results about the energies approximated.

Comparing two methods we have verified that for a small asymmetric or symmetric potential the difference in the effect the differences exerted by one and the other is insignificant. However, when we apply a big asymmetric potential we can observe a much more evident difference between the energies where perturbation theory seems to be a more optimal method than linear variations for providing an energy more approximate to the "exact" one but this is due to that the perturbation theory is not a variational method and in the face of a very big perturbation it can give energies both above and below the "exact" one generating an seism. Therefore, we can conclude by saying that linear variation method is a better mathematical technique for the approximation to "exact" model than perturbation theory time-independent due to linear variation method is better for combining system of comparable weighting and the modification is applied, directly, in the wave function. Nevertheless, perturbation theory is for small changes to a known system where the Hamiltonian is modified, that is to say, perturbation theory works well when the perturbation $\hat{H}'$ is smaller than $\hat{H}°$. Is for this reason that when we applied a big potential, though was the same, the result about the energies are different. Despite, the latter is the best for that.

In addition to this, we also did a comparative between the both method with a more exact numerical method implemented in COMSOL package. Where it is observed that the numerical method applied by COMSOL provided a greater and better approximation of the energies due to it allows doing a discretization stage. This discretization involucres new approximation to the resolution of the numerical process by finite elements method that allows realizing an analysis much more precise of the system.

Regarding the electronic transitions, we also demonstrate the selection rules in the parity transitions. Where from fundamental state to the first excited state it is obtained the great value of transition momentum, that is to say, it is the highest intensity transition.

In conclusion, we can say that quantum chemistry covers abstract and complex concepts which are very difficult to understand. That is the reason why it is convenient to apply the sentence by a great thinker:

"*I hear and I forget, I see and I remember, I do and I understand*" – Confucius

5. Annexes

1. **Nondegenerate perturbation theory** time-independent for an *asymmetric potential* applied in a **one-dimensional box**.

2. **Linear variation method** for an *asymmetric potential* applied in a **one-dimensional box**.

3. **Nondegenerate perturbation theory** time-independent for a *symmetric potential* applied in a **one-dimensional box.**

4. **Linear variation method** for a *symmetric potential* applied in a **one-dimensional box**.

5. Selection Rules of Transitions.

6. Impr. Pant. of **COMSOL** for a big potential applied in a **one-dimensional box** and **rectangular box**.

9. **Nondegenerate perturbation theory** time-independent for an *asymmetric potential* applied in a **two-dimensional box**.

11. **Linear variation method** for an *asymmetric potential* applied in a **two-dimensional box**.

13. **Nondegenerate perturbation theory** time-independent for a *symmetric potential* applied in a **two-dimensional box**.

14. **Linear variation method** for a *symmetric potential* applied in a **two-dimensional box.**

```
(* 1. Nondegenerate Perturbation Theory Time-Independent applied
   for a Big Asymmetric Potential applied in a One-dimensional Box *)

ClearAll["Global`*"];

(* The length of the box *)
a = 1.0;

(* 'ne' is nth-state perturbed and 'lon' is the number
   of states used to calculate the perturbation of each state *)
ne = 5;
lon = 20;
(* Big potential *)
pot[x_] := 4.5 * Exp[-5.5 * x / a];
(* Small potential *)
(* pot[x_]:=0.12*Exp[-3.5*x/a]; *)

(* Introducing the general equations of the system *)
fx[nx_] :=
  If[OddQ[nx] == True, Sqrt[2 / a] * Cos[nx * Pi * x / a], Sqrt[2 / a] * Sin[nx * Pi * x / a]];
ham[fi_] := - (1 / 2.0) * D[fi, {x, 2}];
E0[ii_] := ham[fx[ii]] / fx[ii] // Chop;
E1[ii_] := NIntegrate[fx[ii] * pot[x] * fx[ii], {x, -a / 2, a / 2}] // Chop;

(* The first and second energies corrections *)
For[i = 1, i ≤ ne, i++,
  E2[i] = 0;
   For[j = 1, j ≤ lon, j++,
    If[E0[j] ≠ E0[i],
      as = NIntegrate[fx[j] * pot[x] * fx[i], {x, -a / 2, a / 2}] // Chop;
      as1 = E0[i] - E0[j];
      E2[i] = E2[i] + as ^ 2 / as1];
      ];
    Print["nx=", i, "   E0[", i, "]=", E0[i], "     E1[", i, "] = ",
    E1[i], "    E2[", i, "]=", E2[i], "    E[", i, "]=", E1[i] + E2[i] + E0[i]]
     ];
```

nx=1 E0[1]=4.9348   E1[1] = 7.21657   E2[1]=-3.15484   E[1]=8.99654

nx=2 E0[2]=19.7392   E1[2] = 10.6971   E2[2]=-0.421295   E[2]=30.015

nx=3 E0[3]=44.4132   E1[3] = 11.7462   E2[3]=0.389597   E[3]=56.549

nx=4 E0[4]=78.9568   E1[4] = 12.1637   E2[4]=0.446217   E[4]=91.5667

nx=5 E0[5]=123.37   E1[5] = 12.3672   E2[5]=0.37511   E[5]=136.112

```
(* Obtaining the First-Order Wave-Functions Corrections *)
hij[i_, j_] := NIntegrate[fx[i] * pot[x] * fx[j], {x, -a / 2, a / 2}] // Chop;
c[kk_, ii_] := hij[kk, ii] / (E0[kk] - E0[ii]);
For[k = 1, k ≤ ne, k++,
   li = k - 1; ls = k + 1;
   fk = fx[k] + Sum[c[k, i] * fx[i], {i, 1, li}] + Sum[c[k, i] * fx[i], {i, ls, lon}];
   cte = 1 / NIntegrate[fk^2, {x, -a / 2, 0, a / 2}];
   fun[k] = Sqrt[cte] * fk // Expand // Chop;
    ];

(* Verifying non orthogonality of the perturbed functions *)
solap = Table[0, {i, ne}, {j, ne}];
 For[i = 1, i ≤ ne, i++,
   For[j = i, j ≤ ne, j++,
     solap[[i, j]] = NIntegrate[fun[i] * fun[j], {x, -a / 2, 0, a / 2}, AccuracyGoal → 8] // Chop;
     If[j ≠ i, solap[[j, i]] = solap[[i, j]]];
       ];
     ];
MatrixForm[solap]
```

$$
\begin{pmatrix}
1. & -0.0254106 & 0.116032 & -0.0465786 & -0.0180353 \\
-0.0254106 & 1. & 0.0479004 & 0.0581195 & 0.0262925 \\
0.116032 & 0.0479004 & 1. & -0.036533 & 0.0358754 \\
-0.0465786 & 0.0581195 & -0.036533 & 1. & 0.025688 \\
-0.0180353 & 0.0262925 & 0.0358754 & 0.025688 & 1.
\end{pmatrix}
$$

```
(* Veryfing the asymmetric distributions
 of charge density in the perturbed functions *)
 For[i = 1, i ≤ ne, i++,
  Print["For fun[", i, "]:  ρ between -a/2 and 0 = ", NIntegrate[fun[i]^2, {x, -a / 2, 0}],
    " and ρ between 0 and a/2 = ", NIntegrate[fun[i]^2, {x, 0, a / 2}]];
    ];

(* The shape of the probabilities of the perturbed functions *)
Plot[{pot[x] * 0.05, fun[1]^2, fun[2]^2, fun[3]^2}, {x, -a / 2, a / 2},
 PlotRange → All, PlotStyle → Thickness[0.0045], Axes → {True, False},
 AxesStyle → Directive[Black, Thickness[0.003]], GridLines → {{-a / 2, a / 2}, {}},
 GridLinesStyle → Directive[Black, Thickness[0.003]], Filling -> Axis, AspectRatio → 0.5]
```

For fun[1]: ρ between −a/2 and 0 = 0.216085 and ρ between 0 and a/2 = 0.783915

For fun[2]: ρ between −a/2 and 0 = 0.675636 and ρ between 0 and a/2 = 0.324364

For fun[3]: ρ between −a/2 and 0 = 0.527671 and ρ between 0 and a/2 = 0.472329

For fun[4]: ρ between −a/2 and 0 = 0.579755 and ρ between 0 and a/2 = 0.420245

For fun[5]: ρ between −a/2 and 0 = 0.515578 and ρ between 0 and a/2 = 0.484422

(* **The shape of the perturbed functions with big asymmetric potential applied** *)

```
Plot[{pot[x] * 0.05, fun[1], fun[2], fun[3]}, {x, -a / 2, a / 2},
 PlotRange → All, PlotStyle → Thickness[0.0045], Axes → {True, False},
 AxesStyle → Directive[Black, Thickness[0.003]], GridLines → {{-a / 2, a / 2}, {}},
 GridLinesStyle → Directive[Black, Thickness[0.003]], Filling -> Axis, AspectRatio → 0.5]
```
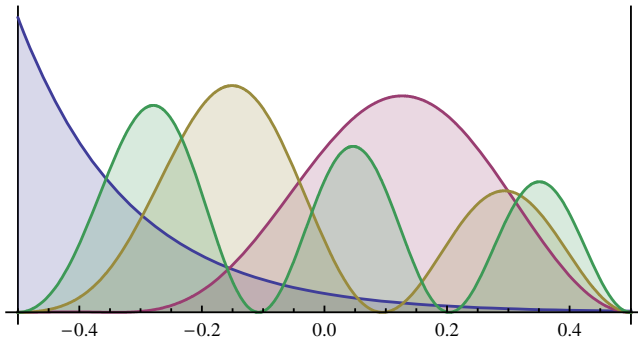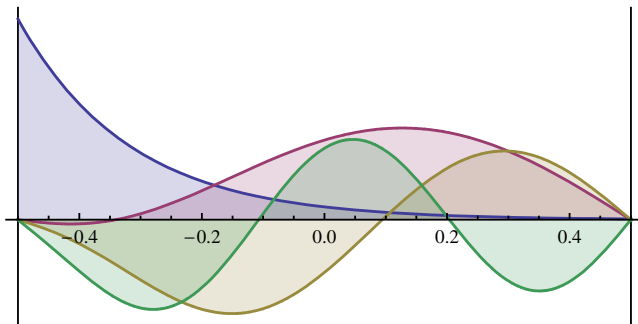
```
                    (* 2. Linear Variation Method for
   an Asymmetric Potential applied in a One-dimensional Box *)

ClearAll["Global`*"];

(* Introducing dates and wavefunction equation *)
nf = 12;
a = 1.0;
fi[nx_] :=
  If[OddQ[nx] == True, Sqrt[2 / a] * Cos[nx * Pi * x / a], Sqrt[2 / a] * Sin[nx * Pi * x / a]];

(* Defining the big asymmetric potential applied *)
pot[x_] := 4.5 * Exp[-5.5 * x / a];
(* Defining the big asymmetric potential applied *)
(* pot[x_]:=0.12*Exp[-3.5*x/a]; *)

(* Defining the hamiltonian operator *)
ham[fi_] := (-1 / 2.0) * D[fi, {x, 2}] + pot[x] * fi;

(* Building the matrix *)
mat = Table[0, {i, nf}, {j, nf}];
For[i = 1, i ≤ nf, i++,
  For[j = i, j ≤ nf, j++,
    mat[[i, j]] = NIntegrate[fi[i] * ham[fi[j]], {x, -a / 2, 0, a / 2}, AccuracyGoal → 10];
    If[j ≠ i, mat[[j, i]] = mat[[i, j]]];
      ];
    ];

(* Matrix diagonalization *)
ene = Eigenvalues[mat] // Chop;
vec = Eigenvectors[mat] // Chop;

(* Ordering of energies an vectors from lowest to highest *)
For[i = 1, i ≤ nf - 1, i++,
  For[j = i + 1, j ≤ nf, j++,
    ei = ene[[i]]; ej = ene[[j]];
    veci = vec[[i]]; vecj = vec[[j]];
    If[ej < ei, ene[[i]] = ej; ene[[j]] = ei; vec[[i]] = vecj; vec[[j]] = veci];
      ];
    ];

(* Graphic plot of big asymmetric potential applied *)
Plot[pot[x], {x, -a / 2, a / 2}, PlotRange → All,
 PlotStyle → Thickness[0.0045], Axes → {True, False},
 AxesStyle → Directive[Black, Thickness[0.003]], GridLines → {{-a / 2, a / 2}, {}},
 GridLinesStyle → Directive[Black, Thickness[0.003]], Filling -> Axis, AspectRatio → 0.5]
ene
```
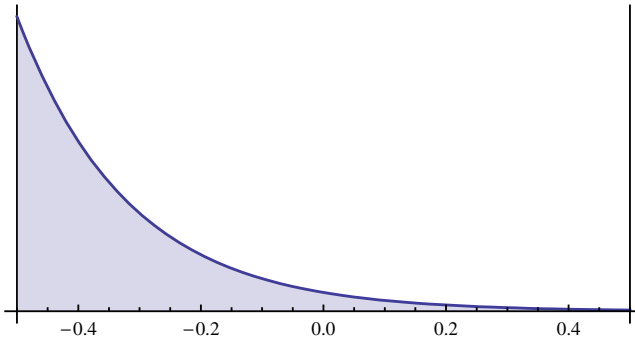
```
{10.1026, 29.4086, 56.1776, 91.451, 136.085,
 190.43, 254.598, 328.622, 412.516, 506.293, 610.021, 724.353}
```

```
(* Building a column vector with basis functions *)
fbasis = Table[0, {i, nf}];
For[i = 1, i ≤ nf, i++,
    fbasis[[i]] = fi[i];
     ];
```

```
(* Obtaining the variational functions *) funV = vec.fbasis;
```

```
Plot[{funV[[1]], funV[[2]], funV[[3]], pot[x] * 0.05}, {x, -a / 2, a / 2},
 PlotRange → All, PlotStyle → Thickness[0.0045], Axes → {True, False},
 AxesStyle → Directive[Black, Thickness[0.003]], GridLines → {{-a / 2, a / 2}, {}},
 GridLinesStyle → Directive[Black, Thickness[0.003]], Filling -> Axis, AspectRatio → 0.5]
```
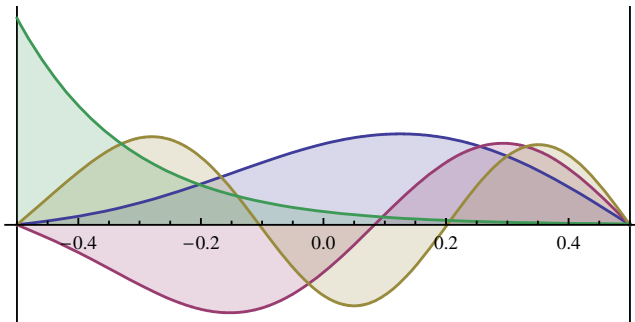


```
(* Verify the asymmetric distribution of charge density of the
 variational functions as consequence big asymmetric potential applied *)
For[i = 1, i ≤ 6, i++,
  Print["For funV[", i,
    "]:  ρ between -a/2 and 0 = ", NIntegrate[funV[[i]]^2, {x, -a / 2, 0}],
    " and ρ between 0 and a/2 = ", NIntegrate[funV[[i]]^2, {x, 0, a / 2}]];
    ];
Plot[{0.05 * pot[x], funV[[1]]^2, funV[[2]]^2, funV[[3]]^2}, {x, -a / 2, a / 2},
 PlotRange → All, PlotStyle → Thickness[0.0045], Axes → {True, False},
 AxesStyle → Directive[Black, Thickness[0.003]], GridLines → {{-a / 2, a / 2}, {}},
 GridLinesStyle → Directive[Black, Thickness[0.003]], Filling -> Axis, AspectRatio → 0.5]
```

For funV[1]: ρ between $-a/2$ and 0 = 0.265678 and ρ between 0 and $a/2$ = 0.734322

For funV[2]: ρ between $-a/2$ and 0 = 0.579364 and ρ between 0 and $a/2$ = 0.420636

For funV[3]: ρ between $-a/2$ and 0 = 0.490089 and ρ between 0 and $a/2$ = 0.509911

For funV[4]: ρ between $-a/2$ and 0 = 0.554533 and ρ between 0 and $a/2$ = 0.445467

For funV[5]: ρ between $-a/2$ and 0 = 0.500901 and ρ between 0 and $a/2$ = 0.499099

For funV[6]: ρ between $-a/2$ and 0 = 0.529013 and ρ between 0 and $a/2$ = 0.470987


```
(* Verify the orthonormality of variational functions *)
overlap = Table[0, {i, nf}, {j, nf}];
For[i = 1, i ≤ nf, i++,
  For[j = i, j ≤ nf, j++,
   overlap[[i, j]] =
    NIntegrate[funV[[i]] * funV[[j]], {x, -a / 2, 0, a / 2}, AccuracyGoal → 8] // Chop;
   If[j ≠ i, overlap[[j, i]] = overlap[[i, j]]];
     ];
    ];
Print["Overlap Mat variational fun = ", MatrixForm[overlap] // Chop]
```

$$\text{Overlap Mat variational fun} = \begin{pmatrix}
1. & 0.\times10^{-10} & 0.\times10^{-10} & 0.\times10^{-9} & 0.\times10^{-9} & 0.\times10^{-9} & 0.\times10^{-9} \\
0.\times10^{-10} & 1. & 0.\times10^{-9} & 0.\times10^{-9} & 0.\times10^{-9} & 0.\times10^{-9} & 0.\times10^{-9} \\
0.\times10^{-10} & 0.\times10^{-9} & 1. & 0.\times10^{-9} & 0.\times10^{-9} & 0.\times10^{-9} & 0.\times10^{-9} \\
0.\times10^{-9} & 0.\times10^{-9} & 0.\times10^{-9} & 1. & 0.\times10^{-9} & 0.\times10^{-9} & 0.\times10^{-10} \\
0.\times10^{-9} & 0.\times10^{-9} & 0.\times10^{-9} & 0.\times10^{-9} & 1. & 0.\times10^{-10} & 0.\times10^{-9} \\
0.\times10^{-9} & 0.\times10^{-9} & 0.\times10^{-9} & 0.\times10^{-9} & 0.\times10^{-10} & 1. & 0.\times10^{-9} \\
0.\times10^{-9} & 0.\times10^{-9} & 0.\times10^{-9} & 0.\times10^{-10} & 0.\times10^{-9} & 0.\times10^{-9} & 1. \\
0.\times10^{-9} & 0.\times10^{-9} & 0.\times10^{-10} & 0.\times10^{-9} & 0.\times10^{-9} & 0.\times10^{-9} & 0.\times10^{-9} \\
0.\times10^{-9} & 0.\times10^{-10} & 0.\times10^{-9} & 0.\times10^{-9} & 0.\times10^{-9} & 0.\times10^{-9} & 0.\times10^{-9} \\
0.\times10^{-10} & 0.\times10^{-9} & 0.\times10^{-9} & 0.\times10^{-9} & 0.\times10^{-9} & 0.\times10^{-9} & 0.\times10^{-9} \\
0.\times10^{-9} & 0.\times10^{-9} & 0.\times10^{-9} & 0.\times10^{-9} & 0.\times10^{-9} & 0.\times10^{-9} & 0.\times10^{-9} \\
0.\times10^{-9} & 0.\times10^{-9} & 0.\times10^{-9} & 0.\times10^{-9} & 0.\times10^{-9} & 0.\times10^{-9} & 0.\times10^{-9}
\end{pmatrix}$$

```mathematica
(* 3. Nondegenerate Perturbation Theory Time-
Independent for a Symmetric Potential applied in a One-dimensional Box *)

ClearAll["Global`*"];

(* The length of the box *)
a = 1.0;

(* ne is nth-state perturbed and lon is the number
  of states used to calculate the perturbation of each state *)
ne = 5;
lon = 20;

(* Vmin is the minimum value V0 so R will be greater than a/2 *)
V0 = Input["Introduce un valor de  V0 menor que a/2"];

(* For a symmetric pontential regarding the centre of the box *)
R = (V0^2 + a^2 / 4) / (2 * V0);
pot[x_] := R - Sqrt[R^2 - x^2];

(* Introducing the general equations of the system *)
fx[nx_] :=
  If[OddQ[nx] == True, Sqrt[2 / a] * Cos[nx * Pi * x / a], Sqrt[2 / a] * Sin[nx * Pi * x / a]];
ham[fi_] := -(1 / 2.0) * D[fi, {x, 2}];
E0[ii_] := ham[fx[ii]] / fx[ii] // Chop;
E1[ii_] := NIntegrate[fx[ii] * pot[x] * fx[ii], {x, -a / 2, a / 2}] // Chop;

(* The first and second correction energies *)
For[i = 1, i ≤ ne, i++,
  E2[i] = 0;
   For[j = 1, j ≤ lon, j++,
    If[E0[j] ≠ E0[i],
      as = NIntegrate[fx[j] * pot[x] * fx[i], {x, -a / 2, a / 2}] // Chop;
      as1 = E0[i] - E0[j];
      E2[i] = E2[i] + as^2 / as1;
      ];
    Print["nx=", i, "  E0[", i, "]=", E0[i], "    E1[", i, "] = ",
    E1[i], "   E2[", i, "]=", E2[i], "    E[", i, "]=", E1[i] + E2[i] + E0[i]]
    ];
```

nx=1 E0[1]=4.9348   E1[1] = 0.0361471   E2[1]=-0.0000517133   E[1]=4.9709

nx=2 E0[2]=19.7392   E1[2] = 0.0807531   E2[2]=-0.0000558346   E[2]=19.8199

nx=3 E0[3]=44.4132   E1[3] = 0.0925738   E2[3]=2.31083×10^{-7} E[3]=44.5058

nx=4 E0[4]=78.9568   E1[4] = 0.0976427   E2[4]=9.74261×10^{-6} E[4]=79.0545

nx=5 E0[5]=123.37   E1[5] = 0.10035   E2[5]=0.0000103024   E[5]=123.47

```
(* Obtaining the First-Order Wave-Functions Corrections *)
hij[i_, j_] := NIntegrate[fx[i] * pot[x] * fx[j], {x, -a / 2, a / 2}] // Chop;
c[kk_, ii_] := hij[kk, ii] / (E0[kk] - E0[ii]);
For[k = 1, k ≤ ne, k++,
   li = k - 1; ls = k + 1;
   fk = fx[k] + Sum[c[k, i] * fx[i], {i, 1, li}] + Sum[c[k, i] * fx[i], {i, ls, lon}];
   cte = 1 / NIntegrate[fk^2, {x, -a / 2, 0, a / 2}];
   fun[k] = Sqrt[cte] * fk // Expand // Chop;
    ];

(* Verifying non orthogonality of the perturbed functions *)
overlap = Table[0, {i, ne}, {j, ne}];
 For[i = 1, i ≤ ne, i++,
   For[j = i, j ≤ ne, j++,
     overlap[[i, j]] =
      NIntegrate[fun[i] * fun[j], {x, -a / 2, 0, a / 2}, AccuracyGoal → 8] // Chop;
     If[j ≠ i, overlap[[j, i]] = overlap[[i, j]]];
       ];
     ];
MatrixForm[overlap]
```

$$
\begin{pmatrix}
1. & 0. \times 10^{-9} & -8.00765 \times 10^{-8} & 0. \times 10^{-10} & -8.67477 \times 10^{-7} \\
0. \times 10^{-9} & 1. & 0. \times 10^{-10} & -7.22136 \times 10^{-8} & 0. \times 10^{-9} \\
-8.00765 \times 10^{-8} & 0. \times 10^{-10} & 1. & 0. \times 10^{-9} & -1.70396 \times 10^{-7} \\
0. \times 10^{-10} & -7.22136 \times 10^{-8} & 0. \times 10^{-9} & 1. & 0. \times 10^{-9} \\
-8.67477 \times 10^{-7} & 0. \times 10^{-9} & -1.70396 \times 10^{-7} & 0. \times 10^{-9} & 1.
\end{pmatrix}
$$

```
(* The shape of the probabilities of the perturbed
 functions and the symmetric distribution of charge density *)
 For[i = 1, i ≤ ne, i++,
   Print["For fun[", i, "]:  ρ between -a/2 and 0 = ", NIntegrate[fun[i]^2, {x, -a / 2, 0}],
     " and ρ between 0 and a/2 = ", NIntegrate[fun[i]^2, {x, 0, a / 2}]];
     ];
Plot[{pot[x], fun[1]^2, fun[2]^2, fun[3]^2}, {x, -a / 2, a / 2},
 PlotRange → All, PlotStyle → Thickness[0.0045], Axes → {True, False},
 AxesStyle → Directive[Black, Thickness[0.003]], GridLines → {{-a / 2, a / 2}, {}},
 GridLinesStyle → Directive[Black, Thickness[0.003]], Filling -> Axis, AspectRatio → 0.5]
```

For fun[1]: ρ between −a/2 and 0 = 0.5 and ρ between 0 and a/2 = 0.5

For fun[2]: ρ between −a/2 and 0 = 0.5 and ρ between 0 and a/2 = 0.5

For fun[3]: ρ between −a/2 and 0 = 0.5 and ρ between 0 and a/2 = 0.5

For fun[4]: ρ between −a/2 and 0 = 0.5 and ρ between 0 and a/2 = 0.5

For fun[5]: ρ between −a/2 and 0 = 0.5 and ρ between 0 and a/2 = 0.5

(* **The shape of the perturbed functions with a symmetric potential applied** *)

```
Plot[{pot[x], fun[1], fun[2], fun[3]}, {x, -a / 2, a / 2},
 PlotRange → All, PlotStyle → Thickness[0.0045], Axes → {True, False},
 AxesStyle → Directive[Black, Thickness[0.003]], GridLines → {{-a / 2, a / 2}, {}},
 GridLinesStyle → Directive[Black, Thickness[0.003]], Filling -> Axis, AspectRatio → 0.5]
```
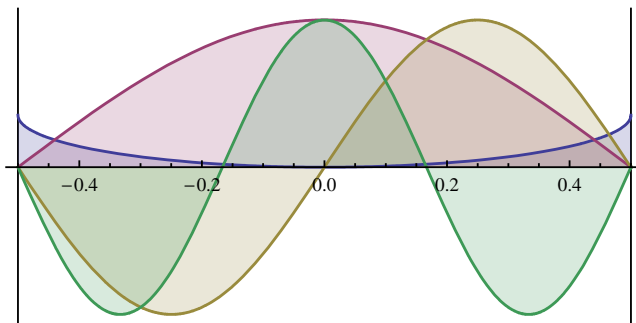
```mathematica
                  (* 4. Linear Variation Method for
    a Symmetric Potential applied in a One-dimensional Box *)

ClearAll["Global`*"];

(* Introducing dates and wavefunction equation *)
nf = 12;
a = 1.0;
fi[nx_] :=
  If[OddQ[nx] == True, Sqrt[2 / a] * Cos[nx * Pi * x / a], Sqrt[2 / a] * Sin[nx * Pi * x / a]];

(* Vmin is the minimum value of V0 so R will be greater than a/2 *)
V0 = Input["Introduce un valor de  V0 menor que a/2"];

(* For a symmetric potential regarding to the centre of the box *)
R = (V0^2 + a^2 / 4) / (2 * V0);
pot[x_] := R - Sqrt[R^2 - x^2];

(* Defining the hamiltonian operator *)
ham[fi_] := (-1 / 2.0) * D[fi, {x, 2}] + pot[x] * fi;

(* Building the matrix *)
mat = Table[0, {i, nf}, {j, nf}];
For[i = 1, i ≤ nf, i++,
  For[j = i, j ≤ nf, j++,
    mat[[i, j]] = NIntegrate[fi[i] * ham[fi[j]], {x, -a / 2, 0, a / 2}, AccuracyGoal → 10];
    If[j ≠ i, mat[[j, i]] = mat[[i, j]]];
      ];
    ];

(* Matrix diagonalization *)
ene = Eigenvalues[mat] // Chop;
vec = Eigenvectors[mat] // Chop;

(* Ordering of energies an vectors from lowest to highest *)
For[i = 1, i ≤ nf - 1, i++,
  For[j = i + 1, j ≤ nf, j++,
    ei = ene[[i]]; ej = ene[[j]];
    veci = vec[[i]]; vecj = vec[[j]];
    If[ej < ei, ene[[i]] = ej; ene[[j]] = ei; vec[[i]] = vecj; vec[[j]] = veci];
      ];
    ];

(* The graphic plot of the symmetric potential applied *)
Plot[pot[x], {x, -a / 2, a / 2}, PlotRange → All,
 PlotStyle → Thickness[0.0045], Axes → {True, False},
 AxesStyle → Directive[Black, Thickness[0.003]], GridLines → {{-a / 2, a / 2}, {}},
 GridLinesStyle → Directive[Black, Thickness[0.003]], Filling -> Axis, AspectRatio → 0.5]
ene
```
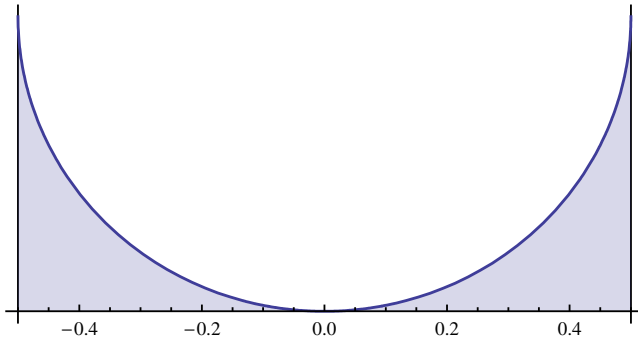
{4.9709, 19.8199, 44.5058, 79.0545, 123.47,
 177.755, 241.908, 315.931, 399.823, 493.585, 597.216, 710.717}

```
(* Building a column vector with basis functions *)
fbasis = Table[0, {i, nf}];
 For[i = 1, i ≤ nf, i++,
    fbasis[[i]] = fi[i];
     ];

(* Obtaining the variational functions *) funV = vec.fbasis;

Plot[{funV[[1]], funV[[2]], funV[[3]], pot[x]}, {x, -a / 2, a / 2},
 PlotRange → All, PlotStyle → Thickness[0.0045], Axes → {True, False},
 AxesStyle → Directive[Black, Thickness[0.003]], GridLines → {{-a / 2, a / 2}, {}},
 GridLinesStyle → Directive[Black, Thickness[0.003]], Filling -> Axis, AspectRatio → 0.5]
```
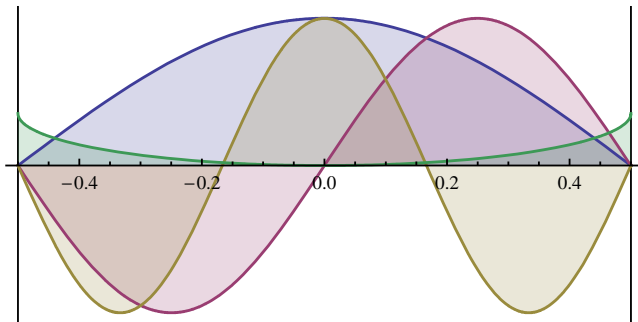


```
(* Verify the symmetric distribution of charge density of the
 variational functions as consequence symmetric potential applied *)
 For[i = 1, i ≤ 6, i++,
   Print["For funV[", i,
    "]:  ρ between -a/2 and 0 = ", NIntegrate[funV[[i]]^2, {x, -a / 2, 0}],
    " and ρ between 0 and a/2 = ", NIntegrate[funV[[i]]^2, {x, 0, a / 2}]];
     ];
Plot[{pot[x], funV[[1]]^2, funV[[2]]^2, funV[[3]]^2}, {x, -a / 2, a / 2},
 PlotRange → All, PlotStyle → Thickness[0.0045], Axes → {True, False},
 AxesStyle → Directive[Black, Thickness[0.003]], GridLines → {{-a / 2, a / 2}, {}},
 GridLinesStyle → Directive[Black, Thickness[0.003]], Filling -> Axis, AspectRatio → 0.5]
```

For funV[1]: ρ between $-a/2$ and $0 = 0.5$ and ρ between 0 and $a/2 = 0.5$

For funV[2]: ρ between $-a/2$ and $0 = 0.5$ and ρ between 0 and $a/2 = 0.5$

For funV[3]: ρ between $-a/2$ and $0 = 0.5$ and ρ between 0 and $a/2 = 0.5$

For funV[4]: ρ between $-a/2$ and $0 = 0.5$ and ρ between 0 and $a/2 = 0.5$

For funV[5]: ρ between $-a/2$ and $0 = 0.5$ and ρ between 0 and $a/2 = 0.5$

For funV[6]: ρ between $-a/2$ and $0 = 0.5$ and ρ between 0 and $a/2 = 0.5$


```
(* Verify the orthonormality of variational functions *)
overlap = Table[0, {i, nf}, {j, nf}];
For[i = 1, i ≤ nf, i++,
  For[j = i, j ≤ nf, j++,
   overlap[[i, j]] =
    NIntegrate[funV[[i]] * funV[[j]], {x, -a / 2, 0, a / 2}, AccuracyGoal → 8] // Chop;
   If[j ≠ i, overlap[[j, i]] = overlap[[i, j]]];
     ];
    ];
Print["Overlap Mat variational fun = ", MatrixForm[overlap]]
```

Overlap Mat variational fun =

$$
\begin{pmatrix}
1. & 0.\times10^{-9} & 0.\times10^{-9} & 0.\times10^{-10} & 0.\times10^{-9} & 0.\times10^{-9} & 0.\times10^{-9} \\
0.\times10^{-9} & 1. & 0.\times10^{-10} & 0.\times10^{-9} & 0.\times10^{-9} & 0.\times10^{-10} & 0.\times10^{-9} \\
0.\times10^{-9} & 0.\times10^{-10} & 1. & 0.\times10^{-9} & 0.\times10^{-10} & 0.\times10^{-9} & 0.\times10^{-10} \\
0.\times10^{-10} & 0.\times10^{-9} & 0.\times10^{-9} & 1. & 0.\times10^{-9} & 0.\times10^{-10} & 0.\times10^{-10} \\
0.\times10^{-9} & 0.\times10^{-9} & 0.\times10^{-10} & 0.\times10^{-9} & 1. & 0.\times10^{-10} & 0.\times10^{-9} \\
0.\times10^{-9} & 0.\times10^{-10} & 0.\times10^{-9} & 0.\times10^{-10} & 0.\times10^{-10} & 1. & 0.\times10^{-9} \\
0.\times10^{-9} & 0.\times10^{-9} & 0.\times10^{-10} & 0.\times10^{-10} & 0.\times10^{-9} & 0.\times10^{-9} & 1. \\
0.\times10^{-9} & 0.\times10^{-10} & 0.\times10^{-10} & 0.\times10^{-9} & 0.\times10^{-9} & 0.\times10^{-9} & 0.\times10^{-9} \\
0.\times10^{-10} & 0.\times10^{-10} & 0.\times10^{-9} & 0.\times10^{-9} & 0.\times10^{-9} & 0.\times10^{-9} & 0 \\
0.\times10^{-9} & 0.\times10^{-9} & 0.\times10^{-9} & 0.\times10^{-9} & 0.\times10^{-9} & 0 & 0.\times10^{-9} \\
0.\times10^{-9} & 0.\times10^{-9} & 0.\times10^{-9} & 0.\times10^{-9} & 0 & 0.\times10^{-9} & 0.\times10^{-9} \\
0.\times10^{-9} & 0.\times10^{-9} & 0.\times10^{-9} & 0 & 0.\times10^{-9} & 0.\times10^{-9} & 0.\times10^{-9}
\end{pmatrix}
$$

```
ClearAll["Global`*"];

(* To hartree from joules *)
a = 1;
fi[nx_] :=
  If[OddQ[nx] == True, Sqrt[2 / a] * Cos[nx * Pi * x / a], Sqrt[2 / a] * Sin[nx * Pi * x / a]];

n = 10;
ini = 1;
filas = Sum[n - i, {i, 1, ini}];
tabla = Table[0, {i, filas}, {j, 4}];
m12 = (2 * Pi / 3) * Integrate[fi[1] * x * fi[2], {x, -a / 2, a / 2}] // N // Chop;
contador = 1;
For[i = 1, i ≤ ini, i++,
  For[f = i + 1, f ≤ n, f += 1,
    as1 = (2 * Pi / 3) * Integrate[fi[i] * x * fi[f], {x, -a / 2, a / 2}] // N // Chop;
    as2 = (as1 / m12) ^ 2;
    tabla[[contador, 1]] = i;
    tabla[[contador, 2]] = f;
    tabla[[contador, 3]] = Abs[as1];
    tabla[[contador, 4]] = as2;
    contador = contador + 1;
      ];
 ];

(* Integral values of <fi[i]*x*fi[f]> *)
TableForm[tabla,
 TableHeadings → {None, {"Est i", "Est f", "|μnm|", "μnm²/μ1,2²"}}, TableAlignments → Left]
```
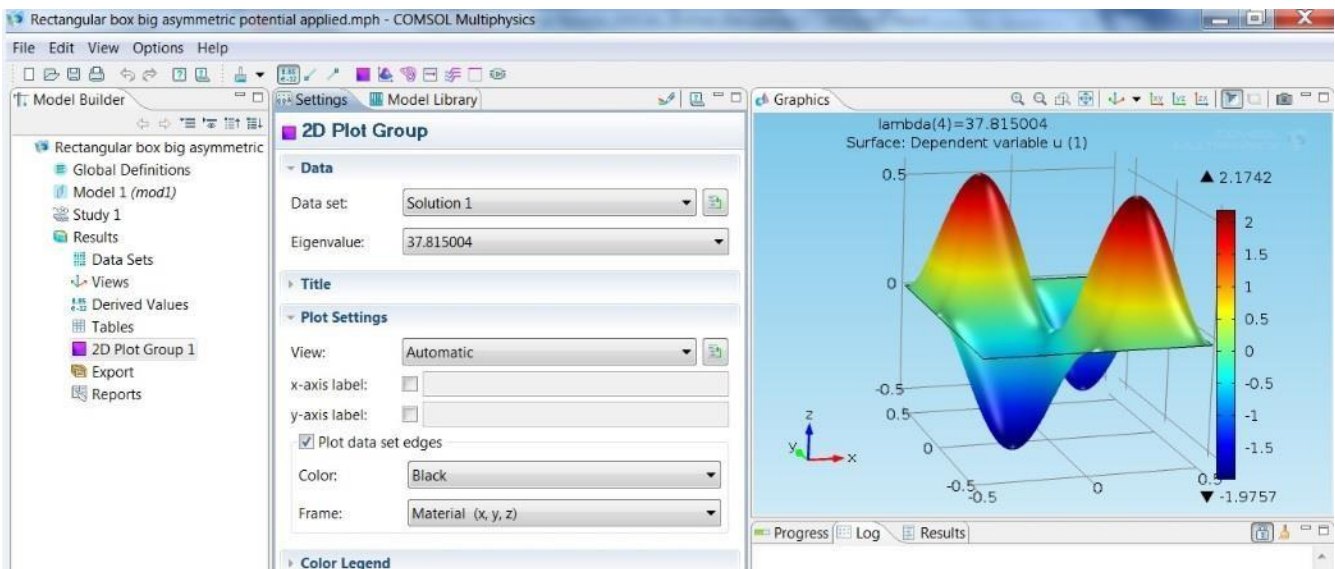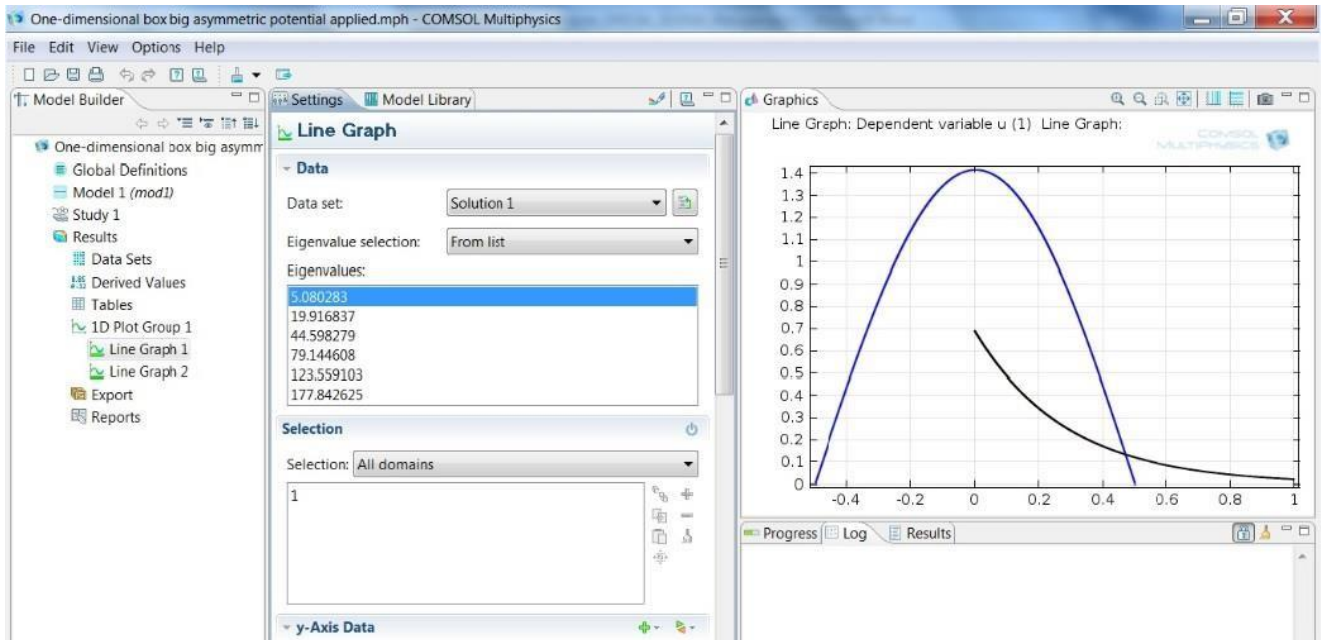
Est i	Est f	$\|\mu_{nm}\|$	$\mu_{nm}^2/\mu_{1,2}^2$
1	2	0.377256	1.
1	3	0	0.
1	4	0.0301805	0.0064
1	5	0	0.
1	6	0.00831503	0.000485798
1	7	0	0.
1	8	0.00342182	0.0000822702
1	9	0	0.
1	10	0.00173212	0.0000210807

6. COMSOL images

```
(* 9. Nondegenerate Perturbation Theory Time-Independent applied
  for an Asymmetric Potential applied in a Two-dimensional Box *)


ClearAll["Global`*"];

(* Rectangular box a ≠ b, to avoid accidental degeneracies *)
a = 1.0;
b = 1.2;
nn = 3;

(* Creating a list of complete set of functions *)
lista = {};
funlis = {};

(* Introducing functions of the system *)
For[i = 1, i ≤ nn, i++,
   For[j = 1, j ≤ nn, j++,
     lista = AppendTo[lista, {i, j}];
       ];
     ];
lon = Length[lista];
fx[nx_] :=
   If[OddQ[nx] == True, Sqrt[2 / a] * Cos[nx * Pi * x / a], Sqrt[2 / a] * Sin[nx * Pi * x / a]];
fy[ny_] := If[OddQ[ny] == True, Sqrt[2 / b] * Cos[ny * Pi * y / b],
     Sqrt[2 / b] * Sin[ny * Pi * y / b]];
fxy[nx_, ny_] := fx[nx] * fy[ny];
For[i = 1, i ≤ lon, i++,
    funlis = AppendTo[funlis, fxy[lista[[i, 1]], lista[[i, 2]]]];
     ];

(* Introducing the big asymmetric potential *)
pot[x_, y_] := 4.15 * Exp[-2.5 * ((x + 0.2) ^ 2 + y)];
(* Introducing the small asymmetric potential *)
(* pot[x_,y_]:=0.15*Exp[-2.5*((x+0.2)^2+y)]; *)

(* The first and second energies corrections *)
ham[fxy_] := - (1 / 2.0) * (D[fxy, {x, 2}] + D[fxy, {y, 2}]);
E0[ii_] := ham[funlis[[ii]]] / funlis[[ii]] // FullSimplify // Chop;
E1[ii_] := NIntegrate[Expand[funlis[[ii]] * pot[x, y] * funlis[[ii]]],
     {x, -a / 2, 0, a / 2}, {y, -b / 2, 0, b / 2}, Method → "LocalAdaptive",
     AccuracyGoal → 6, PrecisionGoal → 6] // Chop;
tabla = Table[0, {i, lon}, {j, 6}];
For[i = 1, i ≤ lon, i++,
   E2[i] = 0;
   For[j = 1, j ≤ lon, j++,
    If[E0[j] ≠ E0[i],
      as =
        NIntegrate[funlis[[j]] * pot[x, y] * funlis[[i]], {x, -a / 2, 0, a / 2}, {y, -b / 2, 0,
           b / 2}, Method → "LocalAdaptive", AccuracyGoal → 6, PrecisionGoal → 6] // Chop;
      as1 = E0[i] - E0[j];
      E2[i] = E2[i] + as^2 / as1];
   ];
   Etot[i] = E1[i] + E2[i] + E0[i];
```

```
   tabla[[i]] = {lista[[i, 1]], lista[[i, 2]], E0[i], E1[i], E2[i], Etot[i]};
  ];
```

(* **Output with the first and second energy corrections**
 and the total energy values of the perturbed functions *)
TableForm[tabla, TableAlignments → Left,
 TableHeadings → {None, {"nx", "ny", "E$^{(0)}$", "E$^{(1)}$", "E$^{(2)}$", "E"}}]

nx	ny	E$^{(0)}$	E$^{(1)}$	E$^{(2)}$	E
1	1	8.36175	4.07721	−0.494139	11.9448
1	2	18.6426	4.73674	0.0171189	23.3964
1	3	35.7773	4.88302	0.385524	41.0459
2	1	23.1662	3.78249	−0.35849	26.5902
2	2	33.447	4.39435	0.0228341	37.8642
2	3	50.5817	4.53005	0.321246	55.433
3	1	47.8402	3.74184	−0.360941	51.2211
3	2	58.121	4.34712	0.128402	62.5965
3	3	75.2557	4.48136	0.338445	80.0755

(* **Graphic plot of the pontentual applied** *)
Plot3D[pot[x, y], {x, −a / 2, a / 2}, {y, −b / 2, b / 2},
 PlotRange → All, PlotStyle → Thickness[0.0045], Axes → {False, False},
 AxesStyle → Directive[Black, Thickness[0.003]], Filling -> Axis, AspectRatio → 0.5]
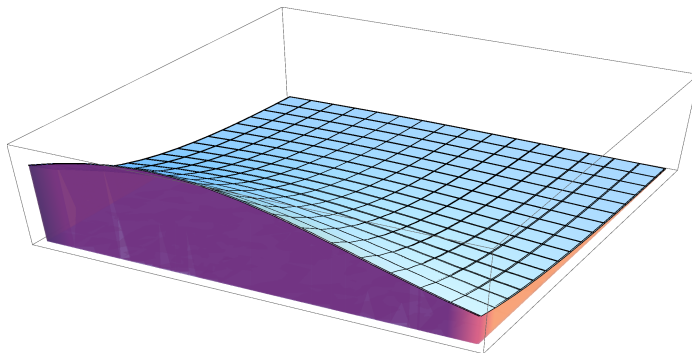
```
(* Obtaining the First-Order Wave-
 Functions Corrections to first perturbation order *)
nf = 5;
hij[i_, j_] := NIntegrate[funlis[[i]] * pot[x, y] * funlis[[j]], {x, -a / 2, 0, a / 2},
    {y, -b / 2, 0, b / 2}, AccuracyGoal → 4, PrecisionGoal → 6] // Chop;
EE0[ii_] := ham[funlis[[ii]]] / funlis[[ii]] // FullSimplify // Chop;
c[kk_, ii_] := hij[kk, ii] / (EE0[kk] - EE0[ii]);
For[k = 1, k ≤ nf, k++,
   li = k - 1; ls = k + 1;
   fk = funlis[[k]] + Sum[c[k, i] * funlis[[i]], {i, 1, li}] +
     Sum[c[k, i] * funlis[[i]], {i, ls, lon}];  cte =
    1 / NIntegrate[fk^2, {x, -a / 2, -a / 4, 0, a / 4, a / 2}, {y, -b / 2, -b / 4, 0, b / 4, b / 2},
      Method → "LocalAdaptive", AccuracyGoal → 6, PrecisionGoal → 6];
   fun[k] = Sqrt[cte] * fk // Expand // Chop;
    ];


(* Verifying non orthogonality of the perturbed functions *)
solap = Table[0, {i, nf}, {j, nf}];
For[i = 1, i ≤ nf, i++,
   For[j = i, j ≤ nf, j++,
     solap[[i, j]] = NIntegrate[fun[i] * fun[j],
        {x, -a / 2, -a / 4, 0, a / 4, a / 2}, {y, -b / 2, -b / 4, 0, b / 4, b / 2},
        Method → "LocalAdaptive", AccuracyGoal → 6, PrecisionGoal → 5] // Chop;
     If[j ≠ i, solap[[j, i]] = solap[[i, j]]];
       ];
     ];
MatrixForm[solap]
```

$$\begin{pmatrix} 1. & -0.00722722 & 0.0305527 & 0.0125515 & -0.0142267 \\ -0.00722722 & 1. & -0.00348536 & 0.0193342 & -0.0126473 \\ 0.0305527 & -0.00348536 & 1. & -0.0187825 & -0.014968 \\ 0.0125515 & 0.0193342 & -0.0187825 & 1. & -0.00926794 \\ -0.0142267 & -0.0126473 & -0.014968 & -0.00926794 & 1. \end{pmatrix}$$

```
For[i = 1, i ≤ lon - 1, i++,
   For[j = i + 1, j ≤ lon, j++,
     eni = Etot[i]; enj = Etot[j]; funi = fun[i];
     funj = fun[j]; lisi = lista[[i]]; lisj = lista[[j]];
     If[enj < eni, Etot[i] = enj; Etot[j] = eni; fun[i] = funj;
      fun[j] = funi; lista[[i]] = lisj; lista[[j]] = lisi];
       ];
     ];
For[i = 1, i ≤ nf, i++,
   Print["nx=", lista[[i, 1]], " ny=", lista[[i, 2]],
     "    E[", lista[[i, 1]], ",", lista[[i, 2]], "]=", Etot[i]];
     ];


nx=1 ny=1    E[1,1]=11.9448

nx=1 ny=2    E[1,2]=23.3964

nx=2 ny=1    E[2,1]=26.5902

nx=2 ny=2    E[2,2]=37.8642

nx=1 ny=3    E[1,3]=41.0459
```

```mathematica
(* Veryfying the asymmetric distributions
 of charge density in the perturbed functions *)
For[i = 1, i ≤ nf, i++,
  Print["Para fun ", lista[[i]], ":  ρ entre -a/2 y 0 = ",
    NIntegrate[fun[i]^2, {x, -a / 2, a / 2}, {y, -b / 2, 0}], " y ρ entre 0 y a/2 = ",
    NIntegrate[fun[i]^2, {x, -a / 2, a / 2}, {y, 0, b / 2}]];
    ];
```

Para fun {1, 1}: ρ entre -a/2 y 0 = 0.334844 y ρ entre 0 y a/2 = 0.665156
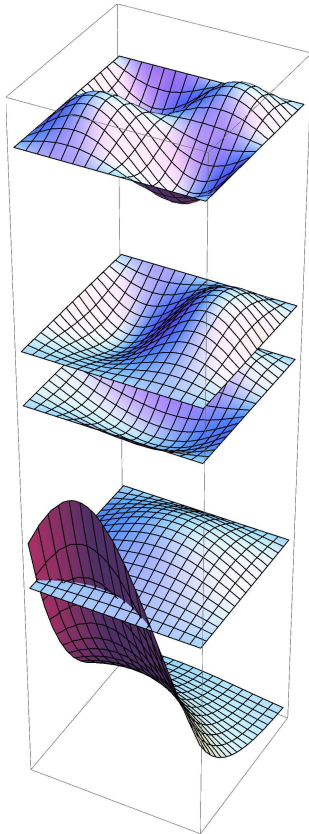
Para fun {1, 2}: ρ entre -a/2 y 0 = 0.599735 y ρ entre 0 y a/2 = 0.400265

Para fun {2, 1}: ρ entre -a/2 y 0 = 0.348837 y ρ entre 0 y a/2 = 0.651163

Para fun {2, 2}: ρ entre -a/2 y 0 = 0.585107 y ρ entre 0 y a/2 = 0.414893

Para fun {1, 3}: ρ entre -a/2 y 0 = 0.56857 y ρ entre 0 y a/2 = 0.43143

```mathematica
(* Shape of the probabilities *)
Plot3D[{1.0 * pot[x, y], Etot[1] + fun[1],
  Etot[2] + fun[2], Etot[3] + fun[3], Etot[4] + fun[4]}, {x, -a / 2, a / 2},
 {y, -b / 2, b / 2}, PlotRange → All, BoxRatios → {1, 1, 4}, Axes → False]
```
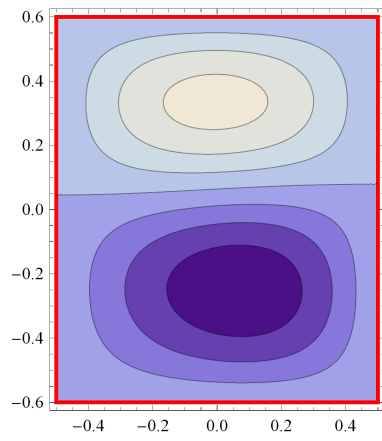


```mathematica
(* Other shapes of perturbed functions *)
For[i = 1, i ≤ nf, i++,
  Print["Energia estado ", i, " = ", Etot[i]] Print[ContourPlot[fun[i], {x, -a / 2, a / 2},
    {y, -b / 2, b / 2}, AspectRatio → b / a, BoundaryStyle → Directive[Red, Thick]]]
    ];
```
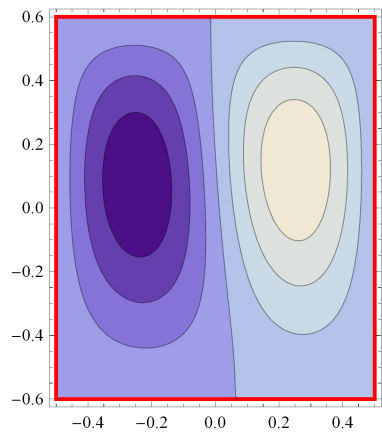
Energia estado 1 = 11.9448
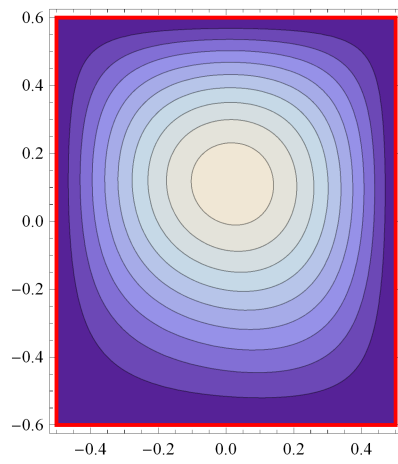
Energia estado 2 = 23.3964

Energia estado 3 = 26.5902

```
              (* 11. Linear Variation Method for
   an Asymmetric Potential applied in a Two-dimensional Box *)

ClearAll["Global`*"];

(* Dimensions of rectangular box and number of functions *)
a = 1.0;
b = 1.2;
nn = 3;

(* Creating a list of complete set of functions *)
lisfun = {};

(* Introducing the big asymmetric potential and
   the corresponding wave functions for a two-dimensional box *)
pot[x_, y_] := 4.15 * Exp[-2.5 * ((x + 0.2) ^ 2 + y)];
(* Introducing the small asymmetric potential and
   the corresponding wave functions for a two-dimensional box *)
(* pot[x_,y_]:=0.15*Exp[-2.5*((x+0.2)^2+y)]; *)

fx[nx_] :=
   If[OddQ[nx] == True, Sqrt[2 / a] * Cos[nx * Pi * x / a], Sqrt[2 / a] * Sin[nx * Pi * x / a]];
fy[ny_] := If[OddQ[ny] == True, Sqrt[2 / b] * Cos[ny * Pi * y / b],
     Sqrt[2 / b] * Sin[ny * Pi * y / b]];
fxy[nx_, ny_] := fx[nx] * fy[ny];
ham[fun_] := - (1 / 2.0) * (D[fun, {x, 2}] + D[fun, {y, 2}]) + pot[x, y] * fun;
For[i = 1, i ≤ nn, i++,
   For[j = 1, j ≤ nn, j++,
     lisfun = AppendTo[lisfun, fxy[i, j]];
       ];
     ];

(* Hamiltonian matrix *)
lon = Length[lisfun];
mat = Table[0, {i, lon}, {j, lon}];
For[i = 1, i ≤ lon, i++,
   For[j = i, j ≤ lon, j++,
     mat[[i, j]] = Integrate[
        lisfun[[i]] * ham[lisfun[[j]]], {x, -a / 2, a / 2}, {y, -b / 2, b / 2}] // Chop;
     mat[[j, i]] = mat[[i, j]];
     ];
 ];

(* Matrix diagonalization *)
ene = Eigenvalues[mat];
vec = Eigenvectors[mat];
For[i = 1, i ≤ lon - 1, i++,
   For[j = i + 1, j ≤ lon, j++,
     enei = ene[[i]]; enej = ene[[j]];
     veci = vec[[i]]; vecj = vec[[j]];
     If[enej < enei,
        ene[[i]] = enej; ene[[j]] = enei;
       vec[[i]] = vecj; vec[[j]] = veci;
       ];
     ];
```

```
    ];
Print[" "];
Print["Potencial fondo caja"];


(* Graphic plot of big asymmetric potential applied  *)
Plot3D[pot[x, y], {x, -a / 2, a / 2}, {y, -b / 2, b / 2},
 PlotRange → All, PlotStyle → Thickness[0.0045], Axes → {True, False},
 AxesStyle → Directive[Black, Thickness[0.003]], Filling -> Axis, AspectRatio → 0.5]
Print[" "];
fun = vec.lisfun;
For[i = 1, i ≤ lon, i++,
  Print["Energia estado ", i, " = ", ene[[i]]]
  (*Print[Plot3D[fun[[i]],{x,-a/2,a/2},{y,-b/2,b/2}]];Print[ContourPlot[
    fun[[i]],{x,-a/2,a/2},{y,-b/2,b/2},BoundaryStyle→Directive[Red,Thick]]];
  Print[" "];*)
    ];
```

Potencial fondo caja
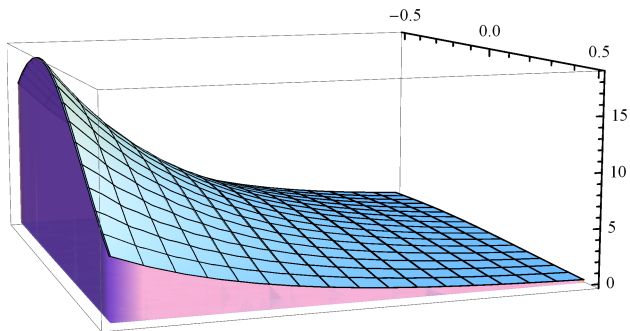

```
Energia estado 1 = 12.0119

Energia estado 2 = 23.3302

Energia estado 3 = 26.635

Energia estado 4 = 37.827

Energia estado 5 = 41.0245

Energia estado 6 = 51.2586

Energia estado 7 = 55.4439

Energia estado 8 = 62.5483

Energia estado 9 = 80.0881
```

```
(* Verify the orthogonality of the first nf functions *)
nf = 5;
solap = Table[0, {i, nf}, {j, nf}];
 For[i = 1, i ≤ nf, i++,
   For[j = i, j ≤ nf, j++,
     solap[[i, j]] = NIntegrate[fun[[i]] * fun[[j]],
        {x, -a / 2, -a / 4, 0, a / 4, a / 2}, {y, -b / 2, -b / 4, 0, b / 4, b / 2},
        Method → "LocalAdaptive", AccuracyGoal → 6, PrecisionGoal → 5] // Chop;
     If[j ≠ i, solap[[j, i]] = solap[[i, j]]];
       ];
     ];
MatrixForm[solap]
```

$$\begin{pmatrix} 1. & 0 & 0 & 0 & 0 \\ 0 & 1. & 0 & 0 & 0 \\ 0 & 0 & 1. & 0 & 0 \\ 0 & 0 & 0 & 1. & 0 \\ 0 & 0 & 0 & 0 & 1. \end{pmatrix}$$

```
(* Verify the big asymmetric distribution of charge density of the
 variational functions as consequence big asymmetric potential applied *)
For[i = 1, i ≤ nf, i++,
  Print["Para funcion ", i, ":  ρ entre -a/2 y 0 = ",
    NIntegrate[fun[[i]]^2, {x, -a / 2, a / 2}, {y, -b / 2, 0}], " y ρ entre 0 y a/2 = ",
    NIntegrate[fun[[i]]^2, {x, -a / 2, a / 2}, {y, 0, b / 2}]];
    ];
```

Para funcion 1: ρ entre -a/2 y 0 = 0.349907 y ρ entre 0 y a/2 = 0.650093

Para funcion 2: ρ entre -a/2 y 0 = 0.576004 y ρ entre 0 y a/2 = 0.423996

Para funcion 3: ρ entre -a/2 y 0 = 0.356809 y ρ entre 0 y a/2 = 0.643191

Para funcion 4: ρ entre -a/2 y 0 = 0.57351 y ρ entre 0 y a/2 = 0.42649

Para funcion 5: ρ entre -a/2 y 0 = 0.573431 y ρ entre 0 y a/2 = 0.426569

```
(* Graphic plots of the variational functions *)
Plot3D[{ene[[1]] + fun[[1]], ene[[2]] + fun[[2]],
  ene[[3]] + fun[[3]], ene[[4]] + fun[[4]]}, {x, -a / 2, a / 2},
 {y, -b / 2, b / 2}, PlotRange → All, BoxRatios → {2, 2, 4}, Axes → False]
```
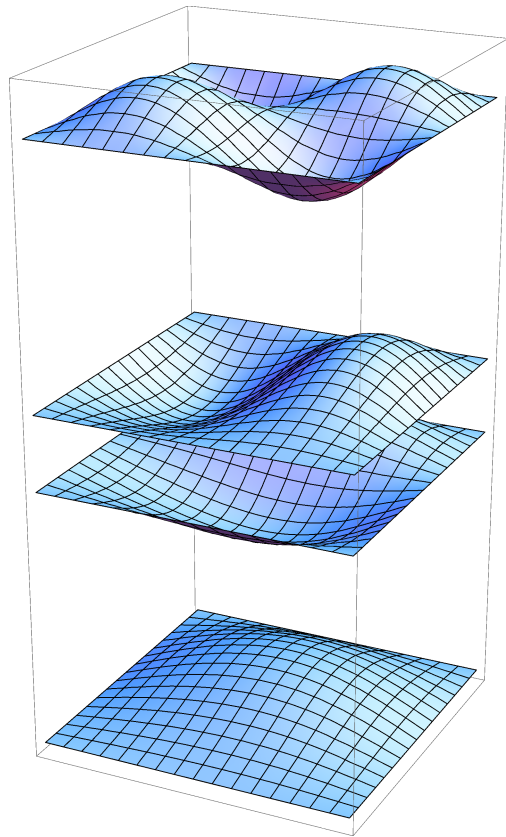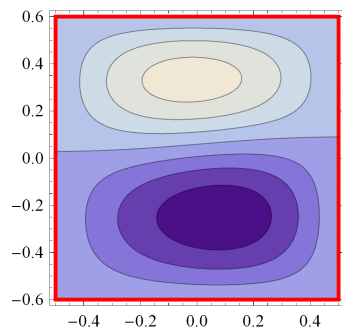


```
(* Graphic plots of the distorted variational functions
 with the corresponding energy values of the states *)
For[i = 1, i ≤ nf, i++,
  Print["Energia estado ", i, " = ", ene[[i]]] Print[ContourPlot[fun[[i]],
    {x, -a / 2, a / 2}, {y, -b / 2, b / 2}, BoundaryStyle → Directive[Red, Thick]]]
   ];
```
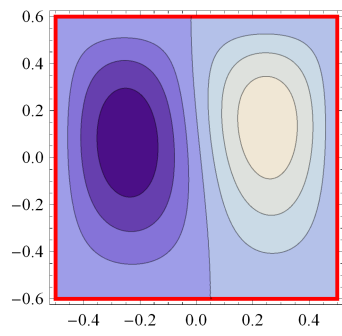
Energia estado 1 = 12.0119
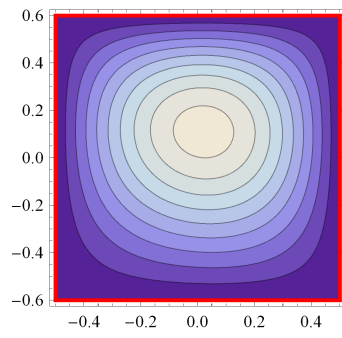
Energia estado 2 = 23.3302

Energia estado 3 = 26.635

```
(* 13. Nondegenerate Perturbation Theory Time
 -Independent applied for a Symmetric Potential applied in a Two-dimensional Box *)

ClearAll["Global`*"];

(* Rectangular box a ≠ b, to avoid accidental degeneracies *)
a = 1.0;
b = 1.2;
nn = 3;

(* Creating a list of complete set of functions *)
lista = {};
funlis = {};

(* Introducing functions of the system *)
For[i = 1, i ≤ nn, i++,
   For[j = 1, j ≤ nn, j++,
     lista = AppendTo[lista, {i, j}];
       ];
     ];
lon = Length[lista];
fx[nx_] :=
   If[OddQ[nx] == True, Sqrt[2 / a] * Cos[nx * Pi * x / a], Sqrt[2 / a] * Sin[nx * Pi * x / a]];
fy[ny_] := If[OddQ[ny] == True, Sqrt[2 / b] * Cos[ny * Pi * y / b],
     Sqrt[2 / b] * Sin[ny * Pi * y / b]];
fxy[nx_, ny_] := fx[nx] * fy[ny];
For[i = 1, i ≤ lon, i++,
    funlis = AppendTo[funlis, fxy[lista[[i, 1]], lista[[i, 2]]]];
     ];

(* Vmin is the minimum value V0 so R will be greater than a/2 *)
V0 = Input["Introduce un valor de  V0 menor que a/2"];

(* For a symmetric pontential regarding the centre of the box *)
R = (V0 ^ 2 + a ^ 2 / 4) / (2 * V0);
pot[x_, y_] := R - Sqrt[R ^ 2 - x ^ 2];

(* Introducing the general equations of the system *)
ham[fxy_] := - (1 / 2.0) * (D[fxy, {x, 2}] + D[fxy, {y, 2}]);
E0[ii_] := ham[funlis[[ii]]] / funlis[[ii]] // FullSimplify // Chop;
E1[ii_] := NIntegrate[Expand[funlis[[ii]] * pot[x, y] * funlis[[ii]]],
     {x, -a / 2, 0, a / 2}, {y, -b / 2, 0, b / 2}, Method → "LocalAdaptive",
     AccuracyGoal → 6, PrecisionGoal → 6] // Chop;
tabla = Table[0, {i, lon}, {j, 6}];

(* The first and second correction energies *)
For[i = 1, i ≤ lon, i++,
   E2[i] = 0;
   For[j = 1, j ≤ lon, j++,
    If[E0[j] ≠ E0[i],
      as =
       NIntegrate[funlis[[j]] * pot[x, y] * funlis[[i]], {x, -a / 2, 0, a / 2}, {y, -b / 2, 0,
          b / 2}, Method → "LocalAdaptive", AccuracyGoal → 6, PrecisionGoal → 6] // Chop;
      as1 = E0[i] - E0[j];
      E2[i] = E2[i] + as ^ 2 / as1];
```

```
     ];
     Etot[i] = E1[i] + E2[i] + E0[i];
     tabla[[i]] = {lista[[i, 1]], lista[[i, 2]], E0[i], E1[i], Chop[E2[i]], Etot[i]};
    ];
   TableForm[tabla, TableAlignments → Left,
    TableHeadings → {None, {"nx", "ny", "E⁽⁰⁾", "E⁽¹⁾", "E⁽²⁾", "E"}}]
```

Out[21]//TableForm=

| nx	ny	$E^{(0)}$	$E^{(1)}$	$E^{(2)}$	E
1	1	8.36175	0.0361471	−0.0000503998	8.39784
1	2	18.6426	0.0361471	−0.0000503999	18.6787
1	3	35.7773	0.0361471	−0.0000503998	35.8134
2	1	23.1662	0.0807532	0	23.2469
2	2	33.447	0.0807533	0	33.5277
2	3	50.5817	0.0807532	0	50.6625
3	1	47.8402	0.092574	0.0000503998	47.9328
3	2	58.121	0.0925738	0.0000503999	58.2136
3	3	75.2557	0.0925738	0.0000503998	75.3484

```
In[22]:= Print[" "];
   Print["Perturbación = ", pot[x, y]];

   (* Shape of the symmetric potential *)
   Plot3D[pot[x, y], {x, -a / 2, a / 2}, {y, -b / 2, b / 2}, PlotRange → All]
```

Perturbación = $0.5 - \sqrt{0.25 - x^2}$

Out[24]=
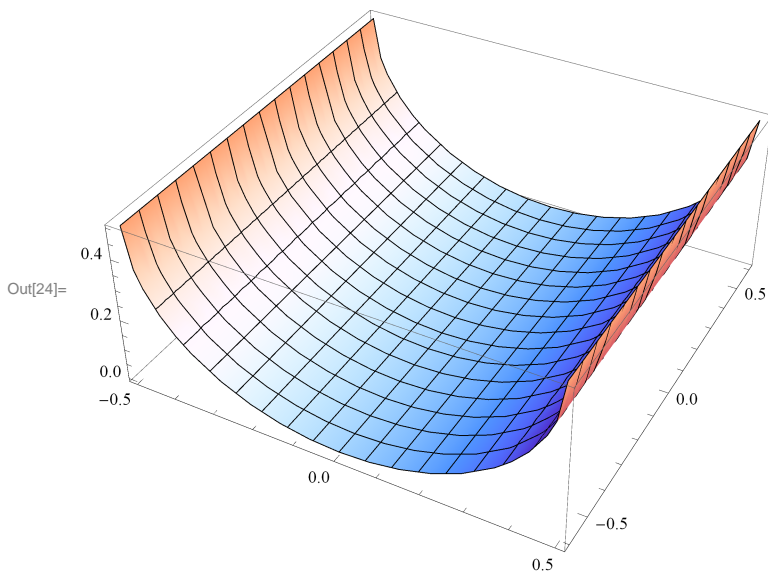
```
In[25]:= (* Obtaining the First-Order Wave-
          Functions Corrections to first perturbation order *)
        nf = lon;
        hij[i_, j_] := NIntegrate[funlis[[i]] * pot[x, y] * funlis[[j]], {x, -a / 2, 0, a / 2},
              {y, -b / 2, 0, b / 2}, AccuracyGoal → 4, PrecisionGoal → 6] // Chop;
        EE0[ii_] := ham[funlis[[ii]]] / funlis[[ii]] // FullSimplify // Chop;
        c[kk_, ii_] := hij[kk, ii] / (EE0[kk] - EE0[ii]);
        For[k = 1, k ≤ nf, k++,
           li = k - 1; ls = k + 1;
           fk = funlis[[k]] + Sum[c[k, i] * funlis[[i]], {i, 1, li}] +
             Sum[c[k, i] * funlis[[i]], {i, ls, lon}];  cte =
           1 / NIntegrate[fk^2, {x, -a / 2, -a / 4, 0, a / 4, a / 2}, {y, -b / 2, -b / 4, 0, b / 4, b / 2},
              Method → "LocalAdaptive", AccuracyGoal → 6, PrecisionGoal → 6];
           fun[k] = Sqrt[cte] * fk // Expand // Chop;
            ];


        (* Verifying orthogonality of the perturbed functions *)
        solap = Table[0, {i, lon}, {j, lon}];
        For[i = 1, i ≤ nf, i++,
           For[j = i, j ≤ nf, j++,
             solap[[i, j]] = NIntegrate[fun[i] * fun[j],
                {x, -a / 2, -a / 4, 0, a / 4, a / 2}, {y, -b / 2, -b / 4, 0, b / 4, b / 2},
                 Method → "LocalAdaptive", AccuracyGoal → 6, PrecisionGoal → 5] // Chop;
             If[j ≠ i, solap[[j, i]] = solap[[i, j]]];
               ];
             ];
        MatrixForm[solap]
```

Out[32]//MatrixForm=

$$
\begin{pmatrix}
1. & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 1. & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 1. & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 1. & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 1. & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 1. & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 1. & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 1. & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1.
\end{pmatrix}
$$

```
In[33]:= For[i = 1, i ≤ lon - 1, i++,
            For[j = i + 1, j ≤ lon, j++,
              eni = Etot[i]; enj = Etot[j]; funi = fun[i];
              funj = fun[j]; lisi = lista[[i]]; lisj = lista[[j]];
              If[enj < eni, Etot[i] = enj; Etot[j] = eni; fun[i] = funj;
               fun[j] = funi; lista[[i]] = lisj; lista[[j]] = lisi];
                 ];
              ];
        For[i = 1, i ≤ nf, i++,
           Print["nx=", lista[[i, 1]], " ny=", lista[[i, 2]],
              "    E[", lista[[i, 1]], ",", lista[[i, 2]], "]=", Etot[i]];
              ];
```

```
nx=1 ny=1    E[1,1]=8.39784

nx=1 ny=2    E[1,2]=18.6787

nx=2 ny=1    E[2,1]=23.2469

nx=2 ny=2    E[2,2]=33.5277

nx=1 ny=3    E[1,3]=35.8134

nx=3 ny=1    E[3,1]=47.9328

nx=2 ny=3    E[2,3]=50.6625

nx=3 ny=2    E[3,2]=58.2136

nx=3 ny=3    E[3,3]=75.3484
```

In[35]:=

```
(* The shape of the probabilities of the perturbed
 functions and the symmetric distribution of charge density *)
For[i = 1, i ≤ nf, i++,
  Print["Para fun ", lista[[i]], ":  ρ entre -a/2 y 0 = ",
    NIntegrate[fun[i]^2, {x, -a / 2, 0}, {y, -b / 2, b / 2}], " y ρ entre 0 y a/2 = ",
    NIntegrate[fun[i]^2, {x, 0, a / 2}, {y, -b / 2, b / 2}]];
    ];
```

Para fun {1, 1}: ρ entre -a/2 y 0 = 0.5 y ρ entre 0 y a/2 = 0.5

Para fun {1, 2}: ρ entre -a/2 y 0 = 0.5 y ρ entre 0 y a/2 = 0.5

Para fun {2, 1}: ρ entre -a/2 y 0 = 0.5 y ρ entre 0 y a/2 = 0.5

Para fun {2, 2}: ρ entre -a/2 y 0 = 0.5 y ρ entre 0 y a/2 = 0.5

Para fun {1, 3}: ρ entre -a/2 y 0 = 0.5 y ρ entre 0 y a/2 = 0.5

Para fun {3, 1}: ρ entre -a/2 y 0 = 0.5 y ρ entre 0 y a/2 = 0.5

Para fun {2, 3}: ρ entre -a/2 y 0 = 0.5 y ρ entre 0 y a/2 = 0.5

Para fun {3, 2}: ρ entre -a/2 y 0 = 0.5 y ρ entre 0 y a/2 = 0.5

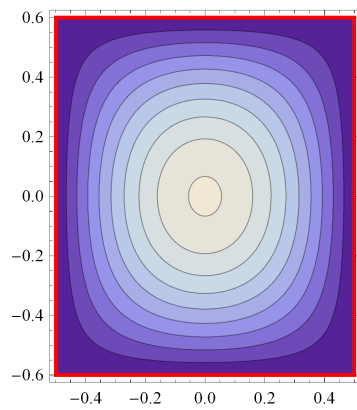Para fun {3, 3}: ρ entre -a/2 y 0 = 0.5 y ρ entre 0 y a/2 = 0.5

In[36]:= `Plot3D[{3 * fun[1], Etot[2] + fun[2], Etot[3] + fun[3], Etot[4] + fun[4]},`
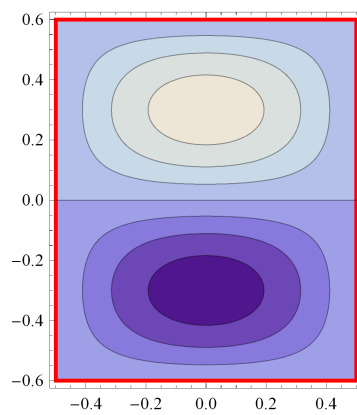`{x, -a / 2, a / 2}, {y, -b / 2, b / 2}, BoxRatios → {2, 2, 5}, Axes → False]`

Out[36]=
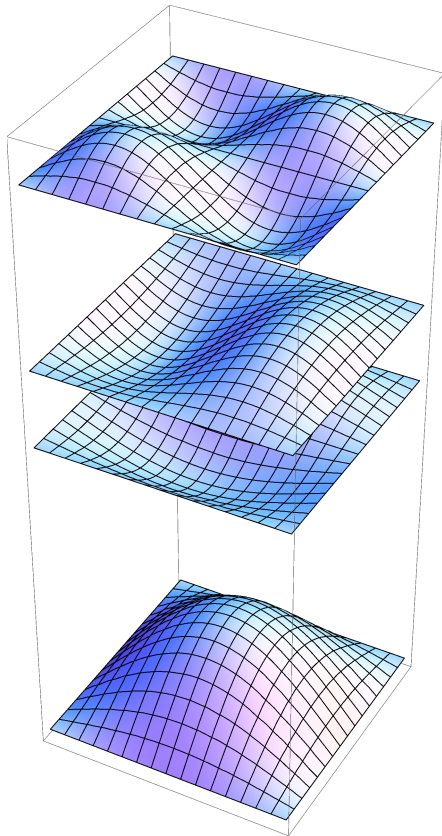
In[37]:= `(* Other shapes of perturbed functions *)`
`For[i = 1, i ≤ nf, i ++,`
` Print["Energia estado ", i, " = ", Etot[i]]`
`  Print[ContourPlot[fun[i], {x, -a / 2, a / 2}, {y, -b / 2, b / 2},`
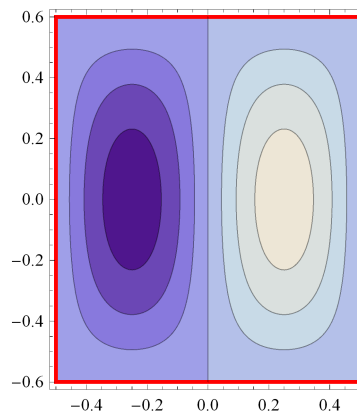`    AspectRatio → b / a, BoundaryStyle → Directive[Red, Thick]]]`
`   ];`

Energia estado 1 = 8.39784

Energia estado 2 = 18.6787

Energia estado 3 = 23.2469

```
                    (* 14. Linear Variation Method for
     a Symmetric Potential applied in a Two-dimensional Box *)

ClearAll["Global`*"];

(* Dimensions of rectangular box and number of functions *)
a = 1.0;
b = 1.2;
nn = 3;

(* Creating a list of complete set of functions *)
lisfun = {};


(* Vmin is the minimum value of V0 so R will be greater than a/2 *)
V0 = Input["Introduce un valor de  V0 menor que a/2"];


(* For a symmetric potential regarding to the centre of the box *)
R = (V0 ^ 2 + a ^ 2 / 4) / (2 * V0);
pot[x_, y_] := R - Sqrt[R ^ 2 - x ^ 2];


(* Introducing the corresponding wave functions for a two
 -dimensional box and the hamiltonian operator *)
fx[nx_] := If[OddQ[nx] == True, Sqrt[2 / a] * Cos[nx * Pi * x / a],
    Sqrt[2 / a] * Sin[nx * Pi * x / a]];
fy[ny_] := If[OddQ[ny] == True, Sqrt[2 / b] * Cos[ny * Pi * y / b],
    Sqrt[2 / b] * Sin[ny * Pi * y / b]];
fxy[nx_, ny_] := fx[nx] * fy[ny];
ham[fun_] := - (1 / 2.0) * (D[fun, {x, 2}] + D[fun, {y, 2}]) + pot[x, y] * fun;
For[i = 1, i ≤ nn, i ++,
   For[j = 1, j ≤ nn, j ++,
     lisfun = AppendTo[lisfun, fxy[i, j]];
       ];
     ];


(* Hamiltonian matrix *)
lon = Length[lisfun];
mat = Table[0, {i, lon}, {j, lon}];
For[i = 1, i ≤ lon, i ++,
   For[j = i, j ≤ lon, j ++,
     mat[[i, j]] = NIntegrate[lisfun[[i]] * ham[lisfun[[j]]], {x, -a / 2, a / 2}, {y, -b / 2,
         b / 2}, Method → "LocalAdaptive", AccuracyGoal → 6, PrecisionGoal → 6] // Chop;
     mat[[j, i]] = mat[[i, j]];
     ];
 ];


(* Matrix diagonalization *)
ene = Eigenvalues[mat];
vec = Eigenvectors[mat];
For[i = 1, i ≤ lon - 1, i ++,
   For[j = i + 1, j ≤ lon, j ++,
```
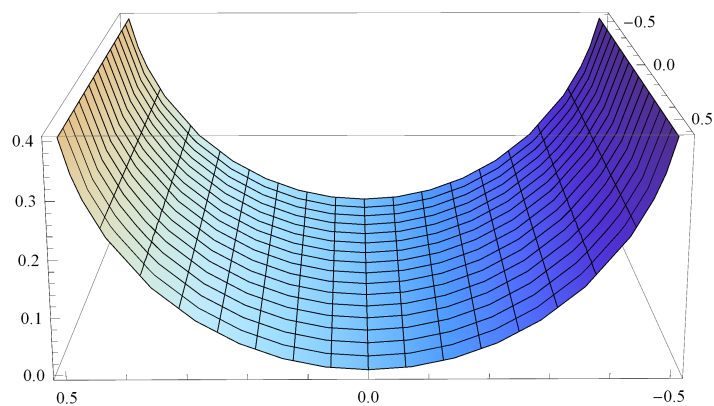
```
    enei = ene[[i]]; enej = ene[[j]];
    veci = vec[[i]]; vecj = vec[[j]];
    If[enej < enei,
        ene[[i]] = enej; ene[[j]] = enei;
       vec[[i]] = vecj; vec[[j]] = veci;
      ];
     ];
    ];
Print[" "];
Print["Potencial fondo caja"];


(* Graphic plot of symmetric potential applied  *)
Plot3D[pot[x, y], {x, -a / 2, a / 2}, {y, -b / 2, b / 2}, PlotRange → All]
Print[" "];
fun = vec.lisfun;
For[i = 1, i ≤ lon, i++,
  Print["Energia estado ", i, " = ", ene[[i]]]
    ];
```

Potencial fondo caja

Energia estado 1 = 8.39674

Energia estado 2 = 18.6776

Energia estado 3 = 23.2442

Energia estado 4 = 33.5251

Energia estado 5 = 35.8123

Energia estado 6 = 47.9294

Energia estado 7 = 50.6598
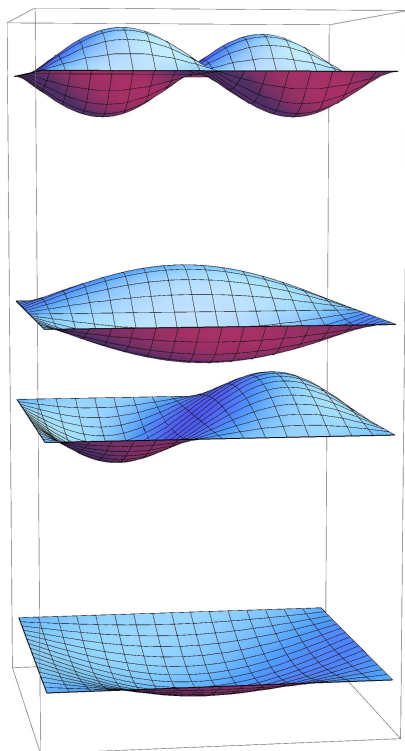
Energia estado 8 = 58.2102

Energia estado 9 = 75.345

```
(* Verify the orthogonality of the first nf functions *)
nf = 5;
solap = Table[0, {i, nf}, {j, nf}];
For[i = 1, i ≤ nf, i++,
   For[j = i, j ≤ nf, j++,
     solap[[i, j]] = NIntegrate[fun[[i]] * fun[[j]],
        {x, -a / 2, -a / 4, 0, a / 4, a / 2}, {y, -b / 2, -b / 4, 0, b / 4, b / 2},
        Method → "LocalAdaptive", AccuracyGoal → 6, PrecisionGoal → 5] // Chop;
     If[j ≠ i, solap[[j, i]] = solap[[i, j]]];
       ];
     ];
MatrixForm[solap]
```

$$\begin{pmatrix} 1. & 0 & 0 & 0 & 0 \\ 0 & 1. & 0 & 0 & 0 \\ 0 & 0 & 1. & 0 & 0 \\ 0 & 0 & 0 & 1. & 0 \\ 0 & 0 & 0 & 0 & 1. \end{pmatrix}$$

```
(* Verify the symmetric distribution of charge density of the
 variational functions as consequence symmetric potential applied *)
For[i = 1, i ≤ nf, i++,
  Print["Para funcion ", i, ":  ρ entre -a/2 y 0 = ",
    NIntegrate[fun[[i]]^2, {x, -a / 2, a / 2}, {y, -b / 2, 0}], " y ρ entre 0 y a/2 = ",
    NIntegrate[fun[[i]]^2, {x, -a / 2, a / 2}, {y, 0, b / 2}]];
    ];
```

Para funcion 1: ρ entre -a/2 y 0 = 0.5 y ρ entre 0 y a/2 = 0.5

Para funcion 2: ρ entre -a/2 y 0 = 0.5 y ρ entre 0 y a/2 = 0.5

Para funcion 3: ρ entre -a/2 y 0 = 0.5 y ρ entre 0 y a/2 = 0.5

Para funcion 4: ρ entre -a/2 y 0 = 0.5 y ρ entre 0 y a/2 = 0.5

Para funcion 5: ρ entre -a/2 y 0 = 0.5 y ρ entre 0 y a/2 = 0.5

```
(* Graphic plots of the variational functions without any distorsion *)
Plot3D[{ene[[1]] + fun[[1]], ene[[2]] + fun[[2]], ene[[3]] + fun[[3]], ene[[4]] + fun[[4]]},
  {x, -a / 2, a / 2}, {y, -b / 2, b / 2}, PlotRange → All, BoxRatios → {2, 2, 4}, Axes → False]
```
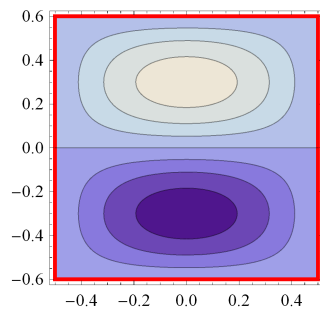


```
(* Graphic plots of the variational functions
 with the corresponding energy values of the states *)
For[i = 1, i ≤ nf, i++,
  Print["Energia estado ", i, " = ", ene[[i]]] Print[ContourPlot[fun[[i]],
    {x, -a / 2, a / 2}, {y, -b / 2, b / 2}, BoundaryStyle → Directive[Red, Thick]]]
  ];
```
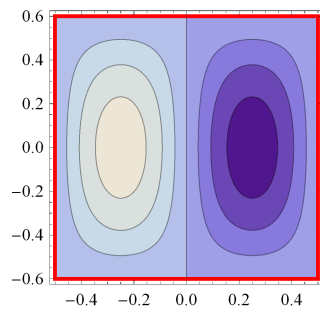
Energia estado 1 = 8.39674
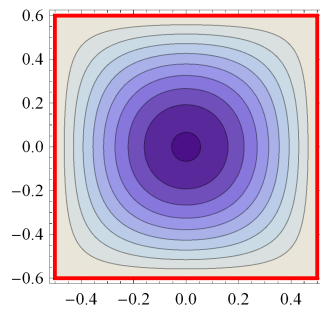
Energia estado 2 = 18.6776

Energia estado 3 = 23.2442

6. References

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[5] R. Chang, *Basic Principles of Spectroscopy,* McGraw Hill, New York, 1971.

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