

# The variational method. Estimating the first few energies of different systems via expansion into orthonormal and non-orthonormal basis functions.

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December 2020

## 1 Introduction

The main objective of this assignment is to apply the variational method to obtain the first few energies for different Hamiltonians. We will use expansions into the quantum harmonic oscillator eigenfunctions and see how the energies obtained change as the number of eigenfunctions considered grows. This will be done for a modified quantum harmonic oscillator, which is of the type that results from a quantum harmonic oscillator under the influence of a constant electric field, and a quartic anharmonic oscillator. For a finite square well we will examine the behaviour of bound states as a function of the depth of the well; we expect the number of bound states to grow as the depth of the well increases. Finally, we will apply an expansion into a non-orthonormal set of functions to the hydrogen atom. We will use Gaussian functions and we will try to optimize their parameters for the ground state. This will be done using a script in Python that implements the variational method.

## 2 The Variational Method

The variational method, also called Rayleigh-Ritz method, is useful for determining upper bounds for the eigenenergies of a system for which the Hamiltonian is known, but neither its eigenvalues nor its eigenstates are known, or can't be obtained in closed form. This method is particularly useful for determining the ground state energy and its eigenstate without explicitly solving the Schrödinger equation.

The idea behind the method is not to attempt to solve the eigenvalue problem for the system

$$\hat{H} |\psi\rangle = E |\psi\rangle \tag{1}$$

but to find the approximate eigenenergies and eigenfunctions from the variational equation

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$$\delta E(\psi) = 0 \quad (2)$$

where  $E(\psi)$  is the expectation value of the energy in the state  $|\psi\rangle$

$$E(\psi) = \frac{\langle\psi|\hat{H}|\psi\rangle}{\langle\psi|\psi\rangle} \quad (3)$$

If  $|\psi\rangle$  depends on a parameter  $\alpha$ , then  $E(\psi)$  will also depend upon  $\alpha$ . This enables us to vary  $\alpha$  as to minimize  $E(\psi)$ .

The minimum value of  $E(\psi)$  provides an upper bound for the true energy of the system. This means that for any trial function  $|\psi\rangle$  chosen,  $E(\psi)$  is always larger than the exact energy  $E_0$ :

$$E(\psi) = \frac{\langle\psi|\hat{H}|\psi\rangle}{\langle\psi|\psi\rangle} \geq E_0 \quad (4)$$

while the equality condition holds only when  $|\psi\rangle$  is proportional to the true ground state  $|\psi_0\rangle$ .

To see this, we expand the trial function  $|\psi\rangle$  into the exact eigenstates of  $\hat{H}$ , which is always possible since they form a complete orthonormal set:

$$|\psi\rangle = \sum_n c_n |\psi_n\rangle \quad \text{where} \quad \hat{H} |\psi_n\rangle = E_n |\psi_n\rangle \quad (5)$$

Then, since  $E_0 \leq E_n$  by definition of ground state:

$$E(\psi) = \frac{\langle\psi|\hat{H}|\psi\rangle}{\langle\psi|\psi\rangle} = \frac{\sum_n |c_n|^2 E_n}{\sum_n |c_n|^2} \geq \frac{E_0 \sum_n |c_n|^2}{\sum_n |c_n|^2} = E_0 \quad (6)$$

## 2.1 Obtaining Eigenenergies

Now, with this in mind, to obtain the ground state energy we make an educated guess of a trial function  $|\phi_0\rangle$  that takes into account physical properties of the ground state (symmetries, smoothness, behaviour at infinity, etc.). For properties we are not confident about, we include adjustable parameters  $\alpha$  so that

$$|\phi_0\rangle = |\phi_0(\alpha_1, \alpha_2, \dots)\rangle \quad (7)$$

Then, using (3), we get the following expression that depends upon the parameters:

$$E_0(\alpha_1, \alpha_2, \dots) = \frac{\langle\phi_0(\alpha_1, \alpha_2, \dots)|\hat{H}|\phi_0(\alpha_1, \alpha_2, \dots)\rangle}{\langle\phi_0(\alpha_1, \alpha_2, \dots)|\phi_0(\alpha_1, \alpha_2, \dots)\rangle} \quad (8)$$

We then minimize with respect to  $\alpha_1, \alpha_2, \dots$ , which will give values  $\alpha_{1_0}, \alpha_{2_0}, \dots$  that minimize  $E_0(\alpha_1, \alpha_2, \dots)$ .

Finally, the value  $E_0(\alpha_{1_0}, \alpha_{2_0}, \dots)$  will be an upper bound for the exact ground state energy  $E_0$ , while the exact ground state  $|\psi_0\rangle$  will be approximated by the state  $|\phi_0(\alpha_{1_0}, \alpha_{2_0}, \dots)\rangle$ .

To find the energy and eigenstate of the first excited state, that will approximate  $E_1$  and  $|\psi_1\rangle$ , we choose a trial function  $|\phi_1\rangle$  that must be orthogonal to  $|\phi_0\rangle$ :

$$\langle\phi_1|\phi_0\rangle = 0 \quad (9)$$

and proceed as before with that added condition. For the second excited state, we choose a trial function  $|\phi_2\rangle$  that must be orthogonal to both  $|\phi_0\rangle$  and  $|\phi_1\rangle$ :

$$\langle\phi_2|\phi_0\rangle = 0 \quad \text{and} \quad \langle\phi_2|\phi_1\rangle = 0 \quad (10)$$

For higher excited state it's the same with the necessary added conditions of orthogonality[1]. These conditions can be included using Lagrange multipliers, by means of a constrained variational problem.

## 2.2 Expansion into Orthonormal Functions

This issue with the added conditions of orthogonality goes away[2] if we expand the trial function  $|\psi\rangle$  into a finite basis set of functions and apply the variational method to find the optimal coefficients of the expansion.

From (3) we can write the following functional:

$$\Lambda(\psi) = \langle\psi|\hat{H}|\psi\rangle - E(\psi) \langle\psi|\psi\rangle \quad (11)$$

If we impose the stationary condition on  $\Lambda(\psi)$  we will get an equation for the expansion coefficients. What we are going to find is the function  $|\psi\rangle$  that better approximates the true ground state, among all functions that can be expressed as linear combinations of the chosen finite basis, since it's not a complete set.

Lets consider a basis of  $N + 1$  functions  $\Upsilon_i$  for which:

$$\langle\Upsilon_i|\Upsilon_j\rangle = \delta_{ij} \quad (12)$$

and the expansion of the trial function  $|\psi\rangle$  into those functions:

$$|\psi\rangle = \sum_{i=0}^N c_i |\Upsilon_i\rangle \quad (13)$$

By replacing this in (11) we get:

$$\Lambda(c_0, c_1, \dots, c_N) = \sum_{ij} \bar{c}_i c_j H_{ij} - E(c_0, c_1, \dots, c_N) \sum_{ij} \bar{c}_i c_j \delta_{ij} \quad (14)$$

where  $\bar{c}_i$  denotes the complex conjugate of  $c_i$  and we have defined:

$$H_{ij} = \langle\Upsilon_i|\hat{H}|\Upsilon_j\rangle \quad (15)$$

Then, we can write:

$$\Lambda(c_0, c_1, \dots, c_N) = \sum_{ij} \bar{c}_i c_j [H_{ij} - \xi \delta_{ij}], \quad \xi = E(c_0, c_1, \dots, c_N) \quad (16)$$

One thing to note is that  $H_{ij}$  is known, and it's a hermitian matrix (symmetric if all entries are real). Now, we minimize the functional  $\Lambda(c_0, c_1, \dots, c_N)$  with respect to the coefficients to get the condition

$$\sum_j c_j [H_{ij} - \xi \delta_{ij}] = 0, \quad i = 0, 1, \dots, N \quad (17)$$

As we know, this system of equations has non-trivial solutions if, and only if, the corresponding matrix is singular. That is

$$\det(H_{ij} - \xi \delta_{ij}) = 0 \quad (18)$$

Thus, the minimization of (11) became an eigenvalue problem of the form

$$H \mathbf{c}^{(i)} = \xi^{(i)} \mathbf{c}^{(i)}, \quad i = 0, 1, \dots, N \quad (19)$$

where  $H$  is a  $(N+1) \times (N+1)$  matrix with  $H_{ij}$  as its entries.

Thus, once solved, we find eigenvectors  $\mathbf{c}^{(i)}$  and eigenvalues  $\xi^{(i)}$ , from which we can get the  $N+1$  solutions to (1) as follows:

$$|\psi^{(i)}\rangle = \sum_{k=0}^N \mathbf{c}_k^{(i)} |\Upsilon_k\rangle \quad \text{and} \quad \hat{H} |\psi^{(i)}\rangle = \xi^{(i)} |\psi^{(i)}\rangle \quad (20)$$

## 2.3 Expansion into Non-Orthonormal Functions

If we were to consider the  $N+1$  functions  $\Upsilon_i$  to be non-orthonormal, we would get

$$\langle \Upsilon_i | \Upsilon_j \rangle = S_{ij} \quad (21)$$

where the elements  $S_{ij}$  can be arranged into a matrix  $S$  known as the overlap matrix. Thus, the minimization of (11) would result in what is known as a generalized eigenvalue problem:

$$H \mathbf{c}^{(i)} = \xi^{(i)} S \mathbf{c}^{(i)}, \quad i = 0, 1, \dots, N \quad (22)$$

where the condition for non-trivial solutions is

$$\det(H - \xi S) = 0 \quad (23)$$

Once solved, solutions can be written as follows:

$$|\psi^{(i)}\rangle = \sum_{k=0}^N \mathbf{c}_k^{(i)} |\Upsilon_k\rangle \quad \text{and} \quad \hat{H} |\psi^{(i)}\rangle = \xi^{(i)} |\psi^{(i)}\rangle \quad (24)$$

### 3 Expansion into the Quantum Harmonic Oscillator Eigenfunctions

As we know, when studying the quantum harmonic oscillator,  $\hat{a}$  and  $\hat{a}^\dagger$ , known as ladder operators, are introduced, so that:

$$\hat{X} = \sqrt{\frac{\hbar}{2m\omega}}(\hat{a}^\dagger + \hat{a}) \quad \text{and} \quad \hat{P} = i\sqrt{\frac{m\hbar\omega}{2}}(\hat{a}^\dagger - \hat{a}) \quad (25)$$

They are known as ladder operators as they satisfy:

$$\hat{a}^\dagger |n\rangle = \sqrt{n+1} |n+1\rangle \quad \text{and} \quad \hat{a} |n\rangle = \sqrt{n} |n-1\rangle \quad (26)$$

$$\langle m|\hat{a}^\dagger|n\rangle = \sqrt{n+1}\delta_{m,n+1} \quad \text{and} \quad \langle m|\hat{a}|n\rangle = \sqrt{n}\delta_{m,n-1} \quad (27)$$

where  $|n\rangle$  and  $|m\rangle$  denote the  $n$ th and  $m$ th eigenfunctions, respectively, of the quantum harmonic oscillator and  $\delta_{m,n}$  denotes the Kronecker delta.

With this in mind, we can obtain the matrix elements of the Hamiltonians that are of interest to us. Specifically, we are considering the modified quantum harmonic oscillator

$$\hat{H}_{MHO} = \frac{\hat{P}^2}{2m} + \frac{1}{2}m\omega^2\hat{X}^2 - \alpha\hat{X}, \quad (28)$$

the quartic anharmonic oscillator

$$\hat{H}_{QAO} = \frac{\hat{P}^2}{2m} + \frac{1}{2}m\omega^2\hat{X}^2 + \beta\hat{X}^4, \quad (29)$$

and a finite square well

$$\hat{H}_{PW} = \frac{\hat{P}^2}{2m} + \hat{V}(\hat{X}) \quad \text{for} \quad V(x) = \begin{cases} -V_0 & |x| \leq b \\ 0 & |x| > b \end{cases}. \quad (30)$$

So, we need matrix elements for  $\hat{P}^2$  and the first, second and fourth powers of  $\hat{X}$ . These can be obtained by using (25) and (27). We get:

$$\langle m|\hat{X}|n\rangle = \sqrt{\frac{\hbar}{2m\omega}}(\sqrt{n+1}\delta_{m,n+1} + \sqrt{n}\delta_{m,n-1}) \quad (31)$$

$$\langle m|\hat{X}^2|n\rangle = \frac{\hbar}{2m\omega}(\sqrt{(n+1)(n+2)}\delta_{m,n+2} + (2n+1)\delta_{m,n} + \sqrt{n(n-1)}\delta_{m,n-2}) \quad (32)$$

$$\begin{aligned} \langle m|\hat{X}^4|n\rangle = & \left(\frac{\hbar}{2m\omega}\right)^2 (\sqrt{(n+1)(n+2)(n+3)(n+4)}\delta_{m,n+4} \\ & + 2(2n+3)\sqrt{(n+1)(n+2)}\delta_{m,n+2} + (6n^2+6n+3)\delta_{m,n} \\ & + 2(2n-1)\sqrt{n(n-1)}\delta_{m,n-2} + \sqrt{n(n-1)(n-2)(n-3)}\delta_{m,n-4}) \end{aligned} \quad (33)$$

$$\langle m|\hat{P}^2|n\rangle = -\frac{m\hbar\omega}{2}(\sqrt{(n+1)(n+2)}\delta_{m,n+2} - (2n+1)\delta_{m,n} + \sqrt{n(n-1)}\delta_{m,n-2}) \quad (34)$$

For the finite well, the matrix elements for the potential have to be represented in terms of an integral:

$$\langle m|\hat{V}(\hat{X})|n\rangle = \frac{-V_0}{\sqrt{\pi x_0 m! n! 2^{m+n}}} \int_{-\frac{b}{x_0}}^{\frac{b}{x_0}} e^{-y^2} H_m(y) H_n(y) dy \quad \text{where} \quad x_0 = \sqrt{\frac{\hbar}{m\omega}} \quad (35)$$

and  $H_m(y)$  are the Hermite polynomials.

### 3.1 Algorithm and Implementation

First thing we will note is that Rydberg Atomic Units will be used, which means that

$$\hbar = 2m = \frac{q^2}{2} = 1 \quad (36)$$

where  $m$  and  $q$  are the mass and charge of the electron. Thus, the matrix elements of our Hamiltonians can be written as:

$$\langle m|\hat{H}_{MHO}|n\rangle = \omega \left( n + \frac{1}{2} \right) \delta_{m,n} - \alpha \sqrt{\frac{1}{\omega}} (\sqrt{n+1}\delta_{m,n+1} + \sqrt{n}\delta_{m,n-1}) \quad (37)$$

$$\begin{aligned} \langle m|\hat{H}_{QAO}|n\rangle = & \omega \left( n + \frac{1}{2} \right) \delta_{m,n} + \beta \frac{1}{\omega^2} (\sqrt{(n+1)(n+2)(n+3)(n+4)}\delta_{m,n+4} \\ & + 2(2n+3)\sqrt{(n+1)(n+2)}\delta_{m,n+2} + (6n^2+6n+3)\delta_{m,n} \\ & + 2(2n-1)\sqrt{n(n-1)}\delta_{m,n-2} + \sqrt{n(n-1)(n-2)(n-3)}\delta_{m,n-4}) \end{aligned} \quad (38)$$

$$\begin{aligned} \langle m|\hat{H}_{PW}|n\rangle = & -\frac{\omega}{4} (\sqrt{(n+1)(n+2)}\delta_{m,n+2} - (2n+1)\delta_{m,n} + \sqrt{n(n-1)}\delta_{m,n-2}) \\ & - \frac{V_0}{\sqrt{\pi x_0 m! n! 2^{m+n}}} \int_{-\frac{b}{x_0}}^{\frac{b}{x_0}} e^{-y^2} H_m(y) H_n(y) dy \end{aligned} \quad (39)$$

where, now,  $x_0$  is  $\sqrt{2/\omega}$ .

The default value for  $\omega$  in the code is 1, but this can be easily changed. Also, we took  $\alpha$  and  $\beta$  as follows

$$\alpha = \sqrt{\omega} \quad \text{and} \quad \beta = \omega^2 \quad (40)$$

so as to simplify further the matrix elements. Again, this can be changed in the code.

Eigenvalue distribution. Five lowest eigenvalues. Modified Harmonic Oscillator.

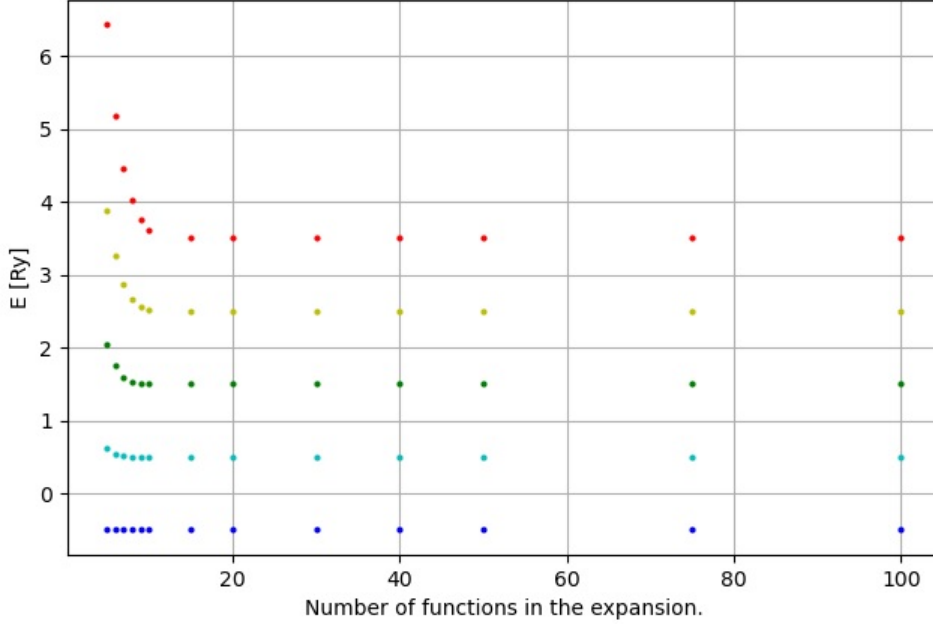


Figure 1: Eigenvalue distribution for the modified harmonic oscillator.

For the square well we take  $V_0$  to be variable but a fixed number of 50 functions in the expansion and

$$b = 5\sqrt{\frac{2}{\omega}} \implies \frac{b}{x_0} = 5 \quad (41)$$

To perform the diagonalizations required, we used the *eigh*<sup>1</sup> function from the *linalg* module of the *SciPy* library. To perform the integration in (39), we used the *trapz*<sup>2</sup> function from *SciPy*'s *integrate* module, which implements the trapezium rule. For this integration, 1000 sample points were taken. In every case we looked at the five lowest eigenvalues of the Hamiltonian, but for the square well ten eigenvalues were plotted.

### 3.2 Results and Discussion

For both oscillators, since we looked at the five lowest eigenvalues, we used expansions into 5, 6, 7, 8, 9, 10, 15, 20, 30, 40, 50, 75 and 100 functions. For the modified harmonic oscillator, results can be seen in Figure 1.

First thing to note, is that we can see that the eigenvalues converge to their exact values. We know how to solve the Hamiltonian in (28). If we introduce the change of variables

$$\hat{Y} = \hat{X} - \frac{\alpha}{m\omega^2} \quad (42)$$

we can write (28) as

<sup>1</sup><https://docs.scipy.org/doc/scipy/reference/generated/scipy.linalg.eigh.html>

<sup>2</sup><https://docs.scipy.org/doc/scipy/reference/generated/scipy.integrate.trapz.html>

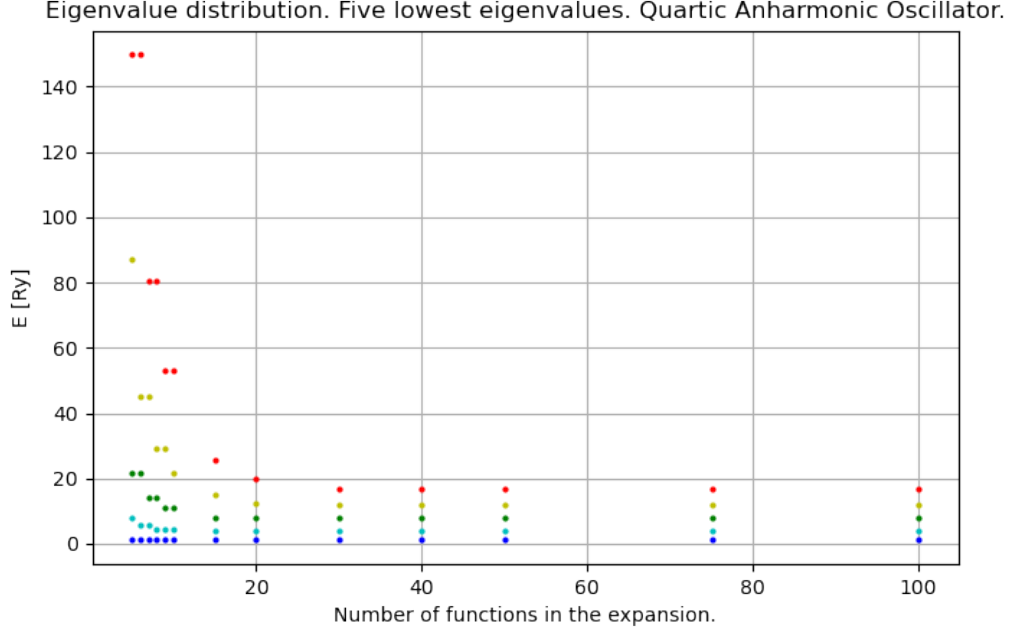


Figure 2: Eigenvalue distribution for the quartic anharmonic oscillator.

$$\hat{H}_{MHO} = \frac{\hat{P}^2}{2m} + \frac{1}{2}m\omega^2\hat{Y}^2 - \frac{\alpha^2}{2m\omega^2} \quad \Rightarrow \quad E_{MHO_n} = \hbar\omega \left( n + \frac{1}{2} \right) - \frac{\alpha^2}{2m\omega^2} \quad (43)$$

Given the units we are working on and the values we chose for  $\omega$  and  $\alpha$  we get

$$E_{MHO_n} = \left( n + \frac{1}{2} \right) - 1 \quad (44)$$

By comparing this with Figure 1, we can see exact convergence. In fact, by checking the values obtained for 5 and 100 functions, we can see they converge exactly to their respective values.

#### Modified Harmonic Oscillator

Eigenvalues obtained for 5 functions in the expansion:  
 $[-0.48855178 \quad 0.6307415 \quad 2.04057273 \quad 3.8884121 \quad 6.42882545]$

Eigenvalues obtained for 100 functions in the expansion:  
 $[-0.5 \quad 0.5 \quad 1.5 \quad 2.5 \quad 3.5]$

Results obtained for the quartic anharmonic oscillator can be seen as a whole in Figure 2 and with more detail in Figure 3. The values obtained for 5 and 100 functions can be seen below.

#### Quartic Anharmonic Oscillator



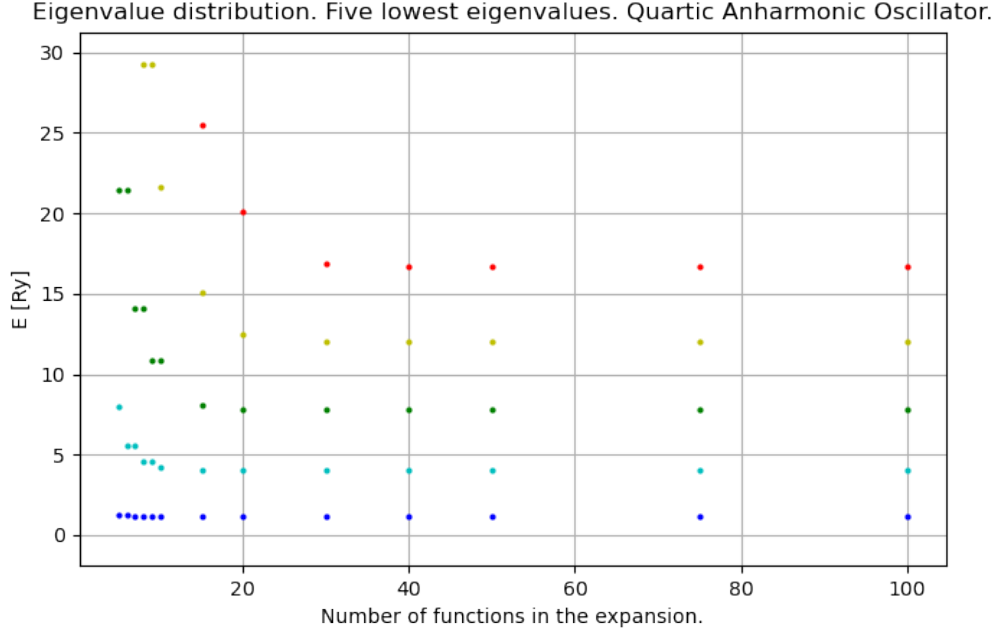


Figure 3: Eigenvalue distribution for the quartic anharmonic oscillator.

Eigenvalues obtained for 5 functions in the expansion:  
[1.28915123    7.99050747    21.46296294    87.00949253    149.74788583]

Eigenvalues obtained for 100 functions in the expansion:  
[1.14878891    4.02156567    7.76398018    12.03129741    16.71931168]

For both oscillators we can see that more functions in the expansion translates to more energies being closer to their exact values and that lower energies converge first, as expected. Also, in both cases, with just five functions in the expansion, the ground state is quite close to it's exact value.

Also, we can see that the number of functions needed to achieve convergence for the five lowest energies is around 40 for the quartic anharmonic oscillator, while around 20 are needed for the modified harmonic oscillator. This is to be expected given the expressions for their respective Hamiltonians. The Hamiltonian of the modified harmonic oscillator has only 3 non-zero diagonals, while the quartic anharmonic oscillator has 5.

For the finite square well, we took 60 evenly spaced values for  $V_0$  between 0 Ry and 3 Ry. Results can be seen in Figure 4. As mentioned previously, the ten lowest energies were plotted.

As expected, we see that as  $|V_0|$  grows, more bound states appear. We know that the number of bound states doesn't grow linearly with the depth of the well. Also worth noting is that the ground state is always present[1], as long as  $V_0 \neq 0$ . Both of these behaviours can be seen in Figure 4.

## 4 Expansion into Gaussian functions

For this expansion we will use Gaussian functions of the form

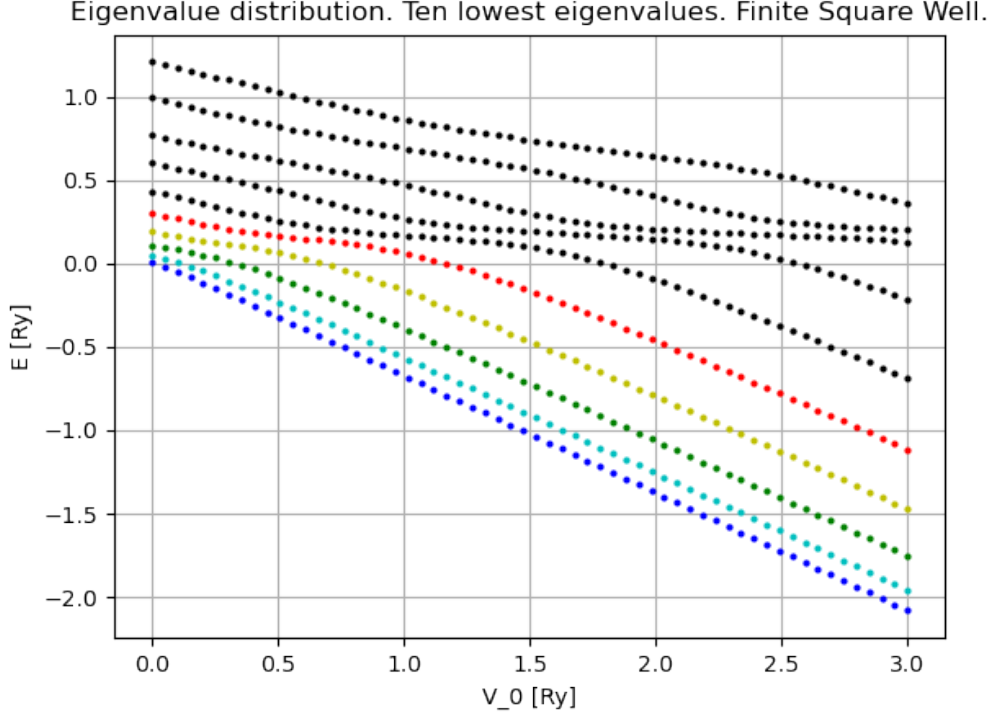


Figure 4: Eigenvalue distribution for the finite square well.

$$\psi_n(r) = e^{-\alpha_n r^2} \quad (45)$$

where we will try to find the optimal coefficients  $\alpha_n$  for the expansion.  
The Hamiltonian for the hydrogen atom is

$$H_{HA} = -\frac{\hbar^2}{2m} \nabla^2 - \frac{q^2}{r} \quad (46)$$

where  $m$  and  $q$  are the mass and charge of the electron, respectively.

So, we need the matrix elements of the Hamiltonian, as well as the matrix elements for the overlap matrix.

For the Hamiltonian we will use the following identities[2]:

$$\int_{\mathbb{R}^3} e^{-\alpha_m r^2} \nabla^2 e^{-\alpha_n r^2} d^3r = -\frac{6\alpha_m \alpha_n}{\alpha_m + \alpha_n} \left( \frac{\pi}{\alpha_m + \alpha_n} \right)^{3/2} \quad (47)$$

$$\int_{\mathbb{R}^3} e^{-\alpha_m r^2} \frac{1}{r} e^{-\alpha_n r^2} d^3r = \frac{2\pi}{\alpha_m + \alpha_n} \quad (48)$$

while for the overlap matrix we will use

$$\int_{\mathbb{R}^3} e^{-\alpha_m r^2} e^{-\alpha_n r^2} d^3r = \left( \frac{\pi}{\alpha_m + \alpha_n} \right)^{3/2} \quad (49)$$

Therefore, we get:

$$\langle \psi_m | \hat{H}_{HA} | \psi_n \rangle = \frac{\hbar^2}{2m} \frac{6\alpha_m \alpha_n}{\alpha_m + \alpha_n} \left( \frac{\pi}{\alpha_m + \alpha_n} \right)^{3/2} - \frac{2\pi q^2}{\alpha_m + \alpha_n} \quad (50)$$

and

$$\langle \psi_m | \psi_n \rangle = \left( \frac{\pi}{\alpha_m + \alpha_n} \right)^{3/2} \quad (51)$$

We know the optimized values for the parameters  $\alpha_n$  for 3[3] and 4[2] Gaussians:

$$\text{- 3 Gaussians: } \alpha_0 = 0.109818 \quad , \quad \alpha_1 = 0.405771 \quad , \quad \alpha_2 = 2.227660 \quad (52)$$

$$\text{- 4 Gaussians: } \alpha_0 = 0.121949 \quad , \quad \alpha_1 = 0.444529 \quad , \quad \alpha_2 = 1.962079 \quad , \quad \alpha_3 = 13.00773 \quad (53)$$

## 4.1 Algorithm and Implementation

As mentioned previously, we will use Rydberg atomic units. With this in mind, we write

$$\langle \psi_m | \hat{H}_{HA} | \psi_n \rangle = \frac{6\alpha_m \alpha_n}{\alpha_m + \alpha_n} \left( \frac{\pi}{\alpha_m + \alpha_n} \right)^{3/2} - \frac{4\pi}{\alpha_m + \alpha_n} \quad (54)$$

while the overlap matrix doesn't change.

We know that, for the ground state, the energy is  $-1$  Ry.

We will optimize the parameters  $\alpha_n$  for expansions into 3 and 4 Gaussian functions since we know their optimized values. The code will use the optimized values as the starting point to set up a sample set, which includes those optimized values, while asking for the number of samples desired. The bounds for this sample sets will be, for each parameter  $\alpha_n$ ,  $\pm 0.03$  of the optimized value.

Again, for diagonalization, the *eigh* function will be used.

## 4.2 Results and Discussion

For 4 Gaussians, we started by taking sample sets for each parameter  $\alpha_n$  of size 11. This number was chosen because it ensures that the optimized values for  $\alpha_n$  are present. This yielded:

4 Gaussians: 11 samples around optimized values for each parameter.

Eigenvalue obtained (6 significant figures, rounded):

$${}^{(4)}_{11}E_0 = -0.998557$$

Coefficients obtained:

$${}^{(4)}_{11}\alpha_0 = 0.121949 \quad , \quad {}^{(4)}_{11}\alpha_1 = 0.444529 \quad , \quad {}^{(4)}_{11}\alpha_2 = 1.962079 \quad , \quad {}^{(4)}_{11}\alpha_3 = 13.00773$$

We see that the energy obtained is quite close to the exact value of 1 Ry. As for the parameters, these are the same as those in (53), but that's likely to be due to the fact that the exact values were among those in the sample set.

To be sure, another run was done, where each sample set was of size 51. This yielded:

4 Gaussians: 51 samples around optimized values for each parameter.

Eigenvalue obtained (6 significant figures, rounded):

$${}_{51}^{(4)}E_0 = -0.998557$$

Coefficients obtained:

$${}_{51}^{(4)}\alpha_0 = 0.121949 \quad , \quad {}_{51}^{(4)}\alpha_1 = 0.444529 \quad , \quad {}_{51}^{(4)}\alpha_2 = 1.962079 \quad , \quad {}_{51}^{(4)}\alpha_3 = 13.00893$$

We can see that the only difference is in the value for  $\alpha_3$ . The energies obtained are practically the same. for reference, these are the exact values obtained (up to Python's float precision):

$$\text{Eigenvalue obtained for 11 samples: } {}_{11}^{(4)}E_0 = -0.9985568113345901$$

$$\text{Eigenvalue obtained for 51 samples: } {}_{51}^{(4)}E_0 = -0.9985568113740363$$

It can be seen that  ${}_{51}^{(4)}E_0$  is slightly smaller than  ${}_{11}^{(4)}E_0$ , but at this point it may be due to the fact that Python's default float precision is only 16 decimal places, which can propagate errors.

An attempt was made to perform reruns with Python's *Decimal* type, which circumvents various issues that arise with floats, but neither *NumPy* nor *SciPy* are capable of handling *Decimal* type data.

For 3 Gaussians, we used the same starting size for the sample sets, which yielded:

3 Gaussians: 11 samples around optimized values for each parameter.

Eigenvalue obtained (6 significant figures, rounded):

$${}_{11}^{(3)}E_0 = -0.990321$$

Coefficients obtained (6 significant figures, rounded):

$${}_{11}^{(3)}\alpha_0 = 0.115818 \quad , \quad {}_{11}^{(3)}\alpha_1 = 0.429771 \quad , \quad {}_{11}^{(3)}\alpha_2 = 2.25766$$

We notice immediately that, while the energy obtained is quite close to 1 Ry, the parameters  $\alpha_n$  differ significantly from those in (52).

Similarly to the case with 4 Gaussian, a rerun was done with a sample set size of 51:

3 Gaussians: 51 samples around optimized values for each parameter.

Eigenvalue obtained (6 significant figures, rounded):

$${}_{51}^{(3)}E_0 = -0.990340$$

Coefficients obtained (6 significant figures, rounded):

$${}_{51}^{(3)}\alpha_0 = 0.118218 \quad , \quad {}_{51}^{(3)}\alpha_1 = 0.435771 \quad , \quad {}_{51}^{(3)}\alpha_2 = 2.25766$$

Which are again different from the ones in (52) and don't appear to stabilize. The parameter  $\alpha_2$  is the same in both runs because it's the biggest value in the sample set.

So what we did was keep feeding the code the values obtained, until stability was reached. This eventually yielded:

3 Gaussians: 21 samples for each parameter until stability was reached.

Eigenvalue obtained (6 significant figures, rounded):

$${}^{(3)}_{21}E_0 = -0.993958$$

Coefficients obtained:

$${}^{(3)}_{21}\alpha_0 = 0.151218 \quad , \quad {}^{(3)}_{21}\alpha_1 = 0.679771 \quad , \quad {}^{(3)}_{21}\alpha_2 = 4.48666$$

We can see that, while the energy obtained is closer to 1 Ry than before, the parameters  $\alpha_n$  are significantly different from the ones provided by Cramer<sup>3</sup>. As to why this is the case, it's hard to say without having a deeper look into the problem. Despite this, the energy estimate is very good.

## References

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<sup>3</sup>Page 170.