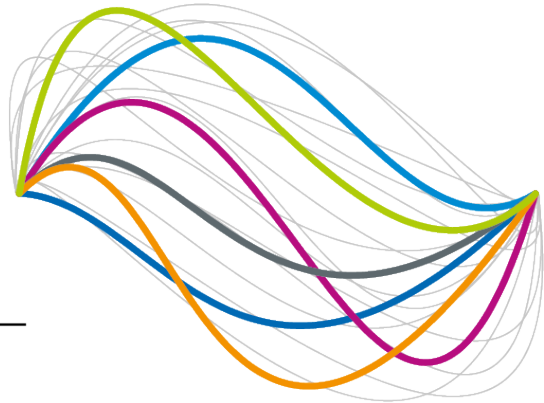

Technical Project 2-Numerical Methods

Technical report submitted to
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1 Introduction

The goal of the project is to calculate the eigenvalues and eigenvectors of the vibration-rotation Hamiltonian of the H_2 molecule by using the shooting method. We further study the effect of various input parameters on the eigenvalues. We use 3 dimensional Schrodinger's equation and find $\Psi(\vec{R})$, the separation of radial (R) and angular (θ, ϕ) variables is used, so the equation becomes:

$$\psi(\vec{R}) = \frac{1}{R} \psi(R) Y_{Jm}(\theta, \phi)$$

where $Y_{Jm}(\theta, \phi)$ are the spherical harmonics with $J = 0, 1, \dots$ denoting the rotational quantum number and $m = -J, \dots, 0, \dots, J$ standing for the magnetic quantum number. The radial part of the equation can be written as:

$$H(R)\psi(R) = \left[-\frac{\hbar^2}{2\mu} \frac{d^2}{dR^2} + V(R) + \frac{\hbar^2 J(J+1)}{2\mu R^2} \right] \psi(R) = E\psi(R)$$

Here, μ is the reduced mass of the two nuclei, $V(R)$ is the potential of the relative motion of the nuclei (vibration) and $\hbar^2 J(J+1)/(2\mu R^2)$ represents the centrifugal repulsion produced by the rotation of the molecule..

This is the equation that we will use to find the wavefunctions and eigenvalues but in reduced form to ease the computations.

2 Theoretical Description

For solving the numerically easily we use the reduced variables which are dimensionless. For the potential $V(R)$ characterized by the position of the minimum R_0 (distance between two atoms) and the potential depth V_0 (dissociation energy of the molecule), we use these parameters to arrive at our reduced variables $r = \frac{R}{R_0}$ and $v(r) = \frac{V(R)}{V_0}$. The schrodinger's

equation becomes:

$$\left[-b \frac{d^2}{dr^2} + v(r) + b \frac{J(J+1)}{r^2} \right] \psi(r) = e \psi(r)$$

Here, $b = \frac{B}{V_o}$ is the reduced value of the rotational constant $B = \frac{\hbar^2}{2\mu R_o^2}$ and $e = \frac{E}{V_o}$ is the reduced value of the proper energy.

We approximate the hydrogen molecule potential with the Morse potential which gives a very reasonable approximation for the weakly excited states. In terms of the reduced variables, the potential is:

$$v(r) = e^{-2a(r-1)} - 2e^{-a(r-1)}$$

The number of the bound states is limited (in case of $J = 0$) and we use a new quantum number called vibrational quantum number (v) to represent these states. In terms of the reduced units the states are given by:

$$e_v = -[1 - a\sqrt{b}(v + \frac{1}{2})]^2, \quad 0 \leq v \leq \frac{1}{a\sqrt{b}} - \frac{1}{2}$$

The second expression gives the number of the states, which is our case went upto $v = 18$. The parameters a and b can be determined by using the experimental data on the spectral lines and by making the assumption of the rigid rotor model.

We use the shooting method to find the energies. Shooting method is an iterative method that means starting with an initial guess, the function computes the eigenvalues and eigenfunctions by assuming the initial guess for the eigenvalue, integrating the Schrodinger's equation numerically, and adjusting the guessed eigenvalue iteratively until the boundary conditions are satisfied. In the case of the Morse potential, we know that the eigenvalues are between -1 and 0, so an initial guess around -1 is reasonable and to go to higher vibrational levels we increase the initial value of the energy.

3 Numerical Studies and results

3.1 Determination of the vibrational energies and their comparison with the theoretical values from the morse potential.

From the table presented below, we see that the Morse potential gives pretty accurate results for the eigenvalues of the H_2 molecule. There is good agreement between the numerically calculated values and values determined through morse potential upto 3 decimal places(for most of eigenvalues, for some it is even better), thus we can say that the Morse potential equation perfectly captures the behaviour of the H_2 potential. We also plotted the wavefunctions for various vibrational levels.

TABLE 1: Vibrational energy values

ν	Experimental Value	Theoretical Value(Morse pot.)
0	-0.9470991	-0.9470802
1	-0.8456891	-0.8455565
2	-0.7499736	-0.7497870
3	-0.6609138	-0.6597718
4	-0.5758257	-0.5755109
5	-0.4974192	-0.4970043
6	-0.4247642	-0.4242520
7	-0.3577143	-0.3572539
8	-0.2965150	-0.2960102
9	-0.2410631	-0.2405208
10	-0.1913456	-0.1907856
11	-0.1470378	-0.1468048
12	-0.1094180	-0.1085782
13	-0.07953787	-0.0761059
14	-0.05237278	-0.0493879
15	-0.0308381	-0.0284243
16	-0.01327256	-0.0132149
17	-0.003762543	-0.0037598
18	-0.000060210	-0.0000589

As seen from the table with increase in the vibrational quantum number, the energy levels get closer and closer and also approach zero (the zone of continuous spectra). This behaviour of the vibrational levels highlights the anharmonicity of the potential, meaning there is a non-linear relationship between the bond length and the potential energy.

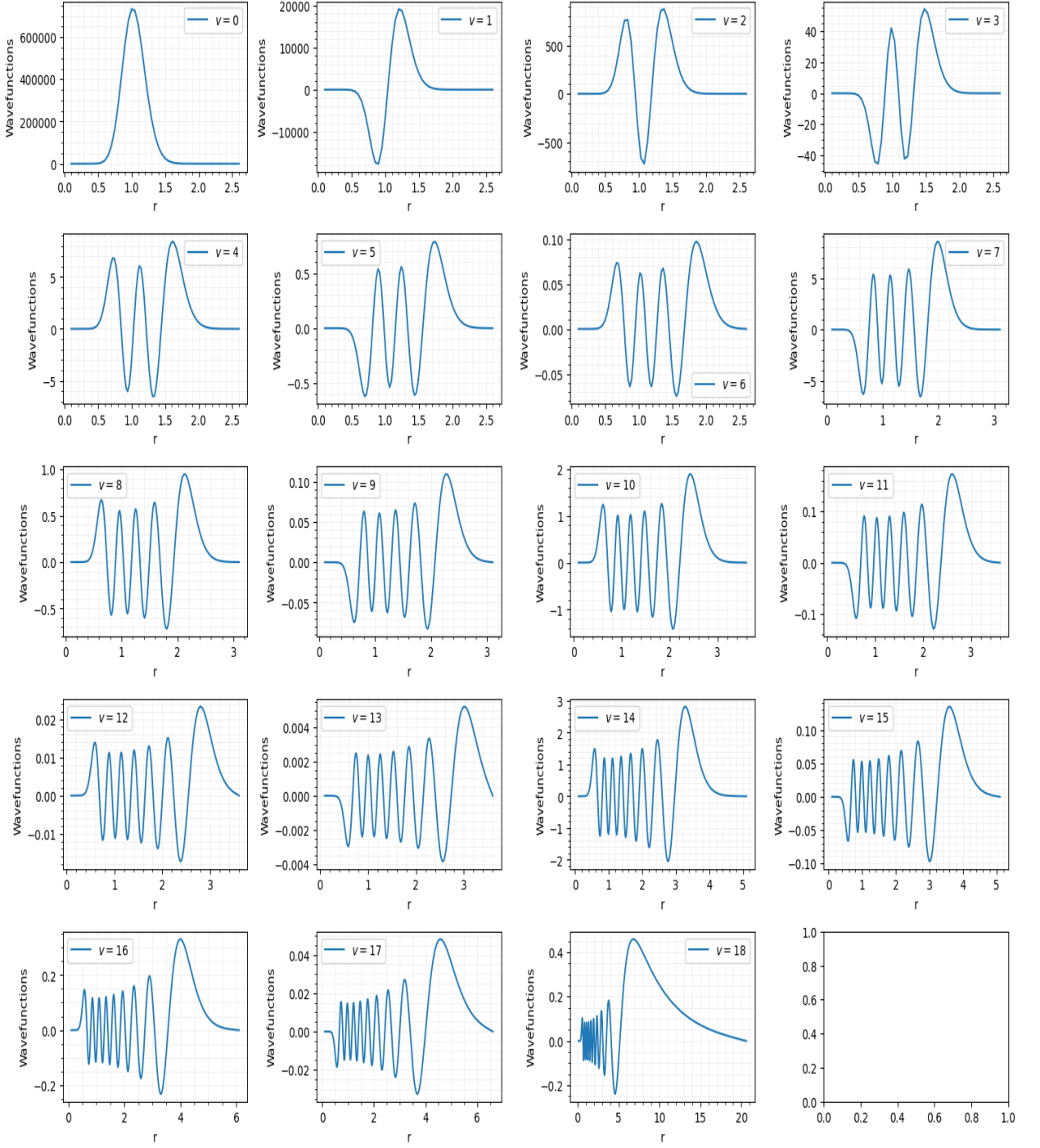


FIGURE 1: Visualization of the Wavefunctions corresponding to the various vibrational states with $J = 0$.

3.2 For $\nu = 0$ and $\nu = 1$ study the variation of the number of iterations in function of the “distance” of the guess value from the finally found eigenvalue.

To check the variation in the number of iterations with the distance between the initial guess and the eigenvalue, we plot the graph between various initial guesses chosen and the absolute distance between initial guess and the eigenvalue. We will also plot the the number of iterations as a function of the initial guess and see the variations in it with that as well.

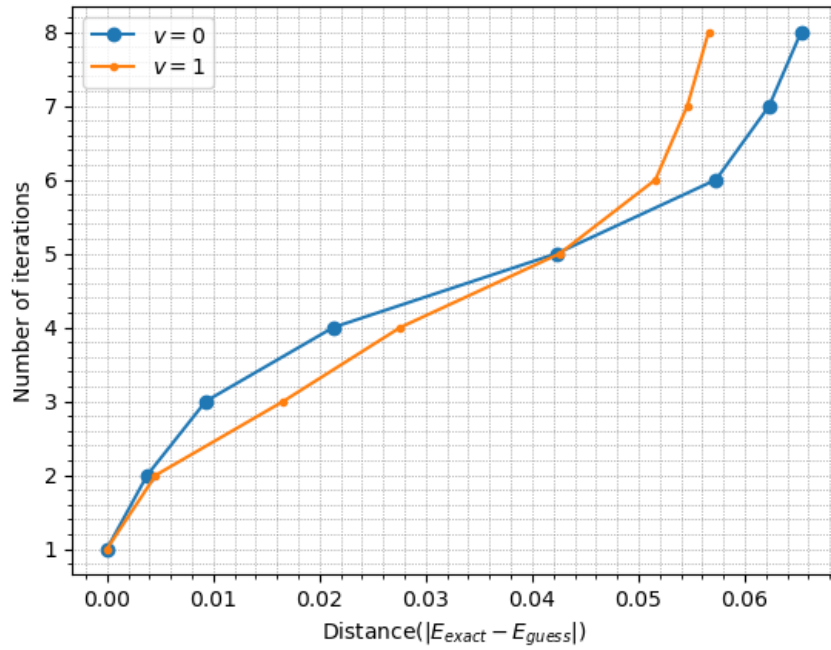


FIGURE 2: Variation of the iterations with respect the difference between guess value and absolute value

From the 3, we see that the distance between the eigenvalue guess and the actual eigenvalue increases the number of the iterations also increases which is expected as the tolerance level is 10^{-4} , so when we choose a value away from the actual away the calculation continues till we reach to this value, which means we will have more iterations. Also, we see this that as distance increases, i.e as we move far away from initial guess, the number of the iterations seems to increase rapidly, this could be due to the fact that the at such a distance from

the initial guess, the shooting method converges to another vibrational level rather than the desired one. Also, that the for $\nu = 1$, the number of iterations increases for lower distance values than that for $\nu = 0$, that means the separation between the successive levels is getting lower.

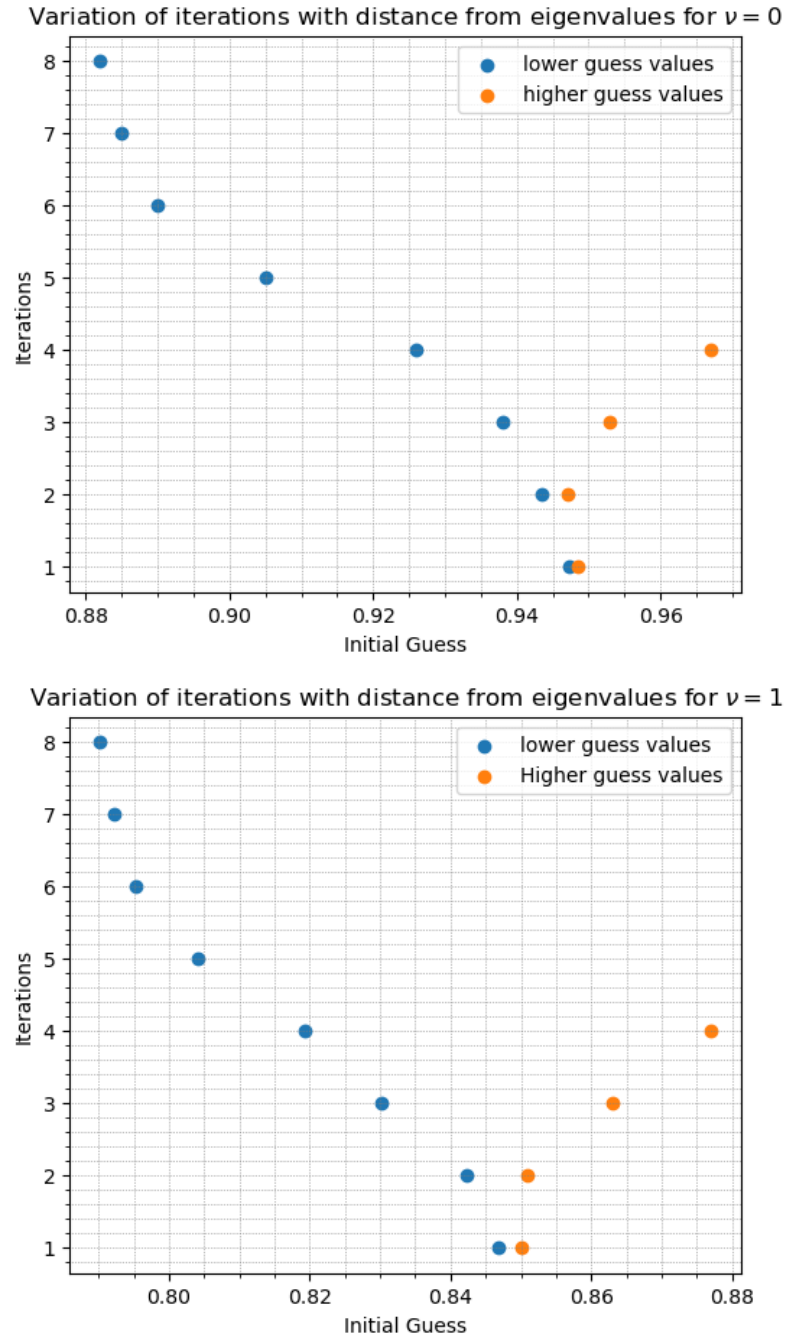


FIGURE 3: Variation of the iterations with respect the different guess values

3.3 Study the influence of R_0, R_N, N, ϵ and τ on the number of iterations and the exactness of the result for $\nu = 0$ and $\nu = 12$.

For $\nu = 0$: Variation with R_0 :

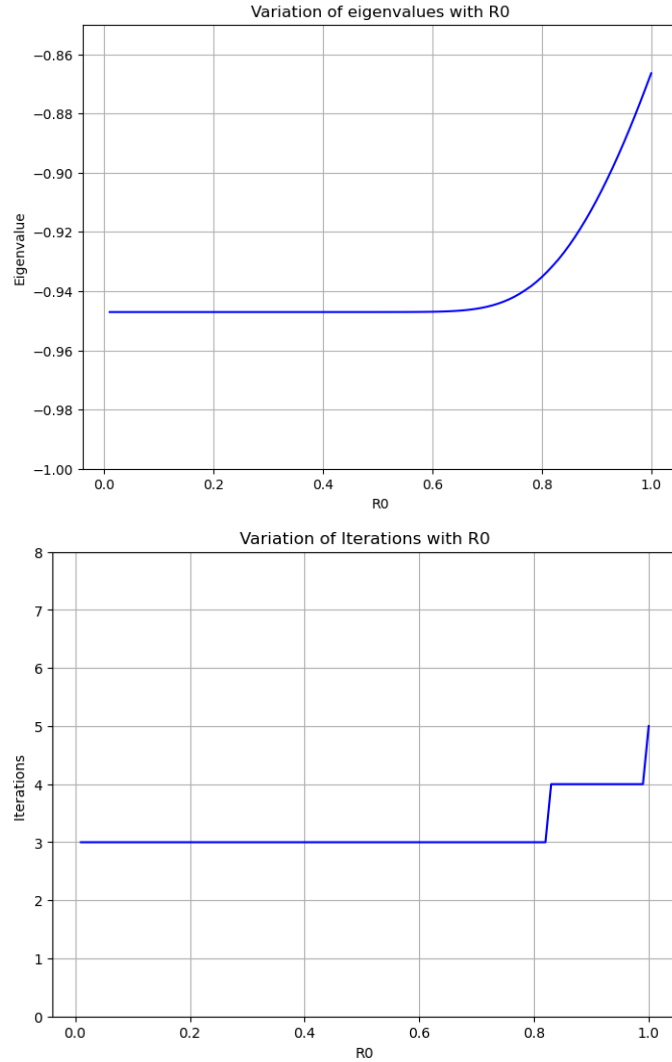


FIGURE 4: Variation of the energy and iterations with R_0

We see that for upto 0.6 value of the R_0 , the change in it has no effect on the eigenvalue but after that the eigenvalue starts to increase, it is because of the now the assumption is that $\psi(r_o) = 0$ is no longer valid, therefore it gives erroneous values. Around the same value, the number of iterations also start to increase as now the shooting method converges to higher values so it takes more iterations to do so.

Variation with R_N :

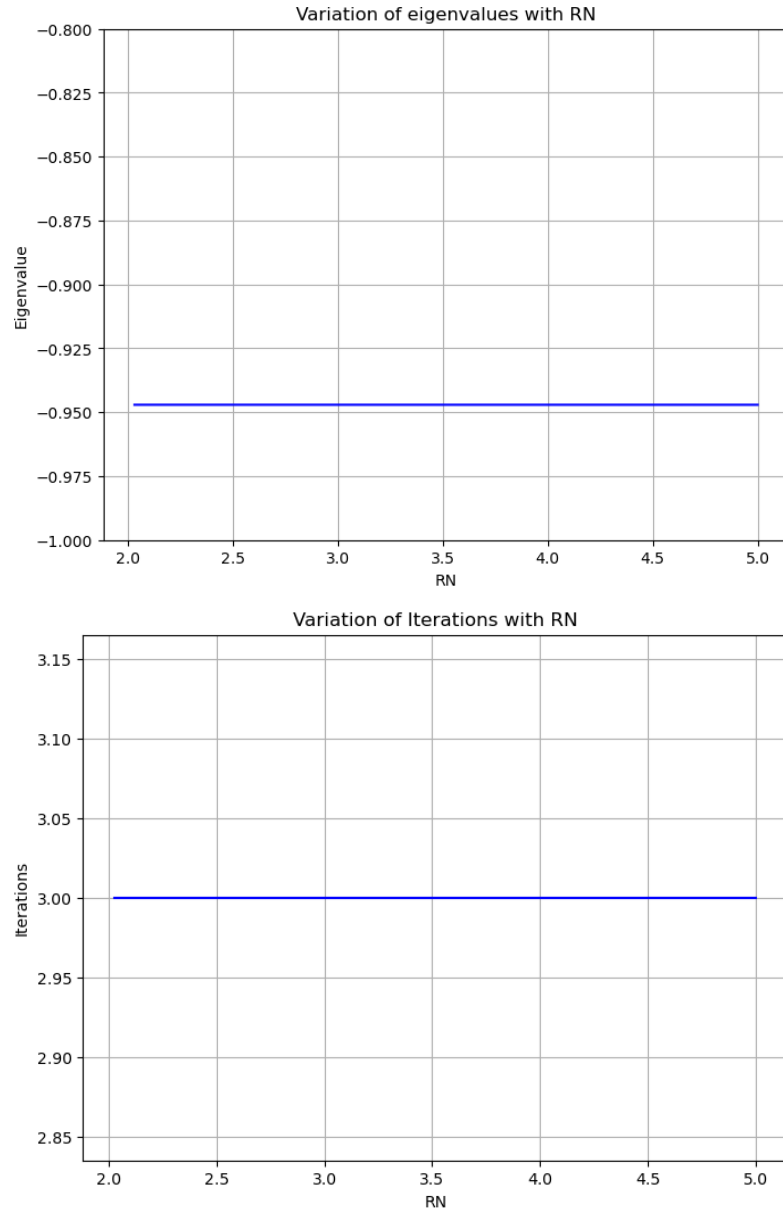


FIGURE 5: Variation of the energy and iterations with R_N

With change in R_N , there is no change in eigenvalue or the number of iterations, because here we have chosen such values of R_N for which we can assume $\psi_{(r_N)} = 0$, so it has no effect on both of the quantities, if we had chosen small enough values of R_N , some of the wavefunction would not be accommodated and we would have seen a behaviour similar to what we saw of the higher values of R_o .

Variation with N :

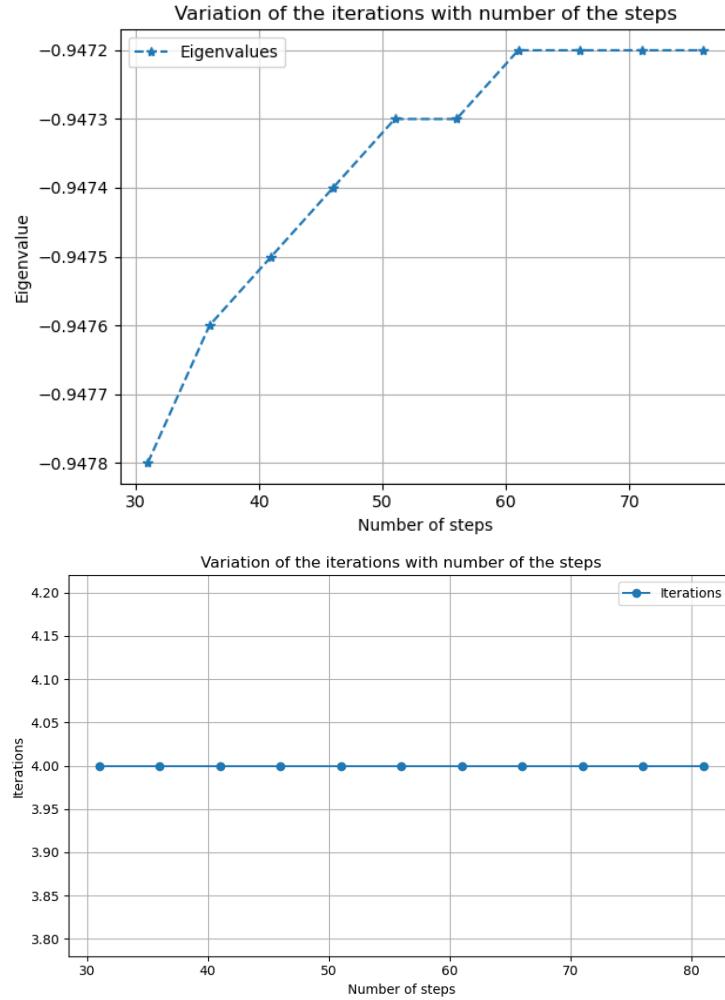


FIGURE 6: Variation of the energy and iterations with N

As we increase the number of the steps, the eigenvalue tends to the accurate value, this can be attributed to the working of the finite differences, we are mapping a continuous function with discrete intervals. Thus, the more number of points we have, the smaller the sub-intervals which means we can approximate the behaviour of the continuous function (i.e. wavefunction) more accurately and will get more precise results. The number of Iterations remains same as the eigenvalue is already correct upto 3 decimal points at the starting, so there won't be much change in its value as N increases, so with the same number of iterations, it will converge to better value of energy.

Variation with ϵ :

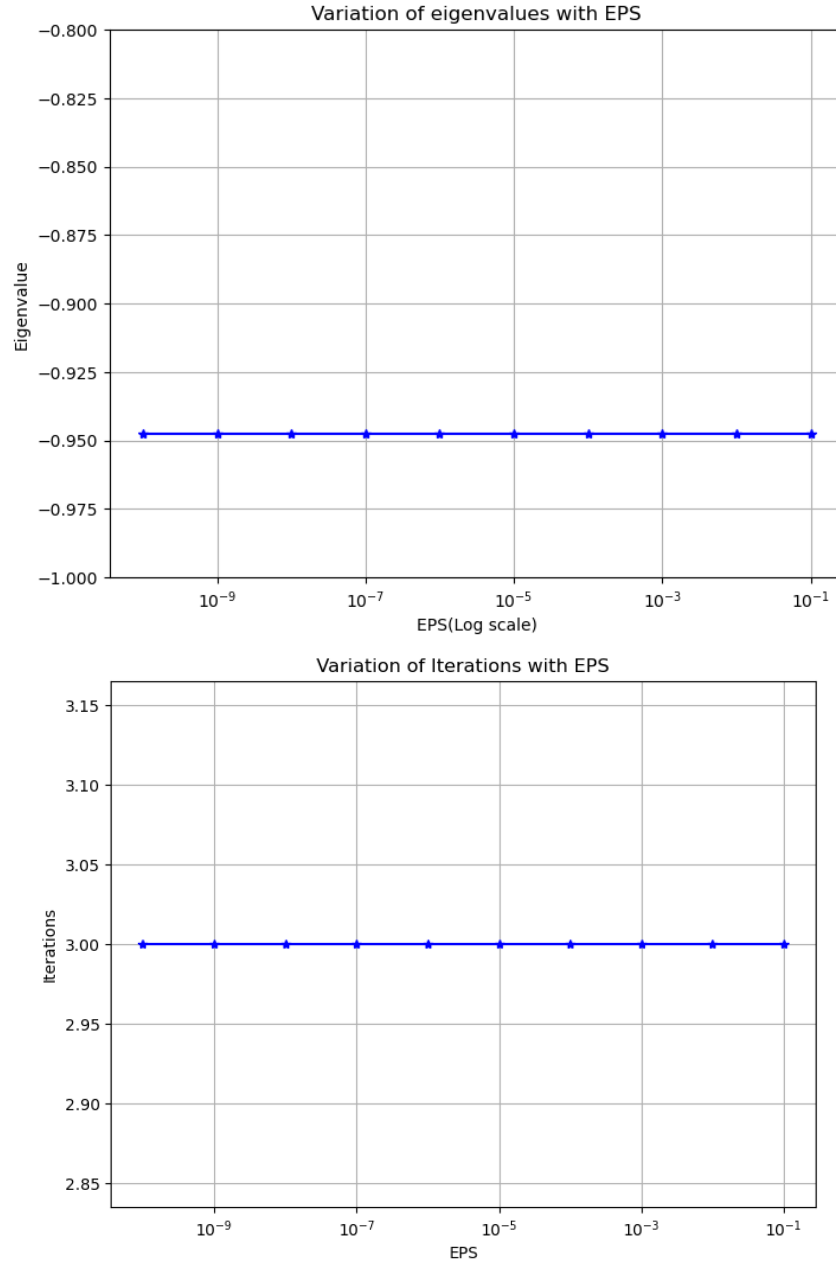


FIGURE 7: Variation of the energy and iterations with ϵ

The ϵ value represents the value given to the ψ_1 and ψ_{N-1} . So, changing this value will have no effect on the eigenvalues obtained and thus the number of iterations required to reach the eigenvalue will also remain unchanged, this is exactly what we see in the provided graphs.

Variation with τ :

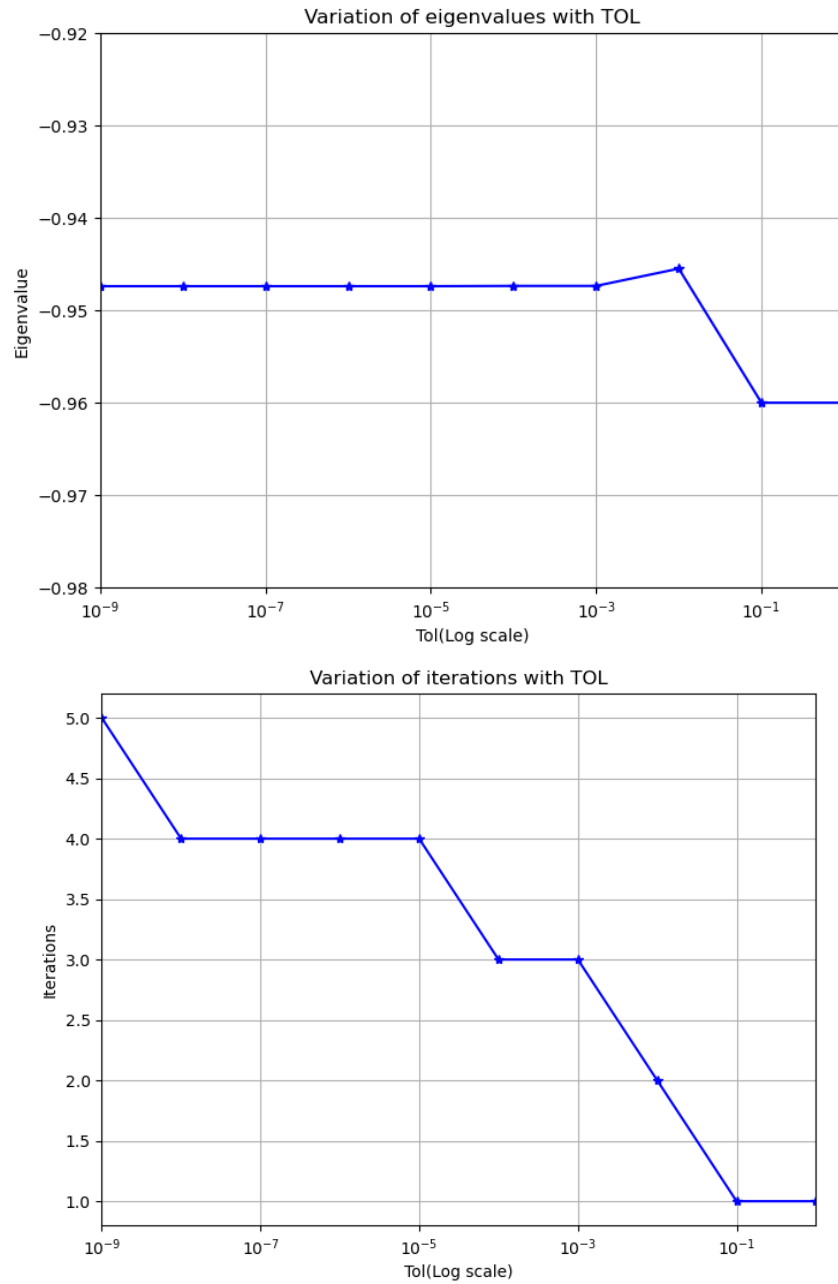


FIGURE 8: Variation of the energy and iterations with τ

The above behaviour is expected, this is because the tolerance limit defines how much accurate we want our result to be, thus when we decrease it, the program converges to a less accurate value (near to the initial guess) with smaller number of iterations, so the number of iterations also decreases with decrease in the tolerance value.

For $\nu = 12$: Variation with R_0

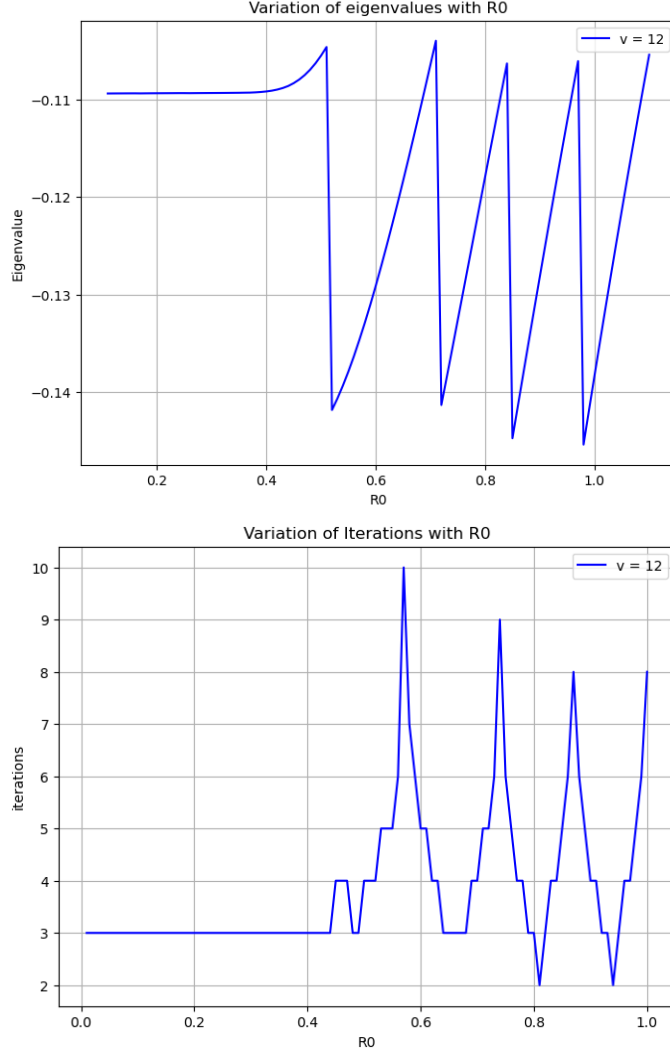
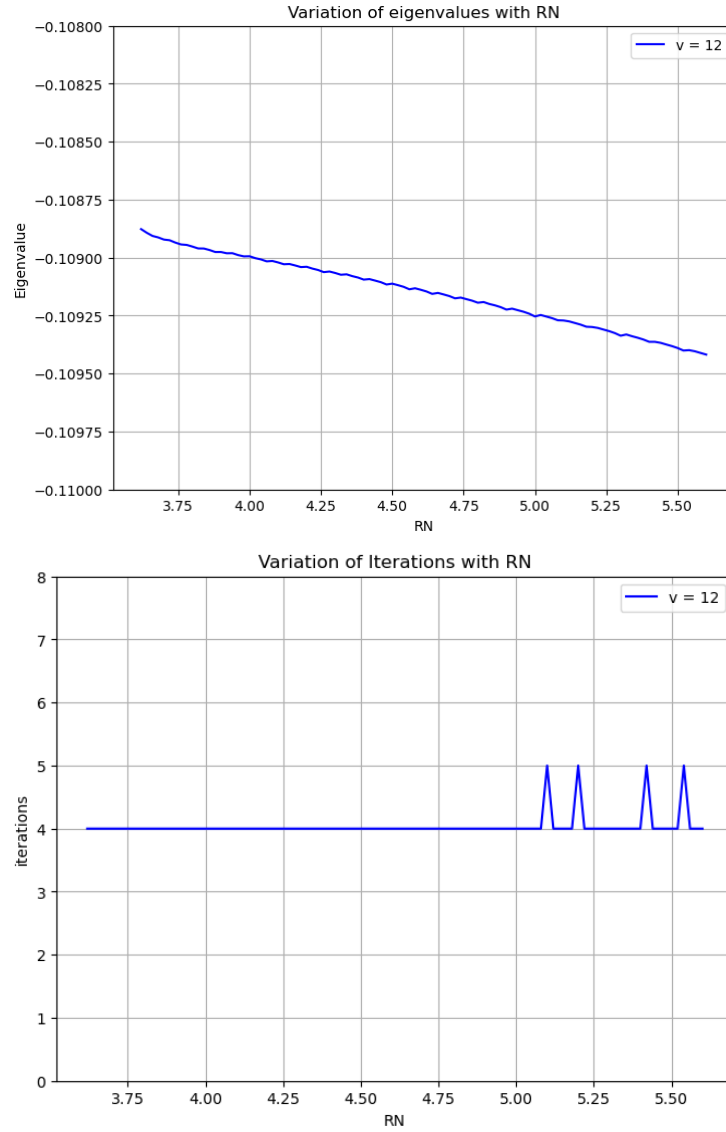
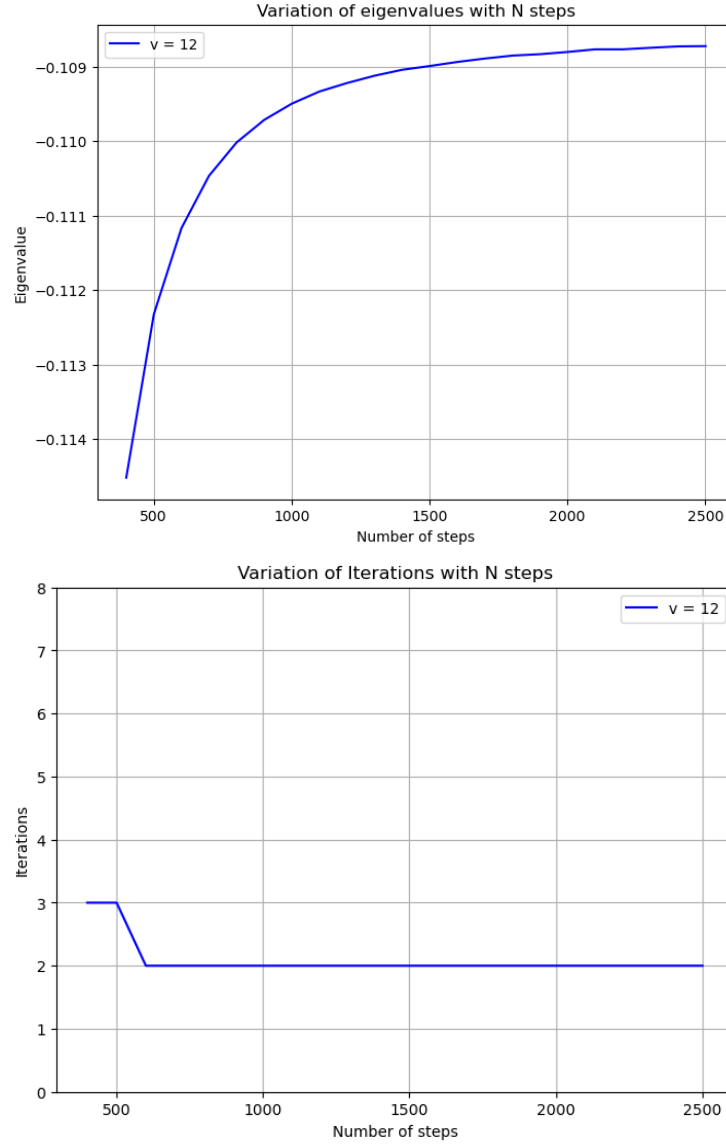


FIGURE 9: Variation of the energy and iterations with R_0

This behaviour can be explained by the fact that as we increase the value of R_0 , $\psi_{(r_0)} = 0$ for some distance but after that the wavefunction is no longer negligible, some of the wavefunction is not present and we see that the method converges to values different from the correct value. This sawtooth behaviour of the eigenvalues is related to the values $\psi_{(r_0)}$ takes as we increase R_0 . It goes from positive to negative domain (which can be confirmed by looking at its wavefunction plot) with occasionally taking 0 values as well, so we see near accurate eigenvalues for some higher R_0 values as well. Since, the method converges to different values, the number of iterations required also changes accordingly.

Variation with R_N FIGURE 10: Variation of the energy and iterations with R_N

As we increase R_N , the condition that $\psi_{(r_N)} = 0$ becomes more valid and thus we get more precise value of the energies, that is exactly what has been depicted in the graph. As for the number of the iterations, we expect it to be constant but we see an abnormal behaviour at some instances, where the number of iterations increases, i think it has to do with the fact that as we get more and more accurate value of eigenvalue, the number of iterations to reach this value increases.

Variation with N FIGURE 11: Variation of the energy and iterations with N

Again, as we saw for $v = 0$, with increase in N , the numerically calculated eigenvalue tends towards more accurate values. The reasoning remains the same as provided for the earlier case but now we see that the number of iterations changes, this is because unlike the $v = 0$ case where the eigenvalue was already pretty accurate, here we have a huge difference between first obtained value of the energy and the accurate value, so naturally more number of iterations are required to converge to this value. From the graph, we see

as the eigenvalue gets near to the accurate value (around $N=500$) the number of iterations remains constant after that even though the accuracy of the eigenvalue keeps on increasing, a behaviour similar to $v = 0$ because now the difference with respect to the accurate value is lesser than it was at the beginning.

Variation with ϵ :

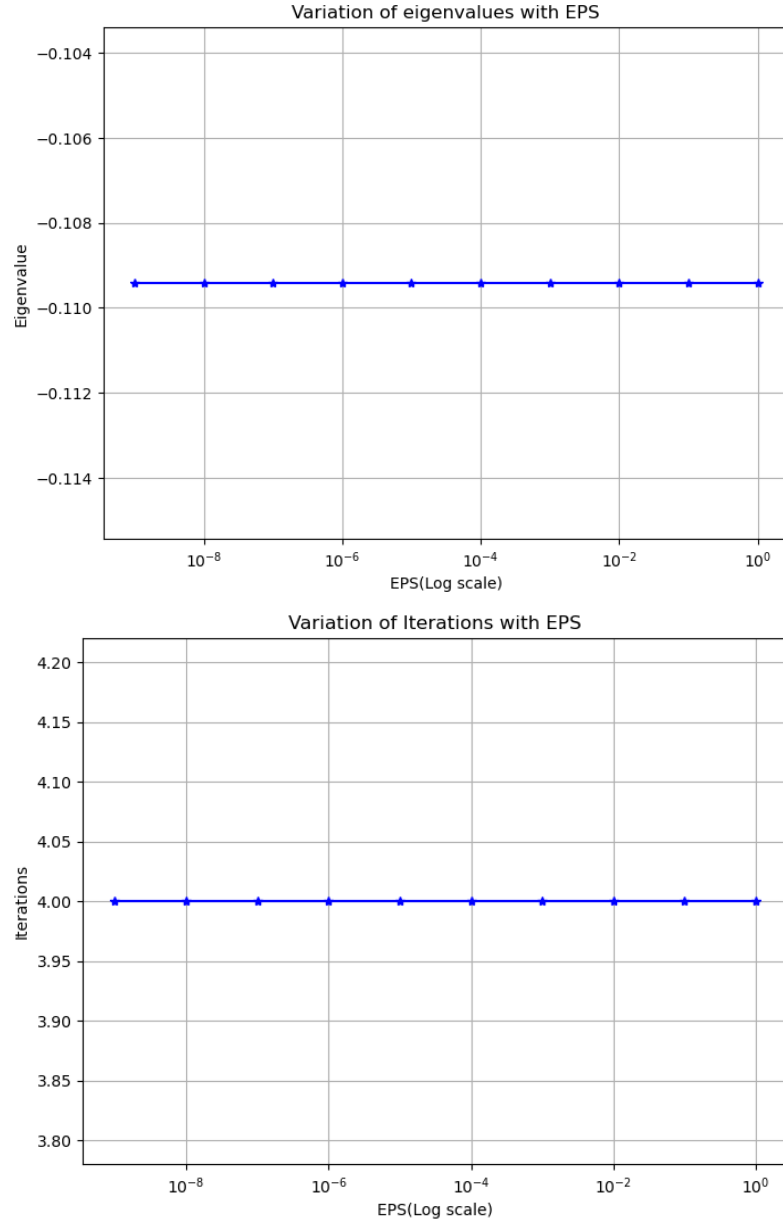


FIGURE 12: Variation of the energy and iterations with ϵ

We see the same behaviour as we recorded earlier for $v = 0$.

Variation with τ

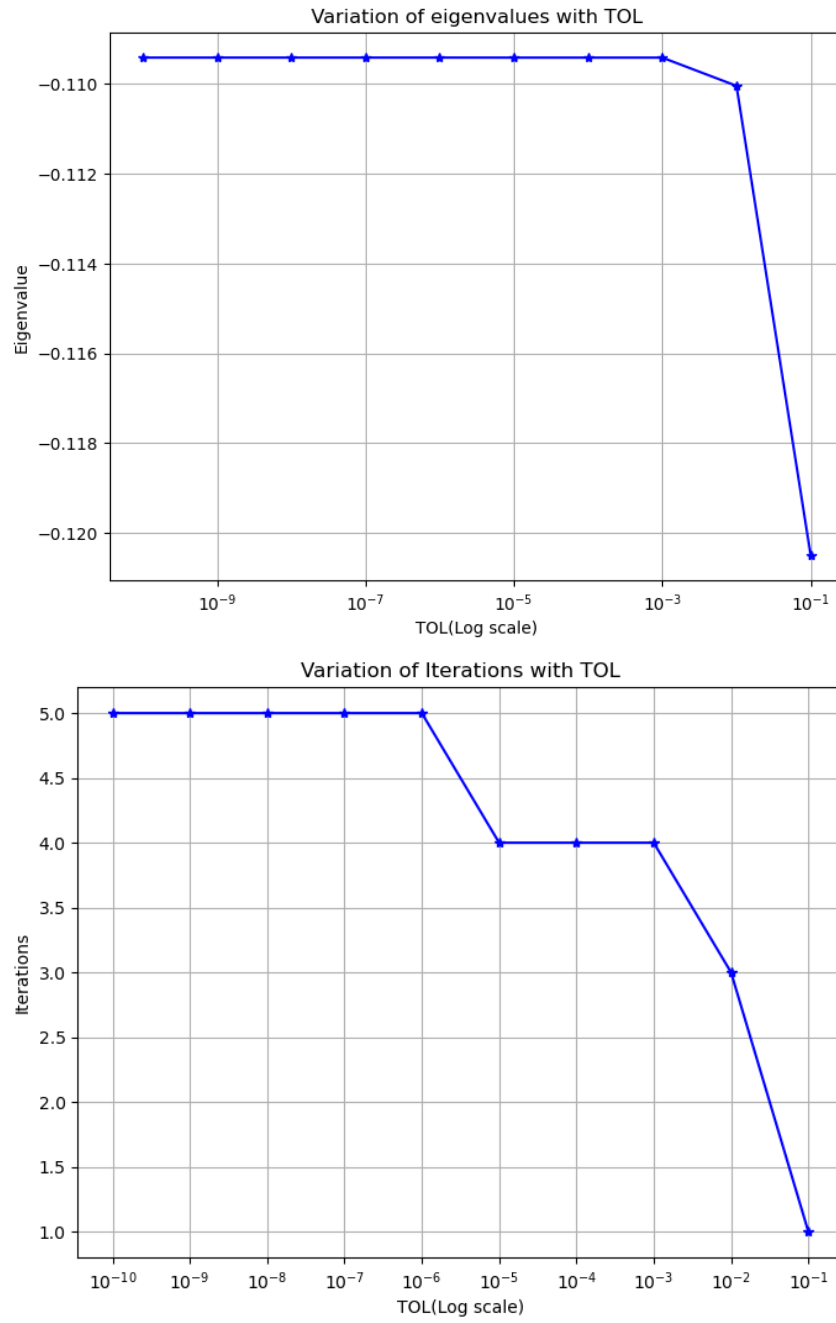


FIGURE 13: Variation of the energy and iterations with τ

We see a behaviour similar to what we saw in the first case. The reason for such behaviour has already been explained in the first case.

3.4 Variation of δe with e :

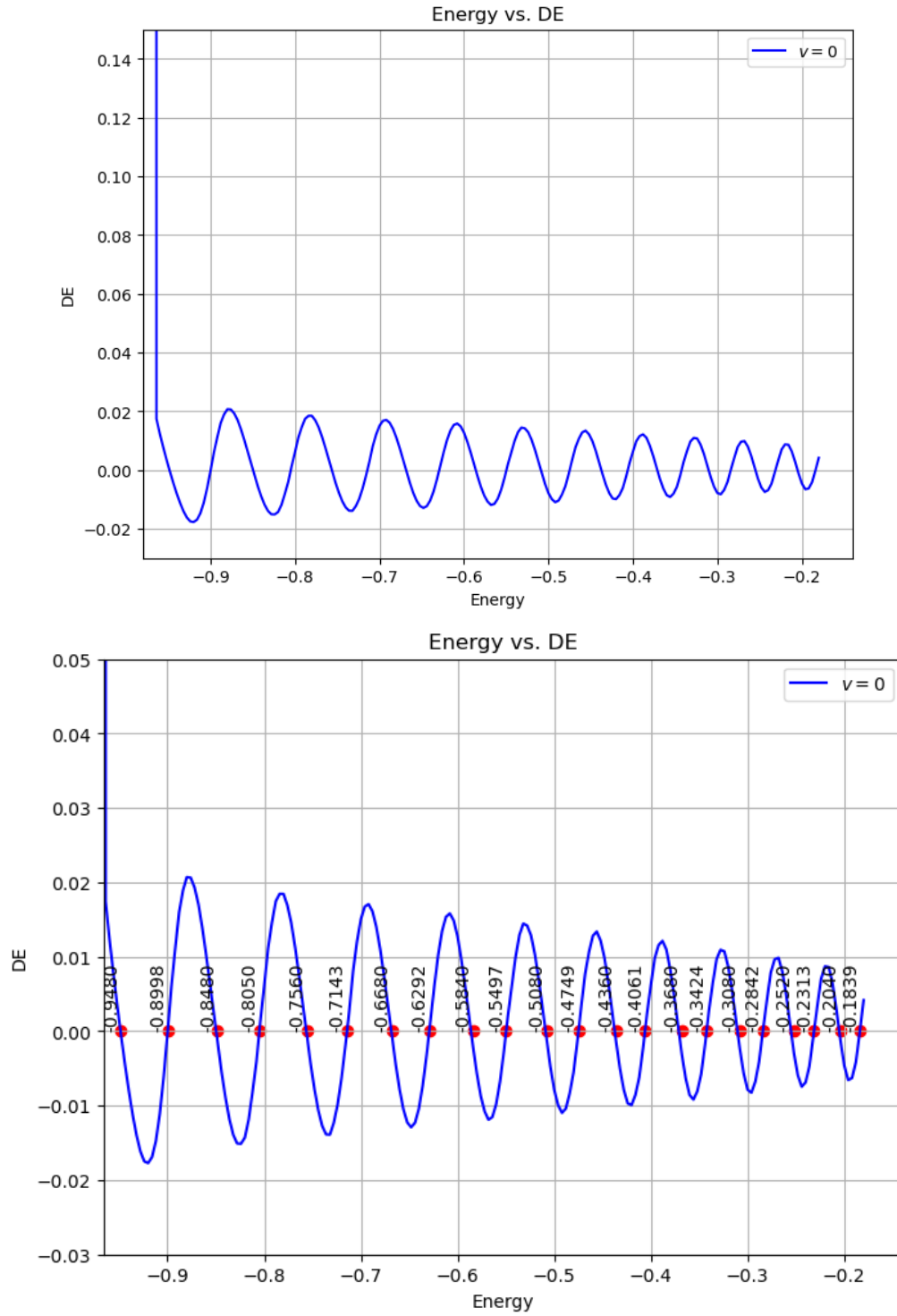


FIGURE 14: Variation of δe with e in the energy range $[0.97, 0.2]$; The red dots represent the theoretical eigenvalues

First thing that we observe from the graph is the damping behaviour of the curve. This can be explained on the basis of the general behaviour of the energies as we go from $v = 0$ to higher levels, the energy levels get closer and closer, so we need smaller and smaller values of the energy correction term (δe) to converge to the actual eigenvalue.

The points of intersection of the graph with e axis which correspond to the negative derivative are $[-0.9480, -0.8480, -0.7560, -0.6680, -0.5840, -0.5080, -0.4380, -0.3680, -0.3080, -0.2520, -0.2040]$ which approximately correspond to the eigenvalues from $v = 0, 1, \dots, 10$. The problem associated with the initial guess that if we put initial guess far away from the actual value the method converges to a different energy state. It can be explained on the basis of the graph we have plotted. If we put an initial guess in the vicinity of the negative derivative domain, the method will converge to the same eigenvalue of the energy and now if we put an initial guess far away from the energy state we want to get, it will be in vicinity of negative derivative domain of a different eigenvalue meaning that the method will still converge but to a different energy value.

3.5 Calculation of B_0 and B_1 by the use of the wavefunctions:

The term B in general represents the rotational constant. It describes the rotational energy levels of a molecule. We used the obtained wavefunctions (that need to be normalized first) to find the rotational constant for $v = 0$ and $v = 1$ and by employing the formula:

$$B_v = B \cdot \langle \psi_v | \frac{1}{r^2} | \psi_v \rangle$$

where $r = \frac{R}{R_o}$.

We find that $B_0 = 59.814183 \text{ cm}^{-1}$ and $B_1 = 57.705493 \text{ cm}^{-1}$.

3.6 Direct Integration of Schrodinger's Equation with rotational term.

We can find the value of the rotational constant for various vibrational levels. To do this we add the rotational term to the initial potential term in the program i.e $E_{v,j}^0 =$

$E_v + BJ(J+1)$. and then find the B values corresponding to $v = 0, 1$ by using different J values for a constant v value. I found B_0 and B_1 values using J values upto 5. The results obtained have been presented in the form of the tables below:

Calculation of B_0 :

TABLE 2: B_0 values

J level	B_0
1	59.41 cm^{-1}
2	59.41 cm^{-1}
3	59.06 cm^{-1}
4	58.79 cm^{-1}
5	58.31 cm^{-1}

Calculation of B_1 :

TABLE 3: B_1 values

J level	B_0
1	57.35 cm^{-1}
2	57.35 cm^{-1}
3	57.01 cm^{-1}
4	56.74 cm^{-1}
5	56.26 cm^{-1}

These tables represent the values of B_0 and B_1 that are calculated by the direct integration of the schrodinger's equation with the centrifugal term. For smaller J values, it gives near accurate values of the rotational constants but as the value of J increases the approximation becomes less and less accurate as for larger J values, the centrifugal term becomes a more significant part of the potential energy, and it can distort the shape of the wave function and the energy levels.

4 Conclusion:

In this project, we found the eigenvalues and eigenfunctions corresponding to $J = 0$ and $v = 0, 1, 2, \dots, 18$ by using the shooting method and compared it to the morse potential

and found out that morse potential provides a very good approximation of the eigenvalues. We also found the variations of eigenvalues as well as the number of iterations taken by the method to converge to this value with the various parameters like $R_0, R_N, N, \epsilon, \tau$. In this study, we found that some parameters have significant impact on the accuracy of the eigenvalue and some did not have any at all. Physical explanation of this behaviour has also been provided in the report. The rotational constants were determined by using two different approaches; from the wavefunctions that were determined earlier by using the shooting method and employing the formulas discussed in [3.5](#) and by the direct integration of the schrodinger's equation with the inclusion of the rotational term.

In nutshell, through this project we determined the accuracy of the approximations provided by the morse potential for eigenvalues of the H_2 molecule or we can say that in general for the diatomic molecules and the impact of various parameters on the eigenvalues. We also studied the impact of the rotational energies on the behaviour of the energies.