Numerical study of Anharmonic Oscillator Using Python Code

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Abstract

In this work, we explore the python code to study the anharmonic oscillator. In obtaining the numerical solution for eigenvalues and eigen-functions, we discretize the spatial coordinates into the finite number of grid points and use the finite difference method. We observe that the effect of anharmonic term in hamiltonian in shifting energy level increases towards higher energy states. We compare eigen functions for ground, first excited and second excited state of the harmonic oscillator with anharmonic oscillator. Further, the corrected wave-functions using first order perturbation theory are compared with wave-functions obtained from the numerical solutions of Schrödinger's equations. The numerical Python code shows consistency of first order perturbation theory for the small value of anharmonic term.

1 Introduction

The quantum harmonic oscillator is one of the most important models in quantum mechanics. It describes the motion of a particle in a parabolic potential well and is widely used to approximate the behavior of atoms near equilibrium positions, molecular vibrations and many physical systems. The Hamiltonian of the harmonic oscillator is given by,

$$H_0 = \frac{p^2}{2m} + \frac{1}{2} m\omega^2 x^2. \tag{1}$$

The first term represents the kinetic energy of the particle, while the second term corresponds to the potential energy of the harmonic oscillator. The parameter m is the mass of the particle and ω is the angular frequency of oscillation. The energy eigenvalues of the unperturbed harmonic oscillator are [1, 2],

$$E_n^{(0)} = \hbar\omega \left(n + \frac{1}{2} \right), \tag{2}$$

where $n = 0, 1, 2, ...$ represents the quantum number. These energy levels are equally spaced and form the basis for studying more complex systems.

In many real physical situations, the potential is not perfectly harmonic. Small deviations from the harmonic potential lead to anharmonic effects. In recent works [3, 4, 5, 6, 7, 8, 9], the anharmonic oscillator is studied with its different aspects. Anharmonic effects can be studied by introducing a perturbation term to the Hamiltonian.

The total Hamiltonian can be written as,

$$H = H_0 + H', \tag{3}$$

where H' represents a small perturbation. In this work, the perturbation is chosen as,

$$H' = \lambda x^4. \tag{4}$$

Here λ is a small parameter that controls the strength of the anharmonicity. This quartic term modifies the potential and leads to shifts in energy levels and wavefunctions.

Perturbation theory is used to calculate approximate corrections to the energy levels and wavefunctions due to this additional term. These analytical results are then compared with numerical solutions obtained using matrix diagonalization. According to first-order perturbation theory, the correction to the energy is given by [1, 2],

$$E_n^{(1)} = \langle \psi_n^{(0)} | H' | \psi_n^{(0)} \rangle \tag{5}$$

This expression represents the expectation value of the perturbing Hamiltonian in the unperturbed state. Physically, it gives the average effect of the anharmonic potential on the energy level.

For the chosen perturbation $H' = \lambda x^4$, the energy correction becomes,

$$E_n^{(1)} = \lambda \langle \psi_n^{(0)} | x^4 | \psi_n^{(0)} \rangle \tag{6}$$

This term shifts the energy levels, with higher states experiencing larger shifts due to their wider spatial distribution.

2 Perturbation Theory Approach

One of the method to solve the Schrödinger for stationary states corresponding time independent Hamiltonian is perturbation theory. Variational method and WKB method also provide the solutions corresponding to the stationary states. However, if solution for a given system is known or solvable, some small deviation in Hamiltonian changes the system slightly and for such case, the perturbation theory is applicable to get the solution for perturbed system. We consider non-degenerate perturbations theory. For such a case, eigenvalues of solvable Hamiltonian are non-degenerate. Eigenvalue E_n and eigenfunction $|\psi_n\rangle$ of perturbed system are expanded in terms of the parameter λ as following,

$$E_n = E_n^0 + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)}....., \tag{7}$$

$$|\psi_n\rangle = |\psi_n^0\rangle + \lambda\, |\psi_n^{(1)}\rangle + \lambda^2\, |\psi_n^{(2)}\rangle ....., \tag{8}$$

where, $E_n^{(1)}$ and $E_n^{(2)}$ are first and second order corrections to eigenvalue E_n^0. Similarly, $|\psi_n^{(1)}\rangle$ and $|\psi_n^{(2)}\rangle$ are the first and second order corrections to eigenfunction $|\psi_n^0\rangle$. $|\psi_n^0\rangle$ is eigenfunction corresponding to Hamiltonian H_0 with eigen value E_n^0. First order correction to eigenvalue is given by Eq. (5) and first order correction to wave function is given by [1, 2]

$$|\psi_n\rangle = |\psi_n^0\rangle + \Sigma_{m\neq n} \frac{\langle\psi_m^0|\, \hat{H}_p\, |\psi_n^0\rangle}{E_n^0 - E_m^0} \,|\psi_m^0\rangle\,. \tag{9}$$

We use these expressions (5) and (9) in python code to obtain the first order corrected wavefunction and eigen values.
In this work, the anharmonic term λx^4 is treated as a small perturbation to the potential energy of the harmonic oscillator.

The first-order correction to the energy levels is calculated using the expectation value of the perturbing Hamiltonian with respect to the unperturbed eigenstates.

This analytical approximation allows estimation of energy shifts without solving the full Hamiltonian numerically. The results obtained from perturbation theory are compared with the exact numerical solutions to analyze its accuracy. Perturbation theory assumes that the anharmonic term is small compared to the harmonic potential. Therefore, its effect can be treated as a small correction to the known energy levels. For weak perturbation strength, first-order correction gives accurate results. However, for stronger perturbations higher order terms become important.

3 Numerical Method

To obtain accurate solutions beyond perturbation theory, a numerical approach is used. The Schrödinger equation is solved by representing the Hamiltonian operator on a spatial grid. One can write the time independent Schrödinger equation as

$$\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + 2(E - V)\psi = 0, \tag{10}$$

where, we consider a particle of mass m. The position space is discretized into a finite number of points between $-x_{max}$ and $+x_{max}$. The second derivative in the kinetic energy operator is approximated using finite difference method as

$$\frac{d^2\psi_i}{dx^2} \approx \frac{\psi_{i-1} - 2\psi_i + \psi_{i+1}}{\Delta x^2},$$

where, ψ_i is value of ψ at point x_i and Δx is step size $x_i - x_{i-1}$ In the discretized form, at point x_i the Schrödinger equation can be written as

$$-\frac{1}{2}\frac{\psi_{i-1} - 2\psi_i + \psi_{i+1}}{\Delta x^2} + V(x_i)\psi_i = E\psi_i \tag{11}$$

For N number of points with $\psi_1 = \psi_N = 0$, we will have $N-2$ set of equations corresponding to Schrödinger equation The kinetic energy operator takes the form of a tridiagonal matrix [10],

$$T = -\frac{\hbar^2}{2m\Delta x^2}\begin{pmatrix} -2 & 1 & 0 & \cdots \\ 1 & -2 & 1 & \cdots \\ 0 & 1 & -2 & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix} \tag{12}$$

and potential energy in matrix form becomes,

$$V = \begin{pmatrix} V(x_2) & 0 & 0 & \cdots \\ 0 & V(x_3) & 0 & \cdots \\ 0 & 0 & V(x_4) & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix}, \tag{13}$$

where $V(x_i)$ is potential energy at x_i. The potential energy is represented as a diagonal matrix where each element corresponds to the potential value at a given position. For the unperturbed case, the harmonic potential is,

$$V(x) = \frac{1}{2}m\omega^2 x^2. \tag{14}$$

For the perturbed system, the potential becomes,

$$V(x) = \frac{1}{2}m\omega^2 x^2 + \lambda x^4. \tag{15}$$

The total Hamiltonian matrix is constructed as,

$$H = T + V. \tag{16}$$

This Hamiltonian matrix is then diagonalized numerically using method of standard linear algebra to obtain the energy eigenvalues and eigenfunctions. The wavefunctions are normalized to ensure physical consistency. This numerical approach allows direct comparison between unperturbed results, perturbation theory predictions and the fully perturbed system.

Implementation Using Python

The numerical solution of the Schrödinger equation was implemented using Python to obtain the eigenvalues and eigenfunctions of the harmonic and anharmonic oscillator. All numerical computations were carried out using the NumPy library, while Matplotlib was used for graphical visualization [11, 12] of the wavefunctions and probability densities .

The Hamiltonian matrix was diagonalized using the `numpy.linalg.eigh()` routine which is specifically designed for Hermitian matrices and provides numerically stable eigenvalues and orthonormal eigenvectors. The obtained eigenvectors correspond to the discretized wavefunctions.

Each eigenfunction was normalized numerically using the condition

$$\sum_i |\psi_n(x_i)|^2 \Delta x = 1$$

to ensure proper probability interpretation. The ground state, first excited state and second excited state wavefunctions were extracted and plotted.

To validate the numerical method, the unperturbed harmonic oscillator energies were compared with the analytical expression

$$E_n = \left(n + \frac{1}{2}\right)$$

showing very good agreement. In the following table, lowest energy eigen values obtained from numerical diagonalization of harmonic oscillator Hamiltonian are given:

Quantum Number n	Energy E_n
0	0.4998
1	1.4992
2	2.4983

The small deviation observed at higher energy levels arises from finite grid size and truncation of the spatial domain. Grid convergence was tested by increasing the number of spatial points, and the eigenvalues were found to stabilize, confirming numerical reliability.

After validation, the anharmonic perturbation was introduced and the shifts in energy levels were calculated. The dependence of energy on the perturbation strength parameter λ was also examined.

Four separate graphical analyses were performed in this work. First, the complete unperturbed harmonic oscillator spectrum was computed and the first three energy eigenstates were plotted together with the harmonic potential.

Subsequently, individual plots were generated for: (i) the ground state, (ii) the first excited state, (iii) the second excited state.

Grid convergence was verified by systematically increasing the number of spatial discretization points. The eigenvalues were found to approach stable limiting values, indicating that the numerical solution is independent of grid size and therefore physically reliable.

This separation allows clearer visualization of the spatial structure, symmetry properties, and nodal behavior of each eigenfunction. The individual plots also help in understanding how probability density distribution changes with increasing quantum number.

The numerical eigenvalues obtained from matrix diagonalization were compared with the analytical energy spectrum and were found to be in close agreement, confirming the correctness of the finite difference discretization and normalization procedure.

All computational implementations are provided in the Appendix, allowing independent verification and reproducibility of the results.

The numerical results reproduce the expected behavior of the quantum harmonic oscillator. The ground state shows a single peak centered at the origin, while higher excited states exhibit increasing the numbers of nodes.

The energy levels are equally spaced, consistent with the analytical result $E_n = \hbar\omega(n + 1/2)$.

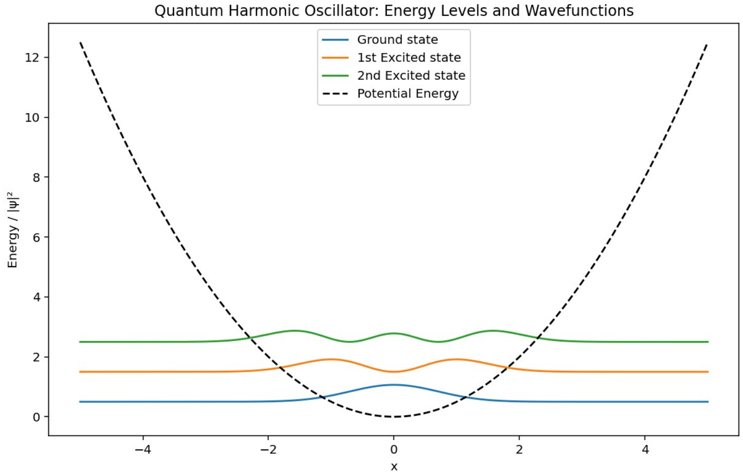

Figure 1: Energy levels and probability densities of the unperturbed quantum harmonic oscillator obtained using numerical diagonalization. The lowest three eigenstates are shown.

4 Ground State of the Quantum Harmonic Oscillator

The ground state corresponds to the lowest energy eigenstate of the quantum harmonic oscillator. It is characterized by a single maximum in the probability density centered at the equilibrium position.

For the unperturbed harmonic oscillator, the ground state energy is given by

$$E_0^{(0)} = \frac{1}{2}\hbar\omega \tag{17}$$

The corresponding wavefunction has a Gaussian form and contains no nodes. When a perturbation is introduced in the form of a quartic anharmonic term, the ground state energy increases and the wavefunction becomes slightly modified. The corrected ground state energy using the first order perturbation theory is found to be 0.5375 $\hbar\omega$. The complete numerical solution gives this correction as 0.54 $\hbar\omega$. Therefore, the first-order perturbation theory predicts a small upward shift in energy, while the full numerical solution shows the exact effect of the perturbation.

By comparing the unperturbed, first-order corrected, and fully perturbed ground state results, we show the validity of perturbation theory. A small difference between the curves shows the effect of the perturbation.

5 First Excited State of the Quantum Harmonic Oscillator

The first excited state corresponds to the second lowest energy level of the quantum harmonic oscillator. Unlike the ground state, the probability density of the first excited state has one node, which is a point where the wavefunction becomes zero.

For the unperturbed harmonic oscillator, the energy of the first excited state is

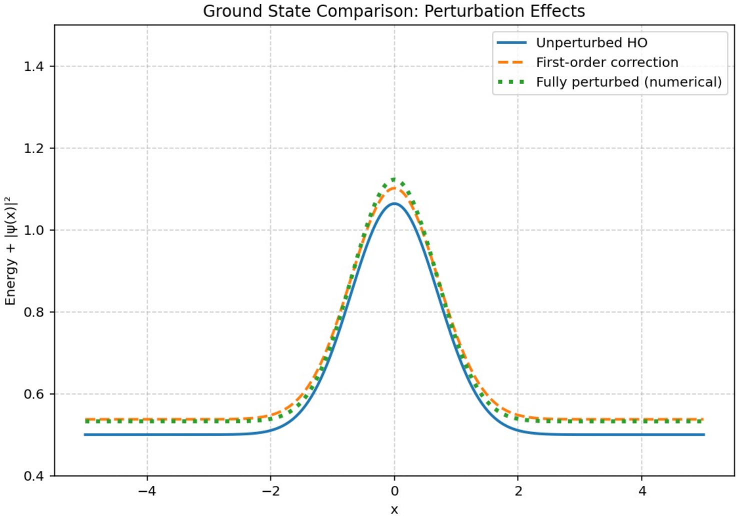

Figure 2: Comparison of the ground state for the unperturbed harmonic oscillator, first-order perturbation correction, and fully perturbed anharmonic oscillator.

$$E_1^{(0)} = \frac{3}{2}\hbar\omega \tag{18}$$

The wavefunction is antisymmetric about the equilibrium position and exhibits two peaks on either side of the center.

When the anharmonic perturbation is introduced, the energy of the first excited state increases. The first-order perturbation theory provides an approximate corrected energy $E_1^{pert} = 1.6875\ \hbar\omega$, while the numerical solution gives the exact modified energy $E_1^{num} = 1.69\ \hbar\omega$.

Comparing the three cases demonstrates how the perturbation affects higher energy states more significantly than the ground state.

The shift in energy increases compared to ground state.

6 Second Excited State of the Quantum Harmonic Oscillator

The second excited state corresponds to the third lowest energy level of the quantum harmonic oscillator. The probability density of this state exhibits two nodes, resulting in three distinct regions of high probability.

For the unperturbed harmonic oscillator, the energy of the second excited state is given by

$$E_2^{(0)} = \frac{5}{2}\hbar\omega \tag{19}$$

The corresponding wavefunction is symmetric about the equilibrium position and has a more extended spatial distribution compared to lower states.

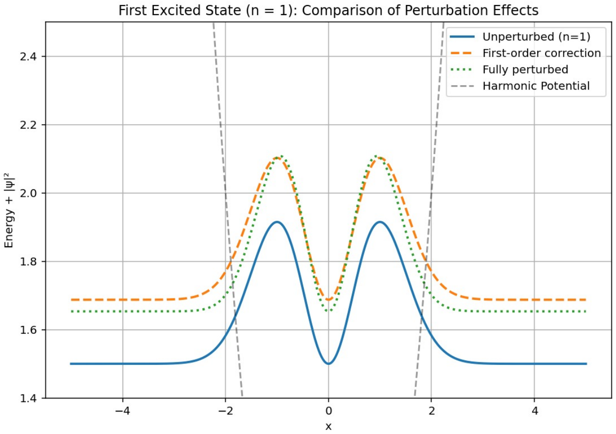

Figure 3: Comparison of the first excited state for the unperturbed harmonic oscillator, first-order perturbation correction, and fully perturbed anharmonic oscillator.

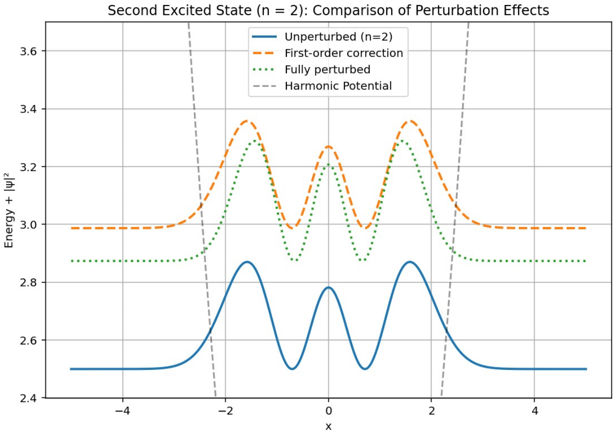

Figure 4: Comparison of the second excited state for the unperturbed harmonic oscillator, first-order perturbation correction, and fully perturbed anharmonic oscillator

When the anharmonic perturbation is applied, the energy shift becomes more pronounced for this state due to its larger spatial extent. The first-order perturbation theory predicts an increase in energy $E_2^{pert} = 2.9875\ \hbar\omega$, while the numerical solution provides the exact modified energy $E_2^{num} = 2.99\ \hbar\omega$.

The comparison between the unperturbed, first-order corrected, and fully perturbed results highlights the increasing influence of perturbation for higher excited states.

The effect of anharmonicity becomes more significant for higher states.

7 Discussion of Results

The numerical simulations clearly show the influence of the anharmonic perturbation on the quantum harmonic oscillator.

For the ground state, the perturbation introduces a small upward shift in the energy level while the wavefunction remains nearly symmetric and localized around the equilibrium position. The first-order perturbation result closely matches the fully perturbed numerical solution.

For the first excited state, the presence of one node is maintained, but the energy level increases due to the additional quartic potential term. The effect of the perturbation becomes more noticeable compared to the ground state.

In the second excited state, the energy shift is even more significant due to the larger spatial extension of the wavefunction. The deviation between the unperturbed and perturbed systems increases with higher quantum number.

Overall, the comparison between unperturbed results, first-order perturbation theory, and full numerical solutions confirms the validity of perturbation theory for weak anharmonic contributions.

8 Conclusion

In this work, the quantum harmonic oscillator with an anharmonic perturbation was studied using numerical diagonalization methods along with perturbation theory.

The unperturbed harmonic oscillator was first solved numerically to verify the known energy spectrum and wavefunctions. The effects of the quartic perturbation term were then analyzed for the ground state, first excited state, and second excited state.

The results demonstrate that the perturbation leads to an increase in energy levels and slight modifications in wavefunctions. The first-order perturbation theory provides accurate approximations for small perturbation strengths.

This study highlights the effectiveness of numerical methods in analyzing quantum systems where analytical solutions become difficult and provides a deeper understanding of anharmonic effects in quantum mechanics. The present work can be extended by considering higher order perturbation corrections or stronger anharmonic terms. Similar numerical methods can be applied to study other quantum systems where analytical solutions are not possible.

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A Python Code for Unperturbed Harmonic Oscillator

```python
import numpy as np
import matplotlib.pyplot as plt

# Constants (atomic units)
hbar = 1
m = 1
omega = 1

# Discretization parameters
N = 200
x_max = 5
x = np.linspace(-x_max, x_max, N)
dx = x[1] - x[0]

# Potential energy
V = 0.5 * m * omega**2 * x**2

# Kinetic energy (using finite difference)
diag = np.ones(N)
off_diag = np.ones(N - 1)
T = (-hbar**2 / (2 * m * dx**2)) * (np.diag(-2 * diag) + np.diag(
   off_diag, 1) + np.diag(off_diag, -1))
```

```
# Hamiltonian
H = T + np.diag(V)

# Solve for eigenvalues and eigenvectors
E, psi = np.linalg.eigh(H)

# Normalize wavefunctions
psi_norm = psi / np.sqrt(np.sum(psi**2, axis=0) * dx)

# Plot ground, first, and second excited states
plt.figure(figsize=(10,6))
plt.plot(x, psi_norm[:,0]**2 + E[0], label='Ground␣state')
plt.plot(x, psi_norm[:,1]**2 + E[1], label='1st␣Excited␣state')
plt.plot(x, psi_norm[:,2]**2 + E[2], label='2nd␣Excited␣state')
plt.plot(x, V, 'k--', label='Potential␣Energy')
plt.xlabel('x')
plt.ylabel('Energy␣/␣|   |  ')
plt.title('Quantum␣Harmonic␣Oscillator:␣Energy␣Levels␣and␣
   Wavefunctions')
plt.legend()
plt.show()

# Print first few energy levels
for n in range(3):
    print(f"Energy␣level␣{n}:␣{E[n]:.3f}")
```

B Python Code for Ground state

```
import numpy as np
import matplotlib.pyplot as plt

# Constants
hbar = 1
m = 1
omega = 1
lam = 0.05   # perturbation strength

# Grid
N = 400
x_max = 5
x = np.linspace(-x_max, x_max, N)
dx = x[1] - x[0]

#  Kinetic Energy
diag = np.ones(N)
```

```
off = np.ones(N-1)
T = (-hbar**2/(2*m*dx**2)) * (
    np.diag(-2*diag) + np.diag(off,1) + np.diag(off,-1)
)


#  UNPERTURBED HARMONIC OSCILLATOR

V0 = 0.5 * m * omega**2 * x**2
H0 = T + np.diag(V0)

E0, psi0 = np.linalg.eigh(H0)
psi0 = psi0 / np.sqrt(np.sum(psi0**2, axis=0)*dx)


#  FIRST-ORDER ENERGY CORRECTION

x4 = np.diag(x**4)
E1 = lam * np.dot(psi0[:,0], x4 @ psi0[:,0]) * dx
E_first = E0[0] + E1


#  FULLY PERTURBED SYSTEM

V = V0 + lam * x**4
H = T + np.diag(V)

E, psi = np.linalg.eigh(H)
psi = psi / np.sqrt(np.sum(psi**2, axis=0)*dx)


plt.figure(figsize=(9,6))

plt.plot(x, psi0[:,0]**2 + E0[0],
         label="Unperturbed␣HO", linewidth=2)

plt.plot(x, psi0[:,0]**2 + E_first,
         label="First-order␣correction", linestyle="--", linewidth
            =2)

plt.plot(x, psi[:,0]**2 + E[0],
         label="Fully␣perturbed␣(numerical)", linestyle=":",
            linewidth=3)

plt.xlabel("x")
plt.ylabel("Energy␣+␣|  (x)|  ")
plt.title("Ground␣State␣Comparison:␣Perturbation␣Effects")
```

```
plt.ylim(E0[0]-0.1, E0[0]+1.0)

plt.grid(True, which="both", linestyle="--", alpha=0.6)
plt.legend()
plt.show()
```

C Python Code for $n = 1$

```


# Choose first excited state
n = 1
psi_un = psi0[:, n]
E_un = E0[n]


x4 = np.diag(x**4)
E1 = lam * np.dot(psi_un, x4 @ psi_un) * dx
E_corr = E_un + E1


V = V0 + lam * x**4
H = T + np.diag(V)

E, psi = np.linalg.eigh(H)
psi = psi / np.sqrt(np.sum(psi**2, axis=0)*dx)

psi_full = psi[:, n]
E_full = E[n]

plt.figure(figsize=(9,6))

plt.plot(x, psi_un**2 + E_un, label="Unperturbed␣(n=1)", linewidth
   =2)
plt.plot(x, psi_un**2 + E_corr, ’--’, label="First-order␣correction"
   , linewidth=2)
plt.plot(x, psi_full**2 + E_full, ’:’, label="Fully␣perturbed",
   linewidth=2)

plt.plot(x, V0, ’k--’, alpha=0.4, label="Harmonic␣Potential")


plt.ylim(E_un - 0.1, E_un + 1.0)

plt.xlabel("x")
```

```
plt.ylabel("Energy␣+␣|   |   ")
plt.title("First␣Excited␣State␣(n␣=␣1):␣Comparison␣of␣Perturbation␣
   Effects")
plt.legend()
plt.grid(True)
plt.show()

print(f"Unperturbed␣Energy␣(n=1):␣{E_un:.5f}")
print(f"First-order␣Corrected␣Energy:␣{E_corr:.5f}")
print(f"Fully␣Perturbed␣Energy:␣{E_full:.5f}")
```

D Python Code for $n = 2$

```

# Choose second excited state
n = 2
psi_un = psi0[:, n]
E_un = E0[n]


x4 = np.diag(x**4)
E1 = lam * np.dot(psi_un, x4 @ psi_un) * dx
E_corr = E_un + E1

V = V0 + lam * x**4
H = T + np.diag(V)

E, psi = np.linalg.eigh(H)
psi = psi / np.sqrt(np.sum(psi**2, axis=0)*dx)

psi_full = psi[:, n]
E_full = E[n]


plt.figure(figsize=(9,6))

plt.plot(x, psi_un**2 + E_un, label="Unperturbed␣(n=2)", linewidth
   =2)
plt.plot(x, psi_un**2 + E_corr, '--', label="First-order␣correction"
   , linewidth=2)
plt.plot(x, psi_full**2 + E_full, ':', label="Fully␣perturbed",
   linewidth=2)

plt.plot(x, V0, 'k--', alpha=0.4, label="Harmonic␣Potential")

```

```
plt.xlabel("x")
plt.ylabel("Energy␣+␣|   |  ")
plt.title("Second␣Excited␣State␣(n␣=␣2):␣Comparison␣of␣Perturbation␣
   Effects")
plt.legend()
plt.grid(True)
plt.show()

#  Print  energies
print(f"Unperturbed␣Energy␣(n=2):␣{E_un:.5f}")
print(f"First-order␣Corrected␣Energy:␣{E_corr:.5f}")
print(f"Fully␣Perturbed␣Energy:␣{E_full:.5f}")
```