
Numerical Analysis of Schrödinger Equation for a Particle in a Double-Well Potential Curve

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Problem Statement

Quantum mechanics, a fundamental theory in physics, describes the behaviour of particles on a microscopic scale, incorporating the wave-like nature of particles. Quantum mechanics differs a lot from the classical mechanics. In classical mechanics, the state of a particle can be precisely determined with well-defined values for properties like position and momentum. In contrast, quantum mechanics operates with probabilities, meaning that it can only predict the likelihood of finding a particle in a particular state. This inherent uncertainty, encapsulated by Heisenberg's Uncertainty Principle, is a fundamental departure from the deterministic worldview of classical physics.

Another significant departure is the concept of wave-particle duality. In quantum mechanics, microscopic particles like electrons and photons exhibit both particle-like and wave-like behaviour, depending on how they are observed or measured. This dual nature challenges the classical idea of distinct particles following definite trajectories.

Superposition is the idea that in quantum mechanics, a particle can exist in multiple states or positions simultaneously. This means that an electron, for instance, can be in a superposition of being in different locations rather than having a single, well-defined position. Superposition also applies to other quantum properties like spin and polarisation.

Just like Newton's laws of motion in classical physics, the Schrödinger equation is one of the most fundamental equations in quantum mechanics. Proposed by Erwin Schrödinger in 1926, it provides a mathematical description of quantum systems and how their quantum state or wavefunction changes over time.

The Schrodinger equations can be divided into two types:

- Time-dependent Schrodinger equations
- Time-independent Schrodinger equations

The goal of this project is to solve the one-dimensional time-independent Schrödinger equation using numerical methods such as the Finite Difference Method (FDM). We aim to apply this approach to study the superposition of a particle in a double well potential. Additionally, we plan to extend this model to explain the Umbrella inversion in ammonia molecules. The specific objectives of the project are presented below:

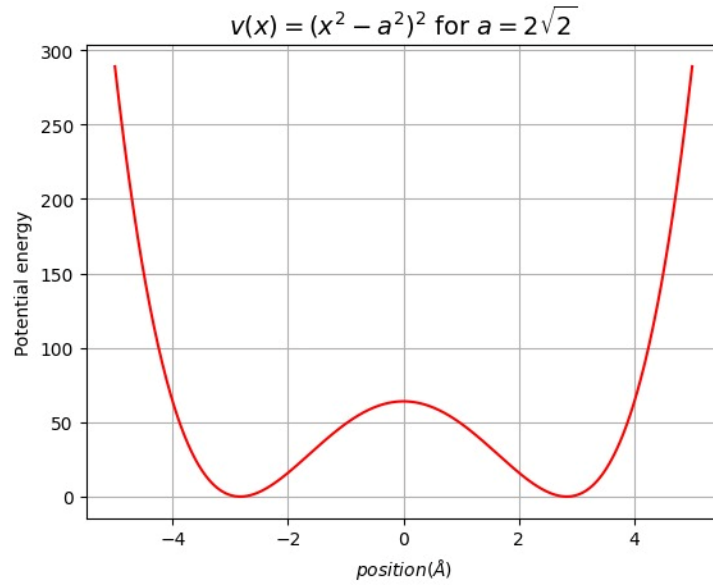
- 1) Develop a double well potential model and solve it using the one-dimensional time-independent Schrödinger equation for a particle like an electron and extend it to the ammonia molecule, including appropriate potential energy functions.
- 2) Make reasonable assumptions to simplify the problem while preserving its essential physical characteristics, ensuring that the problem remains tractable for numerical analysis.
- 3) Derive the governing equations for the one-dimensional Schrödinger equation, taking into account the potential energy profiles involved in the double well potential and the ammonia molecule.
- 4) Formulate the initial conditions and boundary conditions necessary to solve the Schrödinger equation for these systems.
- 5) Implement suitable numerical schemes, including the Finite Difference Method (FDM), to discretise and numerically solve the Schrödinger equation for the chosen systems.
- 6) Develop a computer program capable of solving the discretised Schrödinger equation efficiently and accurately, taking into account the chosen numerical methods.
- 7) To obtain information on the quantum states, energy levels, and wave functions of particles in the double well potential and the behaviour of the ammonia molecule during inversion.

1. The double-well potential model

Consider a particle moving in a one-dimensional space, and its potential energy varies with its position in one-dimensional space and is described by a function:

$$V(x) = (x^2 - a^2)^2 \quad (1)$$

We did the analysis for $a = 2\sqrt{2}$. This function resembles two wells or valleys separated by a hill or finite barrier in the middle, and it is symmetric about $x=0$. The height of the barrier is dependent on the value of a , and it is given by a^4 . The roots of this equation are $x = \pm a$. The two wells represent stable equilibrium positions for the particle, while the barrier represents an energy barrier that the particle must overcome to transition from one well to the other.

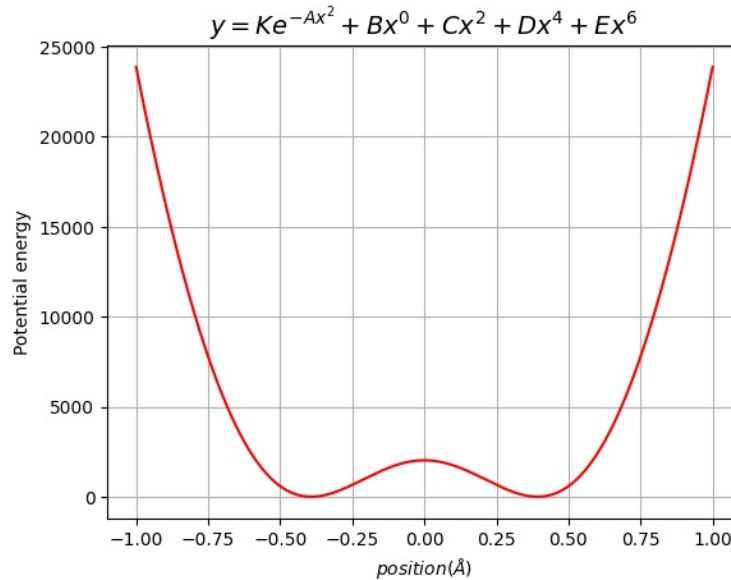


Similarly, in the case of the ammonia molecule, the potential energy curve resembles that of a double well curve whose potential varies with distance, but its function is given by:

$$V(x) = V_0 e^{-Ax^2} + Bx^0 + Cx^2 + Dx^4 + Ex^6 \quad (2)$$

Here V_0 , A , B , C , D , E are constants.

We have constructed this symmetric double-well potential by adding a Gaussian-type function to an even parity power series in x .



For this equation we can find that the height of the barrier is h :

$$h = V_0(1 - e^{-2\rho^2}) - \sum_{k=1}^n A_{2k}\rho^{2k} \quad (3)$$

where $\rho = 0.3925 \text{ Å}$ and 2ρ is the separation between both the minimas of the above function.

2. Assumptions

We have made the following assumptions to simplify our problem:

- 1) **One-dimensional space:** The problem is considered to be confined to one-dimensional space, where the particle's position is described along a single axis (e.g., the x-axis). This simplification reduces the complexity of the mathematical model.
- 2) **Time-Independence:** The Schrödinger equation is solved in a time-independent manner, implying that the quantum states and energy levels of the particle do not change with time. This simplifies the analysis and focuses on the stationary states of the system.
- 3) **Particle in Vacuum:** The analysis assumes that the particle of interest exists in a vacuum, without any external influences or interactions with other particles or fields, except for the potential energy described by the double well potential or the interaction between hydrogen and nitrogen atoms in ammonia molecules.
- 4) **Idealised Potential Energy:** The potential energy function describing the double well potential or the ammonia molecule's inversion is assumed to be idealised and mathematically tractable, allowing for a clear analysis of the quantum states and behaviour of the particle.
- 5) **Neglect of External Forces:** External forces such as gravity or electromagnetic fields are neglected, simplifying the model by focusing solely on the potential energy landscape and its influence on the particle.
- 6) **Neglect of Thermal Effects:** Temperature effects and thermal interactions with the particle are disregarded. This simplification assumes that the particle exists in a temperature-controlled environment, and the focus is primarily on the quantum behaviour.
- 7) **Isolation from Other Particles:** The particle of interest is considered to be isolated from other particles, minimising interactions that could affect its quantum states. This assumption is especially relevant in the context of the double well potential.
- 8) **Sufficient Separation of Energy Levels:** It is assumed that the energy levels within the double well potential or during the ammonia molecule's inversion are well-separated, allowing for the clear identification of discrete quantum states.

3. Governing Equations

In Quantum Mechanics, the Schrodinger equation describes the evolution of the state of a system in time in terms of its wavefunction $\Psi(x, t)$. This wavefunction contains all of the possible information that can be known about the system.

Generally, the Schrodinger equation is given in terms of the wave function and the Hamiltonian operator of the state.

3.1 The Hamiltonian operator

The Hamiltonian operator, often denoted as \hat{H} , is a fundamental concept in quantum mechanics. It represents the total energy operator for a quantum system and is a key component of the Schrödinger equation, which governs the behaviour of quantum systems.

In quantum mechanics, the Hamiltonian operator is represented as the sum of the kinetic energy operator \hat{T} and the potential energy operator \hat{V} . The kinetic energy operator is usually expressed in terms of momentum operators, and the potential energy operator depends on the specific potential energy function of the system.

$$\hat{H} = \hat{T} + \hat{V} \quad (4)$$

To derive the kinetic energy operator in quantum mechanics using the momentum operator, we can use the following steps:

The momentum operator \hat{p} is defined as:

$$\hat{p} = -i\hbar\nabla \quad (5)$$

The kinetic energy operator \hat{T} for a single non-relativistic particle is given by:

$$\hat{T} = \frac{\hat{p}^2}{2m} \quad (6)$$

To derive the kinetic energy operator, we need to square the momentum operator \hat{p}

$$\hat{p}^2 = (-i\hbar\nabla) \cdot (-i\hbar\nabla)$$

Using the properties of the dot product and the chain rule for derivatives, this can be written as:

$$\hat{p}^2 = -\hbar^2\nabla^2 \quad (7)$$

Here, ∇^2 is the Laplacian operator, which is the divergence of the gradient.

Now, substitute the squared momentum operator back into the expression for the kinetic energy operator:

$$\hat{T} = \frac{\hat{p}^2}{2m} = -\frac{\hbar^2}{2m}\nabla^2 \quad (8)$$

This is the kinetic energy operator \hat{T} for a single non-relativistic particle in quantum mechanics. The potential energy function $V(x)$ is the double well potential as defined above.

3.2 1D Time-Independent Schrodinger Equation

The Time-Independent Schrödinger Equation (TISE) is used to describe the stationary states of a quantum system.

The TISE is given by:

$$\hat{H}\psi = E\psi \quad (9)$$

where:

- \hat{H} is the Hamiltonian operator, which represents the total energy of the system. For a single particle, it is typically given by the sum of kinetic and potential energy operators.
- ψ is the wave function of the system. It contains all the information about the system and its interpretation is related to probability amplitudes.
- E is the total energy of the system, which is a scalar quantity.

The Hamiltonian operator for a single particle in a potential $V(x)$ is given by:

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V(\vec{x}) \quad (10)$$

where:

- \hbar is the reduced Planck's constant,
- m is the mass of the particle,
- ∇^2 is the Laplacian operator (which represents taking the second derivative),
- $V(x)$ is the potential energy function.

The solutions to TISE are energy eigenstates, which correspond to the possible outcomes of a measurement of the system's energy. These solutions are important for understanding various phenomena in quantum mechanics. The TISE is used when the Hamiltonian, and hence the potential energy function $V(x)$, does not depend explicitly on time.

4. Boundary Conditions

- 1) The wavefunction must be continuous at the boundaries between regions. So, at the barriers separating the two wells, the wavefunction and its derivative (slope) must be continuous.
- 2) The wavefunction must vanish as you approach infinity in each well. For a finite double well potential, this means the wavefunction goes to zero at the edges of each well.
- 3) The wavefunction and its derivative are zero at the boundaries separating the wells from the infinite barriers.

The boundary conditions ensure the wavefunction and its derivative are continuous everywhere within the allowed regions of the potential, as required for the Schrodinger equation to have a unique, physically meaningful solution.

5. Parameters

5.1 For double well

For the double well potential the equation of potential is given as

$$V(x) = (x^2 - a^2)^2$$

Here we have chosen a reasonable $a = 2\sqrt{2}$ for the visualization of wavefunctions.

For smaller values of the height of the barrier reduces and the well's depth reduces which makes it hard to visualise the wavefunction and superposition of waves.

5.2 Ammonia molecule potential

In ammonia molecule the potential is best resembled by the equation

$$V(x) = V_0 e^{(-Ax^2)} + Bx^0 + Cx^2 + Dx^4 + Ex^6$$

Here the values of constants are

$$V_0 = 17683.5627 \text{ eV}$$

$$A = 3.6530 \text{ \AA}^{-2}$$

$$B = -15661.4233 \text{ eV}$$

$$C = 35750.2356 \text{ eV} - \text{\AA}^{-2}$$

$$D = 3417.3434 \text{ eV} - \text{\AA}^{-4}$$

$$E = -88.7202 \text{ eV} - \text{\AA}^{-6}$$

These are experimentally determined values.

We are going to use both these potential energy functions in Schrodinger equation:

$\hat{H}\psi(x) = (-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{x}))\psi(x)$ one at a time and solve them to get the corresponding eigenvalues and eigenvectors.

6 Solution Methodology

To numerically solve the Schrodinger equation for any potential using the finite difference method, we first break up the space into many small equal-sized pieces. This creates a series of points along the dimension, with each point separated from the next by a tiny distance h . This allows us to approximate the derivatives in the equation as differences between the wavefunction values at each point. We then apply the boundary conditions - like requiring the wavefunction to be continuous and smooth where the potential changes.

Next, we write the Schrodinger equation as a matrix equation involving the Hamiltonian matrix, which contains the potential energy at each grid point. Solving this matrix equation gives us the energy levels and eigenfunctions we want. Making the grid spacing h smaller allows us to get more accurate solutions by better approximating the true derivatives.

7 Numerical Solution

7.1 Finite Difference Method (FDM)

The equation of one-dimension time-independent Schrodinger equations is:

$$\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(\vec{x})\right)\psi(x) = E\psi(x) \quad (11)$$

Multiplying $\psi(x)$ inside the brackets.

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi(x) + V(\vec{x})\psi(x) = E\psi(x) \quad (12)$$

Rearranging the terms.

$$V(\vec{x})\psi(x) - E\psi(x) = \frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi(x) \quad (13)$$

$$(V(\vec{x}) - E)\psi(x) = \frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi(x) \quad (14)$$

Now the RHS term can be rewritten as:

$$\frac{d^2}{dx^2}\psi(x) = \psi(x) = \frac{\frac{d\psi(x)}{dx}_{i+1} - \frac{d\psi(x)}{dx}_i}{\Delta x} = \frac{\psi(x)_{i+1} - 2\psi(x)_i + \psi(x)_{i-1}}{(\Delta x)^2} \quad (15)$$

Substituting the above in original equation we get

$$\frac{\hbar^2}{2m} \left(\frac{\psi(x)_{i+1} - 2\psi(x)_i + \psi(x)_{i-1}}{(\Delta x)^2} \right) = (V(x)_i - E) \psi(x)_i \quad (16)$$

Rearranging the terms

$$\psi(x)_{i+1} - 2\psi(x)_i + \psi(x)_{i-1} = \frac{2m}{\hbar^2} (\Delta x)^2 (V(x)_i - E) \psi(x)_i \quad (17)$$

Finally, we get this equation for any potential $V(x)$

$$-\psi(x)_{i+1} + \left(2 + \frac{2m}{\hbar^2} (\Delta x)^2 (V(x)_i) \right) \psi(x)_i - \psi(x)_{i-1} = \frac{2m}{\hbar^2} (\Delta x)^2 E \psi(x)_i \quad (18)$$

where i goes from 1 to $(n-1)$ and $n \in \mathbb{N}$.

We will get $\psi(x)_0, \psi(x)_1, \psi(x)_2, \psi(x)_3, \dots, \psi(x)_n$.

And when written in matrix format we can see that LHS forms a Tridiagonal matrix of $n \times n$. Now we find Eigenvalues and Eigenvectors for this matrix.

7.2 Computer Program Used

To solve the problem using a computer program, a code was written in Python. The following explains the code used:

- 1) The code starts by importing the necessary libraries: numpy for numerical computations, matplotlib.pyplot for plotting, and scipy.linalg.eigh to solve the eigenvalue problem for a matrix.
- 2) Constants such as the particle mass m , Planck's constant \hbar , potential energy function $V(x)$, grid spacing d , grid points x , and the number of grid points n are defined.
- 3) The potential energy function $V(x)$ is defined. In this example, it's $(x^2 - 8)^2$.
- 4) An empty matrix A of size $(n-1) \times (n-1)$ is created to represent the discretized Schrödinger equation. This empty matrix is now converted to the tridiagonal matrix.
- 5) The diagonal elements of the tridiagonal matrix are

$$A(i, i) = \left(2 + \frac{2m}{\hbar^2} (\Delta x)^2 (V(x)_i) \right)$$

- 6) The off-diagonal elements of the matrix are computed as:

$$\text{If } i < n - 2: \quad A(i, i + 1) = -1$$

$$A(i + 1, i) = -1$$

- 7) Find the eigen vectors and eigen values of the above tridiagonal matrix using eigh function.
- 8) Each eigen vector corresponds to an excited state.

9) Plot the wavefunctions and the square of the wavefunctions for the excited states obtained.

8 Result and Discussion

8.1 Results for the double well potential model

We have constructed a tridiagonal matrix using the equation (18) and the potential given as:

$$V(x) = (x^2 - 8)^2$$

We have calculated the eigen values and eigen vectors of the matrix. Now here each eigen value corresponds to an energy state and each eigen vector corresponds to the wave function of the particle in that energy level.

In quantum mechanics, the concept of parity is used to describe the spatial symmetry of a system. The parity operator, denoted as P , is an operator that reflects a point in space through the origin. Mathematically, it can be defined as:

$$P|\psi(x)\rangle = |\psi(-x)\rangle$$

Given that the potential is symmetric (the same in both wells), the Hamiltonian operator commutes with the parity operator, i.e. $[H, P] = 0$. This means that the Hamiltonian and the parity operator share a set of eigenfunctions in which the energy and parity can be simultaneously determined.

Since $[H, P] = 0$, we can say that H and P have a common set of eigenstates, denoted by $\psi_{\pm(x)}$, where

$$P\psi_{\pm}(x) = \pm\psi_{\pm}(-x)$$

The parity eigenstates $\psi_{\pm(x)}$ represent symmetric and antisymmetric combinations of wave functions corresponding to the two wells. The symmetric state $\psi_+(x)$ (symmetric about y axis) corresponds to even parity, and the antisymmetric state $\psi_-(x)$ (symmetric about origin) corresponds to odd parity. The probability of finding the particle is same in both the wells for at least the ground state energy level because it is an even parity $\psi_+(x)$ and squaring of $\psi_+(x)$ leads to equal probabilities of finding the particle in both the wells. However, this may not be true for higher energy levels but there is always a chance to get a non-zero probability of finding the particle at both the wells.

For ground state, we can see that the graph of $\psi(x)$ is symmetric about the y axis, indicating an even parity.

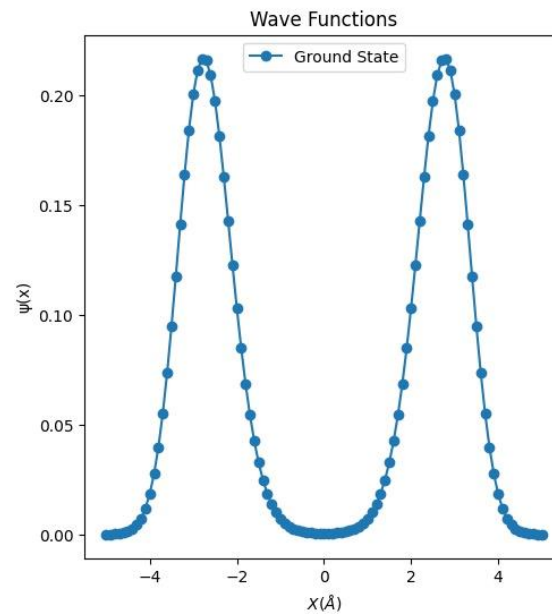


Figure: The ground state wave function of a particle in double well

For the first excited state, we can see that the graph of $\psi(x)$ is symmetric about origin, indicating an odd parity.

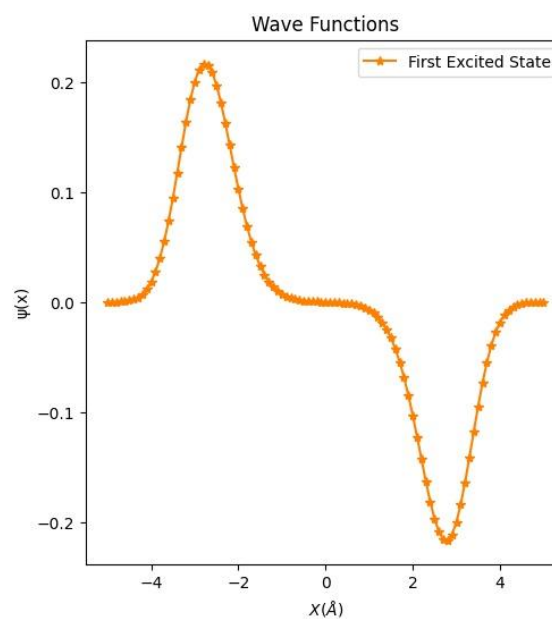


Figure: The first excited state wave function of a particle in double well

We also visualized the probability distribution of electrons in the double well potential as shown in the figure:

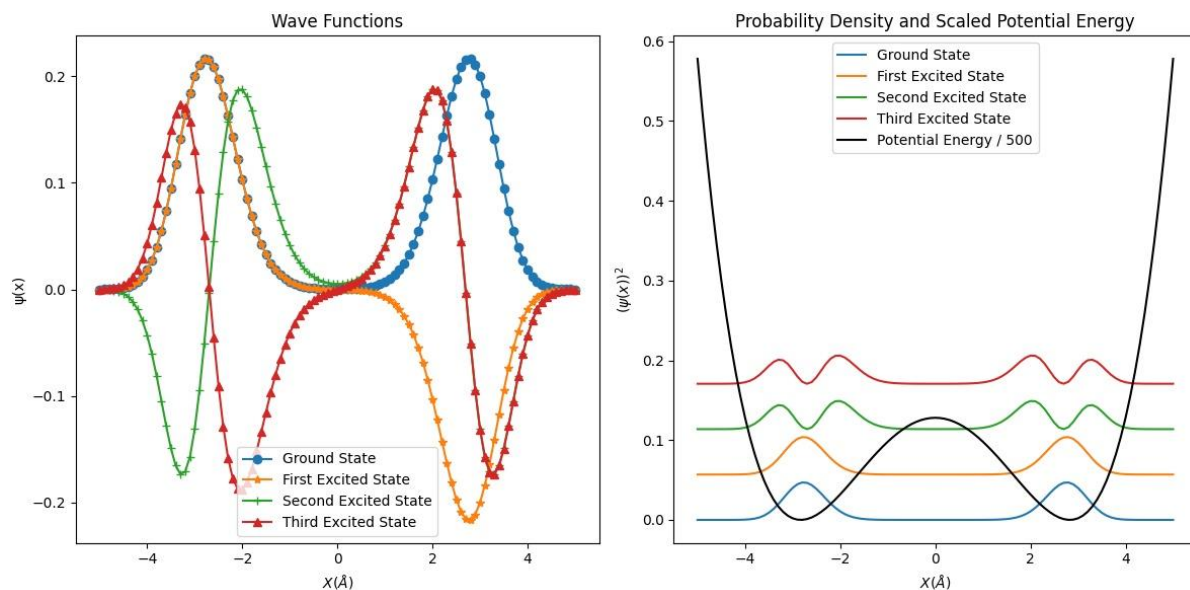


Figure: Wave function and probability density of a particle in double well (Note: A constant value is added for each excited state to create distance between excited states and to visualize the result clearly)

Clearly, from the figure, we can observe that there is an equal and non-zero probability of finding a particle in both the wells of the double well potential curve as per the principles of quantum superposition. This scenario is very different from that of classical mechanics where we expect the particle to be present at either of the wells but here, it is possible for the particle to exist in both the wells simultaneously.

8.2 Umbrella inversion and ammonia molecule

Ammonia (NH_3) demonstrates a fascinating phenomenon known as nitrogen inversion, where the nitrogen atom (N) and three hydrogen atoms (H) oscillate between two potential energy states. This oscillation involves the nitrogen atom shifting between positions above and below the plane formed by the three hydrogen atoms. This behaviour can be likened to a particle in a double well potential, as explained before, where the particle can exist in two distinct energy states. In this analogy, the superposition of states and the wave-like nature of particles are key concepts. The nitrogen atom in ammonia exists in a superposition, much like the particle in a double well potential, occupying both above and below the H-plane with equal probability due to its wave-like behaviour. Correspondingly, the ammonia molecule is at its lowest energy state when the nitrogen atom is farthest from the hydrogen atoms, mirroring the concept of lowest energy states in a potential well. Conversely, when the nitrogen atom is in the H-plane, it experiences the highest potential energy, signifying a barrier that must be surpassed for the transition between the two states, akin to the transition of a particle between potential wells.

The potential energy function in the ammonia molecule is given by:

$$V(x) = V_0 e^{-Ax^2} + Bx^0 + Cx^2 + Dx^4 + Ex^6$$

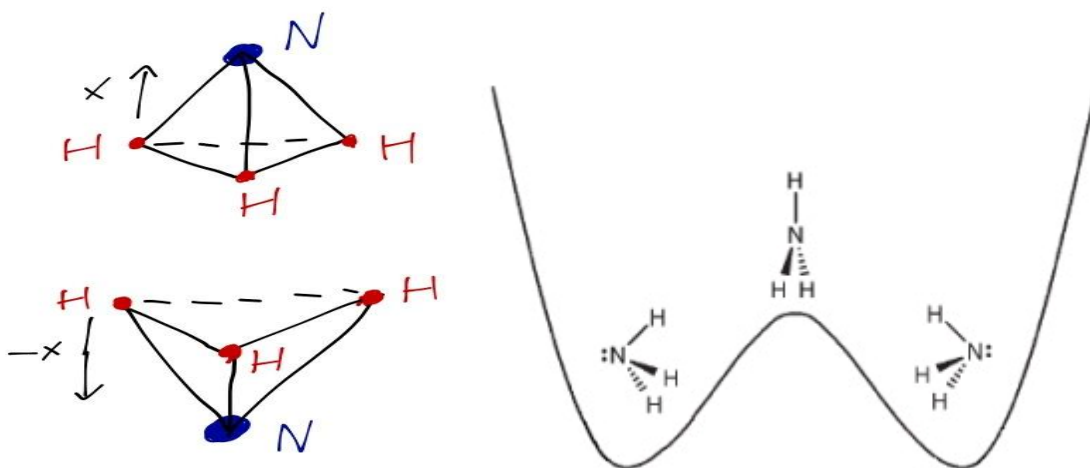


Figure: The potential energy curve for ammonia molecule along with its two stable states.

Similarly, as done before, we have constructed a tridiagonal matrix and calculated the wave functions for the above potential function as show.

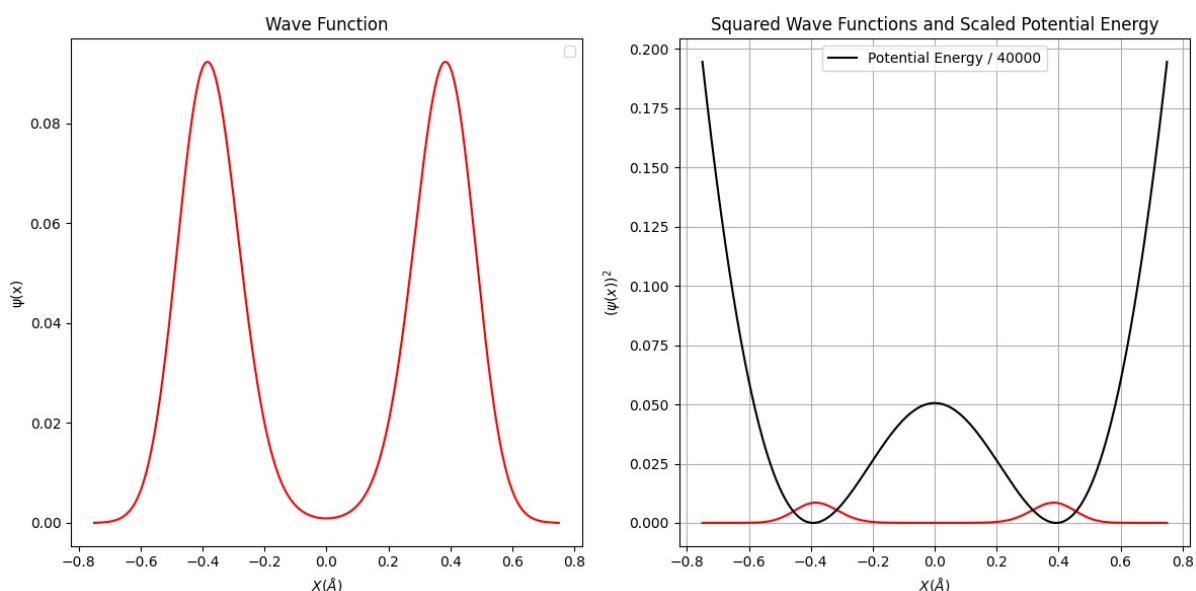


Figure: The probability of finding ammonia in both the states is shown with the help of probability density function.

Clearly, from the figure we can see that the ammonia molecule is in superposition between the two states.

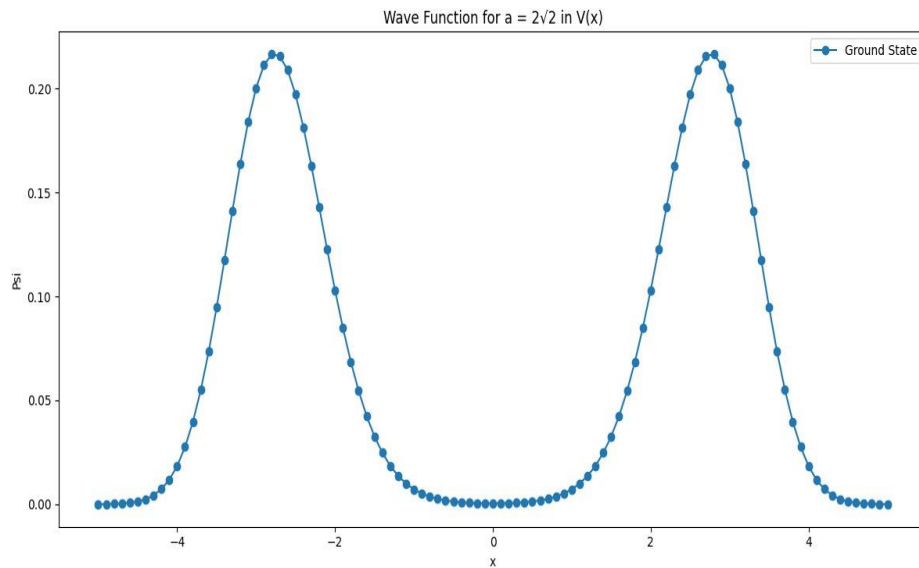
8.3 Some more observations

Constructive interference of wave functions from the two wells:

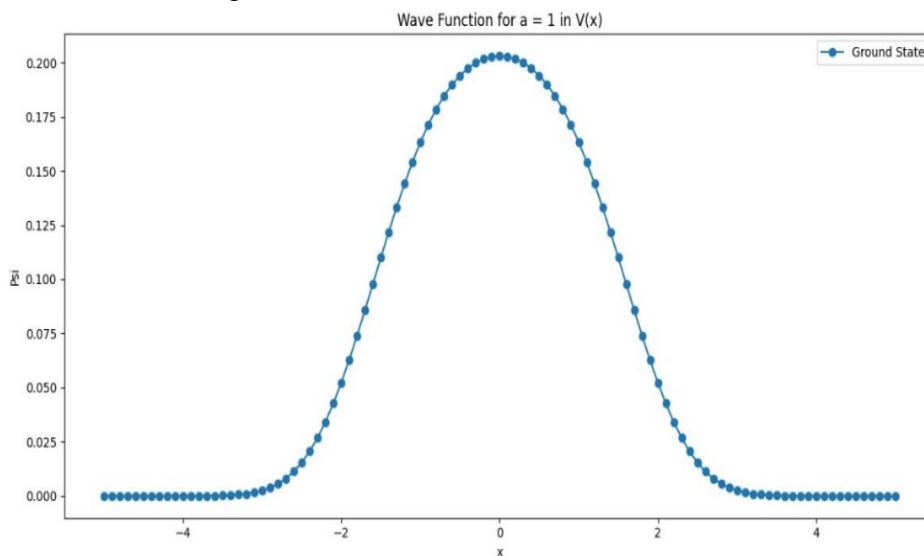
For the potential energy function: $V(x) = (x^2 - a^2)^2$

Here, if the value of a is changed then the distance between the two wells also changes, this causes a significant change in the wave function of the particle.

- 1) If the distance between the two wells is more (i.e., higher value of a like $2\sqrt{2}$) then it is less likely for the particle to traverse the barrier and transition between the wells, hence we see a hump in each well's region of the wave function as shown in the figure:



- 2) If the distance between the two wells is less (i.e., lower value of a like 1) then it is more likely for the particle to traverse the barrier and transition between the wells. The interference between the wave functions from the two wells becomes more pronounced, leading to regions of constructive and destructive interference. The constructive interference regions contribute to the "hump" in the middle, resembling a single hump as shown in the figure:



Effect of probability distribution of particle on reduced barrier height:

We have observed that there is a significant change in the probability distribution of the particle when the barrier height is changed. Consider the example of $V(x)$:

$$V(x) = (x^2 - 64)^2$$

Here in above curve, the barrier height is significantly high, so the particle was not able to cross the barrier even for higher excited states like $n = 100$, but when we multiply $V(x)$ with a factor, say 0.001, the barrier height is large we can observe that the electron at ground state has zero probability of being found at the location of the barrier.

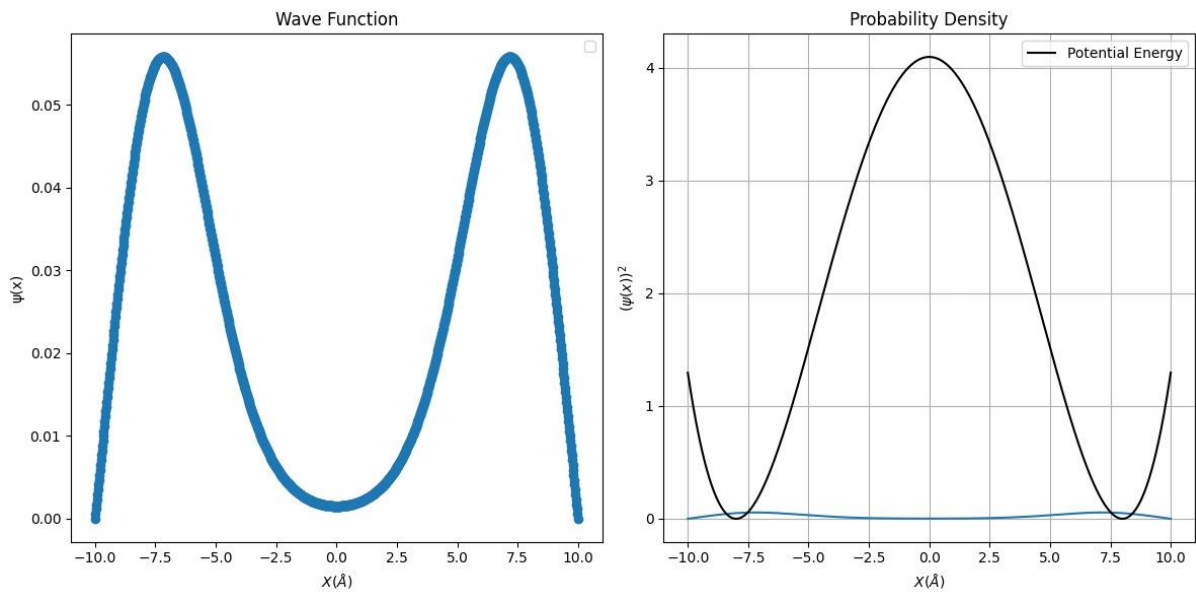


Figure: Potential function is $V(x) = 0.001(x^2 - 64)^2$

But when the barrier is multiplied with an even smaller number like 0.00001, the potential barrier height reduces and we can now see that the particle has non-zero probability of being found at the location of barrier.

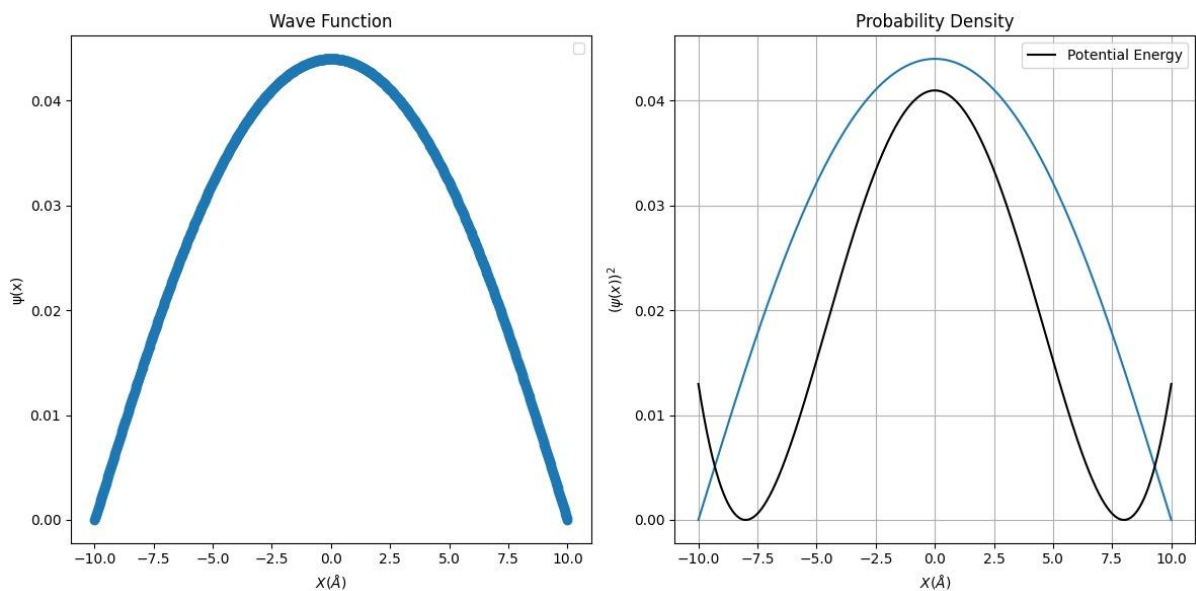


Figure: Potential function is $V(x) = 0.00001(x^2 - 64)^2$

Here, from the above graph we can see that when the barrier height is less, we have chance of finding the particle even at $x = 0$.

9 References

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