

Ammonia in a Double Quantum Well

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Introduction

Quantum physics predicts unusual behaviors that are difficult for our immediate intuition to accept, such as the tunnel effect. In this document, we will study a double quantum well system, a model used in particular to describe the inversion of the ammonia molecule (NH_3). The objective is to progress from a simple case (the single infinite well) to a complex case (the finite double well) in order to isolate and understand some of the key concepts of Quantum physics such as degeneracy and tunneling and conclude about the effects of the Tunnel Effect.

Study

Infinite simple quantum well

The study of the single infinite quantum well serves as the fundamental description of the localized nitrogen atom.

In fact, before considering the interaction between the two equilibrium positions (inversion), we must first characterize the behavior of the nitrogen atom when it is fully confined to a single side of the hydrogen plane.

In this first case, we can model the simple quantum well as having a length L , with infinite barriers. Therefore, the potential $V(x)$ is:

- $V(x) = 0$ inside the well
- $V(x) = +\infty$ outside the well

We can then say that: $\varphi(x) = 0$ outside the well, because the potential is infinite.

However, inside the well, we use the Time Independent Schrödinger's equation:

$$-\frac{\hbar^2}{2m} \frac{d^2\varphi(x)}{dx^2} = E\varphi(x)$$

The general solution of this equation is: $\varphi(x) = A\sin(kx) + B\cos(kx)$, where $k^2 = \frac{2mE}{\hbar^2}$

The wave function must be continuous; therefore, it must be zero at the edges of the well to reach the external solution. By applying this boundary condition, we obtain the eigenenergy:

$$E_n = \frac{n^2\pi^2\hbar^2}{2mL^2}$$

Then, if we apply the normalization condition ($\int |\psi(x)|^2 dx = 1$) on L , we have: $A = \sqrt{\frac{2}{L}}$

In the end, the normalized eigenstates are: $\varphi_n(x) = \begin{cases} \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) & \text{for } 0 < x < L \\ 0 & \text{otherwise} \end{cases}$

The physical meaning here is that the nitrogen atom is trapped in a potential "cage" formed by the hydrogen atoms (width L). The tighter this cage (smaller L), the higher the energy required for the atom to exist there.

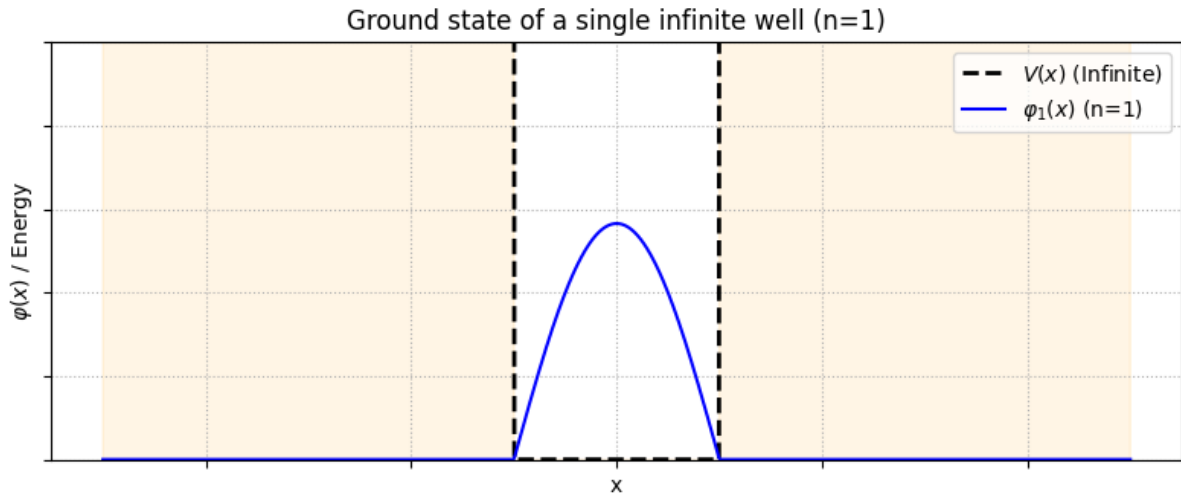
A critical outcome is also the existence of non-zero ground state energy:

$$E_1 = \frac{\pi^2\hbar^2}{2mL^2}$$

So, the nitrogen atom is never at rest; it possesses an intrinsic kinetic energy called zero-point energy.

Here is a representation of the wavefunction:

Image 1:



Double infinite quantum well

While the single well described a particle confined to one location, the infinite double well model introduces the concept of structural duality.

Description of the states

In the case of our idealized scenario where $V_0 \rightarrow \infty$, the central barrier becomes impenetrable. The system is then "decoupled": it is no longer a double well, but two simple infinite potential wells, completely independent of each other.

- Left well (L): An infinite well of width a , located between:
 $x = -b - \frac{a}{2}$ and $x = -b + \frac{a}{2}$
- Right well (R): An infinite well of width a , located between:
 $x = -b + \frac{a}{2}$ and $x = b + \frac{a}{2}$

We can then reuse the results from the previous case.

- If the particle is located in the left well:

$$\varphi_{L,n}(x) = \begin{cases} \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi\left(x + b + \frac{a}{2}\right)}{a}\right) & \text{for } x \in \text{left well} \\ 0 & \text{otherwise} \end{cases}$$

- If the particle is located in the right well:

$$\varphi_{R,n}(x) = \begin{cases} \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi\left(x - b + \frac{a}{2}\right)}{a}\right) & \text{for } x \in \text{right well} \\ 0 & \text{otherwise} \end{cases}$$

These functions $\varphi_{L,n}(x)$ and $\varphi_{R,n}(x)$ describe a state where the particle is exclusively in the left well or exclusively in the right well, with no possibility of moving from one to the other. Since $\varphi_{L,n}(x)$ and $\varphi_{R,n}(x)$ are both valid solutions of the Schrödinger equation for this specific potential (with $V_0 \rightarrow \infty$), they are both eigenstates of the system. The energy of an eigenstate n in an infinite well of width L is given by the result of the previous case. In our case, both wells (L and R) have the same width a . Therefore, replacing L with a : $E_n = \frac{n^2 \pi^2 \hbar^2}{2ma^2}$ for $n \in \mathbb{N}^*$

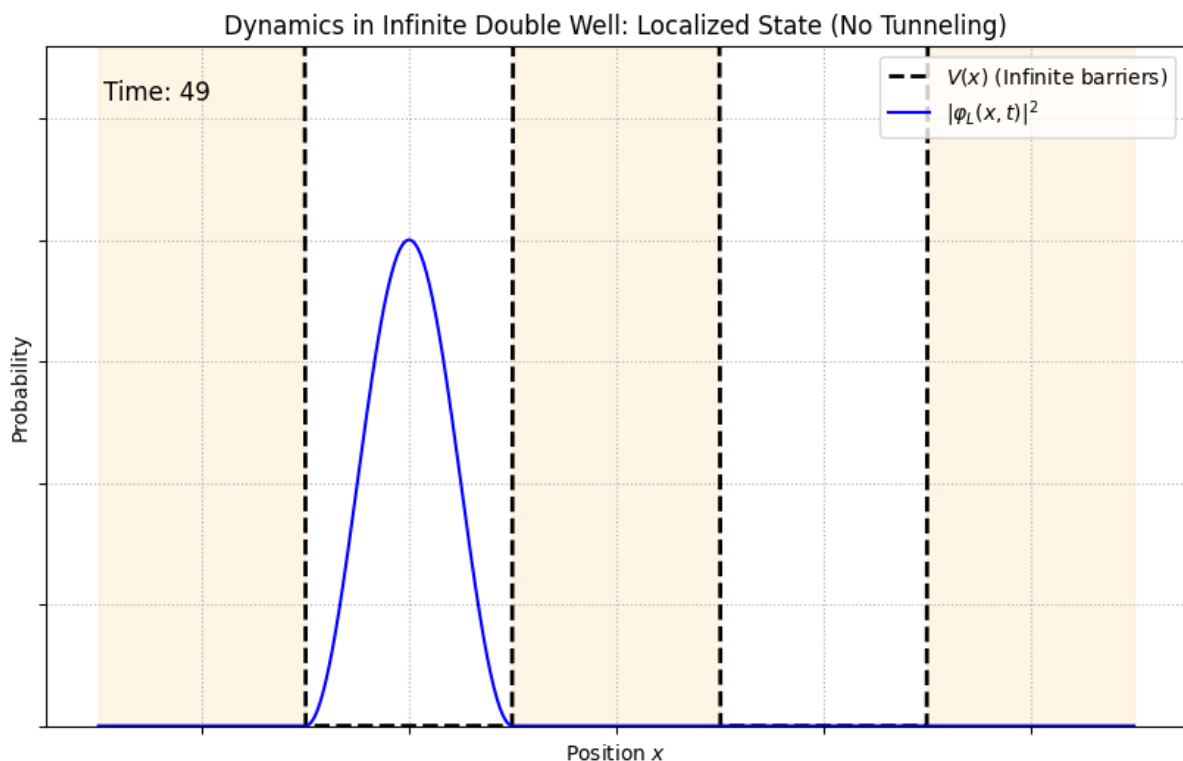
The two states have exactly the same energy.

Degeneracy

Furthermore, we know that degeneracy is the number of distinct (linearly independent) eigenstates that share the same energy level. Then, since two eigenstates correspond to each energy value E_n , each energy level is doubly degenerate (degeneracy of 2).

In this case, the particle is located either in the right-hand well or the left-hand well. Here is a realistic representation, over time, of what actually happens:

Image 2:



In this representation, we can see that the particle can only be in the left well.

Note: We could have chosen to represent the possibility where the particle could only be in the right well.

Symmetry

Let now introduce the symmetrical and antisymmetrical wavefunctions:

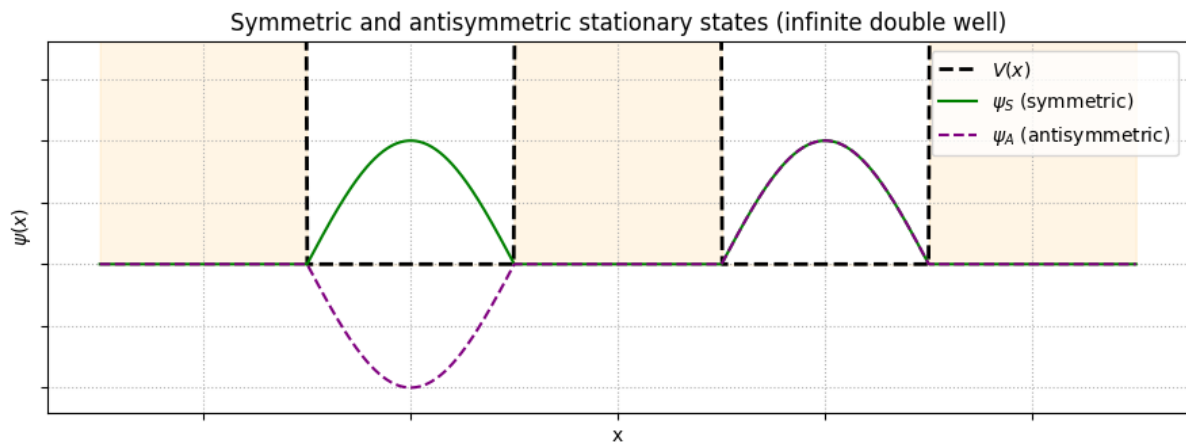
$$\psi_{S,1} = \frac{1}{\sqrt{2}}(\varphi_{R,1} + \varphi_{L,1}) \text{ and } \psi_{A,1} = \frac{1}{\sqrt{2}}(\varphi_{R,1} - \varphi_{L,1})$$

Since any linear combination of degenerate eigenstates is also an eigenstate of the same energy, $\psi_{S,1}$ and $\psi_{A,1}$ are also eigenstates of the system. Also, since the potential is symmetric ($V(x) = V(-x)$), the true stationary eigenstates of the Hamiltonian must have definite parity (either even or odd).

Their energy is $E_{S,1} = E_{A,1} = E_1 = \frac{\pi^2 \hbar^2}{2ma^2}$.

Here is a representation of the different wavefunctions:

Image 3:



Finite double quantum well

In this last case, we lower the potential barrier from infinity to a finite value V_0 . Indeed, this case represents the most realistic modeling and allows us to introduce the tunnel effect, which is central to the problem of the ammonia molecule.

Tunnel effect

Recall that the square modulus of wave function $|\psi(x, t)|^2$ is the probability of finding a particle at a position x at a time t . In the case of a finite double well, the probability of finding the particle decreases upon "passing through the central barrier", but that on the other side of this barrier, the wave function is not equal to 0. This means that there is a probability of finding the particle on the other side of the barrier (i.e. in the other well). This is the tunnel effect. Consequently, because the barrier is finite, the particle is not strictly confined to a single well, it is instead delocalized. Meaning that the particle effectively occupies both wells simultaneously (Image 4).

Solving the problem

But to achieve this result, let's go back to the general expression of the eigenstates of the potential for a finite double quantum well, which is written as:

$$\psi(x) = \begin{cases} A \sin\left(k\left(b - \frac{a}{2} + x\right)\right) & \text{for } -b - \frac{a}{2} < x < -b + \frac{a}{2} \\ C e^{Kx} + D e^{-Kx} & \text{for } -b + \frac{a}{2} < x < b - \frac{a}{2} \\ B \sin\left(k\left(b + \frac{a}{2} - x\right)\right) & \text{for } b - \frac{a}{2} < x < b + \frac{a}{2} \\ 0 & \text{otherwise} \end{cases}$$

The constant K and k were defined from the energy E :

$$k^2 = \frac{2mE}{\hbar^2} \text{ and } K^2 = \frac{2m(V_0 - E)}{\hbar^2}$$

Thus, we have a relation between k and K : $k^2 + K^2 = \frac{2mV_0}{\hbar^2}$

The potential $V(x)$ is perfectly symmetric with respect to the center $x = 0$. We have $V(x) = V(-x)$ in all regions.

Moreover, when the Hamiltonian H (which depends on $V(x)$) is symmetric, its eigenstates $\psi(x)$ must be eigenstates of the parity operator.

This means that the eigenstates must be either even (symmetric $\psi(x) = \psi(-x)$) or odd (antisymmetric, $\psi(x) = -\psi(-x)$).

If we apply this condition to the general expression of $\psi(x)$ that we found, we obtain:

- Symmetrical case: $A = B$ and $C = D$
- Antisymmetrical case: $A = -B$ and $C = -D$

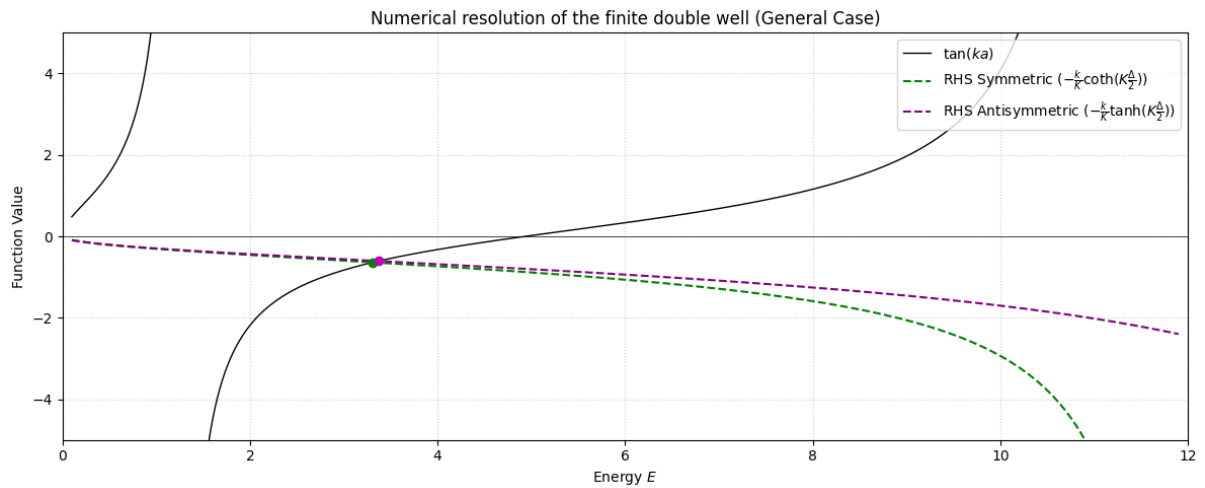
Then, using the continuity of the function and its first derivative, we have a second relation between k and K :

$$\tan(ka) = -\frac{k}{K} \coth\left(K\left(b - \frac{a}{2}\right)\right) \text{ for symmetrical solutions}$$

$$\tan(ka) = -\frac{k}{K} \tanh\left(K\left(b - \frac{a}{2}\right)\right) \text{ for antisymmetrical solutions}$$

These equations are difficult to solve and require a numerical solve shown below:

Image 5:



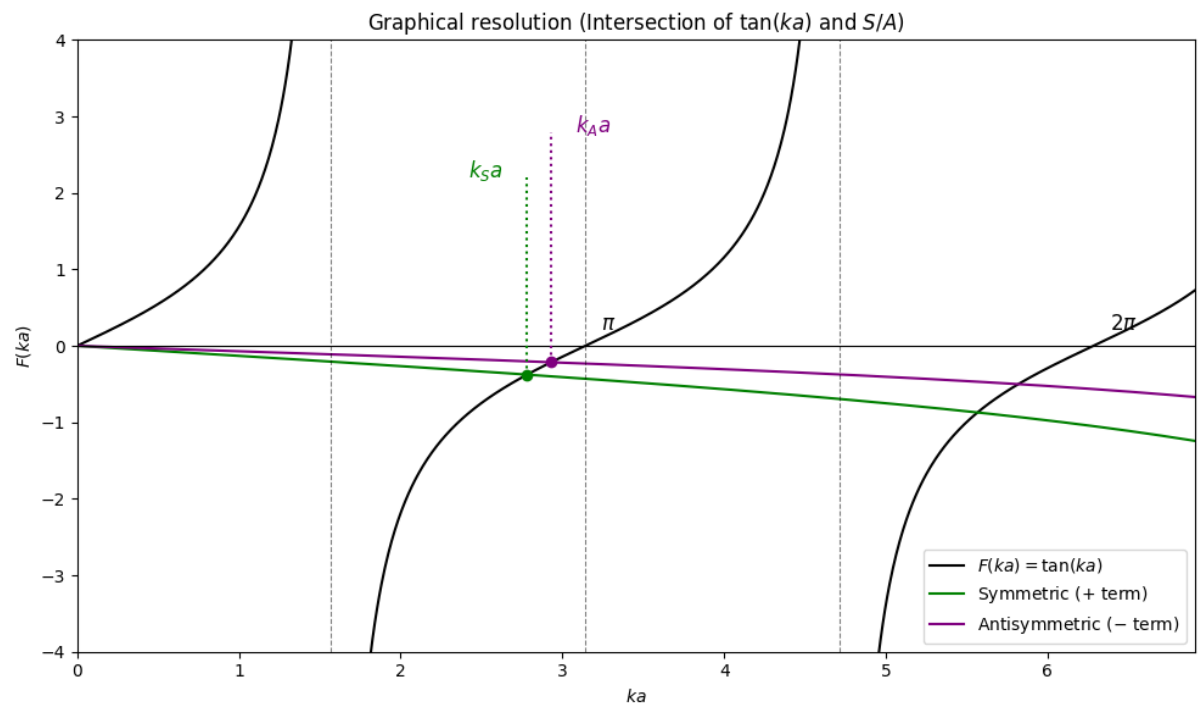
The problem can be simplified by looking at a particular case where the first eigenenergy $E_1 \ll V_0$, in which case $K \gg k$. We can also consider that $K\Delta \gg 1$, with $\Delta = 2b - a$ the width of the barrier. In that case we can show that the relation between k and K can be written as:

$$\tan(ka) = -\frac{k}{K}(1 \pm 2e^{-K\Delta})$$

With + corresponding to the symmetrical case and – corresponding to the antisymmetrical case.

This can be solved graphically as the intersection of $y = \tan(ka)$ and $y = k \in S/A$

Image 6:



The eigenstates (stationary) are the delocalized states ψ_S and ψ_A (assuming $n = 1$).

The "physical" states φ_L (particle on the left) and φ_R (particle on the right) are superpositions of these eigenstates. As seen before (by reversing the relations):

- $\varphi_L = \frac{1}{\sqrt{2}}(\psi_S - \psi_A)$
- $\varphi_R = \frac{1}{\sqrt{2}}(\psi_S + \psi_A)$

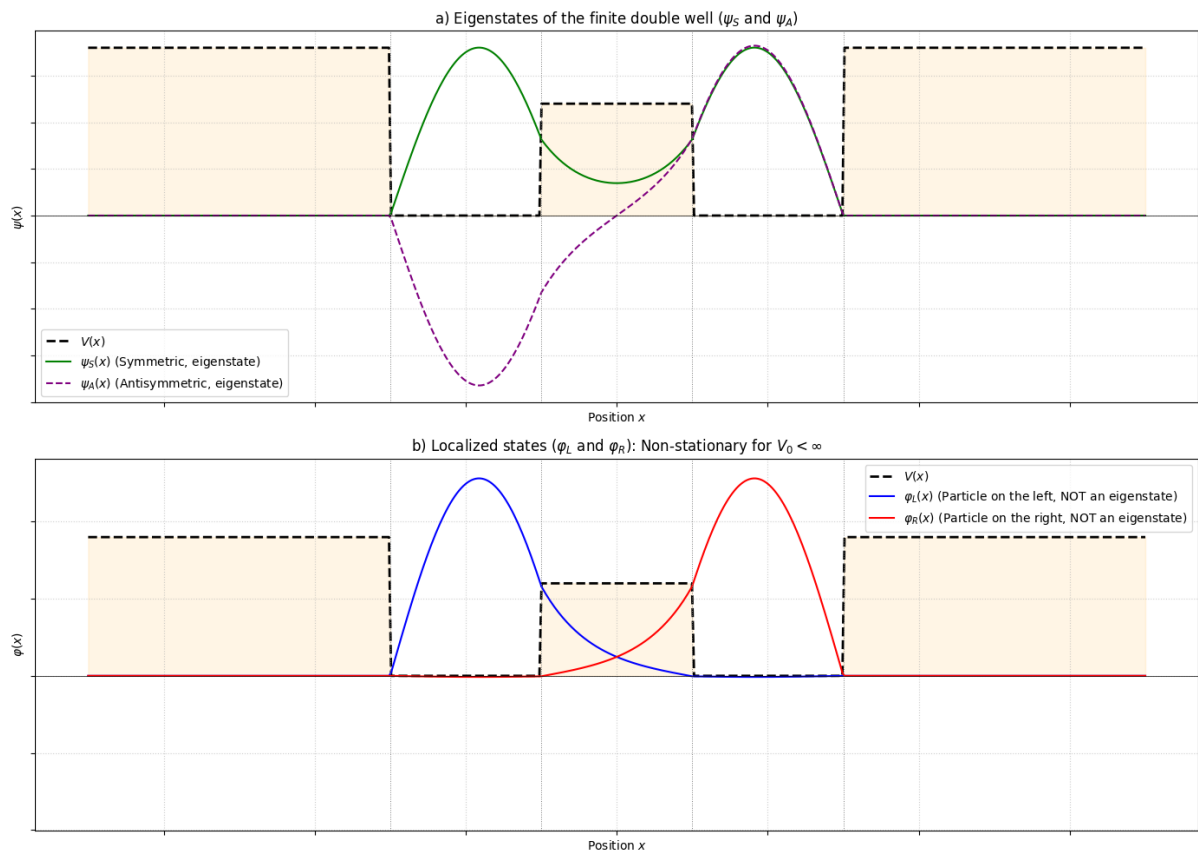
The eigenstates are ψ_S and ψ_A . In the case of the finite barrier, tunneling lifts the degeneracy, which means that ψ_S and ψ_A have different energies: $E_S \neq E_A$.

A superposition of eigenstates with different energies is never an eigenstate (or stationary state). The average energy (expected value) is $\langle E \rangle = \langle \psi | E | \psi \rangle$.

- $\langle E \rangle_L = \frac{E_S + E_A}{2}$
- $\langle E \rangle_R = \frac{E_S + E_A}{2}$

We notice that both energy averages of the two localized states are the same: it's the average of the energies of the first two stationary states.

Image 4:



Conclusion

Let's summarize what we just saw:

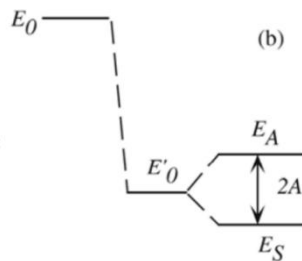
Infinite double quantum well ($V_0 \rightarrow \infty$)

In the infinite well there is no tunnel effect, the wells are decoupled. The energy E_1 is degenerate: $E_S = E_A = E_1$. The localized states φ_L and φ_R are eigenstates (since any linear combination of degenerate states is also an eigenstate). A system prepared in φ_L remains there indefinitely.

Finite double quantum well (realistic case, $V_0 < \infty$)

In the finite well, the tunnel effect exists: the wave function "leaks" through the barrier. This "communication" between the sinks lifts the degeneracy. The energy E_1 splits into two distinct levels: the symmetric state E_S (ground state) and the antisymmetric state E_A (first excited state). This is the "splitting" $2A$ visible in image 7. We have $E_S < E_A$. The symmetric state is more stable because its wave function $\psi \propto \cosh(Kx)$, is «flatter» in the barrier, minimizing the curvature and therefore the kinetic energy, compared to the antisymmetric state $\psi \propto \sinh(Kx)$, which vanishes at $x = 0$. The localized states φ_L and φ_R are no longer eigenstates.

Image 7:

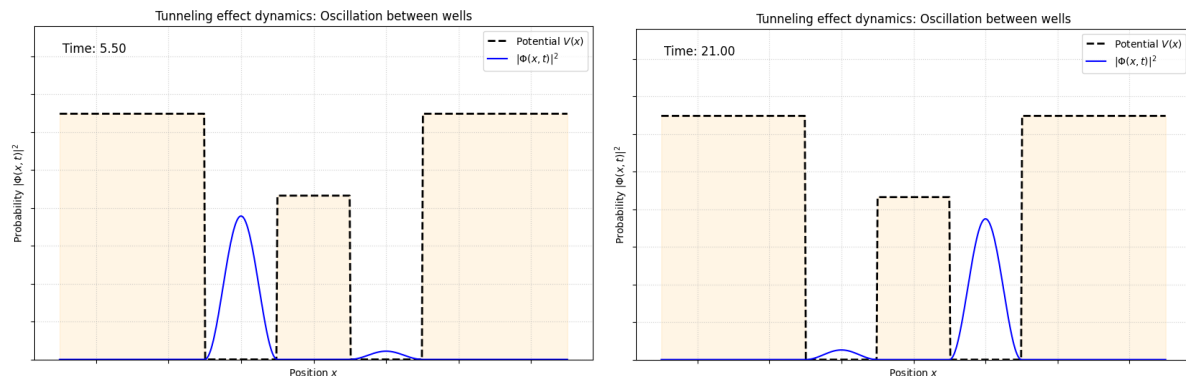


Consequences

We therefore observe that the tunnel effect has the following consequences:

1. **Lifting of degeneracy:** This is the most important consequence on energy. Compared to the case where the two wells were independent (equal energies in each well), we have here a lifting of degeneracy because the two wells "communicate" through tunneling, exactly in the same way as the two pendulums: uncoupled, they have the same natural frequency; coupled, one of the frequencies changes, there is a lifting of degeneracy. A single energy level (in the case $V_0 = \infty$) splits into two levels E_S and E_A . This is why we have two eigenwave functions here: each corresponds to a different energy, thanks to the lifting of degeneracy.
2. **Dynamics (Tunneling):** Since φ_L and φ_R are not stationary states, a system prepared in state φ_L at time $t = 0$ will evolve. It will oscillate between φ_L and φ_R at a frequency $\omega = \frac{E_A - E_S}{\hbar}$. This is the inversion of the ammonia molecule.

Image 8:



These images are the “classical” configurations of the Ammonia molecule. We represent the linear combinations which maximize the probability of being either in the left well or in the right well.

Appendix

Sources

- TD3, part 2: Double Quantum Well
- Wikipedia: https://fr.wikipedia.org/wiki/Effet_tunnel
- CEA: <https://www.cea.fr/multimedia/Documents/publications/clefs-cea/archives/fr/tableau-G.pdf>
- Lecture at Polytechnique (X) by Sylvain Rey about the inversion of the Ammonia Molecule: <https://perso.crans.org/sylvainrey/Agreg%20Cours/Cours/Cours%20divers/Mol%C3%A9cule%20d%27ammoniac%2C%20Masers%20et%20horloges%20atomiques/Mol%C3%A9cule%20d%27ammoniac%20quantique%2C%20masers%2C%20horloges%20atomiques%20et%20GPS.pdf>