

Explorando el efecto túnel en la molécula de amoníaco

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Slide 2. So, this is the table of contents.

First, I will introduce you our work. Second, I will describe the inversion motion of the ammonia molecule. Third, I will determine the stationary states. Fourth, I will demonstrate the creation of non-stationary states and Fifth, We will study its time dynamics. Sixth, We will calculate the survival probability, expected values and *visualize* tunneling. And, finally, the conclusions.

1. Introduction and objectives

Slide 3. *tunneling* is the name given to the penetration and transmission of molecules through potential energy barriers. On a microscopic scale, it is a purely quantum effect, of a probabilistic nature, which occurs in molecules whose energy is less than the barrier, which are transmitted through it through a classically forbidden region for them (red arrow). It is one of the most surprising and paradoxical phenomena of quantum mechanics that describes, in a coherent and formal way, a behavior that breaks with the corresponding classical description (blue arrow), giving quantum theory the explanatory power of the microscopic domain.

The tunneling probability decreases exponentially with the width of the barrier, with the mass of the molecule, and with the square root of the height of the barrier relative to the energy of the molecule.

Slide 4. It is present in all quantum systems and is used in scientific and technological fields such as:

In chemistry, being of great importance in astrochemistry (in adsorption and desorption processes), electrochemistry, radioactive processes, catalysis and any chemical reaction that involves a transition state.

In the same way, it is present in biological systems, such as proteins, and processes of interest such as proton transfer in DNA, which can cause mutations.

And in technological fields such as quantum computing and devices such as the tunnel effect diode or the scanning tunneling microscope (STM).

Slide 5. Our objectives in this work have been the following:

1. Study Quantum Tunneling in a realistic example, such as the inversion motion of NH_3 .
2. Exemplify the creation of non-stationary states as superpositions of stationary states
3. Study time dynamics of these non-stationary states
4. *Visualize* tunneling, in real time, with the help of quantum mechanical simulations.

2. Inversion motion of NH_3

Slide 6. To study the inversion motion of the ammonia molecule, we define the inversion coordinate x as the distance between the N atom and the plane formed by the 3 H atoms. That is, the height of the pyramid.

Slide 7. The pyramidal ammonia molecule (with C_{3v} symmetry) exhibits an umbrella-type vibrational motion in which the hydrogen atoms move vertically, leading to the inversion of the molecule, passing through a plane transition state (of symmetry D_{3h}).

It is a high-amplitude vibrational motion that, although it does not correspond exactly to any normal mode of vibration, represents the angular symmetric or umbrella mode.

Slide 8. According to this definition, the lower energy pyramidal equilibrium geometries (wells) are represented with two identical oscillators, so the potential is symmetric with respect to the reflection of the higher energy planar configuration (barrier). Therefore, the potential energy curve that describes this movement has the form of a double symmetric potential well, so that we consider the inversion motion of ammonia as an anharmonic vibrational motion of the NH_3 molecule between the two potential wells.

3. Determination of stationary states

Slide 9. The first thing we need to study the tunnel effect are the energy levels and the eigenfunctions (stationary states) of the system. To do this, we have to solve the time-independent Schrödinger equation, where the Hamiltonian of our system is [equations], ψ_i are the eigenfunctions and E_i the eigenvalues or energy levels.

Slide 10. To do this, we use the matrix formulation of the linear variational method, taking the set of eigenfunctions of the one-dimensional harmonic oscillator.

Slide 11. By increasing the number of basis functions, the value of the variational energies decreases until the convergence given by the desired precision, which we consider as the energy levels of the system. In this figure, I present the variational energies for the first 4 energy levels versus the number of basis functions N . We can see that, as we expected, the value of the variational energies decreases by increasing N until converged.

Slide 12. In this table, I present the value of the energy levels, which can be seen in the figure, with the potential energy curve. We can appreciate the effect of the energy barrier on the quasi-degeneration of the first two vibrational levels ($v = 0^\pm$), corresponding to the first doublet, and the levels corresponding to the second doublet ($v = 1^\pm$).

Also, we can see that these energy levels are below the height of the barrier. Namely, classically, an ammonia molecule in its fundamental state or any of the first 3 excited states wouldn't be able to carry out the inversion motion, as its energy is less than the energy needed (barrier height) for it to take place. It would need an external energy supply (for example, thermal energy) sufficient for its energy to be greater than the barrier, and thus be able to complete the inversion motion. Otherwise, the molecule would keep oscillating between the return points, around the equilibrium position of the well where it was.

Slide 13. Next, I plot the eigenfunctions of the first four vibrational levels against the inversion coordinate x . The eigenfunctions that fall below the barrier are symmetrically delocalized with respect to the barrier in the two potential wells according to the symmetry properties, with even functions corresponding to even levels,

Slide 14. and odd those corresponding to odd levels.

This symmetric delocalization of the positional probability density in both wells implies that there is an equal probability of finding the ammonia molecule, represented by a stationary state, in either of the two wells. The molecule is then said to be delocalized in the two wells. It is necessary to create localized non-stationary states in one of the wells to follow their quantum mechanical time evolution and to observe the tunnelling effect.

4. Preparation of non-stationary states

Slide 15. We understand by non-stationary state a state of quantum space probability in *motion* formed by a *superposition* of wavefunctions of stationary states of different energies.

Once we have determined the stationary states of our system, we can form linear combinations (superpositions) of these to create non-stationary states, whose energy is the mean of the energies of the states that are in superposition. In our case, we form a superposition of the stationary states $|\psi_0\rangle$, $|\psi_1\rangle$, $|\psi_2\rangle$, $|\psi_3\rangle$ corresponding to the first four energy levels. We give values to α between 0 and 90° to form non-stationary states below the barrier.

Slide 16. In this way, the limit initial non-stationary states, for $\alpha = 0$ and $\alpha = 90^\circ$, are formed by the superposition of the stationary states corresponding to the two doublets, respectively. We see how these states are located in the well on the left.

In the same way, we have created intermediate non-stationary states for different values of α , although I do not include them in this presentation.

5. Time dynamics of non-stationary states

Slide 17. To see how these non-stationary states evolve over time, we need to solve the *time-dependent Schrödinger equation*, where the complete wave function that satisfies this equation is formed by a superposition of stationary states, now including the time dependence.

Slide 18. Although we now include the time dependence in stationary states, the expectation value of an observable for these states does not depend on time. It is for this reason that we create a superposition of non-stationary states of different energy.

We calculate the expectation value of the position as [equation].

The survival probability P_s is defined as the probability that the non-stationary state coincides with the initial state and is therefore given by [equation].

The recurrence time t_r is defined as the time it takes for the non-stationary state to return to its initial state. From the definition of survival probability, we find that the recurrence time is given by [equation], which for limit non-stationary states is equal to [table]. We see how by increasing the width and height of the barrier in the limit case $\alpha = 0$, the recurrence time is much greater than that in the limit case corresponding to $\alpha = 90^\circ$.

Slide 19. Next, I plot the survival probability for the initial non-stationary states corresponding to $\alpha = 0, 15, 30^\circ$.

As expected from the definition of P_s , the survival probability follows a periodicity. The time for which the probability of survival becomes maximum corresponds to the time of recurrence. The first thing we identify is that the survival probability varies in a regular way for the limit non-stationary state and that, as α increases, oscillations appear in the values of $P_s(t)$ that become larger as it increases α .

To better observe these oscillations, I reduce the time scale to 1 picosecond.

Slide 20. Bearing in mind the definition of survival probability, these oscillations or drastic changes of $P_s(t)$ in small intervals imply that the probability of finding the non-stationary state in its initial situation varies drastically in a very small time interval.

If we look, for example, at the graph for $\alpha = 45^\circ$ in the region around $t = 0.5$ ps, we see how the survival probability varies between ~ 0 and ~ 1 in a small time interval. It may be that some of you are wondering: does this result correspond, therefore, to the fact that the non-stationary state is oscillating from one well to another in very small time intervals? Rather, the interpretation of these results implies that the entire non-stationary state does not *penetrate* the barrier whenever it collides with it in these intermediate non-stationary states, unlike in the limit non-stationary states, which are delocalized between the two wells. In the case of intermediate non-stationary states (for example, for $\alpha = 45^\circ$), the state moves from the left well, collides with the barrier, and only a small part (low probability density) manages to penetrate the barrier and be transmitted to the well on the right, while the rest of the state continues to oscillate in the well on the left. As time goes by, the non-stationary state will have collided with the barrier enough times to be transmitted to the other well (the probability density in the well on the right will be higher than that in the one on the left) and the process can be repeated for its return to

the initial situation. This delocalization of the state explains the oscillations in the values of $P_s(t)$.

In order to better understand these observations, we calculate the expectation value of the position and its time evolution

Slide 21. The black horizontal lines [point to] correspond to the cutoff points and the gray lines to the position of the wells. We are especially interested in the thicker black lines, since they correspond to the intersection points with the barrier.

Just like with the survival probability, as α increases, oscillations appear in the expectation value of the position of the state. In the limit case corresponding to $\alpha = 0$, we see how the time evolution of the expectation value of x is regular, which allows us to imagine that the motion between the wells of this non-stationary state is regular. That is, the entire state penetrates and is transmitted through the barrier upon colliding with it. However, as we already anticipated with the survival probability, this is not the case for intermediate non-stationary states. Variations in the expectation value of x indicate that the non-stationary state is delocalized.

Again, I reduce the timescale to 1ps.

Slide 22. We see how, for the limit non-stationary state corresponding to $\alpha = 90^\circ$, we obtain the expected result. However, for $\alpha = 45^\circ$, the expectation value of the position for this time scale shows oscillations and is less than zero (position of the maximum of the barrier), varying around the cutoff point with the barrier (dotted horizontal line around $\approx -0.2 \text{ \AA}$). That is, the non-stationary state is found oscillating in the well on the left, colliding with the barrier and penetrating it slightly. For a sufficient time, as we can see in the graph for $\alpha = 45^\circ$ of the previous figure, the state ends up being transmitted to the other well, and completing the inversion motion. For the rest of the intermediate non-stationary states something similar happens, only with smaller oscillations in the expected value of the position.

Slide 23. We believe that the best way to understand this effect is to visualize it, so we have created a series of quantum mechanical simulations of the time evolution of these non-stationary states. Next, I present those corresponding to the limit states. In them, we see how the probability density in the well on the right increases with time, due to the tunneling of the ammonia molecule.

Slide 24. Conclusions: First. Tunneling is a purely quantum effect, difficult to understand, whose visualization facilitates its understanding.

Second. Quantum Mechanics tells us that a system has a series of eigenvalues of energy and eigenfunctions, which we obtain by solving the Schrödinger equation for a characteristic Hamiltonian operator. However, the system can also be described, as shown in this work, by non-stationary states formed as superpositions of stationary states of different energies. Non-stationary states can be created experimentally using spectroscopic techniques, and only when a measurement is made, the states superposition collapses into the eigenstate obtained from the measured magnitude.

Third. The expected values of an observable corresponding to the eigenfunctions of the Hamiltonian, the stationary states, do not vary with time as it classically occurs. To do this, it is necessary to create a non-stationary state formed by the superposition of stationary states of different energies.

Fourth. In the inversion motion of the ammonia molecule, described by two identical potential wells corresponding to the equilibrium pyramidal geometries of the molecule, separated by a potential barrier corresponding to the planar geometry of the molecule, the stationary states that fall below the barrier are symmetrically delocalized with respect to the barrier and there is no possibility that they evolve in time.

Fifth. To observe tunneling in the inversion motion of the ammonia molecule, it is therefore necessary to even create localized non-stationary states in one of the wells and follow their quantum mechanical time evolution.

Sixth. The initial non-stationary states are constructed as a linear combination of stationary states that allows us to localize that state in one of the potential wells.

Seventh. The initial non-stationary states localized in one of the potential wells evolve over time crossing the barrier and moving to the other potential well by tunneling. This movement is uniform for the initial non-stationary states formed by the superposition of two stationary states and irregular for the combination of more than two stationary states, causing the state to oscillate around its initial equilibrium position. That is, the tunneling probability is greater for non-stationary states formed by the superposition of two stationary states than for non-stationary states constructed as a linear combination of more than two stationary states.