2. Evolution of the particle's wave function

Each of the states \( |\varphi_i\rangle \) with its wave function \( \varphi_i(x) \), describes a stationary state, which leads to time-independent physical predictions. Time evolution appears only when the state vector is a linear combination of several kets \( |\varphi_n\rangle \). We shall consider here a very simple case, for which at time \( t = 0 \) the state vector \( |\psi(0)\rangle \) is:

\[
|\psi(0)\rangle = \frac{1}{\sqrt{2}} \left[ |\varphi_1\rangle + |\varphi_2\rangle \right]
\]

(14)

a. WAVE FUNCTION AT THE INSTANT \( t \)

Apply formula (D-54) of chapter III; we immediately obtain:

\[
|\psi(t)\rangle = \frac{1}{\sqrt{2}} \left[ e^{-i\frac{E_1}{2ma^2}t} |\varphi_1\rangle + e^{-i\frac{E_2}{2ma^2}t} |\varphi_2\rangle \right]
\]

(15)

or, omitting a global phase factor of \( |\psi(t)\rangle \):

\[
|\psi(t)\rangle \propto \frac{1}{\sqrt{2}} \left[ |\varphi_1\rangle + e^{-i\omega_{21}t} |\varphi_2\rangle \right]
\]

(16)

with:

\[
\omega_{21} = \frac{E_2 - E_1}{\hbar} = \frac{3\pi^2\hbar}{2ma^2}
\]

(17)

b. EVOLUTION OF THE SHAPE OF THE WAVE PACKET

The shape of the wave packet is given by the probability density:

\[
|\psi(x,t)|^2 = \frac{1}{2} \varphi_1^2(x) + \frac{1}{2} \varphi_2^2(x) + \varphi_1(x) \varphi_2(x) \cos \omega_{21}t
\]

(18)

We see that the time variation of the probability density is due to the interference term in \( \varphi_1 \varphi_2 \). Only one Bohr frequency appears, \( \nu_{21} = (E_2 - E_1)/\hbar \), since the initial state (14) is composed only of the two states \( |\varphi_1\rangle \) and \( |\varphi_2\rangle \). The curves corresponding to the variation of the functions \( \varphi_1^2 \), \( \varphi_2^2 \) and \( \varphi_1 \varphi_2 \) are traced in figures 4-a, b and c.

Using these figures and relation (18), it is not difficult to represent graphically the variation in time of the shape of the wave packet (cf. fig. 5): we see that the wave packet oscillates between the two walls of the well.

---

**Figure 4**

Graphical representation of the functions \( \varphi_i^2 \) (the probability density of the particle in the ground state), \( \varphi_i^2 \) (the probability density of the particle in the first excited state) and \( \varphi_1 \varphi_2 \) (the cross term responsible for the evolution of the shape of the wave packet).

---

**Figure 5**

Periodic motion of a wave packet obtained by superposing the ground state and the first excited state of a particle in an infinite well. The frequency of the motion is the Bohr frequency \( \omega_{21}/2\pi \).
The variation of $\langle X \rangle (t)$ is represented in figure 6. In dashed lines, the variation of the position of a classical particle has been traced, for a particle moving to and fro in the well with an angular frequency of $\omega_{21}$ (since it is not subjected to any force except at the walls, its position varies linearly with $t$ between 0 and $a$ during each half-period).

We immediately notice a very clear difference between these two types of motion, classical and quantum mechanical. The center of the quantum wave packet, instead of turning back at the walls of the well, executes a movement of smaller amplitude and retraces its steps before reaching the regions where the potential is not zero. We see again here a result of § D-2 of chapter I: since the potential varies infinitely quickly at $x = 0$ and $x = a$, its variation within a domain of the order of the dimension of the wave packet is negligible, and the motion of the center of the wave packet does not obey the laws of classical mechanics (see also chapter III, § D-1-d-γ). The physical explanation of this phenomenon is the following: before the center of the wave packet has touched the wall, the action of the potential on the ”edges” of this packet is sufficient to make it turn back.

**COMMENT:**

The mean value of the energy of the particle in the state $|\psi(t)\rangle$ calculated in (15) is easy to obtain:

$$\langle H \rangle = \frac{1}{2} E_1 + \frac{1}{2} E_2 = \frac{5}{2} E_1$$

as is:

$$\langle H^2 \rangle = \frac{1}{2} E_1^2 + \frac{1}{2} E_2^2 = \frac{17}{2} E_1^2$$

which gives:

$$\Delta H = \frac{3}{2} E_1$$

Note in particular that $\langle H \rangle$, $\langle H^2 \rangle$ and $\Delta H$ are not time-dependent; since $H$ is a constant of the motion, this could have been foreseen. In addition, we see from the preceding discussion that the wave packet evolves appreciably over a time of the order of:

$$\Delta t \approx \frac{1}{\omega_{21}}$$

Using (26) and (27), we find:

$$\Delta H \cdot \Delta t \approx \frac{3}{2} E_1 \times \frac{\hbar}{3 E_1} = \frac{\hbar}{2}$$

We again find the time-energy uncertainty relation.
1. Description of the model

In the ammonia molecule NH₃, the three hydrogen atoms form the base of a pyramid whose apex is the nitrogen atom (cf. fig. 1). We shall study this molecule by using a simplified model with the following features: the nitrogen atom, much heavier than its partners, is motionless; the hydrogen atoms form a rigid equilateral triangle whose axis always passes through the nitrogen atom. The potential energy of the system is thus a function of only one parameter, the (algebraic) distance $x$ between the nitrogen atom and the plane defined by the three hydrogen atoms*. The shape of this potential energy $V(x)$ is given by the solid-line curve in figure 2. The symmetry of the problem with respect to the $x = 0$ plane requires $V(x)$ to be an even function of $x$. The two minima of $V(x)$ correspond to two symmetrical configurations of the molecule in which, classically, it is stable: we shall choose the energy origin such that its energy is then zero. The potential barrier at $x = 0$, of height $V_1$, expresses the fact that, if the nitrogen atom is in the plane of the hydrogen atoms, they repel it. Finally, the increase in $V(x)$ when $|x|$ is greater than $b$ corresponds to the chemical bonding force which insures the cohesion of the molecule.

![Figure 1: Schematic drawing of the ammonia molecule.](image)

![Figure 2: Potential energy $V(x)$ vs. distance $x$.](image)

2. Eigenfunctions and eigenvalues of the Hamiltonian

a. INFINITE POTENTIAL BARRIER

Before calculating the eigenfunctions and eigenvalues of the Hamiltonian corresponding to the “square” potential of figure 2, we are going to assume, in this first stage, that the potential barrier $V_0$ is infinite (in which case, no tunnel effect is possible). This will lead us to a better understanding of the consequences of the tunnel effect across the finite potential barrier of figure 2. We shall therefore consider, first of all, a particle in a potential $V(x)$ composed of two infinite wells of width $a$ centered at $x = \pm b$ (fig. 3). If the particle is in one of these two wells, it obviously cannot go into the other one.

* In the actual model, the potential energy is a function of the internuclear distances $R$, but we can neglect this term and assume the bond lengths $A$ and $B$ fixed.
Each of the two wells of figure 3 is similar to the one studied in complement $H_1$, in § 2-c β. We can therefore use the results obtained in this complement. The possible energies of the particle are:

$$E_n = \frac{n^2\hbar^2}{2m}$$

with:

$$k_n = \frac{n\pi}{a}$$

In the rest of the calculations, it is convenient to change bases, in each of the eigensubspaces of the Hamiltonian of the particle. Since the function $V(x)$ is even, this Hamiltonian $H$ commutes with the parity operator $M$ (cf. complement $H_1$, § 4). In this case, a basis of eigenvectors of $H$ can be found which are even or odd; the wave functions of these vectors are the symmetrical and antisymmetrical linear combinations:

$$\psi_1(x) = \frac{1}{\sqrt{2}} \left[ \psi_1^e(x) + \psi_2^o(x) \right]$$

$$\psi_2(x) = \frac{1}{\sqrt{2}} \left[ \psi_1^e(x) - \psi_2^o(x) \right]$$

In the states $|\psi_1^e\rangle$ and $|\psi_2^o\rangle$, the particle can be found in one or the other of the two potential wells.

In what follows, we shall confine ourselves to the study of the ground state, for which the wave functions $\psi_1^e(x)$, $\psi_2^o(x)$, $\phi_1^e(x)$ and $\phi_2^o(x)$ are shown in figure 5.

![Figure 3](image)

**Figure 3**

When the height $V_0$ of the potential barrier is large, we have two practically infinite potential wells of width $a$ whose centers are separated by a distance of $2b$.

![Figure 5](image)

**Figure 5**

The states $\psi_1^e(x)$ and $\psi_2^o(x)$, shown in figure 5, are stationary states with the same energy, respectively localized in the right-hand well and the left-hand well of figure 3. To use the symmetry of the problem, it is more convenient to choose as stationary states the symmetrical state $\phi_1^e(x)$ and the antisymmetrical state $\phi_2^o(x)$, linear combinations of $\psi_1^e(x)$ and $\psi_2^o(x)$ (figure 6).

![Figure 6](image)

**Figure 6**

When one takes the finite height $V_0$ of the barrier into account, one finds that the energy spectrum of figure 4 is modified: each level splits into two distinct ones. The Bohr frequencies $\Omega_1/2\pi$ and $\Omega_2/2\pi$ corresponding to tunneling from one well to the other are the inversion frequencies of the ammonia molecule for the first two vibration levels. The tunnel effect is more important in the higher vibration level, so $\Omega_2 > \Omega_1$. 
Finally, in figure 7, we have shown the shape of the eigenfunctions \( \chi_0^1(x) \) and \( \chi_1^1(x) \) which are given by equations (5), (7) and (10), once \( k_0^1 \) and \( k_1^1 \) have been determined from (14) and (15). We see that they greatly resemble the functions \( \psi_0^1(x) \) and \( \psi_1^1(x) \) of figure 5, the essential difference being that the wave function is no longer zero in the interval \(-b + a/2 \leq x \leq b + a/2\). The reason for introducing the \( \psi_0^1 \) and \( \psi_1^1 \) basis in the preceding paragraph can now be understood: the eigenfunctions \( \chi_0^1 \) and \( \chi_1^1 \), in the presence of the tunnel effect, resemble \( \psi_0^1 \) and \( \psi_1^1 \) much more than \( \psi_0^1 \) and \( \psi_1^1 \).

\section{EQUILIBRATION OF THE MOLECULE. INVERSION FREQUENCY}

Assume that at time \( t = 0 \), the molecule is in the state:

\[
|\psi(t = 0)\rangle = \frac{1}{\sqrt{2}} \left[ |\chi_0^1\rangle + |\chi_1^1\rangle \right]
\]  

(16)

The state vector \( |\psi(t)\rangle \) at time \( t \) can be obtained by using the general formula (D-54) of chapter III; we obtain:

\[
|\psi(t)\rangle = \frac{1}{\sqrt{2}} e^{-\frac{J_1 t}{2\hbar}} \left[ e^{i\frac{E_0 t}{2\hbar}} |\chi_0^1\rangle + e^{-i\frac{E_0 t}{2\hbar}} |\chi_1^1\rangle \right]
\]  

(17)

From this we deduce the probability density:

\[
|\psi(x, t)|^2 = \frac{1}{2} [\chi_0^1(x)]^2 + \frac{1}{2} [\chi_1^1(x)]^2 + \cos(\Omega t) \chi_0^1(x) \chi_1^1(x)
\]  

(18)

The variation with respect to time of this probability density is simple to obtain graphically from the curves of figure 7. They are shown in figure 8. For \( t = 0 \) (fig. 8-a), we see that the initial state chosen in (16) corresponds to a probability density which is concentrated in the right-hand well (in the left-hand well, the functions \( \chi_0^1 \) and \( \chi_1^1 \) are of opposite sign and very close in absolute value, so their sum is practically zero). It can therefore be said that the particle, initially, is practically in the right-hand well. At time \( t = \pi/2\Omega \) (fig. 8-b), it has moved...