

4.5.1 Model of the NH_3 Molecule

The ammonia molecule NH_3 has the shape of a pyramid (Fig. 4.7a), where the nitrogen atom is at the apex and the three hydrogen atoms form the base in the shape of an equilateral triangle. The plane of the three hydrogen atoms is denoted P and the perpendicular to this plane passing through the nitrogen atom is denoted \mathcal{D} . The distance x represents the position of the intersection of P with \mathcal{D} . The position of the nitrogen atom is chosen as the origin of the x axis. For low excitation energies, the molecule preserves its pyramidal shape and the nitrogen atom remains fixed.

Qualitatively, the variations of the potential energy $\mathcal{V}(x)$ with x are as follows. At the equilibrium position $x = b$, $\mathcal{V}(x)$ has a minimum (Fig. 4.7b). If we force x to become smaller, the energy increases; it goes through a maximum for $x = 0$, which corresponds to an unstable state where the four atoms are in the same plane. If x becomes negative, the molecule is turned over like an umbrella in the wind. For symmetry reasons there exists another minimum for $x = -b$ and the potential energy satisfies $\mathcal{V}(x) = \mathcal{V}(-x)$.

In the following we replace the actual potential $\mathcal{V}(x)$ by the simplified square-well potential $V(x)$ represented by dotted lines in Fig. 4.7b. For this potential, which reproduces the main interesting features of $\mathcal{V}(x)$, we study the quantum motion of a “particle” representing the collective motion of the three hydrogen atoms, assuming that they stay in the same plane. The mass m of the particle is equal to $3m_{\text{H}}$, where m_{H} is the mass of a hydrogen atom.

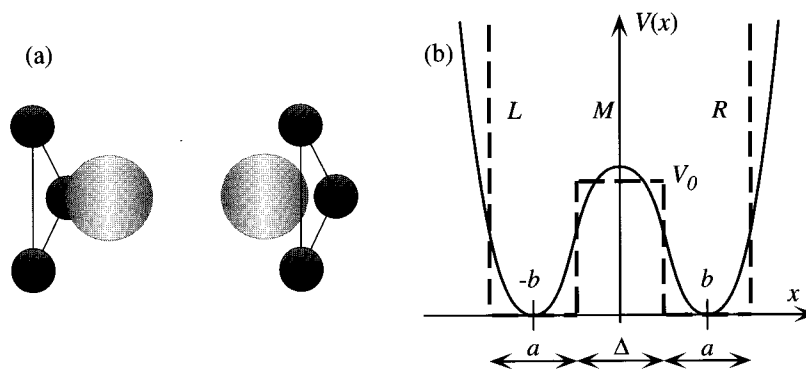


Fig. 4.7. The ammonia molecule: (a) the two classical configurations; (b) the actual potential (*full line*) and the simplified potential (*dotted line*) which describes the inversion of the molecule

4.5.2 Wave Functions

Following the same procedure as in Sect. 4.3, it is straightforward to find the stationary states in this problem. We concentrate on the case $E < V_0$, for which the classical motion of the “particle” is confined in one of the

potential wells (left or right), i. e. the molecule cannot turn over classically. The solutions to the quantum problem are sinusoids in the regions L and R and exponentials in the middle region M. Since the wave functions have to vanish for $x = \pm(b + a/2)$, the eigenstates of the Hamiltonian can be written

$$\begin{aligned} \psi(x) &= \pm\lambda \sin k(b + a/2 + x) && \text{region L,} \\ \psi(x) &= \begin{cases} \mu \cosh Kx & \text{symmetric solution} \\ \mu \sinh Kx & \text{antisymmetric solution} \end{cases} && \text{region M,} \\ \psi(x) &= \lambda \sin k(b + a/2 - x) && \text{region R,} \end{aligned} \quad (4.57)$$

where we set, as previously, $k = \sqrt{2mE}/\hbar$ and $K = \sqrt{2m(V_0 - E)}/\hbar$. These two types of solutions are represented in Fig. 4.8.

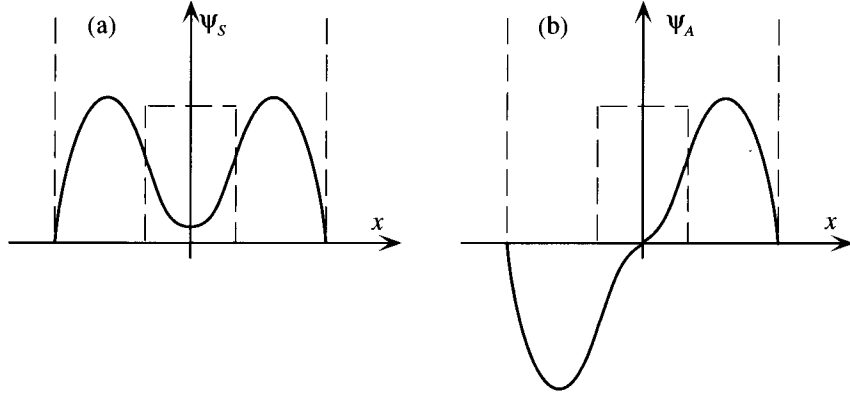


Fig. 4.8. Symmetric solution (a) and antisymmetric solution (b), in the symmetric double-well model of the ammonia molecule

The continuity equations for the wave function and its derivative at the points $x = \pm(b - a/2)$ lead to the conditions

$$\begin{aligned} \tan ka &= -\frac{k}{K} \coth K(b - a/2) && \text{for a symmetric solution } \psi_S, \\ \tan ka &= -\frac{k}{K} \tanh K(b - a/2) && \text{for an antisymmetric solution } \psi_A. \end{aligned}$$

In order to obtain some physical insight with simple algebra, we consider the case where the ground-state energy E is very small compared with the height V_0 of the potential barrier. This leads to $K \sim \sqrt{2mV_0}/\hbar \gg k$. In addition, we assume that the central potential barrier is wide enough that $K\Delta \gg 1$, where $\Delta = 2b - a$ is the width of this barrier. These assumptions hold in the case of the ammonia molecule, as we shall see below. We then have

$$\tan ka \simeq -\frac{k}{K} (1 \pm 2e^{-K\Delta}), \quad (4.58)$$

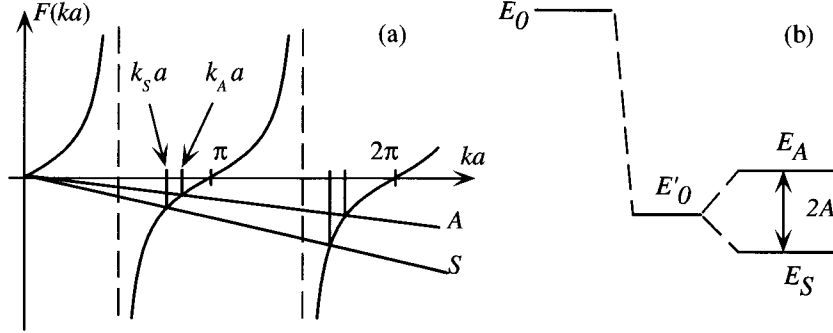


Fig. 4.9. (a) Graphical determination of the energy levels in the double well; (b) positions of the two first energy levels. They are both lower than the ground-state energy of a single potential well similar to L or R ($E_0 \rightarrow E'_0$), and we observe a splitting of these levels ($E'_0 \rightarrow E_A$ and E_S) owing to the coupling between the two wells due to quantum tunneling

where the + sign corresponds to ψ_S and the - sign to ψ_A . This equation allows us to calculate the quantized values of ka . These values appear on the graph in Fig. 4.9 as the abscissae of the intersections of the successive branches of $y = \tan ka$ with the two straight lines $y = -\varepsilon_A ka$ and $y = -\varepsilon_S ka$. These intersections are located in the vicinity of $ka \sim \pi$. The two constants ε_A and ε_S are

$$\varepsilon_A = \frac{1}{Ka} (1 - 2e^{-K\Delta}), \quad \varepsilon_S = \frac{1}{Ka} (1 + 2e^{-K\Delta}). \quad (4.59)$$

They are close to each other and such that $\varepsilon_A < \varepsilon_S \ll 1$, since $Ka \gg ka \sim \pi$.

4.5.3 Energy Levels

We denote by k_S and k_A the two (close) values of k corresponding to the eigenstates ψ_S and ψ_A of lowest energy. The graph in Fig. 4.9 shows the following:

1. The two quantities k_S and k_A are slightly smaller than π/a , which is the lowest value of the wave number in an individual well, similar to L or R, of width a with infinitely high and thick walls.
2. The quantity k_S is slightly smaller than k_A ; consequently the respective energies of the two lowest-lying levels

$$E_S = \hbar^2 k_S^2 / 2m, \quad E_A = \hbar^2 k_A^2 / 2m \quad (4.60)$$

are such that $E_S < E_A$.

In the range of parameters considered here ($K \gg k$, $Ka \gg 1$), we find

$$k_S \sim \frac{\pi}{a(1 + \varepsilon_S)}, \quad k_A \sim \frac{\pi}{a(1 + \varepsilon_A)}, \quad (4.61)$$

with ε_S and $\varepsilon_A \ll 1$. Putting together (4.58), (4.60) and (4.61), we obtain the mean energy $E'_0 = (E_A + E_S)/2$:

$$E'_0 \simeq \frac{\hbar^2 \pi^2}{2ma^2} \left(1 - \frac{2}{Ka} \right). \quad (4.62)$$

The splitting $E_A - E_S$ between these two energy levels will be of particular interest. It is given by

$$E_A - E_S \equiv 2A \simeq \frac{\hbar^2 \pi^2}{2ma^2} \left[\frac{1}{(1 + \varepsilon_A)^2} - \frac{1}{(1 + \varepsilon_S)^2} \right], \quad (4.63)$$

where

$$A \simeq \frac{\hbar^2 \pi^2}{2ma^2} \frac{4e^{-K\Delta}}{Ka}. \quad (4.64)$$

Since K is approximately equal to $\sqrt{2mV_0}/\hbar$, we see that A decreases *exponentially* when the width Δ or the height V_0 of the intermediate potential barrier increases. We also note that A vanishes as $\exp(-\text{const.}/\hbar)$ in the limit $\hbar \rightarrow 0$.

4.5.4 The Tunnel Effect and the Inversion Phenomenon

Classically, for $E < V_0$, the plane of the three hydrogen atoms in the molecule is either on the right or on the left. No transition $L \leftrightarrow R$ is possible. There are two ground states of equal energy, one in the L configuration, the other in the R configuration. In contrast, the two lowest-lying energy states of the quantum molecule have different energies. The two corresponding wave functions have well-defined parities: one is symmetric (ψ_S), the other is anti-symmetric (ψ_A). In both cases the probabilities (modulus squared of ψ) that the particle (or the triangle of hydrogen atoms) is on the right and on the left are *equal*.

For both eigenstates ψ_S and ψ_A the probability density is nonzero in the M region, which is classically forbidden. Again we are facing the possibility that a quantum particle can be located in regions where its total energy is less than the local potential energy. This results in a lowering of the energies of the two lowest eigenstates of the Hamiltonian with respect to the case $V_0 = \infty$. Indeed, in that case there would be two possible ground states for the molecule, corresponding to the L and R configurations (or to any linear combination of these states), with the same energy $E_0 = \hbar^2 \pi^2 / (2ma^2)$. Because V_0 is finite the molecule sees an effective size of each well (L or R) which is slightly larger than a ($a_{\text{eff}} \sim a + K^{-1}$); this explains the lowering of the mean energy $E_0 \rightarrow E'_0$.

This global lowering is followed by a splitting $E'_0 \rightarrow E'_0 \pm A$ into two sublevels. The physical origin of this splitting is the tunneling effect, i. e. the possibility for the particle to cross the potential barrier and pass from one well to the other. We now investigate this very important phenomenon in more detail.

The wave functions ψ_S and ψ_A are eigenstates of the Hamiltonian. We can combine them to form other physically acceptable states of the system. Two linear combinations are particularly interesting:

$$\psi_L = (\psi_S - \psi_A)/\sqrt{2} \quad \text{and} \quad \psi_R = (\psi_S + \psi_A)/\sqrt{2}. \quad (4.65)$$

These wave functions describe states for which the probability density is concentrated nearly entirely on the left for ψ_L and on the right for ψ_R . These correspond to the “classical” configurations, for which the molecule is oriented towards either the left- or the right-hand side (Fig. 4.10).

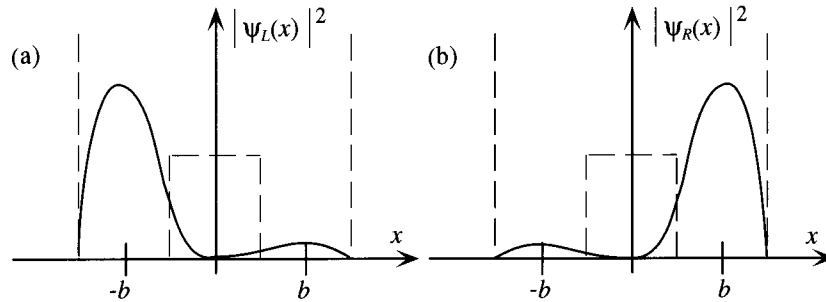


Fig. 4.10. Classical configurations of the ammonia molecule

Consider a wave function $\psi(x, t)$ equal to ψ_R at time $t = 0$. It describes a molecule localized in the “right” configuration. Its time evolution is

$$\begin{aligned} \psi(x, t) &= \frac{1}{\sqrt{2}} \left(\psi_S(x) e^{-iE_S t/\hbar} + \psi_A(x) e^{-iE_A t/\hbar} \right) \\ &= \frac{e^{-iE_S t/\hbar}}{\sqrt{2}} \left(\psi_S(x) + \psi_A(x) e^{-i\omega t} \right), \end{aligned} \quad (4.66)$$

where we have introduced the *Bohr frequency* $\hbar\omega = E_A - E_S = 2A$.

We notice that after a time $t = \pi/\omega = \pi\hbar/(2A)$, the wave function $\psi(x, t)$ is, up to a phase factor, proportional to ψ_L , and the molecule is in the *left* configuration! At time $t = 2\pi/\omega$ the wave function $\psi(x, t)$ is again proportional to ψ_R : the molecule is back to the right configuration. In other words the superposition (4.66) represents a state of the molecule which oscillates from right to left at the Bohr frequency $\nu = \omega/2\pi$. The ammonia molecule prepared in a classical configuration at $t = 0$, *turns over* periodically because of quantum tunneling. This phenomenon, called the *inversion* of the

NH_3 molecule, plays a fundamental role in the principle of the ammonia *maser*, which we shall discuss in Chap. 6.

The quantity A controls the frequency at which the transition from one minimum of the potential to the other occurs. Comparing the expression (4.64) for A with the tunneling probability found in Sect. 3.6.4, we notice that the two expressions are very similar, the essential point being the presence of the exponential term. For ammonia, the energy difference $2A$ is small compared with typical binding energies in atomic and molecular physics: $2A \sim 10^{-4}$ eV. The frequency ν and period T of the oscillation are

$$\nu = \frac{\omega}{2\pi} = \frac{2A}{h} \simeq 24 \text{ GHz}, \quad T = \frac{1}{\nu} = \frac{h}{2A} \simeq 4.2 \times 10^{-11} \text{ s}.$$

As we shall see in Chap. 6, the oscillation is associated with the emission or absorption of electromagnetic radiation. The corresponding wavelength is $\lambda = c/\nu = 1.25 \text{ cm}$. This wavelength can be measured with great accuracy, and it constitutes a “fingerprint” of ammonia, which, for instance, allows us to detect the presence of this molecule in the interstellar medium.

4.6 Other Applications of the Double Well

The general formalism we have just developed for the ammonia molecule can be extended to many other symmetric double-well situations. Consider for instance two identical atoms A_1 and A_2 at a distance Δ from one another. An electron sees a double well, sketched in Fig. 4.11, each minimum being centered on one of the atoms. We choose the origin of energy such that $V \rightarrow 0$ for $x \rightarrow \infty$. If Δ is sufficiently large, one may, to a good approximation, consider that $V \sim 0$ in the middle region between the two atoms.

An electron bound to one atom in a given energy level $E_0 < 0$ must cross a potential barrier of height $|E_0|$ and width Δ in order to jump to the other atom. We want to estimate, in terms of Δ and E_0 , the order of magnitude of the typical time T needed for this transition.

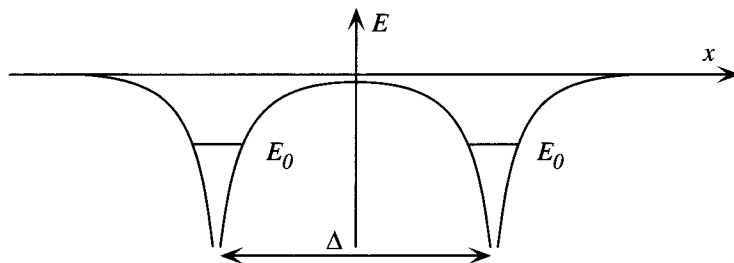


Fig. 4.11. Double well seen by an electron when two atoms are separated by a distance Δ

We shall assume here that the kinetic energy E_k of the bound electron is of the order of $|E_0|$ (for hydrogen atoms, this is exact because of the virial theorem applied to the Coulomb potential). In the exponential related to the tunnel effect, we have $K = \sqrt{2m|E_0|}/\hbar$. Since the electron is bound in an atom, we have $Ka \sim \pi$ (see Chap. 11). The essential result of the previous section, i. e. the exponential dependence of the oscillation frequency on the parameter $K\Delta$, remains valid. Therefore we rewrite (4.64) in the form $A \sim E_k e^{-K\Delta} \sim |E_0| e^{-K\Delta}$, where we neglect a numerical factor of order unity.

In a molecule or in a solid, the interatomic distance is of the order of one or a few angstroms. In a gas at room temperature and atmospheric pressure, the interatomic distance is $\sim 30 \text{ \AA}$. The least bound electrons in an atom (*valence electrons*) have binding energies of a few eV; we then find

$$\begin{aligned} \text{Solid: } \Delta = 2 \text{ \AA}, |E_0| = 4 \text{ eV}, \quad A = 1 \text{ eV}; T = 10^{-15} \text{ s}, \\ \text{Gas: } \Delta = 30 \text{ \AA}; |E_0| = 4 \text{ eV} \quad A = 10^{-12} \text{ eV}; T = 10^{-3} \text{ s}. \end{aligned}$$

We see that tunneling is important for valence electrons inside a molecule or in a solid. These electrons jump rapidly from one atom to another, and they are delocalized in the global molecular structure. In contrast, the corresponding phenomenon is completely negligible in gases. Indeed, because of the thermal motion, two given atoms or molecules in a gas remain at a relative distance of the order of 30 \AA only for a time shorter than 10^{-10} s . The oscillation associated with the tunneling effect has a period of 10^{-3} s and it cannot have an appreciable effect on a timescale as short as 10^{-10} s . In a gas, it is justified to consider that even the least bound electrons “belong” to a given atom.

The essential ingredient in the above reasoning is the exponential variation of A with Δ and $K = \sqrt{2m|E_0|}/\hbar$. This very large variation explains why, in going from a system to another one which seems similar, the characteristic times may be extremely different. For a system where $K\Delta$ is slightly too large, the oscillation period T can become so incredibly large that tunneling may safely be neglected.

The particularly interesting case of NH_3 and the similar molecules ND_3 , PH_3 , AsH_3 , etc. is treated in detail by Townes and Schawlow,² who give more realistic forms of the potentials. Consider, for instance, the passage from NH_3 to AsH_3 :

$$\begin{aligned} \text{NH}_3: V_0 = 0.25 \text{ eV}, b = 0.4 \text{ \AA} : \nu_0 = 2.4 \times 10^{10} \text{ Hz}; \\ \text{AsH}_3: V_0 = 1.5 \text{ eV}, b = 2 \text{ \AA} : \nu_0 = 1.6 \times 10^{-8} \text{ Hz}. \end{aligned}$$

A change by a factor 6 in V_0 and a factor 5 in b induces a dramatic decrease of the inversion frequency, by 18 orders of magnitude! The frequency found for AsH_3 corresponds to one oscillation every two years, and its detection

² C.H. Townes and A.L. Schawlow, *Microwave Spectroscopy*, Chap. 12, McGraw-Hill, New York (1955).

is completely beyond the reach of current experimental techniques. In other words AsH_3 , which seems to differ only moderately from NH_3 , behaves as a classical object from the point of view of the tunneling phenomenon that we have considered here, simply because the As atom is ~ 5 times larger than the nitrogen atom.

The stability of systems which do not have definite symmetry properties is frequently encountered on the microscopic scale. Among many examples, there is the case of optical isomers in organic chemistry. The simplest example is the molecule CHClFBr . The tetrahedral structure of the bonding of carbon results in the fact that two nonequivalent configurations exist. They are represented in Fig. 4.12 and are called optical isomers. Such isomers have different optical, chemical and biological properties. The situation for these isomers is similar to the situation we have just described. Such molecules should, in principle, oscillate from one configuration to the other. However, both types of such molecules are perfectly stable in practice. This is due to the fact that the inversion period T is so large that one cannot detect the oscillation.

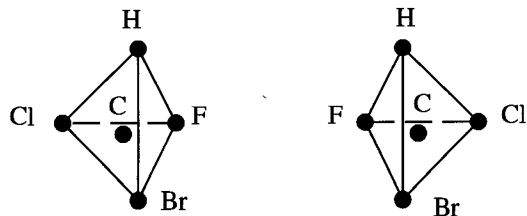


Fig. 4.12. Two optical isomers: can one detect the tunneling oscillation between these two configurations?

Further Reading

- The history of Planck's procedure for explaining the black-body radiation is presented in J. Mehra and H. Reichenberg, *The Historical Development of Quantum Theory* Vol. 1, Chap. 1, Springer, New York (1982).
- The principle and applications of the Penning trap are presented by L.S. Brown and G. Gabrielse, "Geonium theory: physics of a single electron or ion in a Penning trap", *Rev. Mod. Phys.* **58**, 223 (1986). See also G. Gabrielse, "Ultracold antiprotons", *Sci. Am.*, January 1993; J.-L. Basdevant and J. Dalibard, "The Quantum Mechanics Solver: How to Apply Quantum Theory to Modern Physics", Springer, Berlin, Heidelberg (2000), Chap. 13.
- Square-well potentials in semiconductor physics: M.A. Reed, "Quantum dots", *Sci. Am.*, February 1993, p. 98; L.L. Chang and L. Esaki, "Semicon-