An introduction to time-dependent quantum chemistry
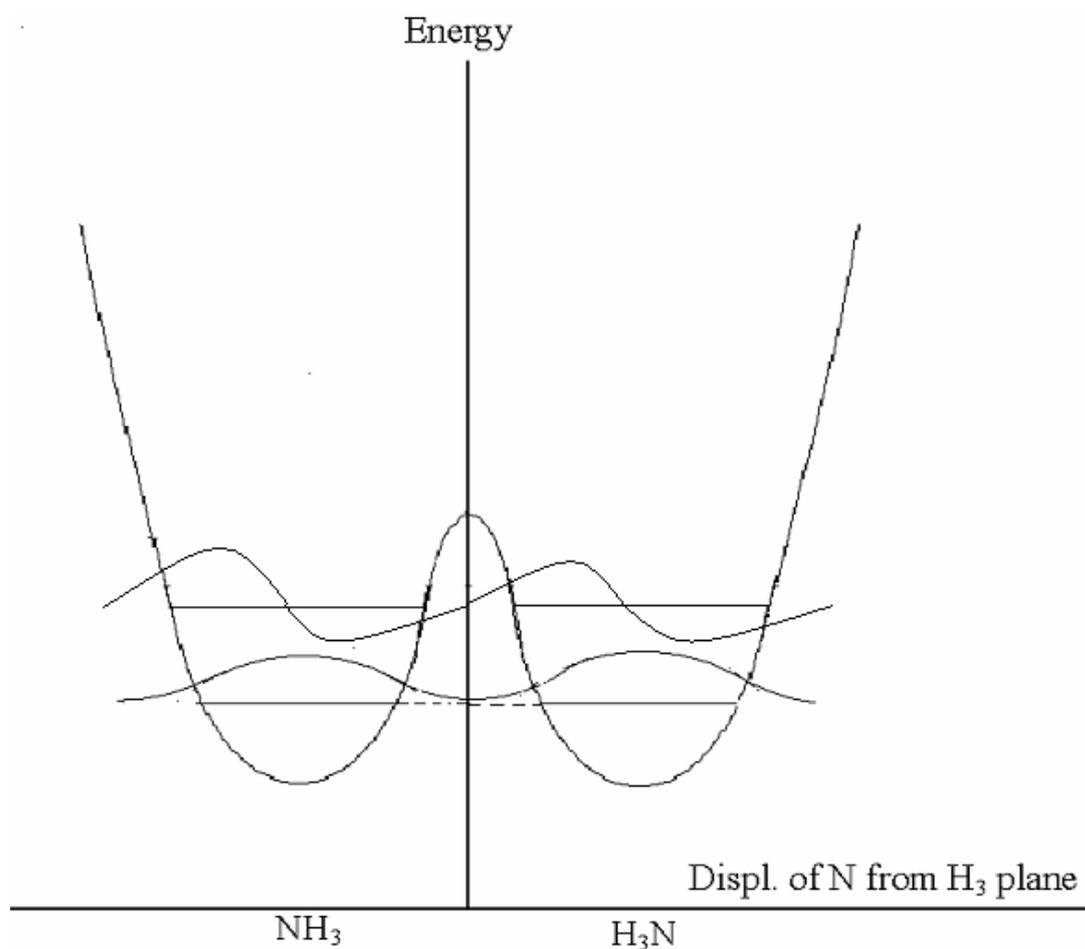
Molecular Inversion in Ammonia

(A chemical example of quantum tunnelling)

Senior Sophister 2014

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Stationary states and time-dependent states

In our quantum chemistry course hitherto we have been concerned principally with stationary states. Although we have had to invoke the motions of electrons in 'correlation energy' and in London long-range forces, we have been describing electrons in atoms and molecules by 'stationary wave' functions such as those describing s, p, d, σ and π orbitals with their characteristic shapes and nodal patterns like violin strings or resonating organ pipes. These wave functions contain no time dependence. The vibration and the rotation of molecules also gives rise to 'standing wave' vibrational and rotational wave functions, which also contain no time component.

(a) Stationary states

The discovery that particles can be diffracted like light waves prompted Schrödinger to apply a wave equation to them. First let's see how they would be described using the language previously applied to wave motion. Suppose that the electrons in the vicinity of an atom or molecule are in a *stationary state*. This means that they have no time dependence, so they resemble the stationary waves that you see in a violin string or organ pipe or sometimes on the surface of your cup of tea after dropping in a lump of sugar. The probability of finding an electron will vary over the atomic region of space and, like the amplitude of the waves in the cases just mentioned, the electron's 'amplitude' would similarly be described by a function. If we confine our discussion to one dimension, such a 'wave function' (WF) could be

$$f(x) = A\sin\frac{2\pi x}{\lambda} \qquad \text{or} \qquad f(x) = A\cos\frac{2\pi x}{\lambda}$$

(Either of them describes a wave which repeats after a distance $x = \lambda$). Because it makes the writing easier let's combine these two in the way that we can with sine and cosine functions ($e^{i\theta} = \cos\theta + i\sin\theta$) to get

$$f(x) = A e^{2\pi i x/\lambda}$$

Now apply to this function to an equation that describes stationary waves

$$\frac{d^2 f(x)}{dx^2} = a\, f(x)$$

where a is a constant. The left hand side is

$$\frac{d^2 f(x)}{dx^2} = -A\left(\frac{2\pi}{\lambda}\right)^2 e^{2\pi i x/\lambda}$$

which is in accord with the previous wave (eigenvalue) equation. But the de Broglie equation ($\lambda = h/p$) allows the wavelength λ to be expressed in terms of momentum so that the last equation continues as

$$\frac{d^2 f(x)}{dx^2} = -A\left[\frac{2\pi p}{h}\right]^2 e^{2\pi i x/\lambda} = -\left[\frac{2\pi p}{h}\right]^2 f(x) = -\left[\frac{p}{\hbar}\right]^2 f(x)$$

The final step is to recognize that if this equation is multiplied by $-\hbar^2/2m$ it produces $p^2/2m$ which is the kinetic energy $\frac{1}{2}mv^2$.

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

If E were the whole of the energy of the particle (as it would be if it were a *free* particle, unaffected by its surroundings) then this eigenvalue equation is

$$\mathscr{H}f(x) = E\,f(x)$$

where $\mathscr{H}$ is the Hamiltonian operator for the system, $\mathscr{H} \equiv -\dfrac{\hbar}{2m}\dfrac{d^2}{dx^2}$, 'extracting' the energy E as an eigenvalue. The next step in the development of Schrödinger's equation is to extend $\mathscr{H}$ so as to include not only the kinetic energy but also the potential energy terms $\mathscr{V}$. And finally the space is extended from one dimension to three dimensions so that the Hamiltonian operator now reads

$$\mathscr{H} = -\frac{\hbar}{2m}\left[\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right] + \mathscr{V}$$

Denoting the factor in brackets as the Laplacian operator ∇^2, the Schrödinger equation is written

$$\left\{ -\frac{\hbar^2}{2m}\left[\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right] + \mathcal{H}(x,\,y,\,z) \right\} \psi(x,\,y,\,z) = E\,\psi(x,\,y,\,z)$$

or simply

$$\mathcal{H}\psi(x,\,y,\,z) = E\,\psi(x,\,y,\,z)$$

When solved, this equation gives the various *quantum states* of the system through its wave function and energy pairs $\psi_1, E_1;\quad \psi_2, E_2;\quad \psi_3, E_3;\quad \psi_4, E_4; \ldots$

(b) Time-dependent states

Now suppose that the wave is moving as you observe on the surface of the sea. Whereas for stationary waves the crest and trough of the wave (such as a resonating violin string) would interchange, the nodal pattern would remain the same. In a moving wave, however, the whole wave, nodes and all, are travelling in time. Let us describe the time dependent part of this wave by

$$\psi(t) = A\,e^{2\pi i\,\nu t}$$

Convince yourself that after one complete *period* $t = \nu^{-1}$ the wave function (WF) returns to the same value $[A\,e^{2\pi i} = A(\cos 2\pi + i\sin 2\pi) = A]$ as it had at $t = 0$. Now differentiate $\psi(t)$ once:

$$\frac{d\psi}{dt} = A\,2\pi i\,\nu\,e^{2\pi i\,\nu t} = 2\pi i\,\nu\psi = \frac{2\pi i h\,\nu}{h}\psi = \frac{iE}{\hbar}\psi$$

i.e. $\qquad \dfrac{\hbar}{i}\dfrac{d\psi}{dt} = E\psi$

which is satisfied by the WF ψ which can be written $\psi(t) = A\,e^{2\pi i\,\nu t}$ or, using $E = h\nu$ as was done above, an alternative form is

$$\psi(t) = A\,e^{Eit/\hbar}$$

The last equation is Schrödinger's time-dependent equation.

A wave function Ψ possessing both space and time variables could be written

$$\Psi = \psi(x,y,z)\,e^{Eit/\hbar}$$

The two Schödinger equations are

time independent: $$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(x,y,z) \right]\Psi = E\Psi$$

time dependent: $$\frac{\hbar}{i}\frac{\partial\Psi}{\partial t} = H\Psi = E\Psi$$

The same WF Ψ can be used for both. If it contains time, the stationary state equation's ∇^2 operator (which involves *partial* derivatives) will act only on the space part, leaving the time factor unchanged. Similarly the space part will not be affected by the $\frac{\partial}{\partial t}$ operator of the time-dependent equation.

A final observation on time dependent and time independent WFs

We are now proposing that in order to describe a system that evolves in time its wave function (WF) should be written as a product of a part depending on space only and a factor that contains time as the only variable, like this:

$$\Psi = \psi(x,y,z)\ e^{Eit/\hbar}$$

But in our Quantum Chemistry course so far we've only bothered with the space part $\psi(x,y,z)$, and completely ignored the time factor $e^{Eit/\hbar}$ which appears to be an innovation. Doesn't the neglect of $e^{Eit/\hbar}$ matter?

Think of how WFs have been used until now. Remember that they are not physically measurable quantities, but may be used to calculate quantities that can be measured. Here are three examples:

(a) Energy $\qquad\qquad\qquad\qquad E = \int \psi * H\psi d\tau$

*(b)* Electron density $\qquad\qquad\qquad \rho = \psi * \psi$

(c) Transition moment integral $\qquad M_{12}^{x} = \int \psi_1^{*} x\psi_2 d\tau$

We have expressed these quantities in the forms that allow the wave function to be complex. They contain $\psi*$ which is the complex conjugate of ψ, i.e. it is the result of changing i (which is $\sqrt{-1}$) into $-i$. What is the effect of including the time factor $e^{Eit/\hbar}$ in the WF when calculating these three quantities? Try it by replacing ψ by $\Psi = \psi e^{Eit/\hbar}$ in the energy integral:

$$E = \int \Psi * H\Psi d\tau = \int \psi * e^{-Eit/\hbar} H\psi e^{Eit/\hbar} d\tau = \int \psi * H\psi d\tau$$

The Hamiltonian *H* of a stationary-state system contains no time-dependent terms. So the result of calculating the energy of such a system is the *same* whether or not the time factor $e^{Eit/\hbar}$ is included. (Show that the same is true in the calculation of ρ and of M_{12}^{x} also.)

Quantum mechanical tunnelling

Oscillator a   Oscillator b
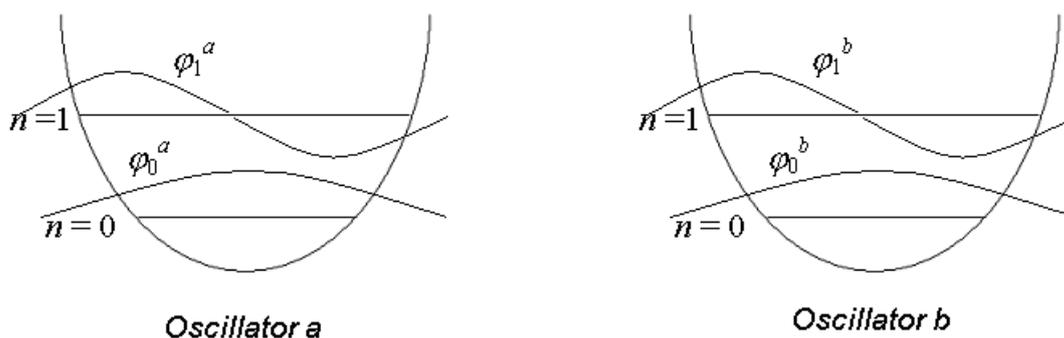
Two non-interacting vibrating systems (harmonic oscillators)

Consider two *independent* harmonic oscillators. Their energies are separately quantized with values given by

$$E_n = (n + \tfrac{1}{2})\hbar\sqrt{\frac{\kappa}{\mu}}$$

where *n* is a quantum number taking values 0, 1, 2, 3, . . . This could be exemplified by the vibrations of two gaseous diatomic molecules at a large separation. We have seen that the vibrational wave functions describing these quantum states are hermite polynomials: for $n = 0$ the WF φ_0^{a} for oscillator **a** and φ_0^{b} for oscillator **b** have maxima at the centre and decay equally right and left. For $n = 1$ the WFs φ_1^{a} and φ_1^{b} have nodes at the centre where they change sign and then also decay to zero. As *n* increases the WF has an increasing number of nodes, and they all decay at large distances from the centre point.

A very important point to notice is that unlike the 'particle in a box' model, despite the decay, the WF does not reach zero at points corresponding to large displacements from the centre. As shown in the diagram, the WFs become small, but remain finite. This is because in the 'particle in a box' system the potential energy

was declared to be infinite outside the line accommodating the particle but for the harmonic oscillator the potential energy $V(x) = \frac{1}{2} kx^2$ is finite until the extension x becomes infinite.

Now suppose that the pair of oscillators approach each other so that they start to interact. The way that we treated the interaction of two hydrogen atoms with AO-WFs φ_a and φ_b to form a molecule was to take combinations of them to form the MO-WFs $\psi_+ = \frac{1}{\sqrt{2}} (\varphi_a + \varphi_b)$ and $\psi_- = \frac{1}{\sqrt{2}} (\varphi_a - \varphi_b)$. We use the same approach here, but where the φs are the harmonic-oscallator vibrational WFs. Just as in MO theory the combined functions describe a greater space than did the separate ('basis') functions.

In order to see where all this is leading to it would probably be helpful to describe a physical example of a pair of coupled oscillators. Consider the ammonia molecule, whose ground state geometry is a triangular pyramid, the three H atoms forming the base, and the N atom the apex, of the pyramid. Now suppose that the NH_3 molecule transforms to its mirror image by pushing the N atom through the triangular base and out on the other side, as happens when a strong wind blows an umbrella inside out. This is called the inversion of the ammonia molecule.
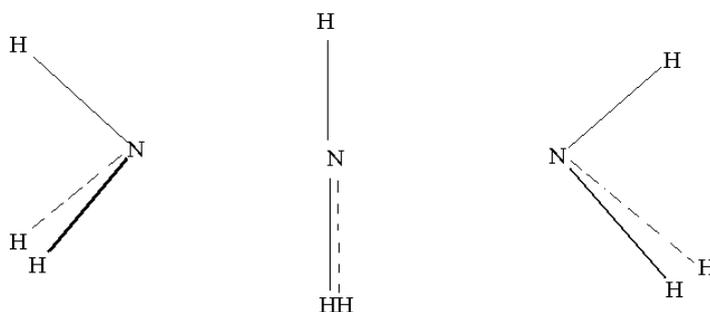
Although the left-hand and right hand molecules are obviously equivalent and so have equal energy, the intermediate structure (in which the N atom is in the plane of the three H atoms) has higher energy. The double-minimum potential energy profile for the transformation is shown in the next diagram.

Let us think about this 'Mexican hat' potential curve for a moment. The energy wells on the left and right describe the molecule vibrating in its most stable configuration. (This vibration is a mode with an oscillating perpendicular distance from the N to the H_3 plane.) These wells are separated by an energy barrier of 25 kJ mol^{-1} which is 10 times greater than thermal energy at room temperature and therefore hinders the inversion of NH_3.

Left-hand energy well (a)   Right-hand energy well (b)
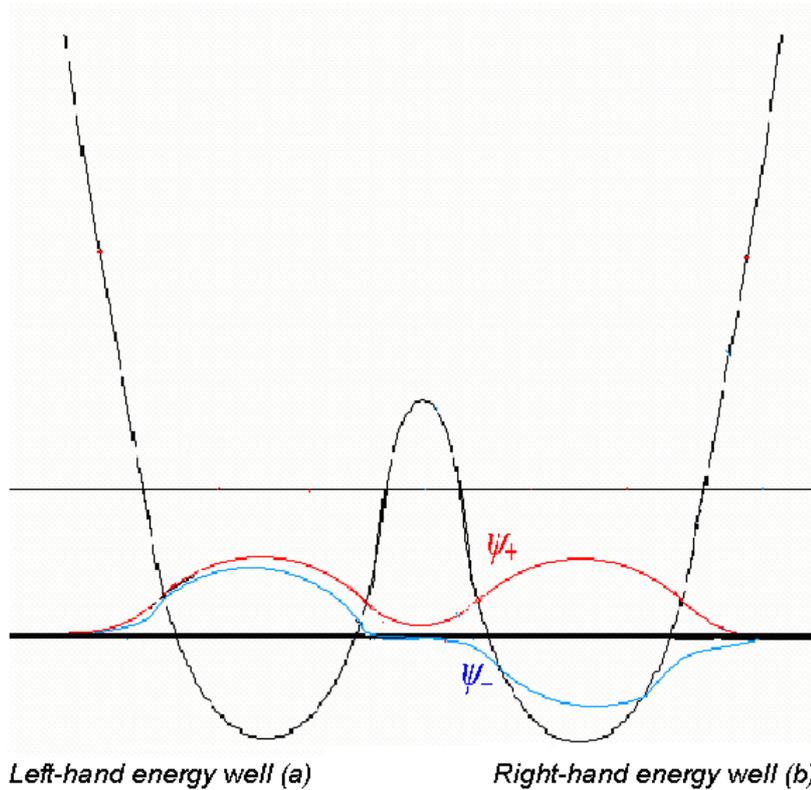
The discussion so far has been on a classical (i.e. non-quantum) level. Now consider the motions of the N and ring of H_3 atoms. This vibration is characterized by the vibrational functions ψ_n and their energy levels E_n. We have seen that since the energy barrier, i.e. the potential energy in the region between the wells, is finite, the vibrational wave functions for the left- and right- hand oscillator do not go to zero in this region, and so they interact. In an analogy with the (H + H) / H_2 case we'll select a vibrational function for a particular energy E in each well and call the left hand call one φ_a and the right hand one φ_b. Then the interaction leads to two states,

$$\psi_+ = \tfrac{1}{\sqrt{2}}(\varphi_a + \varphi_b) \quad \text{and} \quad \psi_- = \tfrac{1}{\sqrt{2}}(\varphi_a - \varphi_b)$$

which will have different energies E_+ and E_- for ψ_+ and ψ_- respectively.

Let's write the time-dependent wave functions for the states ψ_+ and ψ_-. We've seen that these functions, which we'll call Ψ_+ and Ψ_-, are simply ψ_+ and ψ_- multiplied by a time factor $e^{iEt/\hbar}$ where E is the energy of the state:

$$\Psi_+ = \psi_+ e^{iE_+ t/\hbar} \quad \text{and} \quad \Psi_- = \psi_- e^{iE_- t/\hbar}$$

Next, superimpose these functions to produce a time-dependent function

$$\Phi(t) \equiv \frac{1}{\sqrt{2}}\left[\Psi_+ + \Psi_-\right]$$

$$\Phi(t) = \frac{1}{\sqrt{2}}\left[\psi_+ e^{iE_+t/\hbar} + \psi_- e^{iE_-t/\hbar}\right]$$

$$= \frac{1}{\sqrt{2}}\left[\frac{1}{\sqrt{2}}(\varphi_a + \varphi_b)e^{iE_+t/\hbar} + \frac{1}{\sqrt{2}}(\varphi_a - \varphi_b)e^{iE_-t/\hbar}\right]$$

and a time-dependent probability function $\rho(t) = |\Phi(t)|^2 \equiv \Phi(t)^* \times \Phi(t)$:

$$\rho(t) = \frac{1}{4}\left[2|\varphi_a|^2 + 2|\varphi_b|^2 + (\varphi_a + \varphi_b)(\varphi_a - \varphi_b)e^{-iE_+t/\hbar}e^{+iE_-t/\hbar} + (\varphi_a + \varphi_b)(\varphi_a - \varphi_b)e^{+iE_+t/\hbar}e^{-iE_-t/\hbar}\right]$$

$$\rho(t) = \frac{1}{4}\left[2|\varphi_a|^2 + 2|\varphi_b|^2 + (\varphi_a + \varphi_b)(\varphi_a - \varphi_b)e^{+i(E_- - E_+)t/\hbar} + (\varphi_a + \varphi_b)(\varphi_a - \varphi_b)e^{-i(E_- - E_+)t/\hbar}\right]$$

$$\rho(t) = \frac{1}{4}\left[2|\varphi_a|^2 + 2|\varphi_b|^2 + (|\varphi_a|^2 - |\varphi_b|^2) \times 2\cos(2\pi\Delta Et/h)\right]$$

In the last step we have used $e^{i\theta} + e^{-i\theta} = 2\cos\theta$ and replaced $E_- - E_+$ by ΔE. If Planck's equation $\Delta E = h\nu$ is used to associate this splitting of the energy levels of ψ_+ and ψ_- with a frequency ν the probability function becomes, finally

$$\boxed{\rho(t) = \frac{1}{2}\left[|\varphi_a|^2 + |\varphi_b|^2 + (|\varphi_a|^2 - |\varphi_b|^2) \times \cos(2\pi\nu t)\right]}$$

The equation describes the time evolution of the motion. When $t = 0$ we have
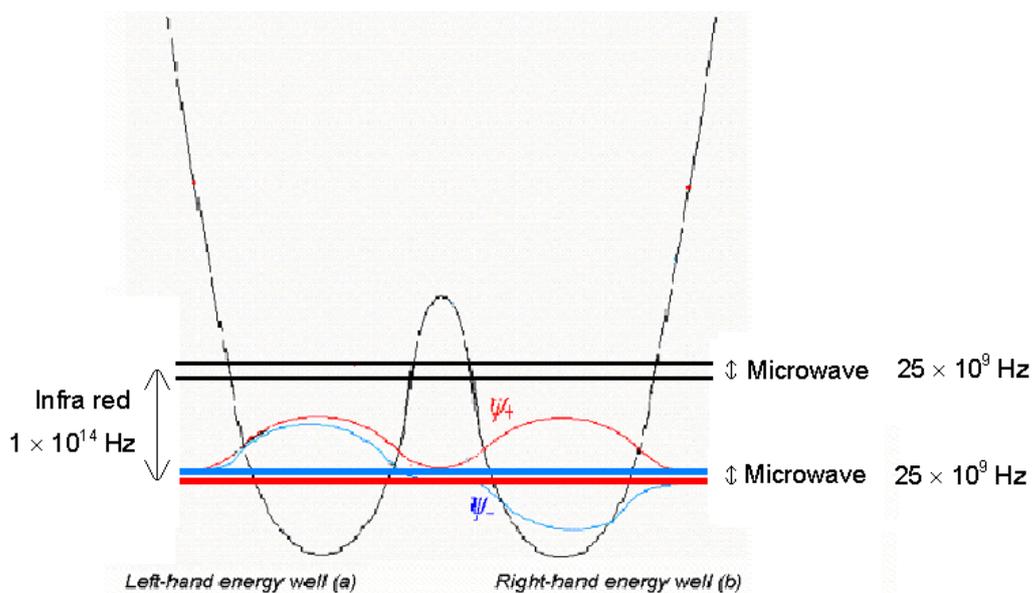
$$\rho(0) = \frac{1}{2}\left[|\varphi_a|^2 + |\varphi_b|^2 + (|\varphi_a|^2 - |\varphi_b|^2)\right]$$

$$= \varphi_a$$

which means that the oscillator is associated with the left-hand well **a**. At a time $t = \frac{1}{2\nu}$ later the density function is

$$\rho(\frac{1}{2\nu}) = \frac{1}{2}\left[|\varphi_a|^2 + |\varphi_b|^2 - (|\varphi_a|^2 - |\varphi_b|^2)\right]$$

$$= \varphi_b$$

i.e. the oscillator is in the right-hand well **b**. After a full vibrational period $t = \frac{1}{\nu}$, or any integral multiple of this time, the system is in the left well and at any half-integral period it is in the right well. The motion describes the inversion of the NH_3 molecule between its two stable configurations and a characteristic *inversion frequency* ν.

Infra red
1×10^{14} Hz

$\updownarrow$ Microwave 25×10^9 Hz

ψ_+

$\updownarrow$ Microwave 25×10^9 Hz

ψ_-

Left-hand energy well (a)   Right-hand energy well (b)

In NH_3 inversion the splitting $E_+ - E_-$ is small (only 0.0096 kJ mol^{-1}), and the corresponding frequency is 24×10^9 Hz which is in the microwave region. It is independent of temperature and is a consequence of the quantum nature of the protons' motion, which results in the penetration of the vibrational wave functions φ_1 and φ_2 in each energy-well into the region of the barrier. If the energy barrier is too high the inversion cannot be detected.

If there were no quantum effects, then provided the energy barrier separating the two ground state configurations were higher than thermal energy the ammonia molecule would remain (in perpetuity) in *one* of these configurations. The possibility of tunnelling means that the molecule can access the second configuration *even if its thermal energy kT is less than the energy barrier*. Thus the phenomenon is often referred to as **quantum mechanical tunnelling**

Radio telescopes operating in the microwave region have been used to identify gaseous NH_3 in space through transitions between the inversion levels ($v_{inv} = 24 \times 10^9$ Hz). But microwave spectroscopy is not required to detect inversion tunnelling in terrestrial ammonia. Transitions between vibrational levels produce signals at infra red frequencies, and since vibrational levels are split the IR signals *will show a splitting*. So ammonia's infra red spectrum also testifies to tunnelling.

The higher the energy barrier V_0 the smaller the possibility of tunnelling, and since the wave functions are negligibly small in the barrier region, if the barrier is very high then no inversion splitting (tunnelling) is observed in this case. This is

illustrated by considering the effect of the increasing barriers along the series NH_3, PH_3, AsH_3 for which the barriers are

	NH_3	PH_3	AsH_3
	25	73	134 kJ mol^{-1}.

We've seen that the inversion frequency in NH_3 is 24×10^9 Hz, but for the other two the tunnelling is too slight to be measured. For PH_3 the inversion has been estimated by calculation to be 0.14×10^6 Hz and for AsH_3 it is one complete cycle every two years!

There are other experimental measurements that relate to the inversion tunnelling in NH_3. Recall that quantum tunnelling arises because the three hydrogen atoms have such low mass that they have quantum properties. So what would be the expected result of comparing the inversion frequencies of the four species NH_3, NH_2D, NHD_2, ND_3? The part of NX_3 that does most of the 'moving' is the X_3 ring where X is hydrogen or deuterium. As the mass of X_3 increases along the series the quantum effect should decrease, and this is confirmed by the inversion frequencies:

| Ammonia isotope	NH_3	NH_2D	NHD_2	ND_3	
Inversion. frequency	24	12	5	2	GHz

Presumably if tritium (^3H) isotopic species were used the decrease would be even more marked.

Effect of temperature on the inversion

As a quantum phenomenon the frequency of the ammonia inversion in the state considered is independent of temperature. (Our equations do not contain the symbol 'T'!) However that is not to say that the observed inversion frequency is independent of temperature. The diagram shows two states separated by an infra red frequency $\sim 10^{14}$ Hz, which is about 40 kJ mol^{-1}. A (considerably) higher temperature would then partially populate the upper state, where the barrier is lower *and consequently the inversion splitting is greater*. Ammonia molecules in this state would show a higher inversion frequency, which might influence the observed frequency.

Other cases of molecular quantum tunnelling

1. Carboxylic acid dimers
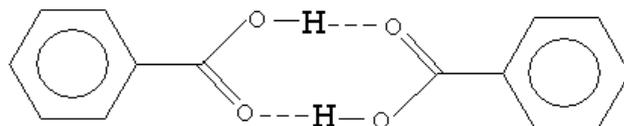
The two H atoms in the hydrogen-bonded carboxylic groups can undergo a concerted switching motion. Thus when, say, the upper H bonded to the left-hand O crosses a rather low energy barrier to bond with the right-hand O, the action will induce the lower H to move in the opposite direction (right to left).

Since the barrier is low, the *interaction* between the left hand and right-hand well is higher than it is in the NH_3 inversion. The splitting of the energy states is therefore significantly higher, and while it was 24 MHz in the inversion in the benzoic acid dimer it is 271 MHz. [CPPC 9 1788 (2008)]

2. In DNA

Consider one of the nucleotide base pairs that binds the double helix strand in DNA – thymine and adenine. The binding occurs by means of two hydrogen-bonds.


Thymine
(lactam)
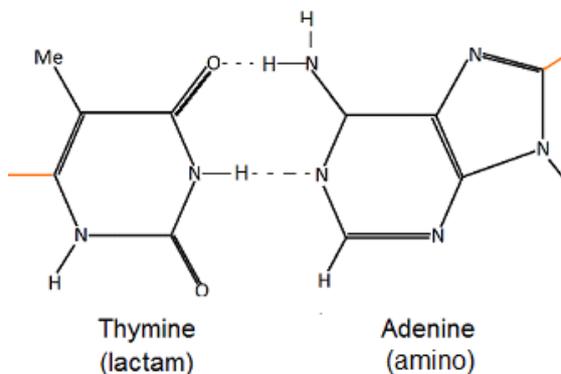
Adenine
(amino)

Now if the thymine molecule were to change from its *lactam* form (above) to a *lactim*

thymine
(lactim form)
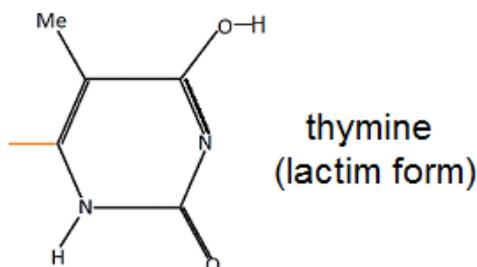
rather than with adenine, it could pair with a different nucleotide (guanine), and a transcription error would be created in the replication. Of interest to us is that the fact

that the lactam could change to a lactim as a result of 'tunnelling' involving the H atoms in the two hydrogen bonds. As a result the lactim could force the adenine from an *amino* to an *imino* form, and the thymine-adenine pair would then be

Thymine   Adenine
(lactim)   (imino)
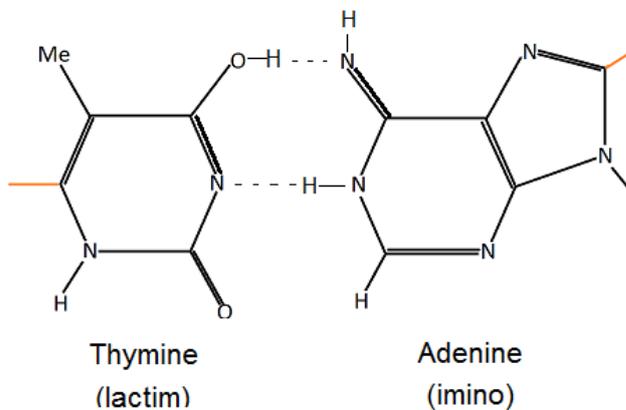
in which there is a concerted 'flipping' of the two H-bond protons between the lactam-amino and the lactim-imino pairs.