An introduction to time-dependent quantum chemistry

Molecular Inversion in Ammonia
(A chemical example of quantum tunnelling)

![Graph showing energy levels for NH₃ and H₃N with displacements of N from H₃ plane]

Senior Sophister 2011

D.A. Morton-Blake
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 $s$, $p$, $d$, $\sigma$ and $\pi$ 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

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

(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

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

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

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

The final step is to recognize that if this equation is multiplied by \(-h^2/2m\) it produces \(p^2/2m\) which is the kinetic energy \(1/2mv^2\).

\[ -\frac{h^2}{2m} \frac{d^2 f(x)}{dx^2} = \frac{p^2}{2m} f(x) = E f(x) \]

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

\[ \mathcal{H} f(x) = E f(x) \]

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

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

Denoting the factor in brackets as the Laplacian operator \( \nabla^2 \), the Schrödinger equation is written
\[
\left\{ -\frac{\hbar^2}{2m} \left[ \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right] + \mathcal{V}(x, y, z) \right\} \psi(x, y, z) = E \psi(x, y, z)
\]

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 \( \psi_1, E_1; \ \psi_2, E_2; \ \psi_3, E_3; \ \psi_4, E_4; \ldots \)

(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
\[
\psi(t) = A e^{\frac{2\pi i}{\nu} t}
\]

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

i.e.
\[
\frac{\hbar}{i} \frac{d\psi}{dt} = E \psi
\]

which is satisfied by the WF \( \psi \) which can be written \( \psi(t) = A e^{\frac{2\pi i}{\nu} t} \) 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 \( \Psi \) possessing both space and time variables could be written
\[
\Psi = \psi(x, y, z) e^{Eit/\hbar}
\]

The two Schödinger equations are
time independent: \[ -\frac{\hbar^2}{2m} \nabla^2 + V(x, y, z) \] \[ \Psi = E\Psi \]

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

The same WF \( \Psi \) can be used for both. If it contains time, the stationary state equation’s \( \nabla^2 \) 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:

\[ \Psi = \psi(x, y, z) e^{\frac{Eit}{\hbar}} \]

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 \( e^{\frac{Eit}{\hbar}} \) which appears to be an innovation. Doesn’t the neglect of \( e^{\frac{Eit}{\hbar}} \) 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 \[ E = \int \psi^* H \psi d\tau \]

(b) Electron density \[ \rho = \psi^* \psi \]

(c) Transition moment integral \[ M_{ij}^x = \int \psi_i^* x \psi_j d\tau \]

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 \( \psi \), i.e. it is the result of changing \( i \) (which is \( \sqrt{-1} \)) into \( -i \). What is the effect of including the time factor \( e^{\frac{Eit}{\hbar}} \) in the WF when calculating these three quantities? Try it by replacing \( \psi \) by \( \Psi = \psi e^{\frac{Eit}{\hbar}} \) in the energy integral:

\[ E = \int \Psi^* H\Psi d\tau = \int \psi^* e^{-\frac{Eit}{\hbar}} H \psi e^{\frac{Eit}{\hbar}} d\tau = \int \psi^* H \psi d\tau \]
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 $e^{iEt/\hbar}$ is included. (Show that the same is true in the calculation of $\rho$ and of $M_{ij}$ also.)

Quantum mechanical tunnelling

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

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

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 $\phi_0^a$ for oscillator $a$ and $\phi_0^b$ for oscillator $b$ have maxima at the centre and decay equally right and left. For $n = 1$ the WFs $\phi_1^a$ and $\phi_1^b$ 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 \( \phi_a \) and \( \phi_b \) to form a molecule was to take combinations of them to form the MO-WFs \( \psi_+ = \frac{1}{\sqrt{2}} (\phi_a + \phi_b) \) and \( \psi_- = \frac{1}{\sqrt{2}} (\phi_a - \phi_b) \). We use the same approach here, but where the \( \phi \)s are the harmonic-oscillator 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.

![Diagram of ammonia molecule and its inversion](image)

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\(_3\).
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 $\psi_n$ 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 $\phi_a$ and the right hand one $\phi_b$. Then the interaction leads to two states, 

$$\psi_+ = \frac{1}{\sqrt{2}} (\phi_a + \phi_b) \quad \text{and} \quad \psi_- = \frac{1}{\sqrt{2}} (\phi_a - \phi_b)$$

which will have different energies $E_+$ and $E_-$ for $\psi_+$ and $\psi_-$ respectively.

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

$$\Psi_+ = \psi_+ e^{i\Delta E/\hbar} \quad \text{and} \quad \Psi_- = \psi_- e^{i\Delta E/\hbar}$$
Next, superimpose these functions to produce a time-dependent function

\[
\Phi(t) = \frac{1}{\sqrt{2}} [\psi_+ + \psi_-]
\]

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

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

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

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

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

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

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

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

The equation describes the time evolution of the motion. When \( t = 0 \) we have

\[
\rho(0) = \frac{1}{2} \left[ |\varphi_a|^2 + |\varphi_b|^2 + (|\varphi_a|^2 - |\varphi_b|^2) \right]
\]

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 NH₃ molecule between its two stable configurations and a characteristic inversion frequency \( \nu \).
In NH$_3$ inversion the splitting $E_+ - E_-$ is small (only 0.0096 kJ mol$^{-1}$), and the corresponding frequency is $24 \times 10^9$ 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 $\varphi_1$ and $\varphi_2$ 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 ($\nu_{inv} = 24 \times 10^9$ 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 NH₃, PH₃, AsH₃ for which the barriers are

<table>
<thead>
<tr>
<th></th>
<th>NH₃</th>
<th>PH₃</th>
<th>AsH₃</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>25</td>
<td>73</td>
<td>134</td>
</tr>
</tbody>
</table>

We’ve seen that the inversion frequency in NH₃ is $24 \times 10^9$ Hz, but for the other two the tunnelling is too slight to be measured. For PH₃ the inversion has been estimated by calculation to be $0.14 \times 10^6$ Hz and for AsH₃ it is one complete cycle every two years!

There are other experimental measurements that relate to the inversion tunnelling in NH₃. 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 NH₃, NH₂D, NHD₂, ND₃? The part of NX₃ that does most of the ‘moving’ is the X₃ ring where X is hydrogen or deuterium. As the mass of X₃ increases along the series the quantum effect should decrease, and this is confirmed by the inversion frequencies:

<table>
<thead>
<tr>
<th>Ammonia isotope</th>
<th>NH₃</th>
<th>NH₂D</th>
<th>NHD₂</th>
<th>ND₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inversion. frequency</td>
<td>24</td>
<td>12</td>
<td>5</td>
<td>2</td>
</tr>
</tbody>
</table>

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.