Study of a two-state system : the ammonia molecule

We first consider the ammonia molecule in the absence of any external perturbation. The nitrogen atom can be above or below the plane *P* defined by the 3 hydrogen atoms. This defines 2 possible states of the molecule. We will denote by $|+\rangle$ the state where the nitrogen atom points towards the $+z$ direction with respect to the plane *P* and by $|-\rangle$ the state where the nitrogen atom points towards the $-z$ direction. The ammonia molecule always switches from the state $|+\rangle$ to the state $|-\rangle$.

1) Represent the molecule in the 2 states $|+\rangle$ and $|-\rangle$.

In the following we will assume the these two states form an orthonormal basis set of the accessible states of the molecule.
If $|\Psi(t)\rangle$ is the state of the system at time *t*, then the evolution of $|\Psi(t)\rangle$ with *t* is given by the time-dependent Schrödinger equation:

$$i\hbar\frac{d|\Psi(t)\rangle}{dt}=\hat{H}|\Psi(t)\rangle,$$

where $\hat{H}$ is the hamiltonian of the system.

2) Are the states $|+\rangle$ and $|-\rangle$ eigenstates of the system ? (justify your answer).

3) At time *t* the system is in the state $|\Psi(t)\rangle = C_+(t)|+\rangle + C_-(t)|-\rangle$ where $C_+(t)$ and $C_-(t)$ are two complex numbers that depend on time. What is their physical meaning ?

4) The matrix representation of the hamiltonian in the basis of the states $|+\rangle$ and $|-\rangle$ can be written as follows:

$$\left[\hat{H}\right]=\begin{pmatrix} H_{++} & H_{+-} \\ H_{-+} & H_{--} \end{pmatrix}.$$

Show that H_{++} and H_{--} are real numbers and that $H_{+-}^{*} = H_{-+}$. Prove that the time-dependent Schrödinger equation is equivalent to:

$$\begin{cases} i\hbar \dfrac{dC_+}{dt} = H_{++}C_+ + H_{+-}C_- \\ i\hbar \dfrac{dC_-}{dt} = H_{-+}C_+ + H_{--}C_- \end{cases}.$$

5) If $|+\rangle$ and $|-\rangle$ are not eigenstates of the system, what are the consequences on the coefficients H_{+-} and H_{-+} ? Prove that if the molecule can switch from the state $|+\rangle$ to the state $|-\rangle$, then switching from $|-\rangle$ to $|+\rangle$ is also possible.

6) For symmetry reasons $H_{++} = H_{--} = E_0$. In addition, the coupling term H_{+-} is assumed to be real and is denoted $-A$ ($A > 0$). What are the normalized eigenvectors $|1\rangle$ and $|2\rangle$ of the hamiltonian ? What are the corresponding energies E_1 and E_2 ? The state $|2\rangle$ is chosen to be the ground state of the molecule, that is the state associated to the lowest energy E_2.

7) If, at time t=0 the molecule is in the state $|+\rangle$, what is the probability that it is found in the state $|-\rangle$ at time t ? **Hint:** solve the time-dependent Schrödinger equation in the basis of the states $|1\rangle$ and $|2\rangle$ ($|\Psi(t)\rangle = C_1(t)|1\rangle + C_2(t)|2\rangle$).

8) We now perturb the system with a static electric field $\vec{E} = E\,\vec{e}_z$ ($E > 0$). The molecule has a permanent dipole moment $\vec{\mu}$. Its interaction energy with the electric field equals (in classical mechanics):

$$W = -\vec{\mu}.\vec{E} = -\mu_z E.$$

When the nitrogen atom is below the plane *P*, $\mu_z = \mu$ ($\mu > 0$).

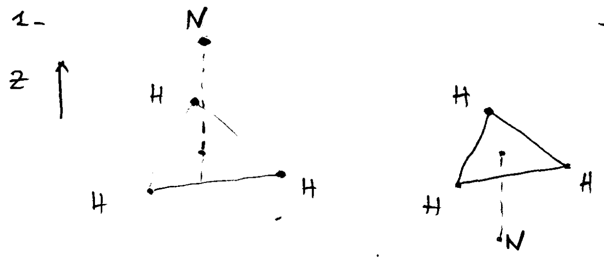
Explain why, in quantum mechanics, $\hat{W}|-\rangle = -\mu E|-\rangle$ and $\hat{W}|+\rangle = \mu E|+\rangle$. Give the matrix representation of the hamiltonian in the presence of the electric field. What are the possible energies for the molecule ? We denote E_2' the ground state energy and $|2'\rangle$ its associated eigenvector.

9) For analysis purposes, we will assume that the geometry of the molecule is not affected by the electric field, which means that the coupling term $-A$ can be considered as a constant. Show that, when the electric field is strong ($\dfrac{A}{\mu E} << 1$) and the molecule is in the ground state $|2'\rangle$, the probability

of finding the nitrogen atom below the plane P is much larger than the probability of finding it above the plane. What are those probabilities equal to in the absence of the electric field ?

Study of a 2-states system

1 -



state $|+\rangle$ state $|-\rangle$

2 - Let us assume that $|+\rangle$ and $|-\rangle$ are eigenstates of $\hat{H}$:
Then $\hat{H}|\pm\rangle = E_\pm|\pm\rangle$. Let us now write the Schrödinger equation $\hat{H}|\psi(t)\rangle = i\hbar \frac{d}{dt}|\psi(t)\rangle$ (1)
and consider that at time $t=0$ the system is in the state $|+\rangle$
(it says in the text that the molecule always switches from $|+\rangle$ to $|-\rangle$, therefore it will be in the state $|+\rangle$ at some time)

$|\psi(t)\rangle = C_+(t)|+\rangle + C_-(t)|-\rangle$ since $|+\rangle$ and $|-\rangle$ form an orthonormal basis of the space of quantum states

$$(1) \Leftrightarrow C_+(t)\underbrace{\hat{H}|+\rangle}_{E_+|+\rangle} + C_-(t)\underbrace{\hat{H}|-\rangle}_{E_-|-\rangle} = i\hbar\left(\dot{C}_+|+\rangle + \dot{C}_-|-\rangle\right)$$

$$\Leftrightarrow \begin{cases} C_+(t)E_+ = i\hbar\dot{C}_+ \\ C_-(t)E_- = i\hbar\dot{C}_- \end{cases} \Leftrightarrow \begin{array}{l} C_+(t) = e^{\frac{E_+t}{i\hbar}}C_+(0) = e^{E_+t/i\hbar} \\ C_-(t) = e^{\frac{E_-t}{i\hbar}}\underbrace{C_-(0)}_{\shortparallel} = 0 \end{array}$$

Therefore $|\psi(t)\rangle = e^{\frac{E_+t}{i\hbar}}|+\rangle \quad \forall t$

meaning that $\langle\psi(t)|-\rangle = e^{\frac{E_+t}{i\hbar}}\langle+|-\rangle = 0$

The probability that the molecule ends up in state $|-\rangle$ is zero which is absurd since it switches from $|+\rangle$ to $|-\rangle$ all the time

Conclusion: $|+\rangle$ and $|-\rangle$ are NOT eigenstates of $\hat{H}$.

3 - $|C_+|^2 = C_+^*C_+ = \langle\psi(t)|+\rangle\langle+|\psi(t)\rangle = |\langle+|\psi(t)\rangle|^2$
is the probability of being in state $|+\rangle$

$|C_-|^2 = \langle\psi(t)|-\rangle\langle-|\psi(t)\rangle = |\langle-|\psi(t)\rangle|^2$
is the probability of being in state $|-\rangle$

4 - $[\hat{H}] = \begin{pmatrix} H_{++} & H_{+-} \\ H_{-+} & H_{--} \end{pmatrix}$ matrix representation

is read as follows: $\hat{H}|+\rangle = H_{++}|+\rangle + H_{-+}|-\rangle$ (2)
$\hat{H}|-\rangle = H_{--}|-\rangle + H_{+-}|+\rangle$ (3)

$\hat{H}$ is hermitian therefore $[\hat{H}]^\dagger = {}^t[\hat{H}]^* = [\hat{H}]$

Comment: If $\mathcal{B} = \{|u_i\rangle\}_i$ is an orthonormal basis and $[\hat{H}]$ the matrix representation of $\hat{H}$ in this basis

The matrix elements $[H]_{ij}$ are defined as follows

$$\forall j \quad \hat{H}|u_j\rangle = \sum_i [\hat{H}]_{ij}\, |u_i\rangle$$

and

$$\langle u_k|\hat{H}|u_j\rangle = \sum_i [\hat{H}]_{ij} \underbrace{\langle u_k|u_i\rangle}_{\delta_{ik}} = \boxed{[\hat{H}]_{kj} = \langle u_k|\hat{H}|u_j\rangle}$$

Since $\hat{H}$ is hermitian: $\langle u_k|\hat{H}|u_j\rangle = \langle u_j|\hat{H}|u_k\rangle^*$

$$\Rightarrow \quad [\hat{H}]_{kj} = [\hat{H}]^*_{jk} = \left({}^t[\hat{H}]^*\right)_{kj}$$

$$\Rightarrow \quad \boxed{[\hat{H}] = [\hat{H}]^\dagger}$$ ($\dagger$ means adjoint)

Thus $H_{++}^* = H_{++}$, $H_{--}^* = H_{--}$

and $H_{+-}^* = H_{-+}$

- $|+\rangle$ and $|-\rangle$ are not eigenvectors of $\hat{H}$ means that $\begin{cases} H_{-+} \neq 0 & \text{(see equation (2))} \\ H_{+-} \neq 0 & \text{(see equation (3))} \end{cases}$

- Time-dependent Schrödinger equation: $\hat{H}|\psi(t)\rangle = i\hbar \dfrac{d|\psi(t)\rangle}{dt}$

  where $|\psi(t)\rangle = c_+(t)|+\rangle + c_-(t)|-\rangle$

According to (2) and (3) we get

$$c_+\left(H_{++}|+\rangle + H_{-+}|-\rangle\right) + c_-\left(H_{--}|-\rangle + H_{+-}|+\rangle\right) = i\hbar\left(\dot{c}_+|+\rangle + \dot{c}_-|-\rangle\right)$$

$\Rightarrow$

$$\begin{cases} i\hbar\dot{c}_+ = c_+H_{++} + c_-H_{+-} & (4) \\ i\hbar\dot{c}_- = c_+H_{-+} + c_-H_{--} & (5) \end{cases}$$

If the molecule can switch from state $|+\rangle$ to state $|-\rangle$ it means that $H_{+-} = H_{-+}^* \neq 0$ (see question 2)

If we now assume that at time $t=0$ the molecule is in state $|-\rangle \Rightarrow c_-(0) = 1$ and $c_+(0) = 0$,

then if the probability that the system ends up in state $|+\rangle$ is zero, it means that $\forall t \quad c_+(t) = 0 \Rightarrow \dot{c}_+ = 0$

$\Rightarrow$ according to (4) $\quad c_-H_{+-} = 0 \quad \forall t \quad (6)$

$\Rightarrow$ according to (5) $\quad i\hbar\dot{c}_- = c_-H_{--}$

$$\Downarrow$$

$$c_- = \underbrace{c_-(0)}_{1}\, e^{\frac{H_{--}t}{i\hbar}}$$

$(6) \Rightarrow \quad e^{\frac{H_{--}t}{i\hbar}} H_{+-} = 0 \Rightarrow H_{+-} = 0$ absurd!

Conclusion: If the system can switch from $|+\rangle$ to $|-\rangle$ then it can also switch from $|-\rangle$ to $|+\rangle$.

$$\begin{cases} H_{++} = H_{--} = E_0 \\ H_{+-} = -A \in \mathbb{R} \Rightarrow H_{-+} = H_{+-}^{*} = -A \end{cases}$$

Thus $$[\hat{H}] = \begin{pmatrix} E_0 & -A \\ -A & E_0 \end{pmatrix}$$

Eigenvalues E of the hamiltonian fulfill $\det\left([\hat{H}] - E\mathbb{1}\right) = 0$

$$\Leftrightarrow \begin{vmatrix} E_0 - E & -A \\ -A & E_0 - E \end{vmatrix} = 0$$

$$\Leftrightarrow (E_0 - E)^2 - A^2 = 0$$

2 solutions $$\boxed{\begin{aligned} E_1 &= E_0 + A \\ E_2 &= E_0 - A \end{aligned}}$$

Eigenvectors:

$$\underbrace{[\hat{H}]\begin{pmatrix} c'_+ \\ c'_- \end{pmatrix}}_{\begin{pmatrix} E_0 c'_+ - A c'_- \\ -A c'_+ + E_0 c'_- \end{pmatrix}} = (E_0 + A)\begin{pmatrix} c'_+ \\ c'_- \end{pmatrix}$$

$$\begin{cases} -A c'_- = A c'_+ \\ -A c'_+ = A c'_- \end{cases} \Leftrightarrow c'_- = -c'_+ = -\frac{1}{\sqrt{2}}$$

to get a normalized eigenvector

$$\boxed{|1\rangle = \frac{1}{\sqrt{2}}\left(|+\rangle - |-\rangle\right)}$$

Comment: we could have guessed the solutions since

$$\hat{H}|+\rangle = E_0|+\rangle - A|-\rangle$$
$$\hat{H}|-\rangle = -A|+\rangle + E_0|-\rangle$$

$$\Rightarrow \hat{H}\left(|+\rangle - |-\rangle\right) = E_0|+\rangle - A|-\rangle - \left(-A|+\rangle + E_0|-\rangle\right)$$
$$= (E_0 + A)\left[|+\rangle - |-\rangle\right]$$

$\Rightarrow |1\rangle = \frac{1}{\sqrt{2}}\left(|+\rangle - |-\rangle\right)$ is eigenvector $\hat{H}$ associated to $(E_0 + A)$

And $$\hat{H}\left(|+\rangle + |-\rangle\right) = E_0|+\rangle - A|-\rangle + E_0|-\rangle - A|+\rangle$$
$$= (E_0 - A)\left[|+\rangle + |-\rangle\right]$$

$\Rightarrow$ $\boxed{|2\rangle = \frac{1}{\sqrt{2}}\left(|+\rangle + |-\rangle\right) \text{ is eigenvector of } \hat{H} \text{ associated to } (E_0 - A)}$

6 – We solve the time-dependent Schrödinger equation in the basis of the eigenvectors of $\hat{H}$ ($|1\rangle$ and $|2\rangle$)

- $\forall t \quad |\psi(t)\rangle = c_1(t)\,|1\rangle + c_2(t)\,|2\rangle$

$$|\psi(0)\rangle = |+\rangle = \frac{1}{\sqrt{2}}\left(|1\rangle + |2\rangle\right)$$

$$\Rightarrow \boxed{c_1(0) = \frac{1}{\sqrt{2}} \text{ and } c_2(0) = \frac{1}{\sqrt{2}}}$$

- $\hat{H}|\psi(t)\rangle = i\hbar \frac{d}{dt}|\psi(t)\rangle$

$$\Rightarrow \sum_{j=1}^{2} c_j(t)\underbrace{\hat{H}|j\rangle}_{E_j|j\rangle} = i\hbar \sum_{j=1}^{2} \dot{c}_j\,|j\rangle$$

$$\Rightarrow \forall j \quad c_j(t)\,E_j = i\hbar\,\dot{c}_j$$

$$\Rightarrow c_j(t) = c_j(0)\,e^{\frac{E_j t}{i\hbar}} \quad (7)$$

$$\Rightarrow \boxed{c_1(t) = \frac{1}{\sqrt{2}}\,e^{(E_1/i\hbar)t} \text{ and } c_2(t) = \frac{1}{\sqrt{2}}\,e^{(E_2/i\hbar)t}}$$

- Probability to be in state $|-\rangle$ at time t:

$$P_-(t) = |\langle -|\psi(t)\rangle|^2 \quad \text{where } \langle\psi(t)|\psi(t)\rangle = 1.$$

Comment: we check that $|\psi(t)\rangle$ is normalized

$$\langle\psi(t)|\psi(t)\rangle = \sum_{j=1}^{2} c_j(t)\,\underbrace{\langle\psi(t)|j\rangle}_{c_j(t)^*}$$

$$= \sum_{j=1}^{2} |c_j(t)|^2$$

$$= \sum_{j=1}^{2} |c_j(0)|^2 = \langle\psi(0)|\psi(0)\rangle = 1$$

according to (7)

- $\underbrace{\langle -|\psi(t)\rangle}_{c_-(t)} = c_1(t)\,\underbrace{\langle -|1\rangle}_{-\frac{1}{\sqrt{2}}} + c_2(t)\,\underbrace{\langle -|2\rangle}_{\frac{1}{\sqrt{2}}}$

$$c_-(t) = \frac{1}{2}\,e^{(E_2/i\hbar)t} - \frac{1}{2}\,e^{(E_1/i\hbar)t}$$

Therefore $P_-(t) = c_-(t)\cdot c_-(t)^*$

$$= \frac{1}{4}\left(e^{(E_2/i\hbar)t} - e^{(E_1/i\hbar)t}\right)\left(e^{-(E_2/i\hbar)t} - e^{-(E_1/i\hbar)t}\right)$$

$$P_-(t) = \frac{1}{4}\left(1 - e^{\frac{(E_2-E_1)t}{i\hbar}} - e^{-\frac{(E_2-E_1)t}{i\hbar}} + 1\right)$$

$$= \frac{1}{4}\left(2 - 2\cos\left(\frac{(E_2-E_1)t}{\hbar}\right)\right)$$

$$\mathcal{P}_-(t) = \frac{1}{2}(1-\cos\omega_{21}t) \qquad \omega_{21} = \frac{E_2-E_1}{\hbar}$$

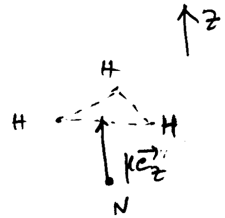
$$\boxed{\mathcal{P}_-(t) = \sin^2\left(\frac{\omega_{21}t}{2}\right)}$$

Therefore the molecule will oscillate between the states $|+\rangle$ and $|-\rangle$ at the frequency $f_{vib} = \frac{\omega_{vib}}{2\pi}$ where $\omega_{vib} = \omega_{21}$

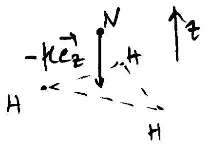
7- In classical mechanics $W = -\vec{\mu}\cdot\vec{\mathcal{E}} = -\mu_z\mathcal{E}$

- In the state $|-\rangle$ $\mu_z = \mu$ which is written formally as

$$\hat{W}|-\rangle = -(\mu)_{|-\rangle}\mathcal{E} = -\mu\mathcal{E}|-\rangle$$



- In the state $|+\rangle$ $\mu_z = -\mu$



$$\Rightarrow \hat{W}|+\rangle = -(-\mu)\mathcal{E}|+\rangle = \mu\mathcal{E}|+\rangle$$

Matrix representation of $\hat{H}_{\mathcal{E}}$ in the presence of the static electric field in the basis $(|+\rangle, |-\rangle)$

$$\hat{H}_{\mathcal{E}} = \hat{H} + \hat{W}$$

$$[\hat{W}] = \begin{pmatrix} \mu\mathcal{E} & 0 \\ 0 & -\mu\mathcal{E} \end{pmatrix}$$

$$\Rightarrow [\hat{H}_{\mathcal{E}}] = \begin{pmatrix} E_0+\mu\mathcal{E} & -A \\ -A & E_0-\mu\mathcal{E} \end{pmatrix}$$

Eigenvalues: $\det([\hat{H}_{\mathcal{E}}] - E\mathbb{1}) = 0 \Leftrightarrow \begin{vmatrix} E_0+\mu\mathcal{E}-E & -A \\ -A & E_0-\mu\mathcal{E}-E \end{vmatrix} = 0$

$$\Leftrightarrow \underbrace{(E_0+\mu\mathcal{E}-E)(E_0-\mu\mathcal{E}-E)}_{(E_0-E)^2-\mu^2\mathcal{E}^2} - A^2 = 0$$

$$\Leftrightarrow (E_0-E)^2 = \mu^2\mathcal{E}^2 + A^2 \Leftrightarrow E = E_0 \pm\sqrt{\mu^2\mathcal{E}^2+A^2}$$

eigenvectors: $E_1' = E_0 + \sqrt{\mu^2\mathcal{E}^2 + A^2}$

$$[\hat{H}]_{\mathcal{E}} \begin{pmatrix} C_+^{1'} \\ C_-^{1'} \end{pmatrix} = E_1' \begin{pmatrix} C_+^{1'} \\ C_-^{1'} \end{pmatrix}$$

$$\begin{cases} (E_0 + \mu\mathcal{E})\, C_+^{1'} - A\, C_-^{1'} = E_1' C_+^{1'} & (8) \\ -A C_+^{1'} + (E_0 - \mu\mathcal{E}) C_-^{1'} = E_1' C_-^{1'} & (9) \end{cases}$$

Let us assume that the field is strong and keep A equal to its value when $\mathcal{E}=0$ (it is not realistic but interesting though...) $\Rightarrow \frac{\mu\mathcal{E}}{A} \gg 1$

$$E_1' = E_0 + \mu\mathcal{E}\left(1 + \frac{A^2}{\mu^2\mathcal{E}^2}\right)^{1/2} \simeq E_0 + \mu\mathcal{E} + \mu\mathcal{E}\cdot\left(\frac{1}{2}\frac{A^2}{\mu^2\mathcal{E}^2}\right)$$

$$E_1' \simeq E_0 + \mu\mathcal{E} + \frac{1}{2}\frac{A^2}{\mu\mathcal{E}}$$

(8) $\Rightarrow$ $$-A C_-^{1'} \simeq \frac{1}{2}\frac{A^2}{\mu\mathcal{E}} C_+^{1'}$$

$\Rightarrow$ $$\boxed{\frac{C_+^{1'}}{C_-^{1'}} \simeq -2\frac{\mu\mathcal{E}}{A} \gg 1}$$

(9) $\Rightarrow$ $-A C_+^{1'} \simeq C_-^{1'}(2\mu\mathcal{E})$ ok!

$E_2' = E_0 - \sqrt{\mu^2\mathcal{E}^2 + A^2}$

$$[\hat{H}]_{\mathcal{E}} \begin{pmatrix} C_+^{2'} \\ C_-^{2'} \end{pmatrix} = E_2' \begin{pmatrix} C_+^{2'} \\ C_-^{2'} \end{pmatrix}$$

$$\begin{cases} (E_0 + \mu\mathcal{E})\, C_+^{2'} - A\, C_-^{2'} = E_2' C_+^{2'} & (10) \\ -A C_+^{2'} + (E_0 - \mu\mathcal{E}) C_-^{2'} = E_2' C_-^{2'} & (11) \end{cases}$$

$$E_2' = E_0 - \mu\mathcal{E}\left(1 + \frac{A^2}{\mu^2\mathcal{E}^2}\right)^{1/2} \simeq E_0 - \mu\mathcal{E}\left(1 + \frac{1}{2}\frac{A^2}{\mu^2\mathcal{E}^2}\right) = E_0 - \mu\mathcal{E} - \frac{1}{2}\frac{A^2}{\mu\mathcal{E}}$$

(11) $\Rightarrow$ $$-A C_+^{2'} \simeq C_-^{2'}\left(-\frac{1}{2}\frac{A^2}{\mu\mathcal{E}}\right)$$

$\Rightarrow$ $$\boxed{\frac{C_+^{2'}}{C_-^{2'}} \simeq \frac{1}{2}\frac{A}{\mu\mathcal{E}} \ll 1}$$

(10) $\Rightarrow$ $-A C_-^{2'} \simeq C_+^{2'}(-2\mu\mathcal{E})$ ok!

Conclusion: When $\mathcal{E}=0$ the ground state of NH_3 is $|2\rangle = \frac{1}{\sqrt{2}}(|+\rangle + |-\rangle)$. When $\mathcal{E}$ becomes large the ground state is $|2'\rangle = C_+^{2'}|+\rangle + C_-^{2'}|-\rangle$ where $C_+^{2'} \ll C_-^{2'}$ which means that the probability of finding N below the plane $\mathcal{P}$ is much larger than the probability of finding it above the plane (without the field those probabilities are both equal to 1/2).