

- Matrices and unitary operators -

Let $\hat{H}\psi_n = E_n \psi_n$ and ψ arbitraryThen $\psi(t) = \sum_n a_n(t) \psi_n$. Let f be an observable.

$$\langle \hat{f} \rangle_\psi \stackrel{\text{def.}}{=} \int \psi^* (\hat{f} \psi) d\varrho$$

$$a_n(t) = a_n(0) e^{-\frac{i}{\hbar} E_n t} \equiv a_n(0) e^{-i\omega_n t}$$

$$\omega_n \equiv \frac{E_n}{\hbar}$$

$$= \int \left(\sum_n a_n \psi_n \right)^* \hat{f} \left(\sum_m a_m \psi_m \right) d\varrho$$

$$= \sum_{n,m} a_n^* a_m \int \psi_n^* (\hat{f} \psi_m) d\varrho$$

$$\equiv f_{nm} \leftarrow \text{matrix element}$$

$$= \sum_{n,m} a_n^*(t) f_{nm} a_m(t)$$

$$= \sum_{n,m} a_n^*(0) f_{nm} a_m(0) e^{i\omega_{nm} t}$$

$$\omega_{nm} \equiv \frac{E_n - E_m}{\hbar}$$

$$\equiv \text{Transition frequency between level } n \text{ and } m$$
By definition, the operator \hat{f} is such that:

$$\langle \hat{f} \rangle_\psi = \frac{d}{dt} \langle \hat{f} \rangle_\psi$$

$$= \frac{d}{dt} \sum_{n,m} a_n^*(0) f_{nm} a_m(0) e^{i\omega_{nm} t}$$

$$= i \sum_{n,m} \omega_{nm} a_n^*(0) f_{nm} a_m(0) e^{i\omega_{nm} t}$$

However, by def:

$$\langle \hat{f} \rangle_{\psi} = \sum_n a_n^*(0) \dot{f}_{nm} a_m(0) e^{i\omega_{nm}t} \Rightarrow$$

$$\Rightarrow \boxed{\dot{f}_{nm} = i\omega_{nm} f_{nm}}$$

It is easy to see that for a generic operator \hat{f} :

$$(\hat{f}^\dagger)_{nm} = (f_{mn})^*$$

because

$$\begin{aligned} (\hat{f}^\dagger)_{nm} &\equiv \int \psi_n^* (\hat{f}^\dagger \psi_m) dq \\ &= \int \psi_m (\hat{f}^* \psi_n^*) dq = \left(\int \psi_m^* (\hat{f} \psi_n) dq \right)^* \\ &= (f_{mn})^* \end{aligned}$$

The Schrödinger equation

$$\boxed{i\hbar \frac{\partial \psi}{\partial t} = \hat{H} \psi} \quad (1.9)$$

can also be written in matrix form

$$\text{Let } \hat{f}: \hat{f} \phi_n = f_n \phi_n \Rightarrow \psi(q, t) = \sum_n a_n(t) \phi_n(q)$$

Multiply 1.9 by $\phi_n^*(q)$ and integrate:

$$\begin{aligned} i\hbar \underbrace{\frac{d}{dt} \int \phi_n^*(q) \psi dq}_{= a_n(t) \text{ by def}} &= \underbrace{\int \phi_n^*(q) \hat{H} \psi dq}_{= \int \phi_n^* \hat{H} (\sum_m a_m(t) \phi_m) dq} \\ &= \sum_m a_m(t) H_{nm} \quad ; \quad H_{nm} \equiv \int \phi_n^* \hat{H} \phi_m dq \end{aligned}$$

Therefore we get:

$$\boxed{i\hbar \frac{d}{dt} a_n(t) = \sum_m H_{nm} a_m(t)} \quad (1.3)$$

If \hat{H} does not depend on t (isolated system)
 this is a first-order differential linear system w/o solution is trivial for finite dimension N :

let $H = [H_{nm}]$ a $N \times N$

and U a unitary matrix such that: (U is time-indep.)

$$U H U^\dagger = D = \text{diag}(E_1, E_2, \dots, E_N)$$

If $|a\rangle = (a_1, a_2, \dots, a_N)$ we rewrite (1.3) as:

$$i\hbar \frac{d}{dt} |a\rangle = H |a\rangle \quad \text{multiply from left by } U:$$

$$\begin{aligned} i\hbar \frac{d}{dt} (U|a\rangle) &= U H |a\rangle \quad \text{identity matrix} \\ &= U H I |a\rangle \\ &= (U H U^\dagger) U |a\rangle \end{aligned}$$

$$\text{Let } |b\rangle = U |a\rangle \Rightarrow$$

$$\Rightarrow \boxed{i\hbar \frac{d}{dt} |b\rangle = D |b\rangle}$$

$$\Leftrightarrow i\hbar \frac{d}{dt} b_n = \lambda_n b_n \Rightarrow b_n(t) = b_n(0) e^{\frac{i}{\hbar} \lambda_n t}$$

Or, equivalently:

$$|b(t)\rangle = e^{-iDt/\hbar} |b(0)\rangle$$

but $|a(t)\rangle = U^\dagger |b(t)\rangle \Rightarrow$

$$\Rightarrow \underbrace{U^\dagger |b(t)\rangle}_{= |a(t)\rangle} = \underbrace{\left(U^\dagger e^{-iDt/\hbar} U \right)}_{= \exp(-iHt/\hbar)} \underbrace{U^\dagger |b(0)\rangle}_{\equiv |a_0\rangle}$$

because
$$U^\dagger e^{-iDt/\hbar} U = U^\dagger \sum_k \frac{(-it/\hbar)^k}{k!} \frac{D^k}{k!} U$$

$$= \sum_k \frac{(-it/\hbar)^k}{k!} \frac{(U^\dagger D U)^k}{k!} = e^{-iHt/\hbar}$$

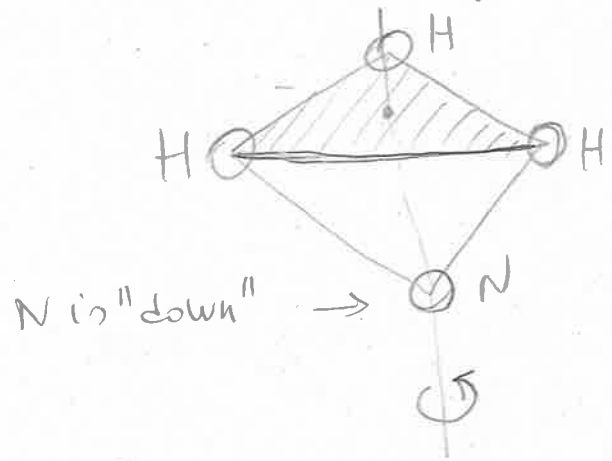
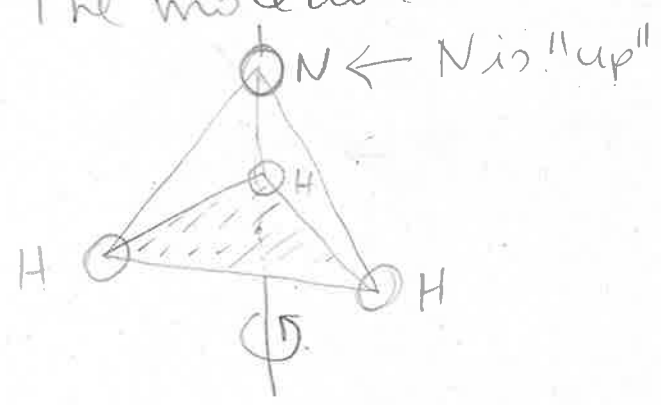
Therefore:

$$|a(t)\rangle = \exp(-iHt/\hbar) |a_0\rangle$$

There are some systems for which it is not important to know the spatial dependence of the state,

- Example of a 2-level system; The Ammonia molecule - From "The Feynman's lectures on physics" chaps. 8 and 9.

The molecule is made like this: NH_3 :



H = 1 proton + 1 electrons
 N = 7 protons + 7 electrons } \Rightarrow

$\Rightarrow NH_3$ has 10 electrons and 10 protons (4 Nuclei)
 $400 \leq \lambda \leq 700 \text{ nm}$ $\lambda < 400 \text{ nm}$

- excitation of electrons requires optical or UV light
- excitation of vibrations requires infrared light ($\lambda > 700 \text{ nm}$)
- excitation of rotations requires for infrared
 $15 \mu\text{m} \leq \lambda \leq 1 \text{ mm}$
 $\Leftrightarrow 20 \text{ THz} \geq \nu \geq 300 \text{ GHz}$

• NITROGEN INVERSION:



The frequency gap is 23.79 GHz $\Leftrightarrow \lambda = 1.26 \text{ cm}$ (Microwave)
 It occurs at room temperature.

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If the molecule is in a given rotational state spinning around the symmetry axis, and does not move in space (zero momentum), and vibrates only a little, we can describe NH_3 a TWO-LEVEL system:

$$N \text{ "up"} \doteq |u\rangle; \quad N \text{ "down"} \doteq |d\rangle$$

here u and d are just label for the state

Then, from (1.3) if we write:

$$|\psi(t)\rangle = a_u(t)|u\rangle + a_d(t)|d\rangle \quad (1.6)$$

The amplitudes a_u, a_d obey The Sch. eq.

$$\begin{cases} i\hbar \frac{da_u}{dt} = H_{uu} a_u + H_{ud} a_d \\ i\hbar \frac{da_d}{dt} = H_{du} a_u + H_{dd} a_d \end{cases} \quad (2.6)$$

What are the values of H_{uu}, H_{ud} , etc? We do not know theoretically!

If H were diagonal, that is $H_{ud} = (H_{du})^* = 0$, then we would have:

$$H = \begin{bmatrix} H_{uu} & 0 \\ 0 & H_{dd} \end{bmatrix} = \begin{bmatrix} E_1 & 0 \\ 0 & E_2 \end{bmatrix}$$

By symmetry, we cannot expect that $E_1 \neq E_2$, therefore we assume:

$$H_{uu} = H_{dd} = E_0$$

Now, consider $H_{ud} \neq 0$: This implies that nitrogen inversion can occur. Let be

$\frac{A}{\hbar}$ rate of nitrogen inversion (flips per second)

experimentally determined. Then we can assume tentatively:

$$H_{ud} = H_{du} = -A \quad \text{with } A \geq 0$$

we take $-A$ instead of A or $e^{i\varphi} A$ for "logical" convenience. (2.6) become:

$$\begin{cases} i\hbar \frac{dq_u}{dt} = E_0 q_u - A q_d \\ i\hbar \frac{dq_d}{dt} = -A q_u + E_0 q_d \end{cases}$$

So, we found that:

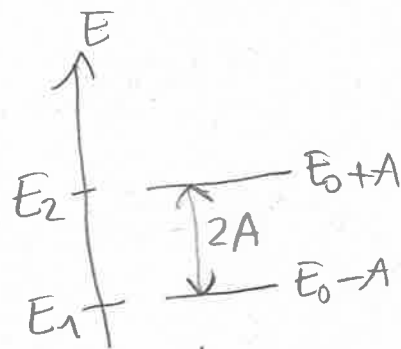
$$H = \begin{bmatrix} E_0 & -A \\ -A & E_0 \end{bmatrix}$$

We diagonalize as usual

$$\det(H - \lambda I) = \det \begin{bmatrix} E_0 - \lambda & -A \\ -A & E_0 - \lambda \end{bmatrix}$$

$$= (E_0 - \lambda)^2 - A^2$$

$$= 0 \Rightarrow \boxed{\lambda_{\pm} = E_0 \pm A}$$



The eigenvectors are:

$$\underline{v}_{\pm} = \frac{1}{\sqrt{2}} (1, \pm 1)$$

$$U H U^{\dagger} = D \quad \text{where} \quad U = \begin{bmatrix} \underline{v}_{+} & \underline{v}_{-} \end{bmatrix} = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 & 1 \\ 1 & -1 \end{bmatrix}$$

$$= \begin{bmatrix} E_0 - A & 0 \\ 0 & E_0 + A \end{bmatrix}$$

$$\text{Then} \quad \exp\left[-i D \frac{t}{\hbar}\right] = \begin{bmatrix} e^{-i\lambda_{-} t/\hbar} & 0 \\ 0 & e^{-i\lambda_{+} t/\hbar} \end{bmatrix}$$

$$\text{and} \quad U^{\dagger} e^{-i D t/\hbar} U = e^{-i E_0 t/\hbar} \begin{bmatrix} \cos\left(\frac{A t}{\hbar}\right) & i \sin\left(\frac{A t}{\hbar}\right) \\ i \sin\left(\frac{A t}{\hbar}\right) & \cos\left(\frac{A t}{\hbar}\right) \end{bmatrix}$$

Therefore

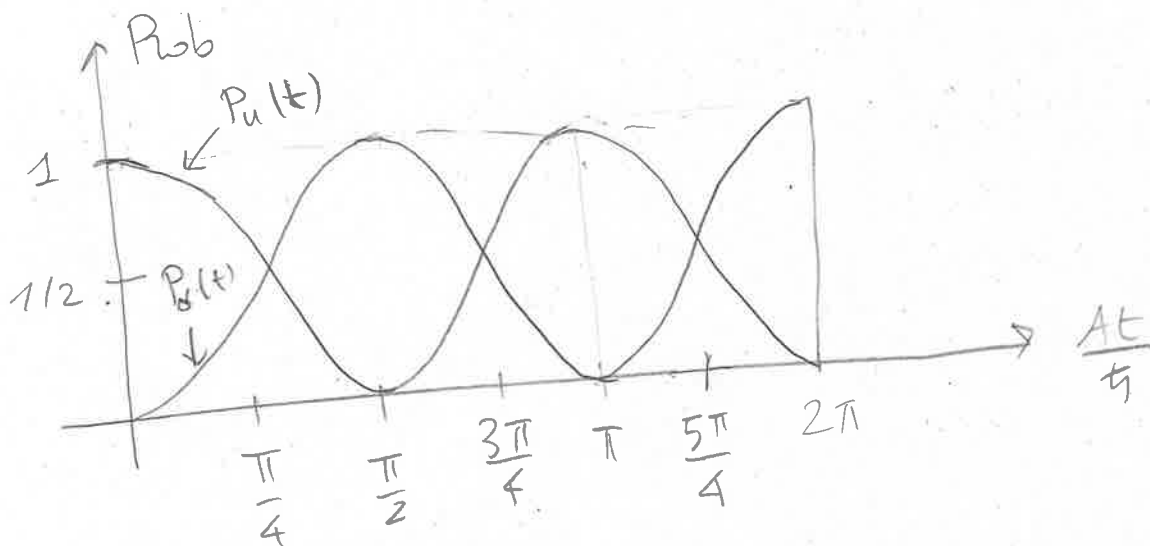
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$$\begin{cases} a_u(t) = e^{-iEt/\hbar} \left[\cos\left(\frac{At}{\hbar}\right) a_u(0) + i \sin\left(\frac{At}{\hbar}\right) a_d(0) \right] \\ a_d(t) = e^{-iEt/\hbar} \left[i \sin\left(\frac{At}{\hbar}\right) a_u(0) + \cos\left(\frac{At}{\hbar}\right) a_d(0) \right] \end{cases} \quad (1.9)$$

What does this mean? If at $t=0$ the molecule is prepared in the state "up", we have

$$a_u(0) = 1, \quad a_d(0) = 0 \quad \Rightarrow$$

$$\Rightarrow |a_u(t)|^2 = \cos^2\left(\frac{At}{\hbar}\right); \quad |a_d(t)|^2 = \sin^2\left(\frac{At}{\hbar}\right)$$

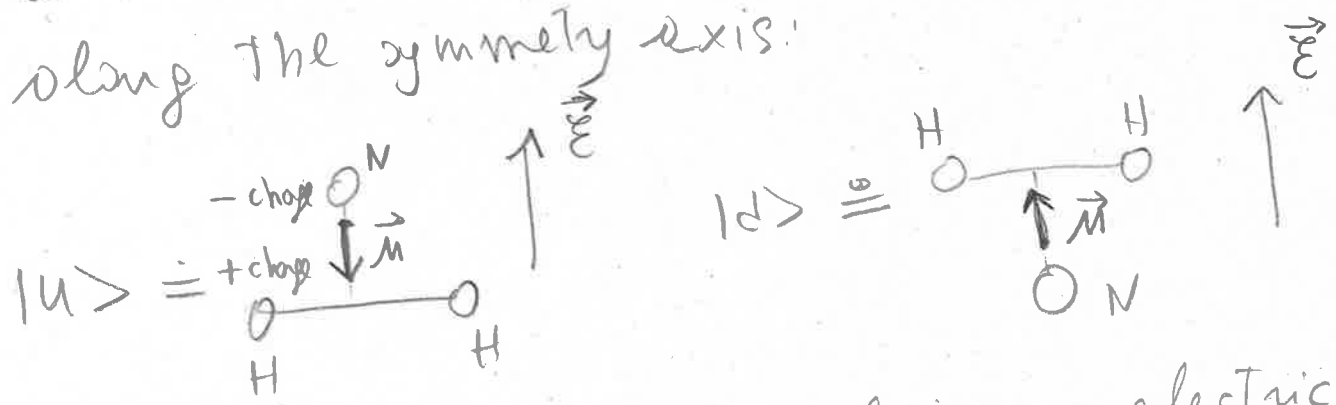


$$P_u(t) = |a_u(t)|^2$$

$$P_d(t) = |a_d(t)|^2$$

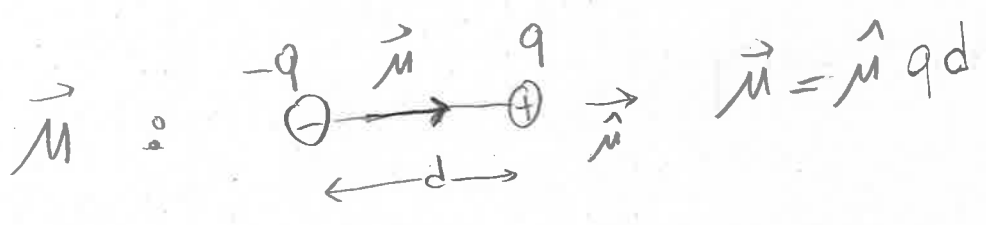
What if I apply a constant (static) electric field \vec{E} ?

In the molecule the electrons tend to stay closer to N. This creates a DIPOLE moment $\vec{\mu}$ directed along the symmetry axis.



The potential energy of a dipole in an electric field \vec{E} is simply:

$$V = -\vec{\mu} \cdot \vec{E}$$



So now $|u\rangle$ gets higher energy than $|d\rangle$. Therefore we put now:

$$H_{uu} = E_0 + \mu E \quad ; \quad H_{dd} = E_0 - \mu E$$

and in the hypothesis that the electric field is so weak to do not change the flip probability, we have:

$$H = \begin{bmatrix} E_0 + \mu \epsilon & -A \\ -A & E_0 - \mu \epsilon \end{bmatrix}$$

As before, we diagonalize H .

$$E_{\pm} = E_0 \pm \sqrt{A^2 + \mu^2 \epsilon^2} \xrightarrow{\mu \epsilon \gg A} E_0 \pm \mu \epsilon$$

The spectrum (Electric-field dependent) is now:

