

The Ammonia Molecule can be thought of as a two-state system. The TDSE in Matrix Mechanics form is

$$i\hbar \frac{d}{dt} \begin{pmatrix} c_1(t) \\ c_2(t) \end{pmatrix} = \begin{pmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{pmatrix} \begin{pmatrix} c_1(t) \\ c_2(t) \end{pmatrix}$$

In this notation, the state $\begin{pmatrix} 1 \\ 0 \end{pmatrix}$ stands for N atoms up, & the state $\begin{pmatrix} 0 \\ 1 \end{pmatrix}$ stands for N atoms down.

If we know the H_{ij} , and the initial conditions $c_1(t=0)$ & $c_2(t=0)$, then we can solve for $c_1(t)$ & $c_2(t)$ for all time.

What Hamiltonian should we use?? Remember, in QM we have no general purpose rules to determine the Hamiltonian. All we can do is guess, and then compare the results that we calculate to observations.

just
one useful
rules of
'thumb'.

The simplest guess that we can make for \hat{H} is that it is diagonal: $H_{ij} = E_i \delta_{ij}$ or

$$H = \begin{pmatrix} E_1 & 0 \\ 0 & E_2 \end{pmatrix}$$

By making this guess, we are essentially guessing that the $|N \text{ atoms up} \rangle$ state and $|N \text{ atoms down} \rangle$ state are stationary states (or eigenstates of \hat{H}).

The TDSE reads as

Solve

$$\begin{aligned} i\hbar \frac{dc_1(t)}{dt} &= E_1 c_1(t) \Rightarrow c_1(t) = c_1(t=0) e^{-iE_1 t/\hbar} \\ \& \quad i\hbar \frac{dc_2(t)}{dt} &= E_2 c_2(t) \quad c_2(t) = c_2(t=0) e^{-iE_2 t/\hbar} \end{aligned}$$

When H is diagonal, the two states evolve independent of each other. If we assume an initial condition such as

$$\begin{pmatrix} c_1(t=0) \\ c_2(t=0) \end{pmatrix} = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad (\text{Assume that } NH_3 \text{ molecule starts with } N \text{ atom up})$$

Then the particular solution is

$$\begin{pmatrix} c_1(t) \\ c_2(t) \end{pmatrix} = \begin{pmatrix} e^{-iE_1 t/\hbar} \\ 0 \end{pmatrix}, \quad \omega_1 \equiv E_1/\hbar$$

As time goes forward, what's the probability to find N atom up? Answer $P(N \text{ atom up}) = |c_1(t)|^2 = 1$.

Similarly, $P(N \text{ atom down}) = |c_2(t)|^2 = 0$.

Nothing is changing in time because we assumed that the $|N \text{ atom up}\rangle$ state is an eigenstate of energy, (i.e., a stationary state.) We made this assumption by guessing that the Hamiltonian is diagonal in the $\{|up\rangle, |down\rangle\}$ basis.

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We can go one step further and guess that $E_1 = E_2$, because the NH_3 molecule is symmetric. So there is no reason why $|\text{up}\rangle$ should have a different energy than $|\text{down}\rangle$. In this case the NH_3 molecule has only one energy, E_0 , and the $|\text{up}\rangle$ & $|\text{down}\rangle$ states are stationary.

However, ~~our~~ observations of NH_3 reveal that it has two energies. To accommodate this, we can either abandon our assumption that NH_3 is symmetric, or abandon our guess that \hat{H} is diagonal in the $\{|\text{up}\rangle, |\text{down}\rangle\}$ basis. Since we have good reasons for believing that NH_3 is symmetric, and no reason for believing that \hat{H} is diagonal, we should try a non-diagonal \hat{H} .

Let's guess $\hat{H} = \begin{pmatrix} E_0 & -A \\ -A & E_0 \end{pmatrix}$, E_0, A real.

Now the TDSE reads as

$$i\hbar \frac{dc_1(t)}{dt} = E_0 c_1(t) - A c_2(t)$$

$$i\hbar \frac{dc_2(t)}{dt} = -A c_1(t) + E_0 c_2(t).$$

Roughly speaking, the off-diagonal term (A) couples the two states together. Physically it means that $|\text{up}\rangle \leftrightarrow |\text{down}\rangle$...

A nice way to solve these equations is to add them & subtract them:

$$i\hbar \frac{d}{dt} (c_1(t) + c_2(t)) = (E_0 - A) (c_1(t) + c_2(t))$$

$$i\hbar \frac{d}{dt} (c_1(t) - c_2(t)) = (E_0 + A) (c_1(t) - c_2(t))$$

Now define $c_I(t) \equiv c_1(t) + c_2(t)$
 and $c_{II}(t) \equiv c_1(t) - c_2(t)$.

Then

$$i\hbar \frac{d c_I(t)}{dt} = (E_0 - A) c_I(t) \Rightarrow c_I(t) = c_I(t=0) e^{-i(E_0 - A)t}$$

$$i\hbar \frac{d c_{II}(t)}{dt} = (E_0 + A) c_{II}(t) \Rightarrow c_{II}(t) = c_{II}(t=0) e^{-i(E_0 + A)t}$$

We have found two states which are stationary. Their time evolution is simple (just multiply by e^{-iEt}), and each has one energy: $E_0 - A = E_I$, $E_0 + A = E_{II}$. We see that E_0 , which is H_{11} & H_{22} , is not an eigenvalue of \hat{H} , so it will not be an observed energy. The eigenvalues are $E_0 - A$ & $E_0 + A$.

So our eigenstates are

$$c_I \equiv c_1 + c_2 \quad \& \quad c_{II} \equiv c_1 - c_2$$

We can write these as $|I\rangle = |Natom\ up\rangle + |Natom\ down\rangle$
 & $|II\rangle = |Natom\ up\rangle - |Natom\ down\rangle$.

But to normalize them we should write

$$|I\rangle = \frac{1}{\sqrt{2}} |up\rangle + \frac{1}{\sqrt{2}} |down\rangle, \text{ energy} = E_0 - A$$

$$\& \quad |II\rangle = \frac{1}{\sqrt{2}} |up\rangle - \frac{1}{\sqrt{2}} |down\rangle, \text{ energy} = E_0 + A$$

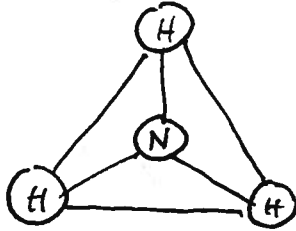
Lecture 32.5

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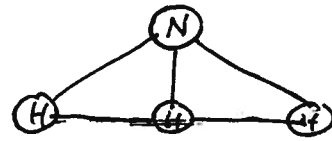
Two-State system: Ammonia Molecule (NH₃)

A triangle of H-atoms:

Nitrogen above or below



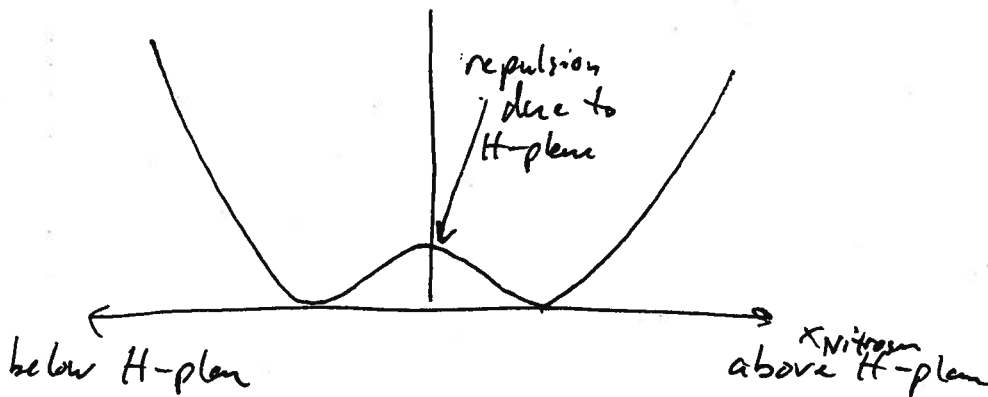
Top View



Side view

"pyramid shape"

Potential seen by N atom:



Roughly speaking, N-atom takes one of two positions: up & down. This is an approximate two-state system.

TDSE in Matrix Mechanics Form

$$i\hbar \frac{d}{dt} \begin{pmatrix} c_1(t) \\ c_2(t) \end{pmatrix} = \begin{pmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{pmatrix} \begin{pmatrix} c_1(t) \\ c_2(t) \end{pmatrix}$$

State $\begin{pmatrix} 1 \\ 0 \end{pmatrix}$ stands for N atom up

State $\begin{pmatrix} 0 \\ 1 \end{pmatrix}$ stand for N atom down.

$c_1(t)$ = amplitude to observe N -atom up
 $c_2(t)$ = " " " " N -atom down

Hamiltonian is
$$\begin{pmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{pmatrix}.$$

If we guess $\hat{0}$

$$H = \begin{pmatrix} H_{11} & \cancel{H_{12}} \\ \cancel{H_{21}} & H_{22} \end{pmatrix}$$

we are guessing that N -atom-up is stationary with energy H_{11} , & we are guessing that N -atom-down is stationary with energy H_{22} .

The potential $V(x)$ is symmetric, so, up & down, should have same energy. Then $H_{11} = H_{22}$. But we observe that Ammonia has 2 energies. So we must add a non-diagonal term \implies N -atom-up & N -atom-down are not stationary.

So we guess
$$H = \begin{pmatrix} E_0 & -A \\ -A & E_0 \end{pmatrix}$$

$$i\hbar \frac{dc_1(t)}{dt} = E_0 c_1(t) - A c_2(t)$$

$$i\hbar \frac{dc_2(t)}{dt} = -A c_1(t) + E_0 c_2(t).$$

Solve by adding & subtracting both equations.

$$i\hbar \frac{d}{dt} (c_1(t) + c_2(t)) = (E_0 - A)(c_1(t) + c_2(t))$$

$$i\hbar \frac{d}{dt} (c_1(t) - c_2(t)) = (E_0 + A)(c_1(t) - c_2(t))$$

Define $c_1(t) + c_2(t) \equiv c_I(t)$

$c_1(t) - c_2(t) \equiv c_{II}(t)$

Then solution: $c_I(t) = c_I(t=0) e^{-i\omega_I t}$ $\omega_I = \frac{E_0 - A}{\hbar}$

$c_{II}(t) = c_{II}(t=0) e^{-i\omega_{II} t}$ $\omega_{II} = \frac{E_0 + A}{\hbar}$

c_I & c_{II} are stationary. They have a simple time dependence.

Use Dirac Notation:

$$|I\rangle = |N_{atom up}\rangle + |N_{atom down}\rangle$$

$$|II\rangle = |N_{atom up}\rangle - |N_{atom down}\rangle$$

But Normalize them correctly:

$$|I\rangle \equiv \frac{1}{\sqrt{2}} (|up\rangle + |down\rangle) \quad \text{energy} = E_0 - A = E_I$$

$$|II\rangle \equiv \frac{1}{\sqrt{2}} (|up\rangle - |down\rangle) \quad \text{energy} = E_0 + A = E_{II}$$

Let's explicitly confirm that $|I\rangle$ & $|II\rangle$ are eigenstates of \hat{H}_0

$$\underbrace{\begin{pmatrix} E_0 & -A \\ -A & E_0 \end{pmatrix}}_{\hat{H}} \underbrace{\begin{pmatrix} \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} \end{pmatrix}}_{|I\rangle} \stackrel{??}{=} E_I \begin{pmatrix} \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} \end{pmatrix}$$

of \hat{H}_0

Is this true?? Answer: Yes

M. H. ... to ...

How do $|I\rangle$ & $|II\rangle$ evolve in time? Answer:

Answer: $|I\rangle_t = |I\rangle e^{-i\omega_I t}$ $|II\rangle_t = |II\rangle e^{-i\omega_{II} t}$

How does $|up\rangle$ evolve in time?

Answer: ~~At $t=0$~~ $|I\rangle = \frac{1}{\sqrt{2}} |up\rangle + \frac{1}{\sqrt{2}} |down\rangle$
 $|II\rangle = \frac{1}{\sqrt{2}} |up\rangle - \frac{1}{\sqrt{2}} |down\rangle$

~~At $t=0$~~

$|up\rangle = \frac{1}{\sqrt{2}} |I\rangle + \frac{1}{\sqrt{2}} |II\rangle$

~~$|down\rangle = \frac{1}{\sqrt{2}} |I\rangle - \frac{1}{\sqrt{2}} |II\rangle$~~

So at $t > 0$,

$|up\rangle_t = \frac{1}{\sqrt{2}} |I\rangle e^{-i\omega_I t} + \frac{1}{\sqrt{2}} |II\rangle e^{-i\omega_{II} t}$

~~$|down\rangle_t = \frac{1}{\sqrt{2}} |I\rangle e^{-i\omega_I t} - \frac{1}{\sqrt{2}} |II\rangle e^{-i\omega_{II} t}$~~

$|up\rangle_t = \frac{1}{\sqrt{2}} \left[\frac{1}{\sqrt{2}} |up\rangle + \frac{1}{\sqrt{2}} |down\rangle \right] e^{-i\omega_I t} + \frac{1}{\sqrt{2}} \left[\frac{1}{\sqrt{2}} |up\rangle - \frac{1}{\sqrt{2}} |down\rangle \right] e^{-i\omega_{II} t}$
 $= \frac{1}{2} \left[e^{-i\omega_I t} + e^{-i\omega_{II} t} \right] |up\rangle + \frac{1}{2} \left[e^{-i\omega_I t} - e^{-i\omega_{II} t} \right] |down\rangle$

Also, $\omega_I = \frac{E_0 - A}{\hbar}$, $\omega_{II} = \frac{E_0 + A}{\hbar}$

$|up\rangle_t = \frac{1}{2} e^{-iE_0 t/\hbar} \left(e^{iA t/\hbar} + e^{-iA t/\hbar} \right) |up\rangle + \frac{1}{2} e^{-iE_0 t/\hbar} \left(e^{iA t/\hbar} - e^{-iA t/\hbar} \right) |down\rangle$

$|up\rangle_t = e^{-iE_0 t/\hbar} \left[\cos(At/\hbar) |up\rangle + i \sin(At/\hbar) |down\rangle \right]$

If we start the system with N atoms up, the system evolves in time like this.

What does this mean? For example, what is

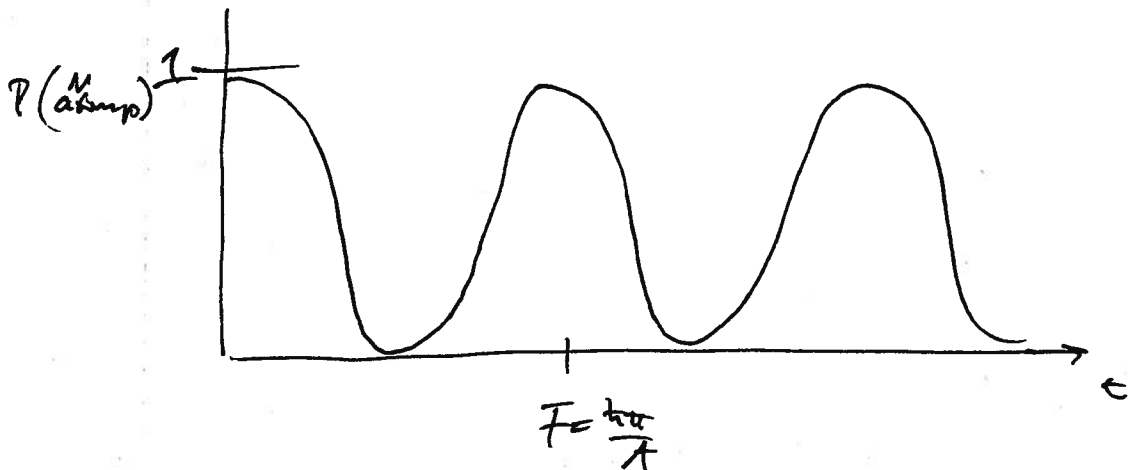
the probability to observe N -atoms-up as a function of time?

Amplitude to observe N -atoms-up

$$= \langle \text{up} | \text{up} \rangle_t = e^{-iE_0 t / \hbar} \cos(\omega t / \hbar)$$

\uparrow base state \uparrow state evolving in time

$$P(\text{up}, t) = |\langle \text{up} | \text{up} \rangle_t|^2 = \cos^2(\omega t / \hbar)$$



Probability slashes back and forth between $|\text{up}\rangle$ & $|\text{down}\rangle$.

The only way to "stop the slashing" is to put the system in an energy eigenstate like $|\text{II}\rangle$ or $|\text{I}\rangle$.

But $|\text{up}\rangle_t$ never evolves into an energy eigenstate on its own.

For the two-state ammonia molecule we have

$$|N_{\text{atom up}}\rangle = |\text{up}\rangle \sim \begin{pmatrix} 1 \\ 0 \end{pmatrix} \text{ in column vector form}$$

$$|N_{\text{atom down}}\rangle = |\text{down}\rangle \sim \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

Essentially, we are imagining that the position of the N atom takes only two discrete values, up & down. This is a good approximation for this molecule.

In our column vector notation, $\begin{pmatrix} c_1 \\ c_2 \end{pmatrix}$, c_1 is

the amplitude to find the N atom up, & c_2 is the amplitude to find N atom down. As time goes forward, these amplitudes can change.

i.e. Our state vector is $\begin{pmatrix} c_1(t) \\ c_2(t) \end{pmatrix}$ for this system.

$$|c_1(t)|^2 = P(\text{N atom up}), \quad |c_2(t)|^2 = P(\text{N atom down})$$

We can also use ket notation:

Since any state can be written this way, $|\psi\rangle = c_1(t)|\text{up}\rangle + c_2(t)|\text{down}\rangle$ from a complete set.
Our Hamiltonian is

$$\hat{H} = \begin{pmatrix} E_0 & -A \\ -A & E_0 \end{pmatrix} \text{ in the } \{|\text{up}\rangle, |\text{down}\rangle\} \text{ basis.}$$

We explicitly solved the TDSE for this system and we found stationary states

$$|I\rangle \sim \text{state I} \sim \begin{pmatrix} \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} \end{pmatrix}, \text{ energy} = E_0 - A$$

$$|II\rangle \sim \text{state II} \sim \begin{pmatrix} \frac{1}{\sqrt{2}} \\ -\frac{1}{\sqrt{2}} \end{pmatrix}, \text{ energy} = E_0 + A.$$

We have put in the $\frac{1}{\sqrt{2}}$ factors to normalize these states : $\langle I | I \rangle = \left(\frac{1}{\sqrt{2}}, \frac{1}{\sqrt{2}} \right) \begin{pmatrix} \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} \end{pmatrix} = \frac{1}{2} + \frac{1}{2} = 1$

$$\text{and } \langle II | II \rangle = \left(\frac{1}{\sqrt{2}}, -\frac{1}{\sqrt{2}} \right) \begin{pmatrix} \frac{1}{\sqrt{2}} \\ -\frac{1}{\sqrt{2}} \end{pmatrix} = \frac{1}{2} + \frac{1}{2} = 1 \checkmark$$

The stationary states evolve in time as

~~the~~

We can explicitly confirm that $|I\rangle$ & $|II\rangle$ are stationary by showing that they are eigenstates of \hat{H} :

$$\hat{H}|I\rangle \stackrel{?}{=} E_I |I\rangle \quad ?? \text{ Is this true?}$$

Try it:

$$\underbrace{\begin{pmatrix} E_0 & -A \\ -A & E_0 \end{pmatrix}}_{\hat{H}} \underbrace{\begin{pmatrix} \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} \end{pmatrix}}_{\uparrow} = \begin{pmatrix} \frac{1}{\sqrt{2}}(E_0 - A) \\ \frac{1}{\sqrt{2}}(E_0 - A) \end{pmatrix} = \underbrace{(E_0 - A)}_{\substack{\text{eigenvalue} \\ \text{eigenvalue}}} \underbrace{\begin{pmatrix} \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} \end{pmatrix}}_{\uparrow \text{eigen vector}} \checkmark$$

Similarly, $\hat{H} |II\rangle = E_{II} |II\rangle$ (Try it.)

states $|I\rangle$ & $|II\rangle$ evolve in time & in a very simple manner:

If $|\psi\rangle_{t=0} = |I\rangle$, then $|\psi\rangle_t = |I\rangle e^{-iE_I t}$

If $|\psi\rangle_{t=0} = |II\rangle$, then $|\psi\rangle_t = |II\rangle e^{-iE_{II} t}$

How do the $|up\rangle$ and $|down\rangle$ states evolve in time?

To answer, re-write $|up\rangle$ & $|down\rangle$ in terms of $|I\rangle$ & $|II\rangle$

This is I, II in terms of $up, down$

$|I\rangle = \frac{1}{\sqrt{2}} |up\rangle + \frac{1}{\sqrt{2}} |down\rangle$
 $|II\rangle = \frac{1}{\sqrt{2}} |up\rangle - \frac{1}{\sqrt{2}} |down\rangle$

Add & Subtract these equations

$|I\rangle + |II\rangle = \sqrt{2} |up\rangle$

$|I\rangle - |II\rangle = \sqrt{2} |down\rangle$

$|up\rangle = \frac{1}{\sqrt{2}} |I\rangle + \frac{1}{\sqrt{2}} |II\rangle$
 $|down\rangle = \frac{1}{\sqrt{2}} |I\rangle - \frac{1}{\sqrt{2}} |II\rangle$

This is $up, down$ in terms of I, II .

Now we can write down how $|up\rangle$ & $|down\rangle$ evolve in time

If $|\psi\rangle = |up\rangle$ at $t=0$, then $|\psi\rangle_t = \frac{1}{\sqrt{2}} |I\rangle e^{-iE_I t} + \frac{1}{\sqrt{2}} |II\rangle e^{-iE_{II} t}$

= Now substitute $I, II \rightarrow up, down$ on right hand side

If $|\psi\rangle = |up\rangle$ at $t = 0$,

$$\begin{aligned}
|\psi\rangle_t &= \frac{1}{\sqrt{2}} \left(\frac{1}{\sqrt{2}} |up\rangle + \frac{1}{\sqrt{2}} |down\rangle \right) e^{-i\omega_I t} + \frac{1}{\sqrt{2}} \left(\frac{1}{\sqrt{2}} |up\rangle - \frac{1}{\sqrt{2}} |down\rangle \right) e^{-i\omega_{II} t} \\
&= \frac{1}{2} \left(e^{-i\omega_I t} + e^{-i\omega_{II} t} \right) |up\rangle + \frac{1}{2} \left(e^{-i\omega_I t} - e^{-i\omega_{II} t} \right) |down\rangle.
\end{aligned}$$

∴ If we start with the Nitrogen atom up, the amplitude to find it up at a later time is

$$\langle up | \psi \rangle_t = \frac{1}{2} \left(e^{-i\omega_I t} + e^{-i\omega_{II} t} \right) \quad \left(\begin{array}{l} \text{Since } \langle up | up \rangle = 1 \\ \& \langle up | down \rangle = 0 \end{array} \right)$$

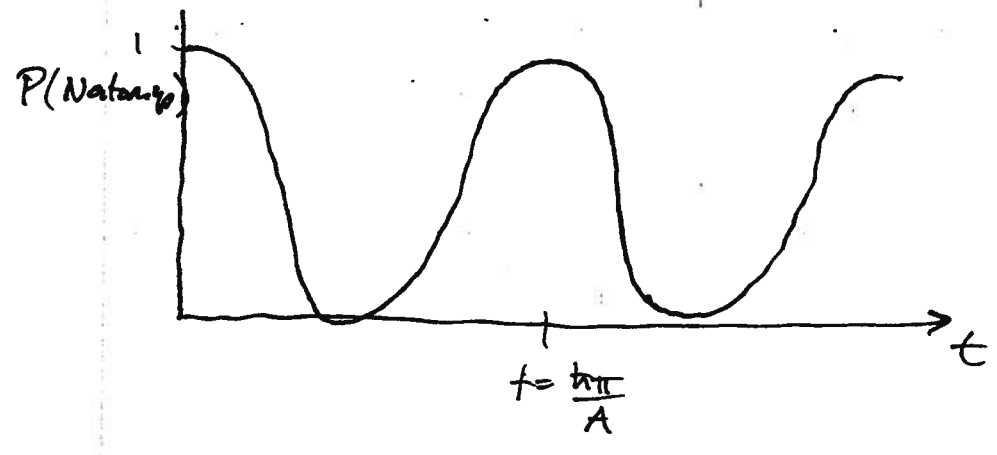
We can simplify further using $\omega_I = (E_0 - A)/\hbar$
& $\omega_{II} = (E_0 + A)/\hbar$

$$\langle up | \psi \rangle_t = \frac{1}{2} e^{-iE_0 t/\hbar} \left(e^{iA t/\hbar} + e^{-iA t/\hbar} \right) = e^{-iE_0 t/\hbar} \cos(A t/\hbar)$$

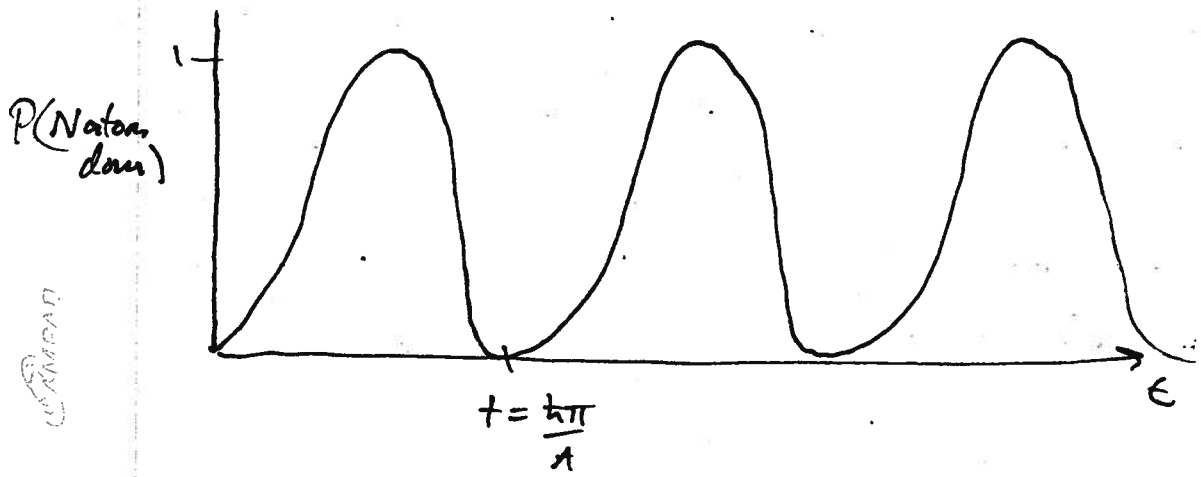
Similarly, if we start with N atom up, the amplitude to find N atom down is

$$\langle down | \psi \rangle_t = e^{-iE_0 t/\hbar} \sin(A t/\hbar)$$

∴ If we start with N atom up, the Probability to find it up at a later time oscillates as $\cos^2(A t/\hbar)$



Where is the Probability going? Answer: into $P(\text{Natom down})$



For any two state system which starts out in a non-stationary state, the probability "sloshes back and forth" between the two states. The only way to "stop the sloshing" is to start in a stationary state \rightarrow an energy eigenstate.