Two - Level Systems ~~Ammonia~~ Part I

First, for n-level systems, when does

$$\frac{d}{dt}\langle \mathcal{O} \rangle = 0 \quad \text{for } \mathcal{O} \text{ static?}$$

① $\boxed{\text{Prepare system in state of definite energy}}$

$$|\psi(0)\rangle = |\varphi_n\rangle \quad \text{where} \quad H|\varphi_n\rangle = E_n|\varphi_n\rangle$$

$t=0$

$$\Rightarrow \langle \psi(t)|\mathcal{O}|\psi(t)\rangle = \langle \varphi_n|e^{i\omega_n t}\mathcal{O}e^{-i\omega_n t}|\varphi_n\rangle$$

$$= \langle \psi(0)|\mathcal{O}|\psi(0)\rangle$$

or

② $\boxed{\text{Measure a quantity which is associated with a symmetry}}$

$$[\mathcal{O}, H] = 0 \quad , \quad |\psi\rangle = \sum_n c_n|\varphi_n\rangle$$

(Not an energy eigenstate)

(If $\mathcal{O}$ is continuous then $e^{i\alpha\mathcal{O}}$ is a symmetry transformation)

$\mathcal{O}|\varphi_n\rangle = |\chi_n\rangle$, where $|\varphi_n\rangle$ & $|\chi_n\rangle$ might be different, but $H|\chi_n\rangle = E_n|\chi_n\rangle$

$$\Rightarrow \langle \psi(t)|\mathcal{O}|\psi(t)\rangle = \sum_{n,m} c_n^* c_m \langle \varphi_n|e^{i\omega_n t}\mathcal{O}e^{-i\omega_m t}|\varphi_m\rangle$$

$$= \sum_{n,m} c_n^* c_m e^{i(\omega_n-\omega_m)t}\underbrace{\langle \varphi_n|\chi_m\rangle}_{=0 \text{ if } E_n \neq E_m}$$

(Since $\mathcal{O}$ can only carry eigenstates of H to other eigenstates of H with same eigenvalue)

$$= \sum_{n,m} c_n^* c_m \langle \varphi_n | \chi_m \rangle$$

for $E_n = E_m$

$$= \langle \psi(0) | \mathcal{O} | \psi(0) \rangle$$

Easier way to show this:

$$\langle \psi(t) | \mathcal{O} | \psi(t) \rangle = \langle \psi(0) | e^{\frac{iH}{\hbar}t} \mathcal{O} e^{-\frac{iH}{\hbar}t} | \psi(0) \rangle$$

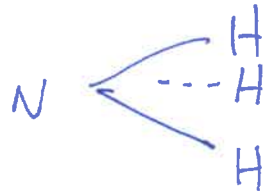
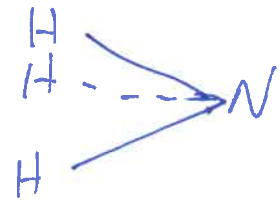
$$= \langle \psi(0) | \mathcal{O} | \psi(0) \rangle \text{ since } [\mathcal{O}, H] = 0$$

What set of observables are symmetries?

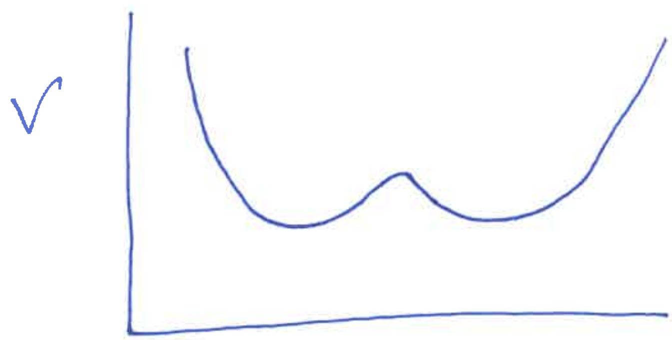
- H is always a symmetry. (Energy is conserved)

- Other quantities such as parity, momentum, etc. can be symmetries, depending on H, or more specifically $V(x)$

Example 2-level System: Ammonia

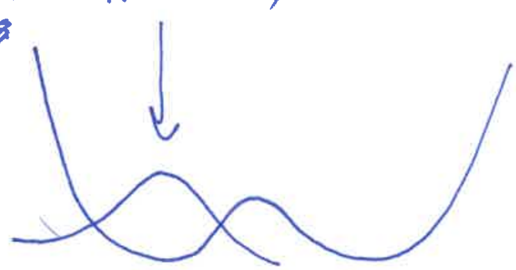
$|L\rangle =$  $|R\rangle =$ 

$z \rightarrow$



z_N (position of N relative to H plane)

$|L\rangle$ is approximately

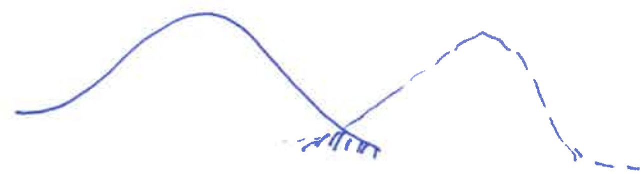


$\approx |R\rangle$

They are approximately harmonic oscillator wave functions in each well. $|L\rangle$ & $|R\rangle$ here represent the ground state H.O. function, but there will also be vibrationally excited states e.g. $|L(v=1)\rangle$

- But this is not a convenient basis, because it's not orthogonal.

- Say $\langle L|L\rangle = \langle R|R\rangle = 1$ (Normalized Gaussians)

$\langle L|R\rangle \neq 0$ because 

- We can, however construct a normalized basis set from $|L\rangle$ + $|R\rangle$

- Let $\eta = \langle L|R\rangle$ ← η is real + positive for our definition of $|L\rangle$ + $|R\rangle$

- $|1\rangle = N(|L\rangle - \alpha|R\rangle)$ $\quad |2\rangle = N(|R\rangle - \alpha|L\rangle)$

$$\frac{\langle 1|2\rangle}{N^2} = \langle L|R\rangle + \alpha^2\langle R|L\rangle - \alpha\langle L|L\rangle - \alpha\langle R|R\rangle$$

$$= \eta + \alpha^2\eta - \alpha - \alpha = 0$$

$$\Rightarrow \eta\alpha^2 - 2\alpha + \eta = 0$$

$$\alpha = \frac{2 \pm \sqrt{4 - 4\eta^2}}{2\eta} = \frac{1 \pm (1-\eta^2)^{1/2}}{\eta}$$

$$(1+x)^{1/2} \approx 1 + \tfrac{1}{2}x + O(x^2) \Rightarrow (1-\eta^2)^{1/2} \approx 1 - \tfrac{1}{2}\eta^2$$

Taking solution which gives small α:

$$\boxed{\alpha = \frac{\eta}{2}}$$

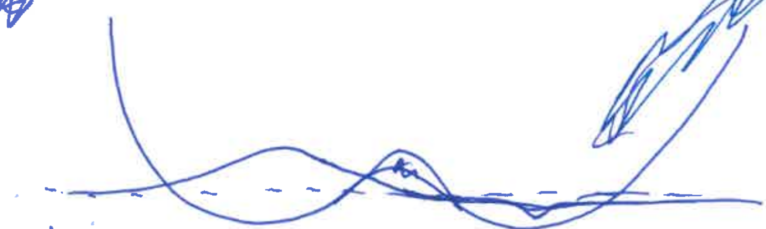
N is chosen to normalize

- Then as $\eta \to 0$, $|1\rangle \to |L\rangle$ & $|2\rangle \to |R\rangle$

- For finite but small η.

$$|1\rangle = |L\rangle + O(\eta)|R\rangle$$

Precisely $|1\rangle =$



$$|2\rangle = |R\rangle + O(\eta)|L\rangle$$

$|2\rangle =$

- Mostly localized, but not completely

- Orthonormal set

$$\langle 1|1\rangle = \langle 2|2\rangle = 1$$

$$\langle 1|2\rangle = 0$$

- So we have some energy expectation value:

$$\langle 1 | H | 1 \rangle = \langle 2 | H | 2 \rangle = E_0$$

- But there is also an off-diagonal ME associated with tunneling probability.

$$\langle 1 | H | 2 \rangle = \Delta$$

- (N pops thru barrier to reorient molecule)
  * Distinct from rotating from $|L\rangle$ to $|R\rangle$ — much more strange than that!!
- Can describe H by 2×2 matrix in basis of $|1\rangle$ $|2\rangle$ states (not eigenstates of H)

$$H = \begin{array}{c|cc} & |1\rangle & |2\rangle \\ \hline |1\rangle & E_0 & -\Delta \\ |2\rangle & -\Delta & E_0 \end{array}$$

(Choice of sign convention will be apparent later)

(How do we know tunnelling happens from $|1\rangle \to |2\rangle$? Because $H|1\rangle \neq E|1\rangle$ + it is clear from position space that if $\langle 2|1\rangle = 0$ that $\langle 2|H|1\rangle \neq 0$

$|+\rangle = \frac{1}{\sqrt{2}}(|1\rangle + |2\rangle)$

Guess that eigenstates are:

$$|+\rangle = \frac{1}{\sqrt{2}}(|1\rangle + |2\rangle) = \frac{1}{\sqrt{2}}\begin{pmatrix}1\\1\end{pmatrix}$$

$$|-\rangle = \frac{1}{\sqrt{2}}(|1\rangle - |2\rangle) = \frac{1}{\sqrt{2}}\begin{pmatrix}1\\-1\end{pmatrix}$$

$|-\rangle = \frac{1}{\sqrt{2}}(|1\rangle - |2\rangle)$

Normalization is correct:

e.g. $\langle + | + \rangle = \left(\frac{1}{\sqrt{2}}\right)^2 \left(\underbrace{\langle 1|1\rangle}_{1} + \underbrace{\langle 2|2\rangle}_{1} + \underbrace{\langle 1|2\rangle}_{0} + \underbrace{\langle 2|1\rangle}_{0} \right) = 1$ ✓

$$\langle + | - \rangle = \frac{1}{2}\left(\langle 1|1\rangle - \langle 2|2\rangle - \langle 1|2\rangle + \langle 2|1\rangle \right) = 0 \checkmark$$

Eigenenergies?

$$H|+\rangle = \begin{pmatrix} E_0 & -\Delta \\ -\Delta & E_0 \end{pmatrix} \cdot \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 1 \end{pmatrix} = \frac{1}{\sqrt{2}}\begin{pmatrix} E_0 - \Delta \\ E_0 - \Delta \end{pmatrix} = (E_0 - \Delta)\frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 1 \end{pmatrix}$$

$$= (E_0 - \Delta)|+\rangle$$

$$H|-\rangle = \begin{pmatrix} E_0 & -\Delta \\ -\Delta & E_0 \end{pmatrix} \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ -1 \end{pmatrix} = \frac{1}{\sqrt{2}}\begin{pmatrix} +E_0 + \Delta \\ -\Delta - E_0 \end{pmatrix} = (E_0 + \Delta) \cdot \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ -1 \end{pmatrix}$$

$$= (E_0 + \Delta)|-\rangle$$

- If $\Delta \to 0$ then we have a degenerate situation

Working w/ non-orth basis

$H|1\rangle = E_0|1\rangle$
$H|2\rangle = E_0|2\rangle$

or

$H|L\rangle = E_0|L\rangle$
$H|R\rangle = E_0|R\rangle$

or

$H|+\rangle = E_0|+\rangle$
$H|-\rangle = E_0|-\rangle$

Working w/ orth. basis

Degenerate 2D subspace. & # of options for basis states w/ same energy

$$H(\alpha|L\rangle + \beta|R\rangle) = E_0(\alpha|L\rangle + \beta|R\rangle)$$

- But presence of coupling between wells lifts the degeneracy + Common story in QM.
  only $|+\rangle$ + $|-\rangle$ states have def. energy.
- Now which state has lower energy?
- Depends on whether Δ is positive or negative.

~~prove later that e. vects must be states of def energy (no nodes)~~

$|+\rangle \approx$

What about the sign of δ?

$p^2 \propto -\frac{d^2}{dx^2}$

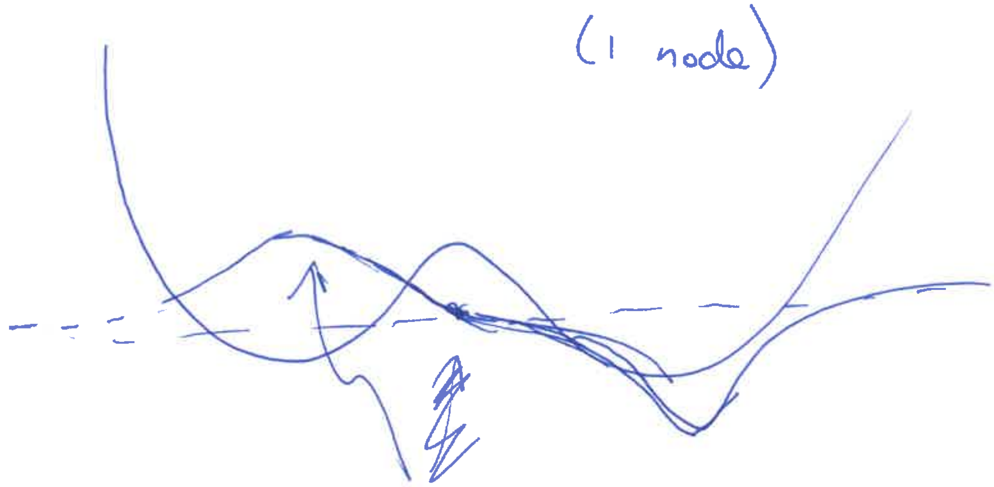
- magnitude of curvature here is a little less than it would be for isolated wells. (where energy is all kinetic)
- curvature $\propto$ K.E. $\Rightarrow$ energy is lower

$\Rightarrow \Delta > 0$

- Symmetric state is g.s. of 2-well problem w/ coupling
- For NH_3, N is both up & down equally, w/ phase same

$|-\rangle \approx$

(1 node)



- Curvature higher than for separated wells. (in order for w.f. to hit zero at $x < \infty$)
- Antisym state has slightly higher energy

- So we have a situation where $|1\rangle \approx |L\rangle$ & $|2\rangle \approx |R\rangle$, the localized states, are not the energy eigenstates

- If you prepare the system in $|\psi(t=0)\rangle = |1\rangle$, what is $|\psi(t)\rangle$?

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

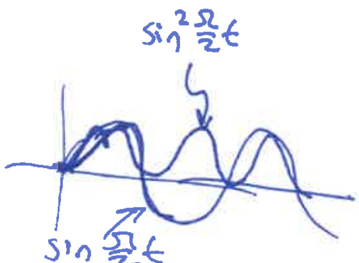
$$|\psi(t)\rangle = \frac{1}{\sqrt{2}}\left(|+\rangle e^{-i\omega_+ t} + |-\rangle e^{-i\omega_- t}\right)$$

$$P_2(t) = |\langle 2|\psi(t)\rangle|^2 = \frac{1}{4}\left|\left(\langle +| - \langle -|\right)\left(e^{-i\omega_+ t}|+\rangle + e^{-i\omega_- t}|-\rangle\right)\right|^2$$

$$= \frac{1}{4}\left|e^{-i\omega_+ t} - e^{-i\omega_- t}\right|^2$$

Define $\Omega = \omega_- - \omega_+ = \frac{2\Delta}{\hbar}$

Then we can pull out a factor of $\left|e^{-i\frac{(\omega_- + \omega_+)}{2}t}\right|^2$ and get



$$\Rightarrow P_2(t) = \frac{1}{4}\left|e^{-i\frac{\Omega t}{2}} - e^{+i\frac{\Omega t}{2}}\right|^2$$

$$= \sin^2 \frac{\Omega}{2} t$$ (which looks like $1 + \sin \Omega t$)

So the system tunnels back and forth, completely, from $|1\rangle \leftrightarrow |2\rangle$ with frequency $\frac{2\Delta}{\hbar}$. If there is no coupling, it never happens. But even with infinitesimal coupling complete flopping happens eventually.

- But what about if we start the system in $|L\rangle$. Will it slosh 100% to $|R\rangle$?

$$|1\rangle = N(|L\rangle - \alpha|R\rangle) \qquad \text{where} \quad \alpha = \frac{\langle L|R\rangle}{2} = \frac{\eta}{2}$$
$$|2\rangle = N(|R\rangle - \alpha|L\rangle)$$

$$\Rightarrow \quad |L\rangle = N(|1\rangle + \alpha|2\rangle)$$
$$|R\rangle = N(|2\rangle + \alpha|1\rangle)$$
$$N = \frac{1}{\sqrt{1+\alpha^2}} \approx 1 - \tfrac{1}{2}\alpha^2$$

If we only consider to order α, we can say $N \approx 1$. If we wanted α^2, we would need to include.

$$= \quad |\psi(t=0)\rangle = |1\rangle + \alpha|2\rangle = \tfrac{1}{\sqrt{2}}\left(|+\rangle + |-\rangle + \alpha|+\rangle - \alpha|-\rangle\right)$$

$$|\psi(t)\rangle = \tfrac{1}{\sqrt{2}}\left[(1+\alpha)e^{-i\omega_+ t}|+\rangle + (1-\alpha)e^{-i\omega_- t}|-\rangle\right] \quad // \quad |R\rangle = \tfrac{1}{\sqrt{2}}\left[(1-\alpha)|+\rangle - (1+\alpha)|-\rangle\right]$$

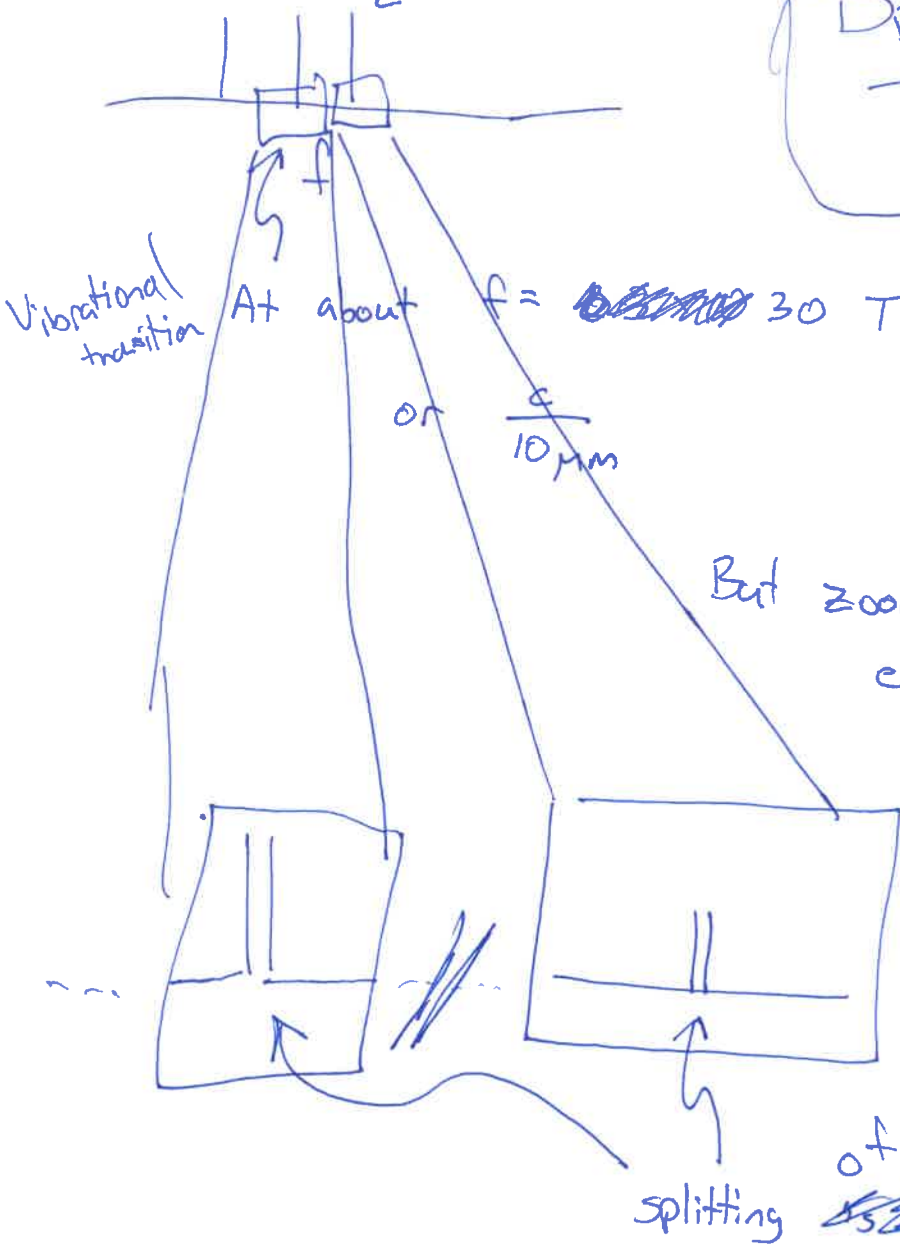
$$P_R(t) = |\langle R|\psi(t)\rangle|^2 = \tfrac{1}{4}\left|(1-\alpha)e^{-i\omega_+ t} - (1+\alpha)e^{-i\omega_- t}\right|^2$$

$$= \tfrac{1}{4}\left|(1-\alpha)e^{-i\frac{\Omega t}{2}} - (1+\alpha)e^{+i\frac{\Omega t}{2}}\right|^2$$

$$|R\rangle \cong \tfrac{1}{\sqrt{2}}(|+\rangle - |-\rangle) - \tfrac{\alpha}{\sqrt{2}}(|+\rangle + |-\rangle)$$

These two rotating phasors are not quite the ~~right~~ same length. As $\alpha \to 0$, i.e. the wells are far apart, the sloshing $\to$ 100%. For finite but small α, the sloshing is nearly 100%, but not quite. Some probability remains in the original localized distribution. ~~So we can in principle tune Δ & α independently by shaping the potential. One controls the tunneling rate & the other controls the maximum tunneling probability. However a few comments: ① For the potentials nature gives us, α & Δ will be related &~~ Comment: We have only analyzed ~~to~~ to order α. So our analysis is only valid in the regime where the sloshing probability is near 100%.

- All other observables for which $[\Theta, H] \neq 0$ will also have $\langle \Theta(t) \rangle$ oscillating at $f = \frac{2\Delta}{h}$.
- For instance z_N
- How fast is f? Easiest way to know is to look at a spectrum.



Discuss measurements

1. Photon emission into spectrometer → H eigenstate
2. Collision → z_p localized state → sloshing

But zoom in and you see each of these lines is split

of each line

- That line splitting involves a pair of levels, e.g. v = 0 & v = 1, but you can measure a couple line splittings to find the splitting of each level. We find that the ground state splitting of 2Δ is 24 GHz. $T = \frac{1}{24\,\text{GHz}} = 42$ ps
- So, if we prepare in |1>, it oscillates to |2> in 20 ps!