Lecture 24: Time dependent perturbation theory (I) — Coherent Rabi flopping (NMR)

We have studied the effect of a perturbation on the shift of the energy eigenstates. These are stationary states of the system - they represent static properties. We now turn to the question of dynamics.

For a quantum system to evolve, it must not be in a stationary state. If it starts in such a state (e.g. the ground state), the Hamiltonian must change so that the system finds itself in a superposition of the new eigenstates.

An important paradigm is the addition of a "small" time dependent perturbation (i.e. a Hamiltonian with an explicitly time dependent parameter)

$$\hat{H}(t) = \underbrace{\hat{H}_0}_{\text{zeroth order}} + \underbrace{\hat{H}_1(t)}_{\text{perturbation}}$$

The state vector evolves according to the T.D.S.E.

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

If $[\hat{H}_0, \hat{H}_1(t)] \neq 0$, then an initial eigenstate of $\hat{H}_0$ is no longer an eigenstate of the full Hamiltonian; the state will change.

In time dependent perturbation theory, we are typically interested in the change in population from some initial eigenstate of $\hat{H}_0$, $|\phi_0^{(i)}\rangle$, to a "final state" $|\phi_0^{(f)}\rangle$

Given $|\Psi(0)\rangle = |\phi_i^{(0)}\rangle$, $\hat{H}_0|\phi_i^{(0)}\rangle = E_i^{(0)}|\phi_i^{(0)}\rangle$

Find prob to be in state $|\phi_f^{(0)}\rangle$ @ time t

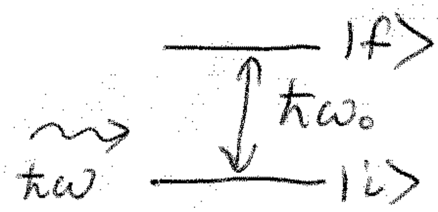
$$P_{f\leftarrow i}(t) = |\langle\phi_f^{(0)}|\Psi(t)\rangle|^2 \quad \text{where } \frac{\partial}{\partial t}|\Psi(t)\rangle = -\frac{i}{\hbar}\hat{H}(t)|\Psi(t)\rangle$$

The "transition rate"

$$W_{f\leftarrow i} = \frac{d}{dt}P_{f\leftarrow i}(t)$$

An important paradigm is <u>resonance</u>, when an oscillating field @ frequency ω is incident on a bound system with naturatal frequency $\omega_0 = \frac{E_f - E_i}{\hbar}$

$\Rightarrow$ Absorption



The transition probability is not the whole story. It is a very "classical" view, the particle is "in" a certain state and then jumps into another definite state. In quantum theory we know that a system can be in a <u>superposition</u> of different state. Time dependent evolution can be <u>coherent</u>, with the state evolving continuously via the time dependent Schrödinger equation.

Magnetic Resonance

An important example of <u>coherent</u> time dependent perturbation theory is nuclear magnetic resonance, the phenomenon underlying MRI = <u>M</u>agnetic <u>R</u>esonance <u>I</u>maging.

Consider a spin-½ proton (e.g. the nucleus of H in H_2O).
Place the sample in a large static $\vec{B}$ field

$$\hat{H}_0 = -\hat{\mu} \cdot \vec{B} \qquad \vec{\mu} = g_p \mu_N \hat{\vec{S}}$$

← spin in units of $\hbar$

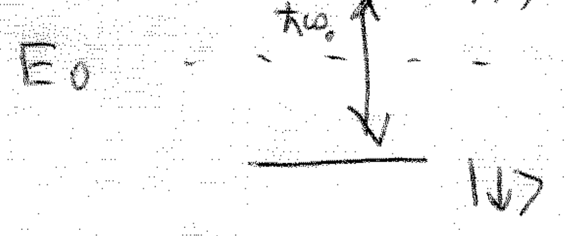
g-factor of proton $\cong 2.8$, $\mu_N = \dfrac{e\hbar}{2M_p c} = h\,(7.62\ \mathrm{MHz/Tesla})$

(Nuclear magneton)

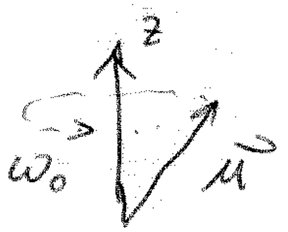
We take direction of $\vec{B}$ to be in $-\vec{e}_z$ direction so "spin down" is ground state $\vec{B} = -B_{\parallel}\,\vec{e}_z$

$$\Rightarrow \hat{H}_0 = +(g_p \mu_N B_{\parallel})\,\hat{S}_z = +\frac{g_p \mu_N B_{\parallel}}{2}\,\hat{\sigma}_z$$

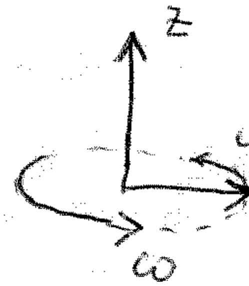
$$\hat{H}_0 \equiv +\frac{\hbar\omega_0}{2}\,\hat{\sigma}_z \quad , \quad \text{Zeroth order } E_{\pm}^{(0)} = \pm\frac{\hbar\omega_0}{2}$$



In the absense of any perturbing field, if the system is not initial in a stationary state it will precess about z-axis with frequency ω_0



We want to apply a perturbation which flips the spin from "down" to "up". Using the picture above, we are guided to consider an oscillating transverse field which rotates w/ spin.



$$\vec{B}_\perp(t) = B_\perp\left(\cos\omega t\, \vec{e}_x + \sin\omega t\, \vec{e}_y\right)$$

If $\vec{B}_\perp(t)$ stays in phase with the precessing $\vec{\mu}$, it will continuously torque it from "up" to "down" or "down" to "up". This is known as "nuclear magnetic resonance".

The total Hamiltonian is

$$\hat{H} = \hat{H}_0 + \hat{H}_1$$

$$\hat{H}_0 = \frac{\hbar\omega_0}{2}\hat{\sigma}_z$$

$$\hat{H}_1 = -\hat{\vec{\mu}}\cdot\vec{B}_\perp(t) = -g_p \mu_N B_\perp (\cos\omega t\, \hat{S}_x + \sin\omega t\, \hat{S}_y)$$

$$= -\frac{\hbar\Omega}{2}\left(e^{-i\omega t}(\hat{S}_x + i\hat{S}_y) + e^{i\omega t}(\hat{S}_x - i\hat{S}_y)\right)$$

$$= -\frac{\hbar\Omega}{2}\left(e^{-i\omega t}\hat{\sigma}_+ + e^{i\omega t}\hat{\sigma}_-\right)$$

where $\hbar\Omega = g_p \mu_N B_\perp$, $\quad \hat{\sigma}_\pm = \hat{S}_x \pm i\hat{S}_y = \hat{S}_\pm$

$$\Rightarrow \hat{H}(t) = \frac{\hbar}{2}\left(\omega_0\hat{\sigma}_z - \Omega\left(e^{-i\omega t}\hat{\sigma}_+ + e^{i\omega t}\hat{\sigma}_-\right)\right)$$

We consider $\Omega \ll \omega_0$ so $\hat{H}_1$ is a "perturbation" to $\hat{H}_0$ (actually, in this problem we need not restrict ourselves to this condition since, as we will see, ~~the~~ an exact solution can always be found)

We seek solutions to the T.D.S.E.

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

Particular given initial state $|\psi(0)\rangle = |\downarrow\rangle$,

we seek probability to be $|\uparrow\rangle$ at a later time.

Expand in basis $\{|\uparrow\rangle, |\downarrow\rangle\}$

$$|\psi(t)\rangle = \begin{bmatrix} c_\uparrow(t) \\ c_\downarrow(t) \end{bmatrix} \qquad \hat{H}(t) \doteq \frac{\hbar}{2}\begin{bmatrix} \omega_0 & -\Omega e^{-i\omega t} \\ -\Omega e^{-i\omega t} & -\omega_0 \end{bmatrix}$$

$$\frac{d}{dt}\begin{bmatrix} c_\uparrow \\ c_\downarrow \end{bmatrix} = -\frac{i}{2}\begin{bmatrix} \omega_0 & -\Omega e^{-i\omega t} \\ -\Omega e^{-i\omega t} & -\omega_0 \end{bmatrix}\begin{bmatrix} c_\uparrow \\ c_\downarrow \end{bmatrix}$$

$$\Rightarrow \left(\dot{c}_\uparrow + \frac{i}{2}\omega_0 c_\uparrow\right) = \frac{i}{2}\Omega e^{-i\omega t} c_\downarrow$$

$$\left(\dot{c}_\downarrow - \frac{i}{2}\omega_0 c_\downarrow\right) = \frac{i}{2}\Omega e^{i\omega t} c_\downarrow$$

Two coupled diff'eq with time dependent coefficients. When time dep most eqns. cannot be solved exactly; here we can.

Consider substitution:

$$C_\uparrow(t) = e^{-i\omega t/2}\,\tilde{C}_\uparrow(t)$$

$$C_\downarrow(t) = e^{i\omega t/2}\,\tilde{C}_\downarrow(t)$$

$$\Rightarrow \quad \dot{\tilde{C}}_\uparrow - \frac{i}{2}\Delta\,\tilde{C}_\uparrow = \frac{i}{2}\Omega\,\tilde{C}_\downarrow$$

$$\dot{\tilde{C}}_\downarrow + \frac{i}{2}\Delta\,\tilde{C}_\downarrow = \frac{i}{2}\Omega\,\tilde{C}_\uparrow$$

$$\Rightarrow \quad \frac{d}{dt}\begin{bmatrix}\tilde{C}_\uparrow \\ \tilde{C}_\downarrow\end{bmatrix} = -\frac{i}{2}\begin{bmatrix}-\Delta & -\Omega \\ -\Omega & +\Delta\end{bmatrix}\begin{bmatrix}\tilde{C}_\uparrow \\ \tilde{C}_\downarrow\end{bmatrix}$$

Schrodinger eq with "Static" Hamiltonian

$$\hat{\tilde{H}} = -\frac{\hbar\Delta}{2}\hat{\sigma}_z - \frac{\hbar\Omega}{2}\hat{\sigma}_x$$

where $\Delta \equiv \omega - \omega_0 \equiv$ "detuning"

Our transformation $c \to \tilde{c}$ is going to the "rotating frame" co-rotating with $\vec{B}_\perp(t)$. In that frame the field is <u>static</u>.

<u>Solution</u>: Take second derivative

$$\ddot{\tilde{c}}_\uparrow - \frac{i}{2}\Delta \dot{\tilde{c}}_\uparrow = \frac{i}{2}\Omega \dot{\tilde{c}}_\downarrow$$

$$\Rightarrow \ddot{\tilde{c}}_\uparrow - \frac{i}{2}\Delta\left(\frac{i}{2}\Delta \tilde{c}_\uparrow + \frac{i}{2}\Omega \tilde{c}_\downarrow\right) = \frac{i}{2}\Omega\left(\frac{-i\Delta}{2}\tilde{c}_\downarrow + \frac{i\Omega}{2}\tilde{c}_\uparrow\right)$$

$$\Rightarrow \ddot{\tilde{c}}_\uparrow + \underbrace{\frac{1}{4}\left(\Omega^2+\Delta^2\right)}_{\equiv \tilde{\Omega}^2} \tilde{c}_\uparrow = 0$$

S.H.O. diff'eq

$$\Rightarrow \text{Solution} \quad \tilde{c}_\uparrow(t) = \tilde{c}_\uparrow(0)\,\left(\frac{\tilde{\Omega}}{2}t\right) + \frac{\dot{\tilde{c}}_\uparrow(0)}{\tilde{\Omega}/2}\sin\left(\frac{\tilde{\Omega}}{2}t\right)$$

Take $c_\uparrow(0) = 0 \quad c_\downarrow(0) = 1 \quad \Rightarrow \tilde{c}_\uparrow(0) = 0, \quad \tilde{c}_\downarrow(0) = 1$

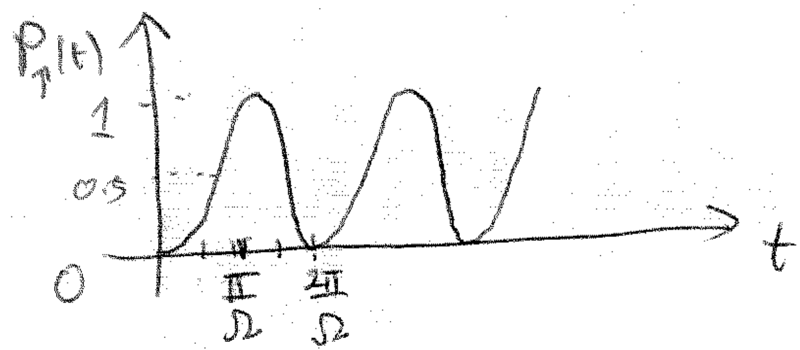
$$\therefore \quad \tilde{c}_\uparrow(t) = i\frac{\Omega}{\tilde{\Omega}}\sin\left(\frac{\tilde{\Omega}}{2}t\right)$$

$$\Rightarrow \boxed{P_\uparrow(t) = |c_\uparrow(t)|^2 = |\tilde{c}_\uparrow(t)|^2 = \frac{\Omega^2}{\Omega^2+\Delta^2}\sin^2\left(\frac{\tilde{\Omega}t}{2}\right)}$$

Rabi solution

"Rabi flopping" (I.I Rabi)

Consider case of <u>resonance</u> $\Delta = 0 \Rightarrow \omega = \omega_0$



Ω = Rabi frequency.

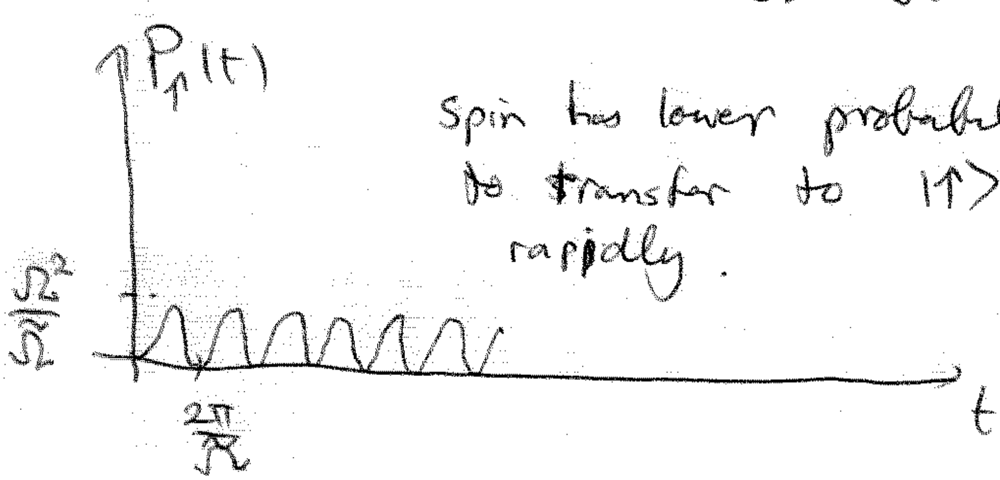
the spin coherently oscillates between $|\downarrow\rangle$ and $|\uparrow\rangle$ @ Rabi frequency. When $\Omega t = \pi \rightarrow$ full transfer

Note when $\Omega t = \pi/2 \Rightarrow |\psi(t)\rangle = \dfrac{|\downarrow\rangle + i|\uparrow\rangle}{\sqrt{2}}$

Coherent superposition

Off resonance: Generalized Rabi freq.

$$\tilde{\Omega} = \sqrt{\Omega^2 + \Delta^2}$$



Spin has lower probability to transfer to $|\uparrow\rangle$ and oscillates rapidly.

Very far off resonance , $\tilde{\Omega} \cong \Delta$

$\Rightarrow$ The maximum probability to be in the excited state

$$P_{\uparrow}(\text{max}) \cong \frac{\Omega^2}{\Delta^2} = \frac{(\hbar\Omega)^2}{\hbar^2(\omega_0-\omega)^2} = \frac{\hbar^2\Omega^2}{(E_f - E_i - \hbar\omega_0)^2}$$

Note the relationship with static perturbation theory.

$$(\hbar\Omega)^2 \sim |\langle\uparrow|\hat{H}_1|\downarrow\rangle|^2 = |\langle f|\hat{H}_1|i\rangle|^2$$

The transition is probable near resonance. Off resonance, the probability of excitation is very small. We say that the system makes a "virtual transition" to the excited state.