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)

\[ \hat{H}(t) = \hat{H}_0 + \hat{H}_1(t) \]

\( \hat{H}_0 \) is the zeroth order Hamiltonian and \( \hat{H}_1(t) \) is the perturbation.
The state vector evolves according to the T.D.S.E.

\[ \frac{2}{\hbar} \frac{\partial}{\partial t} |\psi(t)\rangle = -i \hat{H}(t) |\psi(t)\rangle \]

If \([\hat{H}_0, \hat{H}(t)] \neq 0\), 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 \(\hat{H}_0\), \(|\phi_i^{(0)}\rangle\), to a "final state" \(|\phi_f^{(0)}\rangle\).

Given \(1\hat{\Psi}(0) = 1\phi_i^{(0)}\), \(\hat{H}_0 1\phi_i^{(0)} = E_i^{(0)} 1\phi_i^{(0)}\)

Find \(P_f \leftarrow i\) to be in state \(1\phi_f^{(0)}\) at time \(t\)

\[ P_f \leftarrow i (t) = \left| \langle \phi_f^{(0)} | \psi(t) \rangle \right|^2 \text{ where } \frac{2}{\hbar} \frac{\partial |\psi(t)\rangle}{\partial t} = -i \hat{H}(t) |\psi(t)\rangle \]

The "transition rate"

\[ W_{f \leftarrow i} = \frac{d}{dt} P_{f \leftarrow i} \]
An important paradigm is resonance, when an oscillating field @ frequency $\omega$ is incident on a bound system with natural frequency $\omega_0 = \frac{E_f - E_i}{\hbar}$.

\[ \Rightarrow \text{Absorption} \quad \uparrow_{\hbar\omega_0} \quad 1f\rangle \]

\[ \downarrow_{\hbar\omega} \quad \rightarrow 1i\rangle \]

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 superposition of different states. Time dependent evolution can be coherent, with the state evolving continuously via the time dependent Schrödinger equation.
Magnetic Resonance

An important example of coherent time dependent perturbation theory is nuclear magnetic resonance, the phenomenon underlying MRI - Magnetic Resonance Imaging.

Consider a spin-$\frac{1}{2}$ proton (e.g. the nucleus of H in H$_2$O).

Place the sample in a large static $\vec{B}$ field

$$\hat{H}_0 = -\vec{\mu} \cdot \vec{B}$$

$$\vec{\mu} = g_p \mu_N \frac{\hbar}{2}$$

G-factor of proton $\approx 2.8$, $\mu_N = \frac{e\hbar}{2m_p c} = \hbar \left(7.62 \text{ MHz/Tesla}\right)$ (Nuclear magneton)

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

$$\Rightarrow \hat{H}_0 = +g_p \mu_N B_{\parallel} \hat{S}_z = +g_p \mu_N B_{\parallel} \frac{\hbar}{2}$$

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

Zeroth order

$$E^{(0)}_{\pm} = \pm \frac{\hbar \omega_0}{2}$$

$$E_0 \quad \begin{array}{c} \hline \hline \end{array} \quad \hat{S}_z \quad \begin{array}{c} \hline \hline \end{array}$$

$$\uparrow \uparrow \quad \begin{array}{c} \hline \hline \end{array} \quad \downarrow \downarrow$$
In the absence of any perturbing field, if the system is not initial in a stationary state it will precess about \( z \)-axis with frequency \( \omega_0 \).

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 \( \mathbf{B}_1(t) \) which rotates with spin.

\[
B_1(t) = B_\perp (\cos \omega t \mathbf{e}_x + \sin \omega t \mathbf{e}_y)
\]

If \( \mathbf{B}_1(t) \) stays in phase with the precessing \( \mathbf{B}_0 \), it will continuously torque it from "up" to "down" or "down" to "up". This is known as "nuclear magnetic resonance".
The total Hamiltonian is
\[ \hat{H} = \hat{H}_0 + \hat{H}_1, \]
\[ \hat{H}_0 = \frac{\hbar \omega_0}{2} \hat{\sigma}_z \]
\[ \hat{H}_1 = -\frac{\hbar}{2} \cdot \mathbf{B}_1(t) = -\gamma_p \mu_N B_1 (\cos \omega t \hat{\sigma}_x + \sin \omega t \hat{\sigma}_y) \]
\[ = -\frac{\hbar B_1}{2} \left( e^{-i\omega t} (\hat{\sigma}_x + i \hat{\sigma}_y) + e^{i\omega t} (\hat{\sigma}_x - i \hat{\sigma}_y) \right) \]
\[ = -\frac{\hbar B_1}{2} (e^{-i\omega t} \hat{\sigma}_+ + e^{i\omega t} \hat{\sigma}_- ) \]

where \( \hbar \Omega = \gamma_p \mu_N B_1 \), \( \hat{\sigma}_\pm = \hat{\sigma}_x \pm i \hat{\sigma}_y = \hat{\sigma}_\pm \)

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

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, 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 \( |\psi(t)\rangle = |\uparrow\rangle \)

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

Expand in basis \( \{ |\uparrow\rangle, |\downarrow\rangle \} \)

\[ 12\psi(t) = \begin{bmatrix} C_\uparrow(t) \\ C_\downarrow(t) \end{bmatrix} \]

\[ \hat{H}(t) = \frac{\hbar}{2} \begin{bmatrix} \omega_0 & -\Omega e^{-i\omega t} \\ -\Omega e^{i\omega t} & -\omega_0 \end{bmatrix} \]

\[ \frac{d}{dt} \begin{bmatrix} C_\uparrow(t) \\ C_\downarrow(t) \end{bmatrix} = -\frac{i}{\hbar} \begin{bmatrix} \omega_0 & -\Omega e^{-i\omega t} \\ -\Omega e^{i\omega t} & -\omega_0 \end{bmatrix} \begin{bmatrix} C_\uparrow(t) \\ C_\downarrow(t) \end{bmatrix} \]

\[ \Rightarrow \begin{bmatrix} C_\uparrow(t) + \frac{i}{2} \omega_0 C_\uparrow(t) \\ C_\downarrow(t) - \frac{i}{2} \omega_0 C_\downarrow(t) \end{bmatrix} = \frac{i}{2} \Omega e^{-i\omega t} C_\downarrow(t) \]

Two coupled diff. eqs. with time dependent coefficients. When time dep most eqns. cannot be solved exactly; here we can.
Consider substitution:

\[ C_\uparrow (t) = e^{-i\omega t/2} \hat{C}_\uparrow (t) \]
\[ C_\downarrow (t) = e^{i\omega t/2} \hat{C}_\downarrow (t) \]

\[ \Rightarrow \hat{C}_\uparrow - \frac{i}{2} \hat{\Delta} \hat{C}_\uparrow = \frac{\hat{h}}{2} \Omega \hat{C}_\downarrow \]
\[ \hat{C}_\downarrow + \frac{i}{2} \hat{\Delta} \hat{C}_\downarrow = \frac{\hat{h}}{2} \Omega \hat{C}_\uparrow \]

\[ \frac{d}{dt} \left[ \begin{array}{c} \hat{C}_\uparrow \\ \hat{C}_\downarrow \end{array} \right] = -\frac{i}{2} \left[ \begin{array}{cc} -\Delta & -\Omega \\ -\Omega & +\Delta \end{array} \right] \left[ \begin{array}{c} \hat{C}_\uparrow \\ \hat{C}_\downarrow \end{array} \right] \]

Schrodinger eq with "static" Hamiltonian

\[ \hat{H} = -\frac{\hbar}{2} \frac{\partial^2}{\partial z^2} - \frac{\hbar}{2} \hat{D}_x \]

where \( \Delta = \omega - \omega_o \equiv \text{"detuning"} \)

Our transformation \( C \rightarrow \hat{C} \) is going to the "rotating frame" co-rotating with \( \hat{B}_z (t) \).

In that frame the field is static.
Solution: Take second derivative

\[ \dddot{C}_\uparrow - \frac{i}{2} \Delta \dot{C}_\uparrow = \frac{i}{2} \Omega \dot{C}_\downarrow \]

\[ \Rightarrow \dddot{C}_\uparrow - \frac{i}{2} \Delta \left( \frac{i}{2} \Delta \ddot{C}_\uparrow + \frac{i}{2} \Omega \dot{C}_\downarrow \right) = \frac{i}{2} \Omega \left( -\frac{i}{2} \dot{C}_\downarrow + \frac{i}{2} \Omega \dot{C}_\uparrow \right) \]

\[ \Rightarrow \dddot{C}_\uparrow + \frac{1}{4} (\Delta^2 + \Delta^2) \dddot{C}_\uparrow = 0 \quad \text{S.H.O. diff eq} \]

\[ \Rightarrow \dddot{C}_\uparrow + \frac{1}{4} (\Delta^2 + \Delta^2) \dddot{C}_\uparrow = \frac{\Omega^2}{\Delta} \]

\[ \Rightarrow \text{Solution: } \dddot{C}_\uparrow (t) = \dddot{C}_\uparrow (0) \left( \frac{\Omega}{\Delta} t \right) + \dddot{C}_\downarrow (0) \sin \left( \frac{\Omega}{\Delta} t \right) \]

Take \( C_\uparrow (0) = 0 \), \( C_\downarrow (0) = 1 \) \( \Rightarrow \dddot{C}_\uparrow (0) = 0 \), \( \dddot{C}_\downarrow (0) = 1 \).

\[ \therefore \dddot{C}_\uparrow (t) = \frac{i \Omega}{\Delta} \sin \left( \frac{\Omega}{\Delta} t \right) \]

\[ \Rightarrow P_\uparrow (t) = \left| C_\uparrow (t) \right|^2 = \left| \dddot{C}_\uparrow (t) \right|^2 = \frac{\Omega^2}{\Delta^2 + \Delta^2} \sin^2 \left( \frac{\Omega}{\Delta} t \right) \]

Rabi solution
"Rabi Flickering" (I.I Rabi)

Consider case of resonance $\Delta = 0 \Rightarrow \omega = \omega_0$

$\omega = \text{Rabi frequency}$

The spin coherently oscillates between $|\uparrow\rangle$ and $|\downarrow\rangle$ @ Rabi frequency. When $\Delta t = \pi \Rightarrow$ full transfer

Note when $\Delta t = \frac{\pi}{2} \Rightarrow |\phi(t)\rangle = \frac{|\uparrow\rangle + e^{i\theta}|\downarrow\rangle}{\sqrt{2}}$

Coherent superposition

Off resonance: Generalized Rabi freq.

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

Spin has lower probability to transfer to $|\uparrow\rangle$ and oscillates rapidly.
Very far off resonance, \( \sigma^2 = \Delta \)

The maximum probability to be in the excited state

\[
P_{\text{max}} \propto \frac{\sigma^2}{\Delta^2} = \frac{(\Delta \Delta)^2}{\hbar^2 (\omega_0 - \omega)^2} = \frac{\hbar^2 \sigma^2}{(E_e - E_i - \hbar \omega)^2}
\]

Note the relationship with static perturbation theory,

\[
(\Delta \Delta)^2 \sim |\langle i| \hat{H}_i |i \rangle|^2 = |\langle f| \hat{H}_f |f \rangle|^2
\]

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.