Lecture 25: Time Dependent Perturbation Theory (II) - The Golden Rule

Last time we saw an example of coherent time evolution — spin magnetic resonance. The Rabi solution followed simply because the system was simple — two levels and a single driving frequency. The system was coherent ⇒ well defined phase relationships.

In the real world this is rarely the case. ~~Similar~~ Signals are noisy and samples have many degenerate energy levels. We must, in this case turn to approximation methods.

General problem

Given zeroth order Hamiltonian

$\hat{H}_0$, energy levels $|n\rangle$ (leave out (0) superscript)

Perturbed by $\hat{H}_1(t)$ (explicitly time-dependent)

Start in some initial state $|\psi(0)\rangle = |i\rangle$

Find transition probability to final state

$$P_{f \leftarrow i}(t) = |\langle f|\psi(t)\rangle|^2 = |\langle f|\hat{U}(t)|i\rangle|^2$$

Ansatz.

In the absense of the perturbation, given an arbitrary initial state $|\psi(0)\rangle = \sum_n c_n |n\rangle$

$$|\psi^{(0)}(t)\rangle = \sum_n c_n e^{-i\omega_n t} |n\rangle \qquad \left(\text{where } \omega_n = \frac{E_n}{\hbar}\right)$$

Now let us turn on a "weak" perturbation.

We choose an ansatz:

$$|\psi(t)\rangle = \sum_n c_n(t)\, e^{-i\omega_n t} |n\rangle$$

"slowly varying coefficient"

T.D.S.E.

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

$$\text{where } \hat{H}(t) = \hat{H}_0 + \hat{H}_1(t)$$

$$\Rightarrow \sum_n \left(\dot{c}_n - i\omega_n c_n\right) e^{-i\omega_n t} |n\rangle$$

$$= \sum_n c_n(t)\, e^{-i\omega_n t}\left(-\frac{i}{\hbar}\hat{H}(t)\right)|n\rangle$$

(Next Page)

Now, $\hat{H}(t)|n\rangle = (\hat{H}_0 + \hat{H}_1(t))|n\rangle$

$$= (E_n + \hat{H}_1(t))|n\rangle$$

$$\Rightarrow \sum_n \dot{c}_n e^{-i\omega_n t}|n\rangle = \frac{-i}{\hbar}\sum_n c_n \hat{H}_1(t)|n\rangle$$

having used $\omega_n = E_n/\hbar$

Project with $\langle m|$

$$\Rightarrow \boxed{\dot{c}_m = \frac{-i}{\hbar}\sum_n \langle m|\hat{H}_1(t)|n\rangle c_n(t) e^{-i\omega_n t}}$$

Representation of the T.D.S.E in terms of expansion coeff and matrix elements

$$\frac{d}{dt}\begin{bmatrix} c_1 \\ c_2 \\ c_3 \\ \vdots \end{bmatrix} = \frac{-i}{\hbar}\begin{bmatrix} & & \\ & \hat{H}_1(t) & \\ & & \end{bmatrix}\begin{bmatrix} c_1 \\ c_2 \\ c_3 \\ \vdots \end{bmatrix}$$

Slowly varying terms

weak perturbation

Formal Solution: Integral equation

$$C_m(t) = C_m(0) - \frac{i}{\hbar}\sum_m \int_0^t dt' \langle m|\hat{H}_1(t')|n\rangle C_n(t')\, e^{i\omega_{mn}t'}$$

(Recursive definition)

Iterate:

$$C_m(t) = C_m(0) -$$

$$- \frac{i}{\hbar}\sum_n \int_0^t dt' \langle m|\hat{H}_1(t')|n\rangle e^{i\omega_{mn}t'}\Big(C_n(0) - \frac{i}{\hbar}\sum_{n'}\int_0^{t'} dt'' \langle n|\hat{H}_1(t'')|n'\rangle \overset{e^{i\omega_{nn'}t''}}{\downarrow} C_{n'}(t'')\Big)$$

etc. infinite series in powers of $\langle m|\hat{H}_1|n\rangle$

$\Rightarrow$ "Dyson series"

- Zeroth order

$$C_m^{(0)}(t) = C_m(0)$$

- First order

$$C_m^{(1)}(t) = -\frac{i}{\hbar}\sum_n\left(\int_0^t dt' \langle m|\hat{H}_1(t')|n\rangle e^{i\omega_{mn}t'}\right)$$

- Second order

$$C_m^{(2)}(t) = \left(\frac{-i}{\hbar}\right)^2 \sum_{n,n'}\left(\int_0^t dt' \int_0^{t'} dt'' \langle m|\hat{H}_1(t')|n\rangle \langle n|\hat{H}_1(t'')|n'\rangle\right) C_{n'}(0)$$

$e^{i\omega_{mn}t'}$ $e^{i\omega_{nn'}t''}$

Case under consideration: $|\psi(0)\rangle = |i\rangle$
(eigenstate of $\hat{H}_0$)

$\Rightarrow C_n(0) = \delta_{ni}$

Seek prob to be in some final state $|f\rangle \neq |i\rangle$

$\Rightarrow$ <u>zeroth order</u> $c_f = 0$

<u>First order</u> $c_f^{(1)}(t) = \frac{-i}{\hbar}\int_0^t dt' \langle f|\hat{H}_1(t')|i\rangle e^{-i\omega_{fi}t}$

<u>Second order</u>

$$c_f^{(2)}(t) = \left(\frac{-i}{\hbar}\right)^2 \sum_n \int_0^t dt' \int_0^{t'} dt'' \langle f|\hat{H}_1(t')\underbrace{|n\rangle\langle n|}_{\text{"intermediate states"}}\hat{H}_1(t'')|i\rangle$$

<u>Transition Probability</u>

$P_{f\leftarrow i}(t) = |C_f(t)|^2 \cong |c_f^{(1)}(t)|^2$ to lowest nonvanishing order

$$\Rightarrow P_{f\leftarrow i}(t) \cong \left|\frac{1}{\hbar}\int_0^t dt' \langle f|\hat{H}_1(t')|i\rangle e^{i\omega_{fi}t}\right|^2 \text{ (To first order)}$$

If first order vanishes because $\langle f|\hat{H}_1|i\rangle = 0$

$$\Rightarrow P_{f\leftarrow i}(t) = \left|\frac{1}{\hbar^2}\int_0^t dt' \int_0^{t'} dt'' \langle f|\hat{H}_1(t')|n\rangle\langle n|\hat{H}_1(t'')|i\rangle e^{i\omega_{fn}t'} e^{i\omega_{ni}t''}\right|^2$$

Harmonic perturbation theory

As for magnetic resonance, we consider the case where the ~~applied~~ time dependent perturbation is harmonic, (monochromatic)

$$\hat{H}_1(t) = \underbrace{\hat{H}_1^{(+)}(t)\, e^{-i\omega t}}_{\text{"positive freq comp"}} + \underbrace{\hat{H}_1^{(-)}(t)\, e^{+i\omega t}}_{\text{"negative freq comp"}}$$

To first order $\Longrightarrow$

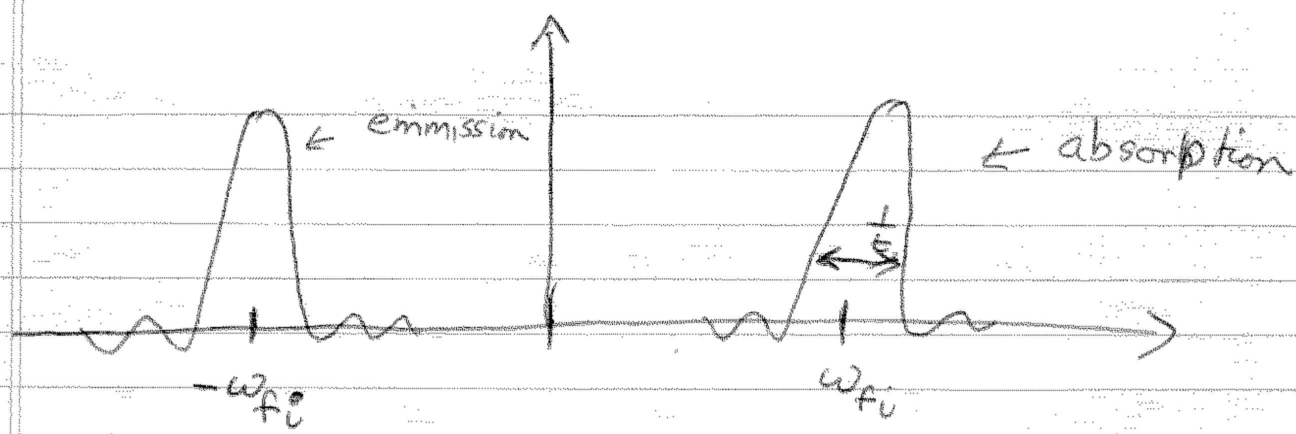
$$C_f^{(1)}(t) = \frac{-i}{\hbar}\int_0^t dt' \langle f|\hat{H}_1^{(+)}|i\rangle e^{-i(\omega-\omega_{fi})t'} - \frac{i}{\hbar}\int_0^t dt' \langle f|\hat{H}_1^{(-)}|i\rangle e^{i(\omega+\omega_{fi})t'}$$

$$C_f^{(1)}(t) = \frac{-i}{\hbar}\langle f|\hat{H}_1^{(+)}|i\rangle \left(\frac{e^{-i(\omega-\omega_{fi})t} - 1}{-i(\omega-\omega_{fi})}\right)$$

$$\frac{-i}{\hbar}\langle f|\hat{H}_1^{(-)}|i\rangle \left(\frac{e^{+i(\omega+\omega_{fi})} - 1}{i(\omega+\omega_{fi})}\right)$$

$$C_f^{(1)} = -\frac{i}{\hbar}\Bigg(\langle f|\hat{H}_1^{(+)}|i\rangle e^{i(\omega_{fi}-\omega)t/2}\, \frac{2\sin\left((\omega_{fi}-\omega)t/2\right)}{\omega_{fi}-\omega}$$

$$+ \langle f|\hat{H}_1^{(-)}|i\rangle e^{i(\omega_{fi}+\omega)t/2}\, \frac{2\sin\left((\omega_{fi}+\omega)t/2\right)}{(\omega_{fi}+\omega)}\Bigg)$$

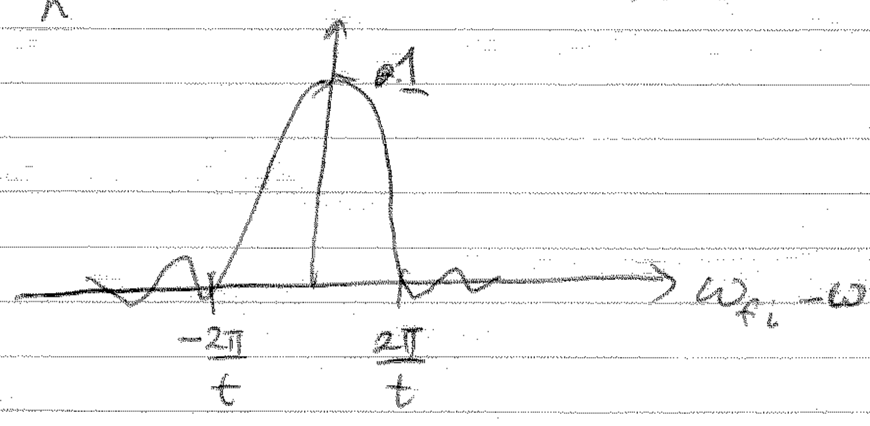


Absorption contribution

$$c_f^{(1)} = \frac{-i}{\hbar} \langle f | \hat{H}_1^{(+)} | i \rangle \, e^{i(\omega_{fi}-\omega)t/2} \, t \, \frac{\sin[(\omega_{fi}-\omega)t/2]}{[(\omega_{fi}-\omega)t/2]}$$

$$= \frac{-i}{\hbar} \langle f | \hat{H}_1^{(+)} | i \rangle \, e^{i(\omega_{fi}-\omega)t/2} \, t \, \mathrm{sinc}\left((\omega_{fi}-\omega)\frac{t}{2}\right)$$

$$P_{f\leftarrow i} = \frac{1}{\hbar^2} \left| \langle f | \hat{H}_1^{(+)} | i \rangle \right|^2 \mathrm{sinc}^2\left[(\omega_{fi}-\omega)\frac{t}{2}\right] t^2$$



$$\Delta E \simeq \frac{2\pi\hbar}{t}$$ ("time-energy uncertainty")

Limit $t \to \infty$

Note $\lim_{t\to\infty} \text{sinc}^2((\omega_{fi} - \omega)t) = \frac{2\pi}{t} \delta(\omega_{fi} - \omega)$

$$\Rightarrow P^{(abs)}_{f\leftarrow i} = \frac{2\pi}{\hbar^2} |\langle f| \hat{H}_1^{(t)} |i\rangle|^2 \, \delta(\omega_{fi} - \omega)\, t$$

Absorption rate $W^{abs}_{f\leftarrow i} = \frac{d}{dt} P^{(abs)}_{f\leftarrow i}$

$$\boxed{W^{(abs)}_{f\leftarrow i} = \frac{2\pi}{\hbar^2} |\langle f| \hat{H}_1^{(t)} |i\rangle|^2 \, \delta(\omega_{fi} - \omega)}$$

Fermi's Golden Rule

Density of States

We started this lecture stating that in many system there are many micro levels with the same final energy (e.g. in a macroscopic solid)

$\Rightarrow$ Many state near ~~final~~ energy E_f

Density of state $g(E)$

$$\Rightarrow dN = \int_{E_f}^{E_f+\Delta E} dE_f \, g(E) = \#\text{ of quantum states in range } E_f \to E_f + \Delta E$$

$\Rightarrow$ True transition rate, we must integrate over density of states

$$W_{f\leftarrow i}^{(abs)} = \int dE_f \, \frac{2\pi}{\hbar^2} |\langle f| \hat{H}_1^{(+)} |i\rangle|^2 \, \delta\left(\frac{E_f}{\hbar} - \frac{E_i}{\hbar} - \omega\right) g(E_f)$$

$$\Rightarrow \boxed{W_{f\leftarrow i}^{(abs)} = \frac{2\pi}{\hbar^2} |\langle f| \hat{H}_1^{(+)} |i\rangle|^2 \, g(E_f = E_i + \hbar\omega)}$$

Fermi's Golden Rule