LECTURE 22

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– Time-dependent perturbation theory –

As in the case of time-independent perturbation theory, let $\hat{H}_0$ be the Hamiltonian of the "unperturbed system" (US) whose eigenvalues and eigenvectors are supposed to be known:

$$\hat{H}_0 |\phi_n\rangle = E_n^0 |\phi_n\rangle \qquad 1.1)$$

The time-evolution of the US is, as usual, ruled by:

$$i\hbar \frac{\partial}{\partial t} |\psi(t)\rangle = \hat{H}_0 |\psi(t)\rangle \qquad 2.1)$$

Suppose that at $t=0$ the system was prepared in the state $|\psi_0\rangle$:

$$|\psi(t=0)\rangle \equiv |\psi_0\rangle$$

We can always write:

$$|\psi(t)\rangle = \sum_n |\phi_n\rangle\langle\phi_n|\psi(t)\rangle$$

$$\equiv \sum_n c_n(t) |\phi_n\rangle \qquad 3.1)$$

where

$$c_n(t) \equiv \langle\phi_n|\psi(t)\rangle$$

At $t=0$:

$$c_n(0) = \langle\phi_n|\psi(0)\rangle$$

$$= \langle\phi_n|\psi_0\rangle$$

Substituting 3.1) in 2.1) and using 1.1) we obtain:

$$i\hbar \sum_n \dot{c}_n(t)|\phi_n\rangle = \hat{H}_0 \sum_n c_n(t)|\phi_n\rangle$$
$$= \sum_n E_n^0 c_n(t)|\phi_n\rangle$$

$$\Leftrightarrow \sum_n \left[i\hbar \frac{dc_n(t)}{dt} - E_n^0 c_n(t) \right] |\phi_n\rangle = 0$$

This equality is satisfied iff:

$$\frac{dc_n(t)}{dt} = -i \frac{E_n^0}{\hbar} c_n(t)$$

whose solution is:

$$\boxed{c_n(t) = c_n(0) \exp\left(-\frac{iE_n^0 t}{\hbar}\right)} \qquad (1.2)$$

Suppose now that the system is perturbed by an external potential (possibly time-dependent)

$$\lambda \hat{V}(t).$$

The new Hamiltonian of the perturbed system is:

$$\hat{H}_0 \xrightarrow{\text{perturbation}} \hat{H} = \hat{H}_0 + \lambda \hat{V}(t) \qquad \text{with } \hat{V}(t) = \hat{V}^\dagger(t)$$

Our aim now is to solve the time-dependent Sch. eq:

$$i\hbar \frac{\partial}{\partial t}|\psi(t)\rangle = \hat{H}|\psi(t)\rangle$$
$$= (\hat{H}_0 + \lambda \hat{V}(t))|\psi(t)\rangle \qquad (2.2)$$

with the initial condition:

$$|\psi(t=0)\rangle \equiv |\psi_0\rangle$$

As before, we look for a solution of the form

$$|\psi(t)\rangle = \sum_n |\phi_n\rangle\langle\phi_n|\psi(t)\rangle$$

$$= \sum_n c_n(t)|\phi_n\rangle$$

It is convenient to isolate from $c_n(t)$ the time evolution of the non-perturbed (or, free) system:

$$c_n(t) = \left[c_n(t)\, e^{i\frac{E_n^0 t}{\hbar}}\right] e^{-i\frac{E_n^0 t}{\hbar}}$$

$$\equiv f_n(t)\, e^{-iE_n^0 t/\hbar}$$

Therefore

$$|\psi(t)\rangle = \sum_n f_n(t)\, e^{-iE_n^0 t/\hbar}|\phi_n\rangle \qquad 1.3)$$

This implies that when $\lambda \Rightarrow 0$, $d_n(t)$ tends to a constant.

Substituting 1.3) into 2.2) we obtain:

$$\sum_n \left[i\hbar \frac{df_n(t)}{dt} + E_n^0 f_n(t)\right] e^{-iE_n^0 t/\hbar}|\phi_n\rangle =$$

$$= \hat{H}|\psi(t)\rangle$$

$$= \sum_n \left[E_n^0 + \lambda \hat{V}(t)\right] f_n(t)\, e^{-iE_n^0 t/\hbar}|\phi_n\rangle$$

That is:

$$\sum_n \left[i\hbar \frac{d f_n(t)}{dt} - \lambda \hat{V}(t) f_n(t) \right] e^{-iE_n^0 t/\hbar} |\phi_n\rangle = 0$$

Now we multiply from left this expression by

$$\langle \phi_n | \, e^{i E_m^0 t/\hbar}$$

to obtain:

(1.4) $$\boxed{i\hbar \frac{d f_m(t)}{dt} = \lambda \sum_n f_n(t) \, e^{i(E_m^0 - E_n^0)t/\hbar} \langle \phi_m | \hat{V}(t) | \phi_n \rangle}$$

where we have used $\langle \phi_n | \phi_m \rangle = \delta_{nm}$

Let us Try to solve this equation to first order in λ;
choosing as initial condition:

$$|\psi(t=0)\rangle = |\phi_k\rangle \qquad (2.4)$$

This means that at $t=0$ the system is in a given eigenvector of the energy. For example, imagine an atom in the lower (fundamental) energy state which is perturbed, from $t=0$, by an electromagnetic wave.

Using (2.4) in 1.3) we obtain:

$$|\psi(t=0)\rangle = \sum_n f_n(0) |\phi_n\rangle = |\phi_k\rangle \Rightarrow f_n(0) = \delta_{nk}$$

If $\lambda = 0$, (1.4) gives:

$$\left.\frac{d f_m(t)}{dt}\right|_{\lambda=0} = 0 \Rightarrow \left. f_m(t)\right|_{\lambda=0} = \left. f_m(0)\right|_{\lambda=0} = \delta_{km}$$

If $\lambda \neq 0$, we look for a power series solution

$$f_m(t) = f_m^0(t) + \lambda f_m^1(t) + \lambda^2 f_m^2(t) + \dots$$

with

$$f_m^0(t) = \left. f_m(t)\right|_{\lambda=0} = \delta_{km} \Rightarrow f_m^\alpha(0) = 0 \quad (\alpha \geq 1)$$

$$\Rightarrow f_m(t) = \delta_{km} + \lambda f_m^1(t) + \lambda^2 f_m^2(t) + \dots \qquad (1.5)$$

Substituting 1.5) into 1.4) gives:

$$i\hbar \frac{d}{dt}\left(\delta_{km} + \lambda f_m^1(t) + \dots\right) =$$

$$= \lambda \sum_n \left(\delta_{kn} + \lambda f_n^1(t) + \dots\right) e^{i\omega_{mn} t} V_{mn}(t) \qquad (2.5)$$

where we have defined the TRANSITION FREQUENCY

$$\omega_{mn} \equiv \frac{E_m^0 - E_n^0}{\hbar}$$

and

$$V_{mn}(t) \equiv \langle \phi_m | \hat{V}(t) | \phi_n \rangle$$

The first-order solution of (2.5) is:

$$i\hbar \frac{d f_m^1(t)}{dt} = e^{i\omega_{mk}t} V_{mk}(t)$$

whose solution is:

$$\boxed{f_m^1(t) = \frac{1}{i\hbar}\int_0^t dt' e^{i\omega_{mk}t'} \langle \phi_m | \hat{V}(t') | \phi_k \rangle} \qquad 1,6)$$

with $\qquad f_m^1(0) = 0$

The probability that at a later time t the system, initially prepared in the state $|\phi_k\rangle$, could be found in the state $|\phi_n\rangle$ with $n \neq k$ is:

$$P_n(t) = |\langle \phi_n | \psi(t) \rangle|^2$$

$$= \left| \langle \phi_n | \left\{ \sum_m f_m(t) e^{-iE_m^0 t/\hbar} |\phi_m\rangle \right\} \right|^2$$

$$= \left| f_n(t) e^{-iE_n^0 t/\hbar} \right|^2 = |f_n(t)|^2$$

$$= \left(\delta_{kn} + \lambda f_n^{1*}(t) + \lambda^2 f_n^{2*}(t) + \dots\right)\left(\delta_{kn} + \lambda f_n^1(t) + \lambda^2 f_n^2(t) + \dots\right)$$

$$= \delta_{kn} + 2\lambda \delta_{kn} \mathrm{Re}\left[f_n^1(t)\right] + \lambda^2 \left[|f_n^1(t)|^2 + 2\delta_{kn} \mathrm{Re}\left[f_n^2(t)\right] \right] + \dots$$

$$= \lambda^2 |f_n^1(t)| + O(\lambda^3)$$

Example

—A particle of electric charge q in a one-dimensional harmonic oscillator is placed in an electric field of strenght $\mathcal{E}$. The potential energy is:

$$\lambda \hat{V}(t) = q\mathcal{E}\hat{x}\, e^{-t^2/\tau^2} \qquad \tau > 0$$

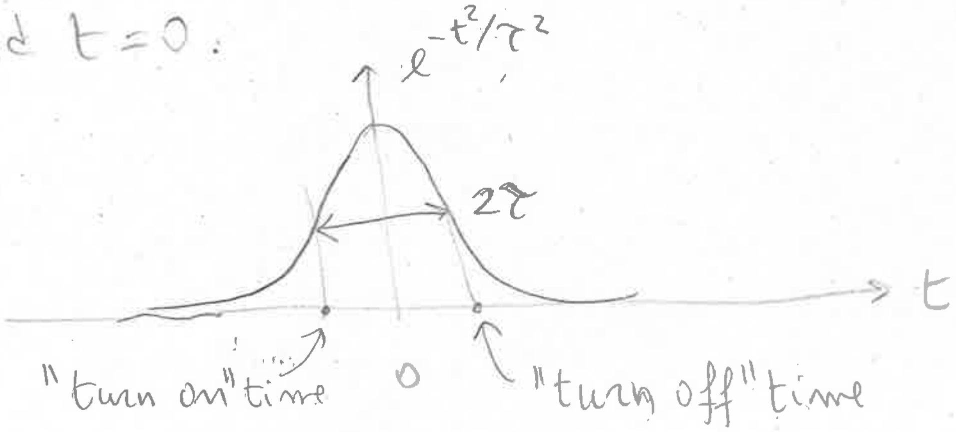
If the particle is in the ground state at $t=-\infty$, what is the probability that at $t \gg \tau$ is in the first (second) excited state? —

In this case
$$\hat{H}_0 = \hbar\omega\left(\hat{a}^+\hat{a} + \tfrac{1}{2}\right)$$

with
$$\hat{H}_0 |n\rangle = \hbar\omega\left(n+\tfrac{1}{2}\right)|n\rangle \; ; \quad n = 0,1,2,\ldots$$

Note that at $t = \pm\infty$ we have
$$\lambda \hat{V}(t) = 0$$

There for the perturbation acts only for a finite time around $t=0$.



According to 1.6 written for $t=-\infty$ instead of $t=0$, we have:

$$f_n^1(t) = \frac{q\mathcal{E}}{i\hbar}\int_{-\infty}^{t} dt' \, e^{i\omega_{n0}t'} \langle n|\hat{x}|0\rangle e^{-(t'/\tau)^2}$$

where $\omega_{n0} = \frac{E_n^0 - E_0^0}{\hbar} = \left[\cancel{\hbar}\omega\left(n+\frac{1}{2}\right) - \cancel{\hbar}\omega\left(0+\frac{1}{2}\right)\right]\frac{1}{\cancel{\hbar}}$

$$= \omega n$$

For $t \gg \tau$, because of the gaussian form, we can replace the upper integration limit with $t=+\infty$ and write

$$f_n^1(\infty) = \frac{q\mathcal{E}}{i\hbar}\langle n|\hat{x}|0\rangle \underbrace{\int_{-\infty}^{\infty} e^{in\omega t} e^{-t^2/\tau^2} dt}$$

$$= \int_{-\infty}^{\infty} e^{-\alpha x^2 + \beta x} dx = e^{\beta^2/(4\alpha)} \left(\frac{\pi}{\alpha}\right)^{1/2}$$

with $\alpha = \frac{1}{\tau^2}$, $\beta = in\omega$

$$= \exp\left[\frac{(in\omega)^2}{4/\tau^2}\right]\sqrt{\pi\tau^2} = e^{-\frac{n^2\omega^2\tau^2}{4}}\sqrt{\pi}\,\tau$$

$$\Rightarrow f_n^1(\infty) = \frac{q\mathcal{E}}{i\hbar}\langle n|\hat{x}|0\rangle \sqrt{\pi}\,\tau \exp\left(-\frac{n^2\omega^2\tau^2}{4}\right)$$

It remains to calculate:

$\langle n|\hat{x}|0\rangle$ where $\hat{x} = \sqrt{\dfrac{\hbar}{2m\omega}}\,(\hat{a}+\hat{a}^+)$

and $\hat{a}|0\rangle = 0$; $\hat{a}^+|0\rangle = |1\rangle$ $\Rightarrow$

$$\Rightarrow \langle n|\hat{x}|0\rangle = \sqrt{\frac{\hbar}{2m\omega}}\,\langle n|\,\hat{a}+\hat{a}^+|0\rangle$$

$$= \sqrt{\frac{\hbar}{2m\omega}}\,\langle n|1\rangle = \delta_{n1}\sqrt{\frac{\hbar}{2m\omega}}$$

Therefore, the probability of transition from the ground state to the first excited state is:

$$\boxed{P_n(\infty) = \delta_{n1}\,\frac{\pi}{2}\,\frac{q^2\mathcal{E}^2\tau^2}{m\hbar\omega}\,e^{-\omega^2\tau^2/2}} \Rightarrow P_2(\infty) = P_3(\infty) = \ldots = 0$$

- Note that for $\omega\tau \gg 1$ (which means that the electric field turns on very slowly), then $P_1(\infty) \to 0$, so the system manages to remain in the ground state.
- Note also that $P_n(\infty) = 0$ for $n \geq 2$ because of the linear dependence $(\hat{x})$ of the perturbation. If it was $\hat{V} \propto \hat{x}^2$, then $P_2(\infty) \neq 0$. This is called a

SELECTION RULE.

Harmonic variation of the perturbation

In many cases of practical interest, like in the interaction of an atom with an electromagnetic wave, the potential has a harmonic time-dependence:

$$\hat{V}(t) = \hat{M}\, e^{\mp i\omega t} \qquad \omega \geq 0$$

where $\hat{M}$ is some time-independent operator.

In this case (1.6) gives:

$$f_m^1(t) = \frac{1}{i\hbar} \langle \phi_m | \hat{M} | \phi_k \rangle \underbrace{\int_0^t e^{i(\omega_{mk} \mp \omega)t'} dt'}$$

$$= \frac{e^{i(\omega_{mk} \mp \omega)t} - 1}{i(\omega_{mk} \mp \omega)}$$

$$= e^{i(\omega_{mk} \mp \omega)t/2} \, \frac{\sin\left(\frac{t\Delta}{2}\right)}{\Delta/2}$$

where $\Delta \equiv \dfrac{E_m^0 - E_k^0 \mp \omega\hbar}{\hbar}$

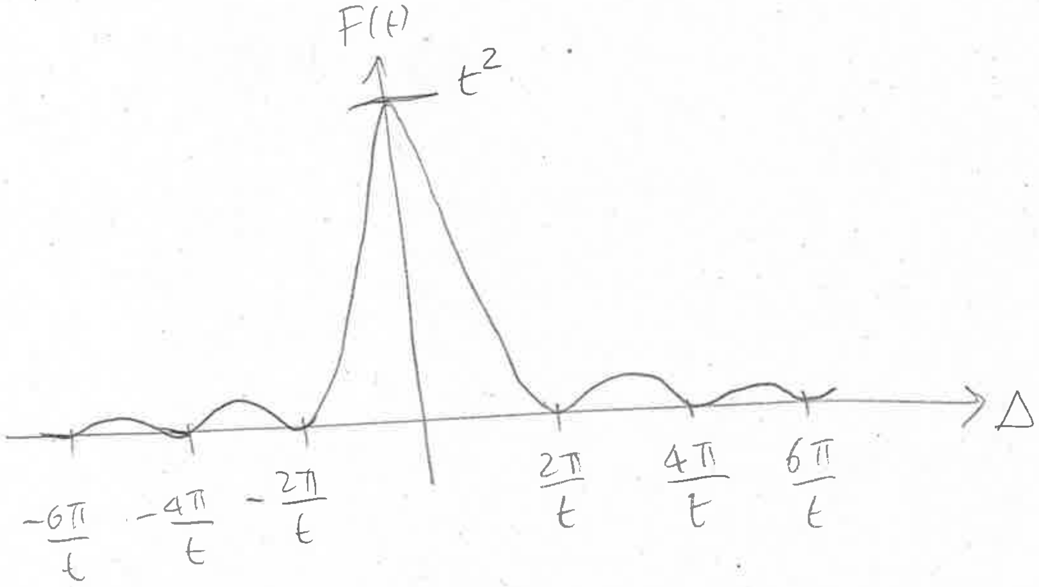
Therefore:

$$\boxed{|f_m^1(t)|^2 = \frac{1}{\hbar^2} |\langle \phi_m | \hat{M} | \phi_k \rangle|^2 \left[\frac{\sin(t\Delta/2)}{\Delta/2} \right]^2}$$

The function

$$F(t) = \left[\frac{\sin(t\Delta/2)}{\Delta/2}\right]^2$$

has a Dirac-delta behaviour:



In fact, if $f(x)$ is a smooth test function

$$\int_{-\infty}^{\infty} f(\Delta)\,\frac{4}{\Delta^2}\sin^2\left(\frac{t\Delta}{2}\right)d\Delta \underset{t\Delta \gg 1}{\approx} f(0)\int_{-\infty}^{\infty} d\Delta\,\frac{4}{\Delta^2}\sin^2\frac{t\Delta}{2}$$

$$= 2t\,f(0)\underbrace{\int_{-\infty}^{\infty} dy\,\frac{\sin^2 y}{y^2}}_{=\pi}$$

So, for large t:

$$\frac{4}{\Delta^2}\sin^2\left(\frac{t\Delta}{2}\right) \to 2\pi t\,\delta(\Delta) = 2\pi\hbar t\,\delta(E_m^0 - E_k^0 \mp \hbar\omega)$$

and

$$\boxed{|f_m'(t)|^2 \to \frac{2\pi}{\hbar}|\langle\phi_m|\hat{M}|\phi_k\rangle|^2\,t\,\delta(E_m^0 - E_k^0 \mp \hbar\omega)}$$

This equation shows that the transition probability after a long time grows linearly with t (can it exceed 1???).

However, the TRANSITION PROBABILITY PER UNIT OF TIME is finite and time-independent:

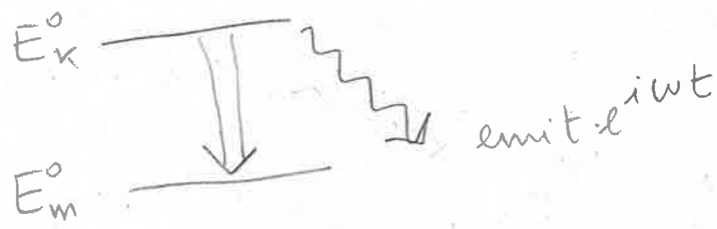
$$\Gamma_{k\to m} \equiv \lambda^2 \frac{d}{dt} |f_m^1(t)|^2 = \frac{2\pi}{\hbar} |\langle \phi_m | \lambda \hat{M} | \phi_k \rangle|^2 \delta(E_m^0 - E_k^0 \mp \hbar\omega)$$

The delta function shows that transitions are induced only if:

$$\hbar\omega = |E_m^0 - E_k^0|$$

If $E_k^0 < E_m^0$ then the system is excited from the lower level E_k^0 to the upper level E_m^0:

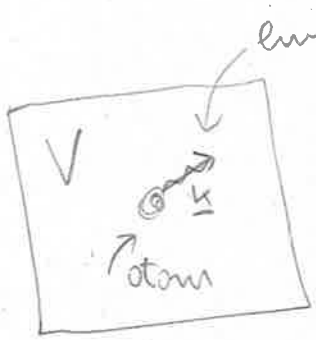
If $E_k^0 > E_m^0$, the system decay to the lower level



The delta function is not physical, it is actually integrated over, if we take in account that the photon energy $\hbar\omega$ does not specify uniquely the photon state. The photon will in general be detected in some momentum interval $(\underline{k}, \underline{k}+\Delta\underline{k})$ in the vicinity of $|\underline{k}| = \omega/c$, and the transition rate that is measured is really

$$R_{k\to m} = \sum_{\Delta \underline{k}} \Gamma_{k\to m}$$

The sum is over all states in the range $\Delta\underline{k}$. It is possible to show (but we do not do it here) that for a particle emitted within a volume V:



$$R_{k\to m} = \frac{2\pi V}{\hbar}\int \frac{d^3k}{(2\pi)^3} |\langle \phi_m | \lambda \hat{M} | \phi_k\rangle|^2 \delta(E_m^0 - E_k^0 + \hbar\omega)$$