Q02 - Lecture 3

Transitions between discrete levels by time-dependent interaction

Let's review perturbation theory!

Start with a Hamiltonian $\hat{H}_0$, with eigenstates $|n\rangle$, eigenvalues E_n. Then we can write any state:

$$|\psi(t=0)\rangle = \sum \gamma_n |n\rangle$$

And after some time t, we have:

$$|\psi(t)\rangle = \sum \gamma_n e^{-iE_n t/\hbar} |n\rangle$$

Now we add a time-dependent interaction:

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

We can treat this as a perturbation if its matrix elements are small compared to the spacing between levels:

$$\langle n|\hat{H}_1(t)|m\rangle \ll |E_n - E_m|$$

The perturbation will cause transitions between eigenstates.

The probability of making a transition to state $|\phi\rangle$ after time t is given by:

$$P_{\psi(0)\to\phi}(t) = |\langle\phi|\psi(t)\rangle|^2$$

Example I: Interaction of atom with EM field:

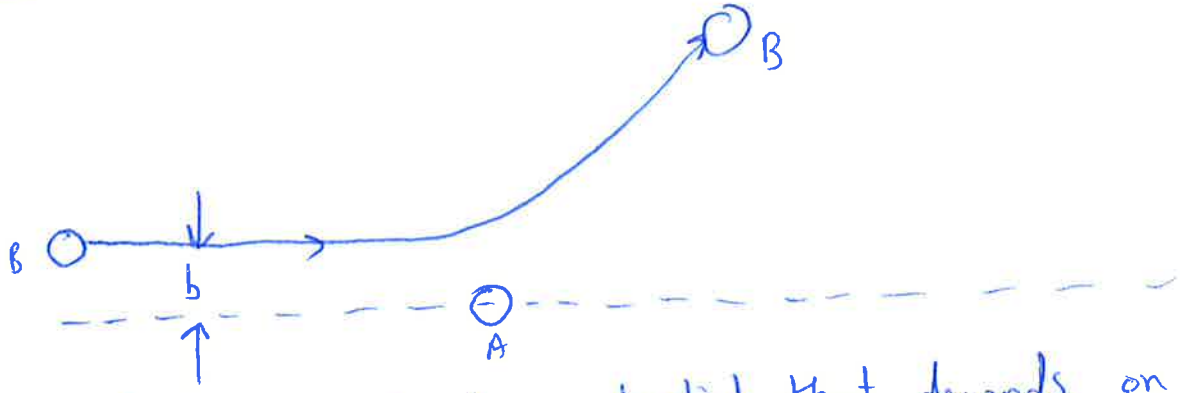
$$\vec{E}(t) = \vec{E}\cos(\omega t + \phi)$$

We will see later that: $H_1(t) = -\hat{\vec{D}}\cdot\vec{E}(t)$ where $\hat{\vec{D}} = q\hat{\vec{r}}$

Notice that $\hat{\vec{D}}$ is an operator, but $\vec{E}$ is just a number!

This is called the "semi-classical treatment"

Example II: Collision processes



If $\hat{V}$ is an interaction potential that depends on R, the distance between A & B, then if R depends on time, $\hat{V}$ depends on time.

For a collision, $\hat{V} \to 0$ @ $t = -\infty, +\infty$

If the collision causes a change in internal state, it is called inelastic. b is called the "impact parameter"

Perturbation Theory

The SE gives: $i\hbar \frac{d}{dt}|\Psi(t)\rangle = (H_0 + H_1(t))|\Psi(t)\rangle$

We will solve this by making use of the fact that $H_1(t)$ is "small"

Re-scale it: $\hat{H}_1(t) = \lambda H_1'(t)$

where now $\langle n|H_1'(t)|m\rangle \approx |E_n - E_m|$, & $\lambda \ll 1$.

This approach does not always work:

Example I: $\hat{E}$ must be small.

Example II: b must be small.

Now we have: $i\hbar \frac{d}{dt}|\Psi(t)\rangle = (\hat{H}_0 + \lambda H_1'(t))|\Psi(t)\rangle$

Recall that we can express every solution as an expansion of the eigenstates of the original Hamiltonian H_0:

$$|\Psi(t)\rangle = \sum \gamma_n(t) e^{-iE_n t/\hbar} |n\rangle$$

but now, the γ's are a function of time!

Take the SE, multiply by $\langle k|$.

Remembering: $H_0|n\rangle = E_n|n\rangle$ & $\sum_n |n\rangle\langle n| = \mathbb{I}$

Then we get:

$$i\hbar \frac{d}{dt}\gamma_k(t) = \lambda \sum_n \langle k|\hat{H}_1'(t)|n\rangle e^{i(E_k-E_n)t/\hbar}\gamma_n(t)$$

So far, this is exact.

Now, let's expand γ in a power series of λ:

$$\gamma_k(t) = \gamma_k^{(0)}(t) + \lambda\gamma_k^{(1)}(t) + \lambda^2\gamma_k^{(2)}(t) + \dots$$

This is useful because, since λ is small, most of the behaviour of γ will be captured by the first few orders. Substitute this in and collect terms of the same order of λ:

Order 0

$$i\hbar \frac{d}{dt}\gamma_k^{(0)}(t) = 0$$

In other words, $\gamma_k^{(0)}$ = constant and just given by the initial condition of the problem.

Order 1

$$i\hbar \frac{d}{dt}\gamma_k^{(1)}(t) = \sum_n \langle k|\hat{H}_1'(t)e^{i(E_k-E_n)t/\hbar}\gamma_n^{(0)}(t)$$

Order r

$$i\hbar \frac{d}{dt}\gamma_k^{(r)}(t) = \sum_n \langle k|\hat{H}_1'(t)|n\rangle e^{i(E_k-E_n)t/\hbar}\gamma_n^{(r-1)}(t)$$

Please Notice

- each order (r) depends only on the solution to the $(r-1)^{th}$ order $\Rightarrow$ CAN SOLVE ITERATIVELY
- λ itself has disappeared!

First Order Theory

Let's work out the probability of making a transition from state $|i\rangle$ to ~~state~~ $|k\rangle$ using first order PT.

Zeroth order: $\gamma_k^{(0)} = \delta_{ki}$

Then the first order is simply:

$$i\hbar \frac{\partial}{\partial t}\gamma_k^{(1)}(t) = \sum_n \langle k|\hat{H}_1'(t)|n\rangle e^{+i(E_k-E_n)t/\hbar}\,\delta_{ni}\,\gamma_n^{(0)}(t)$$

$$= \langle k|\hat{H}_1'(t)|i\rangle e^{+i(E_k-E_i)t/\hbar}$$

Now integrate to get the answer!

$$\gamma_k^{(1)}(t) = \frac{1}{i\hbar}\int_{t_0}^{t} d\tau \langle k|\hat{H}_1'(\tau)|i\rangle e^{i(E_k-E_i)\tau/\hbar}$$

But recall that the transition amplitude is:

$$\gamma_k(t) = \underbrace{\gamma_k^{(0)}(t)}_{0} + \lambda\gamma_k^{(1)}(t) + \cdots$$

So $S_{ki} = \lambda\gamma_k^{(1)}(t)$, but also recall $\lambda\hat{H}_1'(t) = \hat{H}_1(t)$

then:

$$\boxed{S_{ki} = \frac{1}{i\hbar}\int_{t_0}^{t} d\tau \langle k|\hat{H}_1(t)|i\rangle e^{i(E_k-E_i)\tau/\hbar}}$$

And $P_{i\to k} = |S_{ki}|^2 = \frac{1}{\hbar^2}\left|\int_{t_0}^{t} d\tau \langle k|\hat{H}_1(t)|i\rangle e^{i(E_k-E_i)\tau/\hbar}\right|^2$

Now imagine a perturbation of the type:

$$\hat{H}_1(t) = \hat{W} f(t)$$

$\hat{W}$: operator acting on atomic variables; $f(t)$: function

if $W_{ki} = \langle k|\hat{W}|i\rangle$, then we have (for $t_0 = -\infty$, $t = \infty$)

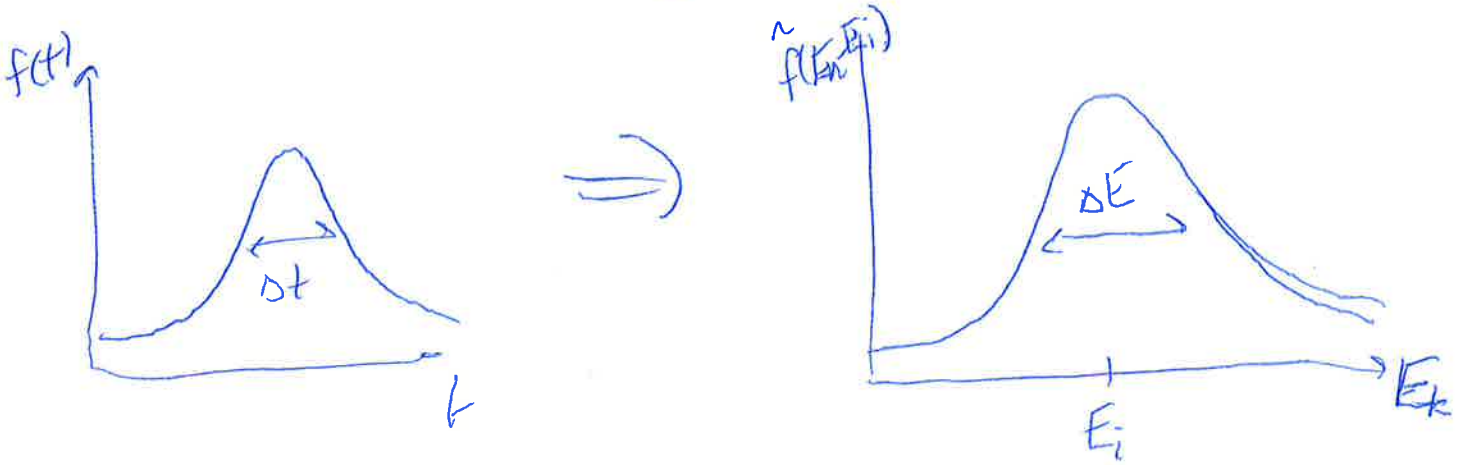
$$S_{ki} = \frac{W_{ki}}{i\hbar}\int_{-\infty}^{\infty} d\tau\, f(t)\, e^{i(E_k - E_i)\tau/\hbar}$$

But this is just the Fourier transform of $f(t)$!!!

Writing $\tilde{f}(E) \equiv \frac{1}{\sqrt{2\pi}\hbar}\int_{-\infty}^{\infty} d\tau f(t) e^{iEt/\hbar}$

then $$P_{i\to k} = |S_{ki}|^2 = \frac{2\pi}{\hbar}|W_{ki}|^2 \left|\tilde{f}(E_k - E_i)\right|^2$$

Example: Collision taking place in time Δt then $f(t)$ looks like gaussian with width Δt:

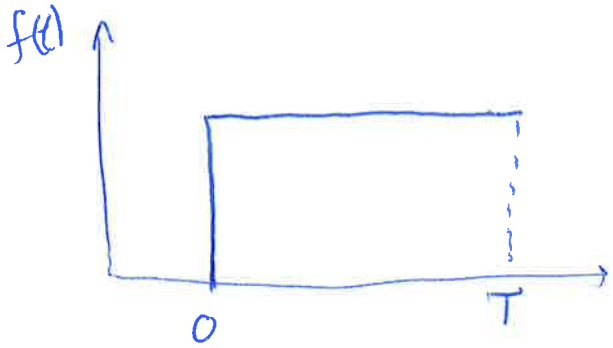


where $\Delta E \approx \frac{\hbar}{\Delta t}$

Thus a collisional interaction for Δt duration will only significantly populate levels for which

$$|E_k - E_i| < \hbar/\Delta t$$

Next example, consider a perturbation suddenly turned on:



We know the Fourier transform of a square pulse; So,

$$S_{ki} = \frac{W_{ki}}{\hbar} \frac{e^{i(E_k - E_i)T/\hbar} - 1}{i(E_k - E_i)/\hbar}$$

or

$$P_{i\to k}(T) = \frac{|W_{ki}|^2}{\hbar^2} g_T(E_k - E_i)$$

where $g_T(E) = \frac{\sin^2(ET/2\hbar)}{(ET/2\hbar)^2} T^2$

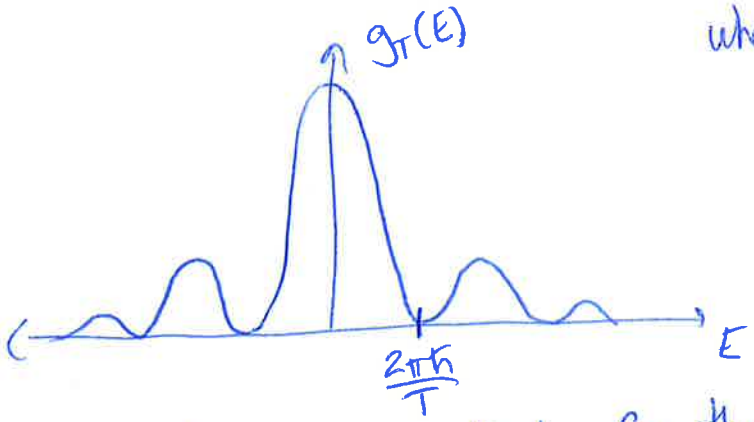
Corrections:

$$\delta_T(E) = \frac{g_T(E)}{2\pi\hbar T}$$

then

$$P_{i\to k}(T) = T \frac{2\pi}{\hbar} |W_{fi}|^2 \delta_T(E_k - E_i)$$

where $\lim_{T\to\infty} \delta_T(E) = \delta(E)$



So, as before, we have an estimate for the efficiently populated states:

$$E_i - \frac{\pi\hbar}{T} < E_k < E_i + \frac{\pi\hbar}{T}$$

The energy is conserved to a precision $\frac{2\pi\hbar}{T}$, or

$$\Delta E \cdot T \simeq \frac{\hbar}{2}$$

"energy-time uncertainty principle" ?!

Final example, a sinusoidal perturbation:

$$f(t) = \cos(\omega t + \phi)$$

Taking the fourier transform:

$$S_{ki} = -\frac{W_{ki}}{2\hbar}\left[\frac{e^{i(\omega_{ki}-\omega)t - i\phi} - e^{i(\omega_{ki}-\omega)t_0 - i\phi}}{\omega_{ki}-\omega} + \frac{e^{i(\omega_{ki}+\omega)t + i\phi} - e^{i(\omega_{ki}+\omega)t_0 + i\phi}}{\omega_{ki}+\omega}\right]$$

where $\hbar\omega_{ki} = E_k - E_i$.

This has two terms, with denom. $\omega_{ki}-\omega$ and $\omega_{ki}+\omega$. Since $\omega_{ki} \sim \omega$ (quasi-resonant condition), the second term is MUCH smaller (so let's ignore it!) → QUASI-RESONANT APPROXIMATION

And:

$$P_{k\to i} = \frac{T|W_{ki}|^2}{4}\left(\frac{2\pi}{\hbar}\right)\delta_T(E_k - E_i - \hbar\omega)$$

δ_T is the same as before!

Comparing this to the pulsed excitation, we have two differences:

1) A factor of 4

2) $E_k - E_i \to E_k - E_i - \hbar\omega$

The first term is because half the amplitude is lost in the off-resonant term (the one with $\omega_{ki}+\omega$ in the denom). This is also called the "ROTATING WAVE APPROXIMATION"

We can construct a similar constraint on the efficiently populated states as before:

$$E_i + \hbar\omega - \frac{\pi\hbar}{T} < E_k < E_i + \hbar\omega + \frac{\pi\hbar}{T}$$

For long T, the only states efficiently populated are those with $|E_k - E_i| = \hbar\omega$. THE CHANGE IN THE ATOMIC ENERGY OCCURS BY THE ABSORPTION OR EMISSION OF A QUANTUM OF ENERGY $\hbar\omega$!

We could call this a photon, but this is not necessary.

Exact Solution of the Problem

Now consider a much simpler case: a two-level atom.

$\hat{H} = \hat{H}_0 + \hat{W}$ as before

$|a\rangle \rightarrow H_0|a\rangle = E_a|a\rangle$

$|b\rangle \rightarrow H_0|b\rangle = E_b|b\rangle$

and $\hat{W}$ gives transitions between these levels:

$W_{aa} = W_{bb} = 0$, $W|a\rangle = |b\rangle$, $W|b\rangle = |a\rangle$

This system can be solved exactly!

$$H = \begin{pmatrix} E_a & W \\ W & E_b \end{pmatrix}$$

Diagonalize it!

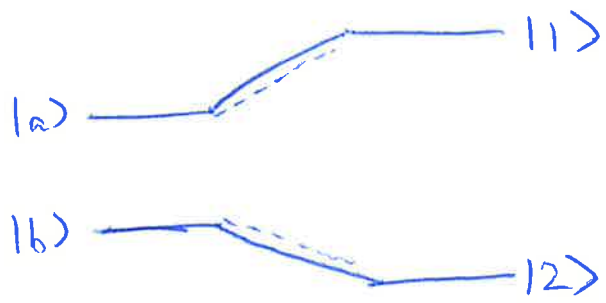
You will find:

$$\begin{cases} |\phi_1\rangle = \cos\theta|a\rangle + \sin\theta|b\rangle \\ |\phi_2\rangle = -\sin\theta|a\rangle + \cos\theta|b\rangle \end{cases}$$

where $\tan 2\theta = \frac{2W}{(E_a - E_b)}$

and $E_{1,2} = \left(\frac{E_a+E_b}{2}\right) \pm \underbrace{\frac{1}{2}\sqrt{(E_a-E_b)^2+4W^2}}_{\hbar\Omega}$

Pictorally:



To get the dynamics, we decompose our state into $|1\rangle + |2\rangle$, time evolve @ $e^{-iE_{1,2}t/\hbar}$ and project onto desired final state.

If initial state is $|a\rangle$, then probability of transition to $|b\rangle$ at time T is given by:

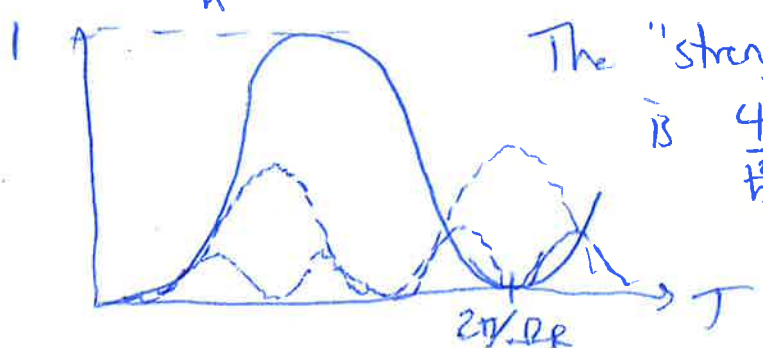
$$P_{a\to b}(T) = \frac{4W^2}{(E_a-E_b)^2+4W^2}\sin^2\left(\frac{\Omega T}{2}\right)$$

$$\boxed{P_{a\to b}(T) = \frac{4W^2}{\hbar^2\Omega^2}\sin^2\left(\frac{\Omega T}{2}\right)}$$

1) These are called "Rabi Oscillations"

2) $\Omega_R = \frac{2W}{\hbar}$ is the "Rabi frequency" by convention and does not depend on anything but the transition matrix element.

3) $\Omega = \frac{\sqrt{(E_a-E_b)^2+4W^2}}{\hbar}$ is the "generalized Rabi frequency"



The "strength" of the oscillation is $\frac{4W^2}{\hbar^2\Omega^2} = \frac{\Omega_R^2}{\Omega^2}$

ie) if $E_a = E_b$

$$P = \sin^2\left(\frac{WT}{\hbar}\right)$$

So $P=1$ when $\frac{WT}{\hbar} = \pi/2$ or $\Omega_R T = \pi$

However, when $E_a \neq E_b$, you never get 100% population transfer.