

TIME-DEPENDENT PERTURBATION THEORY.

QUANTUM DYNAMICS - STATEMENT OF THE PROBLEM

How does transition occur between stationary states? (e.g. Atomic transitions)

Transition occurs when system is perturbed by a time dependent Hamiltonian

Let us consider a system with time-independent Hamiltonian \hat{H}_0 .

Schrödinger Equation: $i\hbar \frac{\partial |\Psi\rangle}{\partial t} = \hat{H}_0 |\Psi\rangle$.

Stationary states: $|\varphi_{E_n}\rangle = |\varphi_{E_n}\rangle e^{-iE_n t/\hbar}$ spectrum may be continuous or discrete
where, $\hat{H} |\varphi_{E_n}\rangle = E_n |\varphi_{E_n}\rangle$.

Any general state is a linear combination of stationary states

$$|\Psi(t)\rangle = \sum_n c_n |\varphi_{E_n}\rangle e^{-iE_n t/\hbar}$$

which can have a non-trivial time evolution.

- If the system is in a stationary state $|\varphi_{E_a}\rangle$ it lives in that state forever!
- In the physical world often it is found that system is in a stationary state $|\varphi_{E_a}\rangle$ at $t=0$, but at some later time the system has a non-zero probability $P_{a \rightarrow b}(t)$ to be found in another stationary state $|\varphi_{E_b}\rangle$
- This can happen if 'in the mean-while' the hamiltonian of the system changes i.e. we have a time-dependent Hamiltonian $\hat{H}(t)$.

- The form of the time-dependence is as follows

$$\hat{H}(t) = \hat{H}_0 + \hat{H}_{(1)}(t).$$

i.e. a time dependent piece is added to the original Hamiltonian, often as a perturbation, which may become zero after sometime.

- Due to the presence of $\hat{H}_{(1)}(t)$ the transition probability $P_{a \rightarrow b}(t)$ will typically be non-zero.
- The physical problem is to compute $P_{a \rightarrow b}(t)$ for any two states with energy eigenvalues E_a and E_b , given some $\hat{H}_{(1)}(t)$
- This problem is often solved considering $\hat{H}_{(1)}(t)$ as a small (amplitude) perturbation of \hat{H}_0 \rightarrow "TIME-DEPENDENT PERTURBATION THEORY".

X

TWO-LEVEL SYSTEMS :

Consider a two-level system where \hat{H}_0 has two discrete non-degenerate energy eigen-values :

$$\hat{H}_0 |\varphi_a\rangle = E_a |\varphi_a\rangle, \quad \hat{H}_0 |\varphi_b\rangle = E_b |\varphi_b\rangle$$

$$E_a \neq E_b, \quad \langle \varphi_a | \varphi_b \rangle = \delta_{ab}.$$

Then any state is a linear combination (normalized) -

$$|\psi\rangle(t) = C_a |\varphi_a\rangle e^{-iE_a t/\hbar} + C_b |\varphi_b\rangle e^{-iE_b t/\hbar}.$$

Probability of finding system in state 'a' or 'b' : $P_a = |C_a|^2$, $P_b = |C_b|^2$
 we have, $P_a + P_b = |C_a|^2 + |C_b|^2 = 1$. Also, $P_{a \rightarrow b}(t) = 0$.

Now, the full hamiltonian is of the form

$$\hat{H}(t) = \hat{H}_0 + \hat{H}_{\text{int}}(t). \quad \hat{H}(t)|\psi\rangle = i\hbar \frac{\partial |\psi\rangle}{\partial t}.$$

If dimension of Hilbert space does not change due to the presence of $\hat{H}_{\text{int}}(t)$, we can still express any state, which solves Schrödinger equation with full Hamiltonian $\hat{H}(t)$, in the old basis as

$$|\psi\rangle(t) = C_a(t) |\varphi_a\rangle e^{-iE_a t/\hbar} + C_b(t) |\varphi_b\rangle e^{-iE_b t/\hbar}.$$

The superposition coefficients become general function of time (not just $e^{-iEt/\hbar}$).

The time dependence of $C_n(t)$ is determined by $\hat{H}_{\text{int}}(t)$.

Let us determine $C_n(t)$:

$$i\hbar \frac{\partial |\psi\rangle}{\partial t} = \hat{H}(t) |\psi\rangle = \hat{H}_{(0)} |\psi\rangle + \hat{H}_{(1)}(t) |\psi\rangle$$

where,

$$|\psi\rangle(t) = C_a(t) |\varphi_a\rangle e^{-iE_a t/\hbar} + C_b(t) |\varphi_b\rangle e^{-iE_b t/\hbar}.$$

Putting into Schrödinger equation we get-

$$\begin{aligned} & i\hbar \left[\dot{C}_a e^{-iE_a t/\hbar} |\varphi_a\rangle - \frac{i}{\hbar} E_a C_a e^{-iE_a t/\hbar} |\varphi_a\rangle + \dot{C}_b e^{-iE_b t/\hbar} |\varphi_b\rangle - \frac{i}{\hbar} E_b C_b e^{-iE_b t/\hbar} |\varphi_b\rangle \right] \\ &= C_a \underbrace{\hat{H}_{(0)} |\varphi_a\rangle}_{E_a |\varphi_a\rangle} e^{iE_a t/\hbar} + C_a \hat{H}_{(1)}(t) |\varphi_a\rangle e^{-iE_a t/\hbar} + C_b \underbrace{\hat{H}_{(0)} |\varphi_b\rangle}_{E_b |\varphi_b\rangle} e^{-iE_b t/\hbar} + C_b \hat{H}_{(1)}(t) |\varphi_b\rangle e^{-iE_b t/\hbar} \\ \Rightarrow & i\hbar \dot{C}_a e^{-iE_a t/\hbar} |\varphi_a\rangle + i\hbar \dot{C}_b e^{-iE_b t/\hbar} |\varphi_b\rangle \\ &= C_a e^{-iE_a t/\hbar} \hat{H}_{(1)}(t) |\varphi_a\rangle + C_b e^{-iE_b t/\hbar} \hat{H}_{(1)}(t) |\varphi_b\rangle \end{aligned}$$

Taking inner product with $\langle \varphi_a |$ and $\langle \varphi_b |$ respectively and using orthogonality we get

$$\begin{cases} i\hbar \dot{C}_a e^{-iE_a t/\hbar} = C_a e^{-iE_a t/\hbar} \langle \varphi_a | \hat{H}_{(1)}(t) |\varphi_b \rangle + C_b e^{-iE_b t/\hbar} \langle \varphi_a | \hat{H}_{(1)}(t) |\varphi_b \rangle \\ i\hbar \dot{C}_b e^{-iE_b t/\hbar} = C_a e^{-iE_a t/\hbar} \langle \varphi_b | \hat{H}_{(1)}(t) |\varphi_a \rangle + C_b e^{-iE_b t/\hbar} \langle \varphi_b | \hat{H}_{(1)}(t) |\varphi_a \rangle \end{cases}$$

$$\Rightarrow \begin{cases} \dot{C}_a = -\frac{i}{\hbar} [C_a \hat{H}_{aa}^{(1)} + C_b \hat{H}_{ab}^{(1)} e^{-i(E_b - E_a)t/\hbar}] \\ \dot{C}_b = -\frac{i}{\hbar} [C_b \hat{H}_{bb}^{(1)} + C_a \hat{H}_{ba}^{(1)} e^{i(E_b - E_a)t/\hbar}] \end{cases}$$

Integrating we get $C_a(t)$, $C_b(t)$.

A particular simplification occurs if

$$\hat{H}_{aa}^{(1)} = 0 = \hat{H}_{bb}^{(1)}$$

We then have

$$\left. \begin{aligned} \dot{C}_a &= -\frac{i}{\hbar} C_b \hat{H}_{ab}^{(1)}(t) e^{-i\omega t} \\ \dot{C}_b &= -\frac{i}{\hbar} C_a \hat{H}_{ab}^{(1)}(t) e^{i\omega t} \end{aligned} \right\} \omega = \frac{\epsilon_b - \epsilon_a}{\hbar}$$

Note that $\hat{H}_{ab}^{(1)} + \hat{H}_{ba}^{(1)} = \hat{H}_{ba}^{(1)}$ \rightarrow Hermitian Hamiltonian.

Ex. Such 2-level system can be solved exactly (see Assignment).

Expand out the exact solution and match with perturbation results above.

Perturbation Theory

Let us consider time-dependent part of hamiltonian to be

$$\hat{H}^{(1)} = \lambda \hat{W}.$$

where λ is a small parameter. We wish to solve the problem order by order in λ .

We need to solve $\hat{H}(t)|\Psi\rangle = i \frac{\partial}{\partial t} |\Psi\rangle$

where, $|\Psi\rangle = \sum_n C_n(t) e^{-iE_n t/\hbar} |\phi_n\rangle$

and, $\hat{H}(t) = \hat{H}_0 + \hat{H}^{(1)}(t)$.

Plugging into schrödinger equation

$$\text{it } \sum_n \left[\dot{C}_n(t) e^{-iE_n t/\hbar} |\phi_n\rangle - \frac{i}{\hbar} C_n E_n e^{iE_n t/\hbar} |\phi_n\rangle \right] \\ = \sum_n \left(C_n E_n |\phi_n\rangle e^{-iE_n t/\hbar} + \lambda C_n \hat{W} |\phi_n\rangle e^{-iE_n t/\hbar} \right).$$

Taking inner product with $\langle \phi_m |$

$$\text{it } \dot{C}_m e^{-iE_m t/\hbar} = \lambda \sum_n C_n \langle \phi_m | \hat{W} | \phi_n \rangle e^{-iE_n t/\hbar}.$$

$$\frac{d}{dt} C_m(t) = -\frac{i\lambda}{\hbar} \sum_n C_n W_{mn}^{(1)} e^{i\omega_{mn} t}$$

where, $\omega_{mn} = E_m - E_n$, $W_{mn} = \langle \phi_m | \hat{W} | \phi_n \rangle$.

We could have taken $|\Psi(t)\rangle = \sum_n b_n(t) |\phi_n\rangle$
but assuming this form of b_n helps algebra later

orthonormal
 $\langle \phi_n | \phi_m \rangle = \delta_{mn}$.
 $\hat{H}_0 |\phi_n\rangle = E_n |\phi_n\rangle$

The sum in general makes it a very hard problem to solve.
 (coupled equations).

Simplify : Set up a perturbation

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

Ansatz: perturbative expansion of coefficients.

$$= \sum_P \lambda^P C_m^{(P)}(t)$$

Putting back :

$$\sum_{P=0}^{\infty} \lambda^P \frac{d}{dt} C_m^{(P)}(t) = -\frac{i}{\hbar} \sum_{P=0}^{\infty} \lambda^{P+1} \sum_n C_n^{(P)}(t) \omega_{mn} e^{i\omega_{mn} t}$$

Now compare powers of λ

$$\frac{d}{dt} C_m^{(P)}(t) = -\frac{i}{\hbar} \sum_n C_n^{(P-1)}(t) \omega_{mn} e^{i\omega_{mn} t}$$

$$\text{with, } \frac{dC_m^{(0)}(t)}{dt} = 0$$

(stationary states at zeroth order!)

- Every order is determined by the solution at previous order.
- No longer a coupled problem at any given order.

Let us look at this perturbation series in slightly more detail.

0th order :

$$\frac{d C_m^{(0)}}{dt} = 0$$

$C_m^{(0)}$ are constant (Stationary states), when there is no perturbation.

Example: Consider the two level system with $\omega_{aa} = 0 = \omega_{bb}$.

at $t=0$, say $C_a(t=0) = 1$, $C_b(t=0) = 0$.

then upto zeroth order : $\frac{d C_m^{(0)}}{dt} = 0$

$\Rightarrow C_a^{(0)}(t) = 1$, $C_b^{(0)}(t) = 0$ at all times!

For system with many levels we can consider

$C_m(t=0) = \delta_{mi}$ initially system in Eigenstate 'i'.

$\Rightarrow C_m^{(0)}(t) = \delta_{mi}$ \leftarrow stationary states upto zeroth ord.
at all times!

First order :

$$\frac{d C_m^{(1)}(t)}{dt} = -\frac{\Omega}{\hbar} \sum_n C_n^{(0)}(t) W_{mn}(t) e^{i \omega_{mn} t}.$$

$\delta_{ij} = 1, \text{ if } i=j$
 $= 0, \text{ otherwise}$

$C_n^{(0)}(t)$ determined at previous order.
 δ_{ni} System initially in Eigenstate 'i'.

Hence,

$$\frac{d C_m^{(1)}(t)}{dt} = -\frac{i}{\hbar} \omega_{mi}(t) e^{i\omega_{mi} t}$$

$$\Rightarrow C_m^{(1)}(t) = -\frac{i}{\hbar} \int_0^t dt' \omega_{mi}(t') e^{i\omega_{mi} t'}.$$

All $C_m^{(1)}$ can become non-zero at first order.

We can now calculate the probability of transition:

If the system is in state 'i' at $t=0$,

what is the probability of finding it in state 'f' at t ?

$$\underset{(1)}{\mathcal{P}_{i \rightarrow f}}(t) = |C_f(t)|^2$$

$$\begin{aligned} & \text{transition} \\ & = |C_f^{(0)} + \lambda C_f^{(1)}(t)|^2 \end{aligned}$$

probability

$$\text{to first order} = \lambda^2 |C_f^{(1)}|^2$$

in perturbation

$$\text{theory.} = \frac{\lambda^2}{\hbar^2} \left| \int_0^t dt' \omega_{fi}(t') e^{i\omega_{fi} t'} \right|^2$$

$$\boxed{\mathcal{P}_{i \rightarrow f}^{(1)} = \frac{1}{\hbar^2} \left| \int_0^t dt' (\lambda \omega_{fi}(t')) e^{i\omega_{fi} t'} \right|^2.}$$

Example: For 2-level system $\omega_{aa} = \omega_{bb} = 0$.

At first order $C_a^{(1)}(t) = 0$, since $\omega_{aa} = 0$.

But, $C_b^{(1)} = -\frac{i}{\hbar} \int_0^t dt' W_{ba}(t') e^{i\omega_{ba} t}$.

Hence, $C_a = 1 + \mathcal{O}(\lambda^2)$.

$$C_b = -\frac{\lambda i}{\hbar} \int_0^t dt' W_{ba}(t') e^{i\omega_{ab} t} + \mathcal{O}(\lambda^2).$$

Second order:

determined at previous order.

$$\frac{d C_m^{(2)}}{dt} = -\frac{i}{\hbar} \sum_n C_n^{(1)}(t) W_{mn}(t) e^{i\omega_{mn} t}.$$

Assuming $C_n^{(0)} = \delta_{ni}$

$$C_n^{(1)}(t) = -\frac{i}{\hbar} \int_0^t dt'' W_{ni}(t'') e^{i\omega_{ni} t''}$$

Integrating one more time we get

$$\begin{aligned}
 C_m^{(2)}(t) &= \left(-\frac{i}{\hbar}\right) \sum_n \int_0^t dt' C_n^{(1)}(t') W_{mn}(t') e^{i\omega_{mn} t'} \\
 &= \left(-\frac{i}{\hbar}\right)^2 \sum_n \int_0^t dt' \int_0^{t'} dt'' W_{ni}(t'') e^{i\omega_{ni} t''} W_{mn}(t') e^{i\omega_{mn} t'} \\
 &= \left(-\frac{i}{\hbar}\right)^2 \sum_m \int_0^t dt' \int_0^{t'} dt'' e^{iE_m t'/\hbar} W_{mn}(t') e^{-iE_n(t'-t'')} W_{ni}(t'') e^{-iE_i t''/\hbar}
 \end{aligned}$$

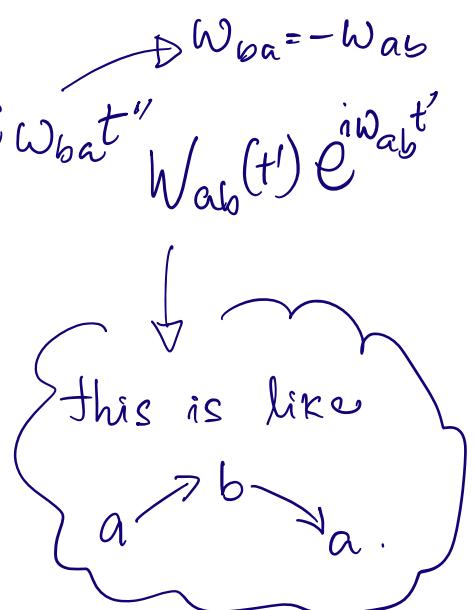
More instructively

$$C_m^{(2)} e^{-iE_m t} = \left(-\frac{i}{\hbar}\right)^2 \sum_n \int_0^t dt' \int_0^{t'} dt'' e^{iE_m(t-t')} W_{mn}(t') e^{-iE_n(t'-t'')} W_{ni}(t'') e^{-iE_i t''/\hbar}$$

Example: 2-level system

$$C_a^{(2)} = \left(-\frac{i}{\hbar}\right)^2 \int_0^t dt' \int_0^{t'} dt'' W_{ba}(t'') e^{i\omega_{ba} t''} W_{ab}(t') e^{i\omega_{ab} t'}$$

$$C_b^{(2)} = 0 \text{ since } W_{bb} = 0$$



Summary of 2-level system upto 2nd order:

$$C_a(t) = 1 + \lambda \cdot 0 + \lambda^2 \left(\frac{-i}{\hbar}\right)^2 \int_0^t \int_0^{t'} W_{ba}(t'') e^{i\omega_{ba} t''} W_{ab}(t') e^{i\omega_{ab} t'}.$$

$$C_b(t) = 0 + \lambda \left(\frac{i}{\hbar}\right) \int_0^t W_{ba}(t') e^{i\omega_{ba} t'}.$$

Summary upto second order :

$$\begin{aligned} G_f^{(2)}(t) e^{-iE_f t/\hbar} &= \delta_{fi} e^{-it_i t/\hbar} + \lambda \left(\frac{-i}{\hbar}\right) \int_0^t e^{-iE_f(t-t')} W_{fi}(t') e^{-ie_i t'/\hbar} \\ &+ \lambda \left(\frac{-i}{\hbar}\right)^2 \sum_n \int_0^t \int_0^{t'} W_{fn}(t') e^{-iE_n(t'-t'')} W_{ni}(t'') e^{-ie_i t''/\hbar}. \end{aligned}$$

Can you guess the third order by analogy, without doing the calculation?

Sinusoidal Perturbations.

$$\hat{W}(t) \Rightarrow \hat{W}^{(0)} \sin \omega t = 2 \hat{W}^{(0)} \left[\frac{e^{i\omega t} - e^{-i\omega t}}{2i} \right].$$

Let us assume $C_{mi}^{(0)}(t) = \delta_{mi}$ \rightarrow initial state (φ_i) .

Upto first order in perturbation

$$\begin{aligned} C_{mi}^{(1)}(t) &= \left(\frac{-i}{\hbar}\right) \int_0^t dt' W_{mi}(t') e^{i\omega_{mi} t'} \\ &= \left(\frac{-i}{\hbar}\right) \int_0^t dt' \left(W_{mi}^{(0)} \right) \left(\frac{e^{i\omega t'} - e^{-i\omega t'}}{2i} \right) e^{i\omega_{mi} t'} \\ &= -\frac{W_{mi}^{(0)}}{2\hbar} \int_0^t \left[e^{i(\omega + \omega_{mi})t'} - e^{i(\omega_{mi} - \omega)t'} \right] dt' \\ &= -\frac{W_{mi}^{(0)}}{2\hbar} \left[\frac{1 - e^{i(\omega + \omega_{mi})t}}{\omega + \omega_{mi}} - \frac{1 - e^{i(\omega_{mi} - \omega)t}}{\omega_{mi} - \omega} \right] \end{aligned}$$

Probability:

$$P_{i \rightarrow f}^{(s)}(t) = \frac{\lambda^2 |W_{fi}^{(0)}|^2}{4\hbar^2} \left| \frac{1 - e^{i(\omega + \omega_{fi})t}}{\omega + \omega_{fi}} - \frac{1 - e^{i(\omega_{fi} - \omega)t}}{\omega_{fi} - \omega} \right|^2$$

If we considered $\hat{W}(t) = \hat{W}^0 \cos \omega t$

$$\underset{i \rightarrow f}{P}_{\text{Cs}}^{(C)}(t) = \frac{\lambda^2 |W_{fi}^0|^2}{4\hbar^2} \left| \frac{1 - e^{i(\omega + \omega_{fi})t}}{\omega + \omega_{fi}} + \frac{1 - e^{i(\omega_{fi} - \omega)t}}{\omega_{fi} - \omega} \right|^2$$

Special case : $\omega = 0$ ie $\hat{W}(t) = \hat{W}^0 \rightarrow$ a constant.

$$\underset{i \rightarrow f}{P}_{\text{Cs}}^{(C)}(t) = \frac{\lambda^2 |W_{fi}^0|^2}{4\hbar^2} \left| \frac{2 - 2 e^{i\omega_{fi}t}}{\omega_{fi}} \right|^2$$

$$= \frac{\lambda^2 |W_{fi}^0|^2}{\hbar^2 \omega_{fi}^2} |1 - e^{i\omega_{fi}t}|^2$$

$$= \frac{\lambda^2 |W_{fi}^0|^2}{\hbar^2} \left[\frac{\sin(\omega_{fi}t/2)}{(\omega_{fi}/2)} \right]^2$$

NOTE :

- 1. In this way, we can use time-dependent perturbation theory setup even when the perturbation Hamiltonian \hat{H}_1 is time-independent.
- 2. For constant perturbation, if there are off-diagonal elements, then transition probability has oscillatory behavior

Ex: What is the smallest time for which you should keep the perturbation on to ensure maximum transition probability?

RESONANCE .

Another special case occurs when driving frequency is close to one transition frequency.

Recall, for sinusoidal perturbation

$$\mathcal{P}_{i \rightarrow f}^{(s)}(t) = \frac{|W_{fi}|^2}{4t^2} \left| \frac{1 - e^{i(\omega + \omega_{fi})t}}{\omega + \omega_{fi}} - \frac{1 - e^{i(\omega_{fi} - \omega)t}}{\omega_{fi} - \omega} \right|^2$$

At fixed t , this function has a maximum near

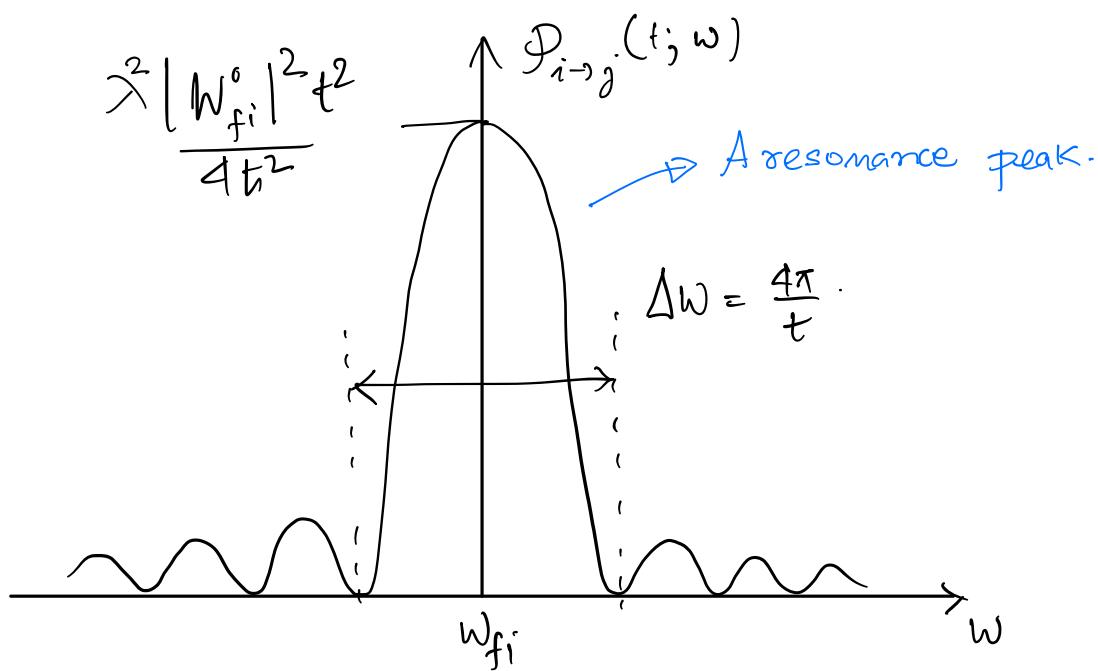
$$\omega \approx \omega_{fi} \quad \text{or} \quad \omega \approx -\omega_{fi}$$

$$\mathcal{P}_{i \rightarrow f}^{(s)}(t) = \frac{|W_{fi}|^2}{4t^2} \left| \frac{1 - e^{i(\omega + \omega_{fi})t}}{\omega + \omega_{fi}} - \frac{1 - e^{i(\omega_{fi} - \omega)t}}{\omega_{fi} - \omega} \right|^2$$

↙ More important ↘ this term dominates
 $\omega \approx -\omega_{fi}$ when $\omega \approx \omega_{fi}$.

Let us assume $\omega \approx \omega_{fi}$.

$$\mathcal{P}_{i \rightarrow f}^{(s)}(t) = \frac{|W_{fi}|^2}{4t^2} \frac{\sin^2 \left[\frac{(\omega_{fi} - \omega)t}{2} \right]}{\left[\frac{\omega_{fi} - \omega}{2} \right]^2}$$



At large time t , the peak becomes higher and narrower. Strictly as $t \rightarrow \infty$, this becomes the δ -function (see later).

Ex: Show that $P_{i \rightarrow f} = P_{f \rightarrow i}$

The peak corresponds to a 'resonance' when energy is absorbed from external agency to drive transition to excited state. It corresponds to 'anti-resonance' when the external perturbation (tuned at right frequency), forces the system to go from excited state to state of lower energy.

In the later case the system gives away energy to external agency, but the presence of external agency is essential for transition to take place (otherwise $H=0 \Rightarrow P_{i \rightarrow f}=0$). This concept, applied to atomic physics, is the idea behind stimulated emission.

(transition in presence of stimulation through external perturbation)

Maximum transition probability

FERMI GOLDEN RULE.

Special case when the final state is a part of continuum.

$$\rho_{i \rightarrow f}(t) = |\langle \varphi_f | \psi(t) \rangle|^2.$$

$|\varphi_f\rangle \rightarrow \text{continuum}$

e.g. States of a free particle.

$$\delta \rho_{i \rightarrow f}(t) = \int d^3 p \quad |\langle \vec{p} | \psi(t) \rangle|^2$$

$\vec{p} \in \text{Some neighbourhood of } p_f$

$$\delta \rho_{i \rightarrow f}(t) = \int d\Omega_p \underbrace{p^2 dp}_{\text{write in terms of Energy.}} |\langle \vec{p} | \psi(t) \rangle|^2$$

$$E = \frac{p^2}{2m} \Rightarrow dE = \frac{p}{m} dp$$

$$\Rightarrow p^2 dp = m p dE$$
$$= m \sqrt{2m E} dE.$$

$$\begin{aligned} \delta \rho_{i \rightarrow f}(t) &= \int d\Omega_p m \sqrt{2m E} dE |\langle E, \Omega_p | \psi(t) \rangle|^2 \\ &= \int d\Omega_p \underset{\substack{\uparrow \\ \text{degeneracy.}}}{f(E)} dE |\langle E, \Omega_p | \psi(t) \rangle|^2. \end{aligned}$$

More generally, A general degeneracy parameter.

$$\delta P_{i \rightarrow f}^{(t)} = \int_{\beta \in \delta \beta_f} d\beta \int_{E \in \delta E_f} dE \ g(\beta, E) | \langle E, \beta | \psi(t) \rangle |^2.$$

In general the density of states can have a degeneracy dependence.

If we have a constant perturbation. ($\omega = 0$).

$$P_{i \rightarrow f}^{(t)} = \frac{\lambda^2 |W_{fi}^{(0)}|^2}{\hbar^2} \left[\frac{\sin(\omega_{fi} t / 2)}{(\omega_{fi} / 2)} \right]^2$$

↓ continuum final states.

$$P_{i \rightarrow f}^{(t)} = \int_{\beta \in \delta \beta} d\beta \int_{E \in \delta E} dE | \langle \beta, E | \omega W^{(0)} | \phi_i \rangle |^2 \left(\frac{\sin(\omega_{fi} t / 2)}{\omega_{fi} / 2} \right)^2$$

Late times

$$\lim_{t \rightarrow \infty} \left(\frac{\sin \frac{\omega_{fi} t}{2}}{\omega_{fi} / 2} \right)^2 = \pi t \delta\left(\frac{\omega_{fi}}{2}\right) = 2\pi \hbar t \delta(E - E_i).$$

Aside: How to show $\lim_{t \rightarrow \infty} \left(\frac{\sin tx}{x} \right)^2 = \pi t \delta(x)$.

First show that $\lim_{t \rightarrow \infty} \frac{\sin xt}{x} = \pi \delta(x)$.

$$\frac{\sin x}{x} = \text{Sinc}x$$

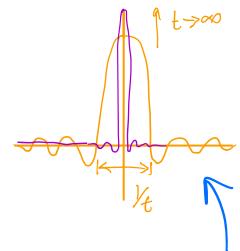
Easy way: use

$$\delta(x) = \lim_{t \rightarrow \infty} \frac{1}{2\pi} \int_{-t}^t e^{ikx} dk$$

$$\Rightarrow 2\pi \delta(x) = \lim_{t \rightarrow \infty} \frac{e^{itx} - e^{-itx}}{ix} = \lim_{t \rightarrow \infty} \frac{2 \sin tx}{x}$$

$$\Rightarrow \delta(x) = \lim_{t \rightarrow \infty} \frac{\sin tx}{\pi x}$$

$$\lim_{t \rightarrow \infty} \left(\frac{\sin x}{x} \right) = \pi \delta(x).$$



Now, $\lim_{t \rightarrow \infty} \left(\frac{\sin tx}{x} \right)^2$

- is also proportional to delta
- proportionality constant must be determined.
- this can be found by integration.

$$\int_{-\infty}^{\infty} \lim_{t \rightarrow \infty} \left(\frac{\sin tx}{x} \right)^2 dx = N, \text{ then } \lim_{t \rightarrow \infty} \left(\frac{\sin tx}{x} \right)^2 = N \delta(x).$$

What is N?

$$\begin{aligned} \lim_{t \rightarrow \infty} \left[- \int_{-\infty}^{\infty} \frac{d}{dx} \left(\frac{1}{x} \right) \sin^2 tx dx \right] &= \int_{-\infty}^{\infty} \frac{1}{x} (2 \sin tx \cos tx) t dx \\ &= t \int_{-\infty}^{\infty} \lim_{2t \rightarrow \infty} \left(\frac{\sin[(2t)x]}{x} \right) dx \rightarrow \pi \delta(x). \end{aligned}$$

$$= \pi t = N$$

✓ you may perform these steps putting in some regular $f(x)$ within integral, and show $\int f(x) \delta(x) dx = f(0)$.

$$\delta P_{i \rightarrow f}(t) = \delta \beta_f \frac{2\pi}{\hbar} t \left| \langle \beta_f, E_f = E_i | W | \varphi_i \rangle \right|^2 \rho(\beta_f, E_f = E_i).$$

$\delta P_{i \rightarrow f} = 0$ when E_i does not belong to any continuum Energy value.

transition probability per unit time per unit "degeneracy measure"

$$f_{i \rightarrow f} = \frac{\delta P_{i \rightarrow f}}{\delta \beta_f}, \quad \delta f_{i \rightarrow f} = \frac{d P_{i \rightarrow f}}{dt}.$$

$$P_{i \rightarrow f} = \frac{2\pi}{\hbar} \left| \langle \beta_f, E_f = E_i | W | \varphi_i \rangle \right|^2 \rho(\beta_f, E_f = E_i).$$

Probability

- (i) Proportional to density of states.
- (ii) Energy of final state equal to initial state.

↙ this fact is only true if $\omega=0$. If $\omega \neq 0$, $E_f = E_i + \hbar\omega$ as we will see below.

Revisit Scattering problem:

The interaction potential $V(r)$ is a time independent perturbation on free particle hamiltonian

$$\mathcal{H} = \mathcal{H}^0 + V(r) \Rightarrow \lambda \hat{W}^0 \text{ in above notation.}$$

$$f_{\vec{P}_i \rightarrow \vec{P}_f} = \frac{2\pi}{\hbar} |\langle \vec{P}_f | V | \vec{P}_i \rangle|^2 \delta(E_f - E_i).$$

Let us write the quantity $\langle \vec{P}_f | V(r) | \vec{P}_i \rangle$ in position coordinates

$$\begin{aligned} \langle \vec{P}_f | \hat{V}(r) | \vec{P}_i \rangle &= \int d^3 \vec{r}_1 \int d^3 \vec{r}_2 \underbrace{\langle \vec{P}_f | \vec{r}_1 \rangle}_{\substack{\text{Insertion of} \\ \text{Identity}}} \langle \vec{r}_1 | \hat{V}(r) | \vec{r}_2 \rangle \underbrace{\langle \vec{r}_2 | \vec{P}_i \rangle}_{\substack{\text{Insertion of} \\ \text{Identity}}} \\ &= \int d^3 \vec{r}_1 \int d^3 \vec{r}_2 \left(\frac{1}{2\pi\hbar} \right)^3 e^{-i\vec{P}_f \cdot \vec{r}_1} \underbrace{\langle \vec{r}_1 | \hat{V}(r) | \vec{r}_2 \rangle}_{\substack{\text{Momentum} \\ \text{Eigenstate in} \\ \text{position space.}}} \left(\frac{1}{2\pi\hbar} \right)^3 e^{i\vec{P}_i \cdot \vec{r}_2} \\ &\quad \downarrow \qquad \qquad \qquad \downarrow \qquad \qquad \qquad \downarrow \qquad \qquad \qquad \downarrow \\ &\quad \langle \vec{r}_1 | \hat{V}(r) | \vec{r}_2 \rangle \text{ position operator acting on position eigenstate.} \\ &= V(\vec{r}_2) \langle \vec{r}_1 | \vec{r}_2 \rangle \\ &= V(\vec{r}_2) \delta(\vec{r}_1 - \vec{r}_2). \end{aligned}$$

$$\langle \vec{P}_f | \hat{V}(r) | \vec{P}_i \rangle = \int d^3 \vec{r}_1 \int d^3 \vec{r}_2 \left(\frac{1}{2\pi\hbar} \right)^3 e^{-i\vec{P}_f \cdot \vec{r}_1 + i\vec{P}_i \cdot \vec{r}_2} V(\vec{r}_2) \delta(\vec{r}_1 - \vec{r}_2)$$

performing integration over $\vec{r}_2 \rightarrow$ delta func. clicks.

$$= \left(\frac{1}{2\pi\hbar} \right)^3 \int d^3 \vec{r}_1 e^{-i(\vec{P}_f - \vec{P}_i) \cdot \vec{r}_1} V(\vec{r}_1).$$

We can rename integration variable from \vec{r}_1 to \vec{r} .

Putting it together we get,

$$f_{\vec{p}_i \rightarrow \vec{p}_f} = \frac{2\pi}{\hbar} \left(m \sqrt{2mE} \right) \left(\frac{1}{2\pi\hbar} \right)^6 \left| \int d^3r e^{i(\vec{p}_i - \vec{p}_f) \cdot \vec{r}/\hbar} V(r) \right|^2$$

Probability Current for free incoming particle. (see lecture note-1 on scattering).

$$\vec{J} = \left(\frac{1}{2\pi\hbar} \right)^3 \sqrt{\frac{2E_i}{m}}$$

$$\frac{f_{\vec{p}_i \rightarrow \vec{p}_f}}{|\vec{J}|} = \frac{m^2}{4\pi^2\hbar^4} \left| \int d^3r e^{i(\vec{p}_i - \vec{p}_f) \cdot \vec{r}/\hbar} V(r) \right|^2$$

This is the result for First Born approximation.

Fermi Golden Rule for Sin ωt perturbations.

Consider $\hat{W} = \hat{W}^{(0)} \sin\omega t$

The transition probability we found above

$$P_{i \rightarrow f}(t) = \frac{|W_{fi}^{(0)}|^2}{4\hbar^2} \left| \frac{\sin(\omega_{fi} - \omega)t/2}{(\omega_{fi} - \omega)/2} \right|^2$$

If final states are continuous we should write.

$$\delta P_{i \rightarrow f}(t) = \int_{\substack{\beta \in \delta \beta_f \\ E \in \delta E_f}} d\beta f(\epsilon) dE \left[\frac{|W_{fi}^{(0)}|^2}{4\hbar^2} \left| \frac{\sin(\omega_{fi} - \omega)t/2}{(\omega_{fi} - \omega)/2} \right|^2 \right]$$

$$\frac{|W_{fi}^{(0)}|^2}{4\hbar^2} \pi t \delta\left(\frac{\omega_{fi} - \omega}{2}\right)$$

$$\frac{|W_{fi}^{(0)}|^2}{4\hbar^2} (2\hbar\pi t) \delta(E_f - (E_i + \hbar\omega))$$

$$\delta P_{i \rightarrow f}(t) = (\delta\beta_i t) \left(\frac{|W_{fi}^{(0)}|^2}{4\hbar} \right) (2\pi\hbar) g(\beta_f, E_f) \Big|_{E_f = E_i + \hbar\omega}$$

So probability per unit time per unit degeneracy measure.

$$p_{i \rightarrow f}(t) = \left(\frac{|W_{fi}^{(0)}|^2}{4\hbar} \right) (2\pi\hbar) g(\beta_f, E_f) \Big|_{E_f = E_i + \hbar\omega}$$

Key concept of Fermi-Golden rule :

Probability of transition to continuum states is proportional to the density of states around the value of E_f , the value of E_f being completely determined by E_i and nature of perturbation.

SELECTION RULES FOR ATOMIC TRANSITIONS.

SCALAR AND VECTOR OPERATORS (Action of rotational symmetry).

1. Generators of symmetry.

First lets take the case of translations. \hat{T} .

$$\hat{T} = \exp\left(-\frac{i}{\hbar} a \hat{p}\right) \quad \hat{p} \rightarrow \text{linear momentum operator.}$$

Action on a state in position representation: $(\hat{T}|\psi\rangle)$

$$\exp\left(-\frac{i}{\hbar} a \left(-i\hbar \frac{\partial}{\partial x}\right)\right) \psi(x) \quad \rightarrow \text{Expanding}$$

$$= 1 - a \frac{\partial \psi}{\partial x} + \frac{a^2}{2} \frac{\partial^2 \psi}{\partial x^2} + \dots \quad \rightarrow \text{Taylor series expansion.}$$

$$= \psi(x-a)$$

Similarly rotation operators have angular momentum generators

$$\hat{R}_n^{(\theta)} = \exp\left(-\frac{i}{\hbar} \theta \hat{L} \cdot \hat{n}\right).$$

Rotation by angle θ along \hat{n} .

Now consider expectation value of operator $\hat{\Theta}$: $\langle \psi | \hat{\Theta} | \psi \rangle$

$$\text{Under action of rotation } |\tilde{\psi}\rangle = R_n^{(\theta)} |\psi\rangle$$

And the expectation changes as

$$\langle \tilde{\psi} | \hat{\Theta} | \tilde{\psi} \rangle = \langle \psi | \underbrace{R_n^{(\theta)} + \hat{\Theta} R_n^{(\theta)}}_{\text{Action of rotation on operators.}} R_n^{(\theta)} | \psi \rangle.$$

Action of rotation on operators.

For simplicity let us consider $\hat{h} = \hat{z}$.

$$\begin{aligned}\hat{\theta} &= R_z^\theta + \hat{\theta} R_z^\theta \\ &= \exp\left(\frac{i}{\hbar}\theta \hat{L}_z\right) \hat{\theta} \exp\left(-\frac{i}{\hbar}\theta \hat{L}_z\right)\end{aligned}$$

If θ is small we can expand.

$$\hat{\theta} = \left(1 + \frac{i}{\hbar}\theta \hat{L}_z + \dots\right) \hat{\theta} \left(1 - \frac{i}{\hbar}\theta \hat{L}_z + \dots\right).$$

$$= \hat{\theta} + \frac{i}{\hbar}\theta \left(\hat{L}_z \hat{\theta} - \hat{\theta} \hat{L}_z\right) + \mathcal{O}(\theta^2).$$

$$\nearrow \delta_{\theta} \hat{\theta} = \frac{i}{\hbar}\theta [\hat{L}_z, \hat{\theta}]$$

Change in
operator under
infinitesimal
parameter θ

\uparrow
Generators of a Symmetry acts on Operators
as anti-commutators.

SCALAR OPERATOR :

Definition: $[\vec{L}_i, \hat{F}] = 0, i=1,2,3$.

This immediately has implication for a system enjoying rotational symmetry.

The stationary states in a system with rotational symmetry (Discrete) has the form $|n, l, m\rangle$ (e.g. Hydrogen atom).

↑
Energy eigen value

What is the matrix elements of F in such a system

$$\langle n', l', m' | \hat{F} | n, l, m \rangle$$

Remember such matrix elements occur in perturbation theory.

Now, given F is a scalar i.e. $[\vec{L}, F] = 0$ we can make some generic conclusions about these matrix elements.

$$\text{eg: } \langle n', l', m' | [\hat{L}_z, \hat{F}] | n, l, m \rangle = 0$$

$$\Rightarrow (m' - m) \langle n', l', m' | \hat{F} | n, l, m \rangle = 0$$

i.e. the matrix elements must vanish unless $m' = m$.

$$\text{Also, } [\hat{L}_i, \hat{F}] = 0 \Rightarrow [L^2, F] = 0$$

$$\text{then, } \langle n', l', m' | [L^2, F] | n, l, m \rangle = 0$$

$$\Rightarrow [l(l'+1) - l(l+1)] \langle n', l', m' | F | n, l, m \rangle = 0$$

i.e. Matrix elements are zero unless $m' = m$ and $l' = l$.

Ex show that

$\langle n', l, m | \hat{F} | n', l, m \rangle$ is independent of m .

[Hint: use $[\hat{L}_+, \hat{F}] = 0$]

VECTOR OPERATORS.

Before, defining generic vector operators, let us write how the rotation acts on position operator $\hat{\vec{r}}$.

This will be known if we know $[\hat{L}_i, \hat{\vec{r}}_j]$.

Let us see how to compute it for one component, say $[\hat{L}_z, \hat{x}]$

We know, in position representation

$$\hat{L}_z = (-i\hbar) \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right)$$

So computing commutator in position representation:

$$\begin{aligned} & [\hat{L}_z, \hat{x}] \psi \\ &= (-i\hbar) \left[\left(x \frac{\partial}{\partial y} (\hat{x}\psi) - y \underbrace{\frac{\partial}{\partial x}(\hat{x}\psi)}_{y\psi + xy\frac{\partial\psi}{\partial x}} \right) - \left(\cancel{x^2 \frac{\partial\psi}{\partial y}} - \cancel{xy \frac{\partial\psi}{\partial x}} \right) \right] \\ &= (i\hbar) y \psi \end{aligned}$$

Hence in operator form we can write

$$[\hat{L}_z, \hat{x}] = i\hbar \hat{y}.$$

Like wise all the commutators can be computed!

The full result may be expressed as

$$[L_i^{\circ}, x_j^{\circ}] = i\hbar \epsilon_{ijk} x_k$$

C.g. \rightarrow 3 1 312 $x_2 = y$

$$\epsilon_{312} = 1$$

$\epsilon_{123} = 1$ Symmetric permutation = 1
 $\epsilon_{312} = -1$ Antisymmetric permutations = -1
 $\epsilon_{123} = 0$ Repeated index = 0
 i.e. $\epsilon_{123} = 1, \epsilon_{312} = 1, \epsilon_{231} = 1$
 $\epsilon_{132} = -1, \epsilon_{112} = 0$ etc.

Vector operator definition:

$$[L_i^{\circ}, V_j^{\circ}] = i\hbar \epsilon_{ijk} V_k \rightarrow ①$$

Any set of 3 operators on which angular momentum acts in the same way as position vector.

just like scalar operators, we can now set up rules for matrix elements of vector operators.

From ① we can derive

$$[L_z, V_z] = 0 \quad V_{\pm} = V_x + i V_y$$

$$[L_z, V_{\pm}] = \pm \hbar V_{\pm} \quad L_{\pm} = L_x + i L_y$$

$$[L_{\pm}, V_{\pm}] = 0$$

$$[L_{\pm}, V_z] = \mp \hbar V_{\pm}$$

$$[L_+, V_-] = +2\hbar V_z, [L_-, V_+] = -2\hbar V_z$$

$$\begin{aligned}
 \text{eg: } [L_+, V_-] &= [L_x + iL_y, V_x - iV_y] \\
 &= [L_x, V_x] \underset{0}{\cancel{+}} i[L_x, V_y] + i[L_y, V_x] \underset{0}{\cancel{+}} [L_y, V_y] \\
 &= (-i)(i\hbar) V_z + (i)(-i)\hbar V_z \\
 &= 2\hbar V_z
 \end{aligned}$$

Now, consider

$$\langle n'l'm' | [L_z, V_{\pm}] | nlm \rangle = \pm \hbar \langle n'l'm' | V_{\pm} | nlm \rangle$$

$$\Rightarrow [m' - (m \pm 1)] \langle n'l'm' | \hat{V}_{\pm} | nlm \rangle = 0.$$

$$\langle n'l'm' | [L_z, V_z] | nlm \rangle = 0$$

$$\Rightarrow (m' - m) \langle n'l'm' | V_z | nlm \rangle = 0.$$

$$\langle n'l'm' | V_+ | nlm \rangle = 0 \quad \text{unless } m' = m+1$$

$$\langle n'l'm' | V_- | nlm \rangle = 0 \quad \text{unless } m' = m-1$$

$$\langle n'l'm' | V_z | nlm \rangle = 0 \quad \text{unless } m' = m.$$

$$\langle n'l'm' | V_i | nlm \rangle = 0 \quad \text{unless } \Delta m = 0, \pm 1.$$

Most generally one can show that the matrix elements are related to Clebs-Gordan coefficients in the following way

$$\langle n' l' m' | V_+ | n l m \rangle = -\sqrt{2} C_{m_1 m'}^{l_1 l'} \langle \mathcal{G} \rangle$$

$$\langle n' l' m' | V_- | n l m \rangle = \sqrt{2} C_{m-1 m'}^{l_1 l'} \langle \mathcal{G} \rangle$$

$$\langle n' l' m' | V_z | n l m \rangle = C_{m_1 m'}^{l_1 l'} \langle \mathcal{G} \rangle$$

some common matrix element.

$$C_{m_1 m_2 M}^{j_1 j_2 J} = 0 \text{ unless } M = m_1 + m_2$$

$$\text{and } J = j_1 + j_2 \geq j_1 + j_2 - 1, \dots, |j_1 - j_2|.$$

Inspecting the coefficients appearing in the matrix elements one can conclude

$$\langle n' l' m' | \hat{V}_z | n l m \rangle = 0 \text{ unless}$$

and

$$\Delta l = 0, \pm 1$$

$$\Delta m = 0, \pm 1$$

gives selection

rules for electric dipole transitions in atomic physics.

ELECTRIC DIPOLE TRANSITIONS.

{ Dipole moment of electron $\vec{d} = -q\vec{r}$
 } Electric field in EM wave $E_0 \cos \omega t \hat{n}$ ↗ polarization vector.

$$\text{Energy in dipole} - \vec{d} \cdot \vec{E} = E_0 q \vec{r} \cdot \hat{n} \cos \omega t.$$

If polarization is in z-direction, perturbation Hamiltonian is

$$H_{(1)} = q E_0 z \cos \omega t.$$

Put it into formula

$$P_{i \rightarrow f} = \frac{E_0^2}{\hbar^2} |\langle \vec{d} \cdot \hat{n} \rangle|^2 \left[\frac{\sin^2[(\omega_{fi} - \omega)t/2]}{(\omega_{fi} - \omega)^2} \right].$$

Average Energy density over a full cycle

$$\mathcal{E} = \frac{\epsilon_0}{2} E_0^2$$

$$P_{i \rightarrow f} = \frac{2}{\epsilon_0 \hbar^2} \mathcal{E} |\langle \vec{d} \cdot \hat{n} \rangle|^2 \left[\frac{\sin^2[(\omega_{fi} - \omega)t/2]}{(\omega_{fi} - \omega)^2} \right]$$

In coherent radiation \rightarrow with a diffuse spread \rightarrow we need to integrate

$$P_{i \rightarrow f} = \frac{2}{\epsilon_0 \hbar} |\langle \vec{d} \cdot \hat{n} \rangle|^2 \int_{-\infty}^{\infty} g(\omega) d\omega \left[\frac{\sin^2[(\omega_{fi} - \omega)t/2]}{(\omega_{fi} - \omega)^2} \right]$$

large time

$$P_{if}(t) = \frac{2}{4\epsilon_0 \hbar} |\langle \vec{d} \cdot \hat{n} \rangle|^2 g(\omega_{fi}) (2\pi t)$$

Probability per unit time

$$P_{i \rightarrow f}(t) = \pi \frac{|\langle \vec{d} \cdot \hat{n} \rangle|^2}{\epsilon_0 \hbar} g(\omega_{fi})$$

There is a radiation bath from all direction so we need to take average

$$\begin{aligned} |\langle \vec{d} \cdot \hat{n} \rangle|_{\text{avg}}^2 &= \left| q \langle \varphi_f | \vec{r} | \varphi_i \rangle \cdot \hat{n} \right|_{\text{avg}}^2 \\ &= \frac{1}{4\pi} \int \left| q \langle \varphi_f | \vec{r} | \varphi_i \rangle \right|_{\text{avg}}^2 \cos^2 d\Omega \\ &= \left| q \langle \varphi_f | \vec{r} | \varphi_i \rangle \right|^2 \cdot \frac{1}{3}. \end{aligned}$$

↗ along z direction.

Means both kind of mod (complex & vector)

$$|\langle \varphi_f | \vec{r} | \varphi_i \rangle|^2 = |\langle \varphi_f | x | \varphi_i \rangle|^2 + |\langle \varphi_f | y | \varphi_i \rangle|^2 + |\langle \varphi_f | z | \varphi_i \rangle|^2.$$

Hence, under incoherent bath of radiation transition probability per unit time

$$P_{i \rightarrow f} = \frac{\pi}{3\epsilon_0 \hbar} |\langle \varphi_f | q \vec{r} | \varphi_i \rangle|^2 g(\omega_{fi}).$$

transition probability for stimulated Emission \rightarrow bath provides $H(t)$.

↑
Energy density
in frequency ω_{fi} .

✓ Stimulated Emission \rightarrow Presence of radiation bath

✓ Spontaneous Emission \rightarrow No bath (due to vacuum fluctuations of EM field).
 ↴ In this sense this
 Hard to calculate \rightarrow Was estimated by Einstein. is also "stimulated"

EINSTEINS ARGUMENT.

Say we have some transition rate (probability per unit time) R for one atom to go from state a to b . If we have N_b atoms in state b , then rate of change of N_b is $N_b R$. This should be true if N_b is large \rightarrow Probabilities are realized by repeating same experiment large no. of times.

For atomic transitions between states 'a' and 'b' there are 3 transition rates involved.

$$(\text{say } E_b > E_a) \left\{ \begin{array}{l} A \rightarrow \text{Spontaneous emission rate } b \rightarrow a \text{ Unknown so far.} \\ B_{ba} S(\omega_{ba}) \rightarrow \text{Stimulated emission rate } b \rightarrow a \\ B_{ab} S(\omega_{ab}) \rightarrow \text{Stimulated absorption rate } a \rightarrow b. \end{array} \right. \begin{array}{l} \text{Calculated above.} \\ (B_{ba} = B_{ab}). \end{array}$$

Consider N_b excited atoms, N_a unexcited atoms in a incoherent radiation bath at finite temperature in equilibrium.

For large N_a, N_b , using the equivalence of transition rate (probability) with the rate of change of these numbers we can write.

$$\frac{dN_b}{dt} = -N_b A - N_b B_{ba} S(\omega_{ba}) + N_a B_{ab} S(\omega_{ba})$$

Rate of change of no. of excited atoms.
 Spontaneous decay to N_b Stimulated decay to N_b .
 — $N_b \times$ decay rate to unexcited N_a

No. of N_a atoms getting excited to N_b by stimulated absorption.

$$\text{Equilibrium } \frac{dN_a}{dt} = 0.$$

$$\Rightarrow S(\omega_{ba}) = \frac{N_b A}{N_a B_{ab} - N_b B_{ba}} = \frac{A}{\left(\frac{N_a}{N_b} \right) B_{ab} - B_{ba}}$$

Distribution of Atoms in two states given by Boltzmann at temperature T

$$\frac{N_a}{N_b} = \frac{e^{-E_a/k_B T}}{e^{-E_b/k_B T}} = e^{\hbar\omega_{ba}/k_B T}.$$

$$\Rightarrow g(\omega_{ba}) = \frac{A}{e^{\hbar\omega_{ba}/k_B T} B_{ab} - B_{ba}} \rightarrow ①$$

The radiation bath in equilibrium with atoms at temperature T has a frequency distribution given by Planck distribution.

$$g_p(\omega) = \frac{\hbar}{\pi^2 c^3} \frac{\omega^3}{e^{\hbar\omega/k_B T} - 1} \rightarrow \text{We can take } g_p \text{ to be our } g(\omega_{ab}) = g_p(\omega_{ab}). \rightarrow ②$$

Comparing ① and ② implies:

$$B_{ab} = B_{ba}. \quad (\text{which follows from QM, as we have seen before})$$

$$A = \frac{\omega_{ab}^3 \hbar}{\pi^2 c^3} \quad B_{ba} = \frac{\omega_{ab}^3 \hbar}{\pi^2 c^3} \left[\frac{\pi}{3\epsilon_0 \hbar} |\langle \varphi_a | \vec{a}^\dagger | \varphi_b \rangle|^2 \right]$$

Value of A is quantum Electromagnetism (QED) result.

This is not easy to calculate with QED.

In some sense, the quantum nature of Electromagnetic fields was put in through the planck's formula.

SELECTION RULES FOR ELECTRIC DIPOLE TRANSITIONS.

Finally we see, the electric-dipole transition probability is proportional to

$$\langle \psi_f | \vec{r} | \psi_i \rangle$$

But we know for hydrogen atom energy levels

$$\langle n' l' m' | \vec{r} | n l m \rangle = 0 \text{ unless selection rules are obeyed}$$

Vector selection rules are $\Delta l = 0, \pm 1$, $\Delta m = 0, \pm 1$.

But here there is more: Parity $\hat{X} \rightarrow -\hat{X}$, $\hat{P} \rightarrow -\hat{P}$, $\hat{L} \rightarrow \hat{L}$
Vectors pseudo-Vectors.

The hydrogen atom eigenstates are also parity eigen states :

$$\Pi |n l m\rangle = (-1)^l |n l m\rangle$$

This implies under parity

$$\begin{aligned} \langle n' l' m' | \vec{r} | n l m \rangle &= - \langle n' l' m' | \Pi^+ \vec{r} \Pi | n l m \rangle \\ &\quad (\text{since } \Pi^+ \vec{r} \Pi = -\vec{r}) \\ &= (-1) \langle n' l' m' | (-1)^{l'} \vec{r} (-1)^l | n l m \rangle \\ &= (-1)^{l+l'+1} \langle n' l' m' | r | n l m \rangle \end{aligned}$$

Matrix element vanishes unless $l+l'$ is odd.

$\Rightarrow \Delta l = 0$ NOT ALLOWED.

Vector operator selection rules apply for \vec{r}

Thus to conclude, for hydrogen atom energy levels

$$\langle n_f \ l_f \ m_f \mid \vec{r} \mid n_i \ l_i \ m_i \rangle = 0$$

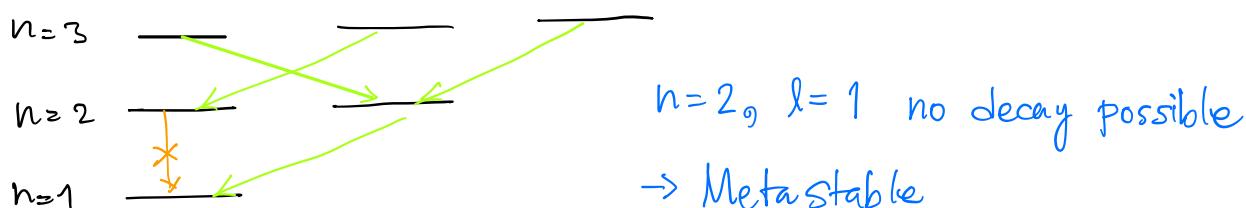
unless $\begin{cases} \Delta l = l_f - l_i = \pm 1 \\ \Delta m = m_f - m_i = 0, \pm 1. \end{cases}$

These are the selection rules for atomic transitions. ✓

$l=0$

$l=1$

$l=2$



Forbidden transitions do happen because of several factors

- (i) higher order effects.
- (ii) Finite size of atom sees spatial spread of EM wave.
- (iii) Collisions. etc.