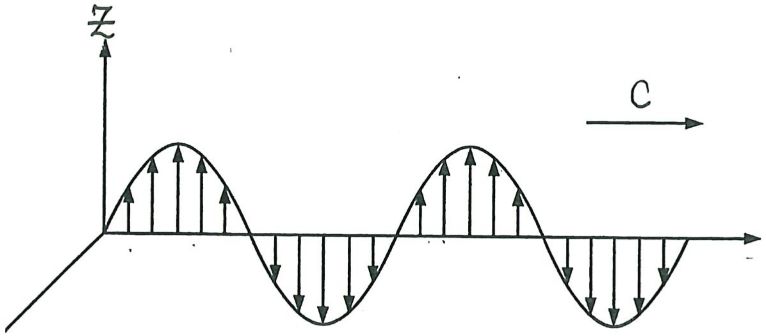
D. (Stimulated) Absorption and Emission: Time-Dependent Perturbation Theory

Physical Picture of the Problem



arrows show $\vec{\mathcal{E}}$ field in EM wave

$\lambda \sim$ hundreds of nm

[Picture here has $\underbrace{\vec{\mathcal{E}} \parallel \hat{z}}_{\text{linearly polarized}}$]

(could be circularly polarized)

($\hat{H}_{atom}$)

Atom

○

$\sim \mathring{A}$ ($\underbrace{0.1}$ nm)

Physics is governed by

$$\boxed{\hat{H} = \hat{H}_{atom} + \underbrace{\hat{H}'(t)}_{\text{light-atom interaction}} \quad (8)}$$

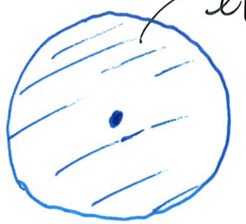
Initially, atom in ψ_i

> Q: Prob. of finding atom in ψ_f at time t after $\hat{H}'(t)$ is turned on?

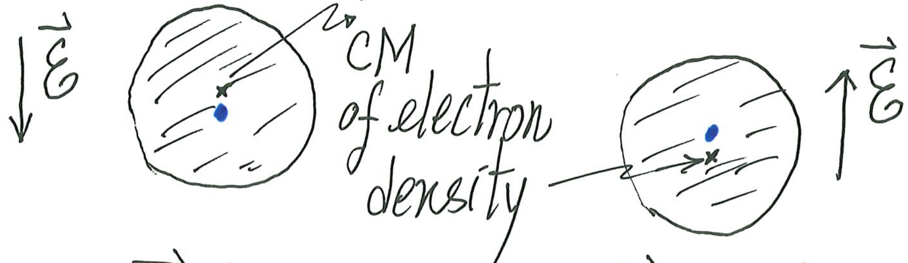
(a) What is the form of $\hat{H}'(t)$? Electric Dipole Mechanism

- Classical EM thinking

Oscillating $\vec{\mathcal{E}}$-field (in EM wave)



"Atom" (no $\vec{\mathcal{E}}$-field)



$\vec{\mu}$ ↓ ($-\hat{z}$ direction) $\qquad$ $\vec{\mu}$ ↑ ($\hat{z}$-direction)

electric dipole

time ⟶

oscillating electric dipole moment due to $\vec{\mathcal{E}}(t)$

- can radiate EM wave [emission]
- can carry characteristic frequency [absorption]

- Electric dipole effect is most important

  [ignore magnetic dipole effect and electric quadrupole effect, ...]

- For simplicity, consider one electron[+] (−e charge) at location $\vec{r}$

$$\vec{\mu} = -e\,\vec{r}$$ (electric dipole moment) (EM theory)

- $\hat{H}'$ is an energy (interaction energy)

$$\boxed{\vec{\mu} \text{ interacts with } \vec{\mathcal{E}}\text{-field in EM wave is the dominant mechanism}}$$

$$\hat{H}' = -\vec{\mu}\cdot\vec{\mathcal{E}} \qquad (9)$$ ["electric dipole" approximation]

[+] For many electrons, sum them up or invoke electron density

- $\vec{\mathcal{E}}$ in EM wave : $\vec{\mathcal{E}} = \mathrm{Re}[\vec{\mathcal{E}}_0 e^{i\vec{k}\cdot\vec{r}-i\omega t}]$ (propagating in $\vec{k}$)

$$= \vec{\mathcal{E}}_0 \cos(\vec{k}\cdot\vec{r}-\omega t)$$ (could have a phase)

[OR $\vec{\mathcal{E}} = \mathcal{E}_0 \hat{z} \cos(kx-\omega t)$ (in figure on LMI-I-20)]

$\mathcal{E}_0$: amplitude of field

- At the atom, i.e. $x \sim \underbrace{1\,\mathrm{nm}}_{a\,=\,\text{typical size of atom}}$ (about nucleus at origin)

$$ka = \frac{2\pi}{\lambda}\cdot a \sim \frac{a}{\lambda} \ll 1 \; (\approx 0)$$ [$|\vec{\mathcal{E}}|$ practically the same across atom]

$$\therefore \boxed{\vec{\mathcal{E}} = \vec{\mathcal{E}}_0 \cos\omega t} \quad (10)$$ (this is how time-dependence enters)

e.g. for linearly polarized light polarized in $\hat{z}$-direction

$$\vec{\mathcal{E}} = \mathcal{E}_0 \hat{z} \cos\omega t$$

It follows from Eq. (9) and Eq. (10) that

$$\boxed{\hat{H}' = -\vec{\mu}\cdot\vec{\mathcal{E}}_0 \cos\omega t} \quad (11) \qquad \text{OR} \qquad \boxed{\hat{H}' = e\,\vec{r}\cdot\vec{\mathcal{E}}_0 \cos\omega t} \quad (12)$$

(general form of electric dipole effect) (one electron at $\vec{r}$)

$\boxed{\hat{H}' \text{ is time-dependent}}$

e.g. $\vec{\mathcal{E}}_0 = \mathcal{E}_0 \hat{z}$, Eq. (12) becomes[+]

$$\boxed{\hat{H}' = \overbrace{e\mathcal{E}_0}^{\text{constant}}\ \overset{\text{position operator } \hat{z} = z}{z}\ \underbrace{\cos\omega t}_{\text{time-dependent perturbation}}} \quad (13)$$

[+] H' can be thought of $(-e)\cdot$(electric potential) $= (-e)\cdot\underbrace{(-\mathcal{E}_0 z \cos\omega t)}_{\text{"-gradient" gives } \vec{\mathcal{E}}}$

[+] For circularly polarized wave propagating in $\hat{z}$-direction, Eq. (12) will pick up x and y of the electron (as $\vec{\mathcal{E}}$ has x- and y-components)

[+] This way of handling EM wave is called "semi-classical".

The problem is now:

$$\boxed{\hat{H} = \hat{H}_{atom} + \hat{H}'(t) = \hat{H}_{atom} + \underbrace{ez\mathcal{E}_0\cos\omega t}_{\text{[starting from time 0 onward]}}} \quad (14)$$

with given $\underbrace{\text{initial condition}}_{\text{initially, atom is an eigenstate}}$

To solve the problem, we need to develop

<u>Time dependent perturbation theory</u>[+]

We write $\hat{H} = \hat{H}_0 + \hat{H}'(t)$ in developing the formulation.

[+] Of course, only to 1^{st} order in $\hat{H}'$

(b) Time-dependent Perturbation Theory

- Governing equation is TDSE $\hat{H}\Psi = i\hbar \frac{\partial \Psi}{\partial t}$ (3)
- Idea :

(i) If $\hat{H} = \hat{H}_0$ (time-dependent) and $\hat{H}_0 \psi_n = E_n \psi_n$,

then $\Psi(x,t) = \sum_n \underbrace{a_n} \psi_n e^{-iE_n t/\hbar}$ given $\Psi(x,0) = \sum_n \underbrace{a_n} \psi_n$

the same
(do not depend on time)

(ii) Now $\hat{H} = \hat{H}_0 + \hat{H}'(t)$ (our problem)

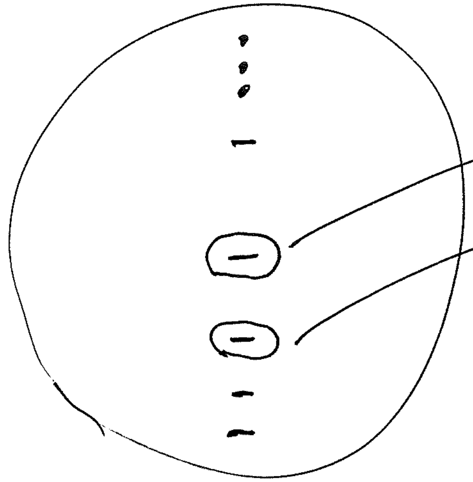
Key idea

$$\boxed{\Psi(x,t) = \sum_n \underbrace{a_n(t)}_{\substack{\text{time dependence} \\ \text{must come from } \hat{H}'(t)}} \psi_n \underbrace{e^{-iE_n t/\hbar}}_{\substack{\text{time evolution} \\ \text{due to } \hat{H}_0}}} \quad (15)$$

Problem is to solve for $a_n(t)$

- Want to get equations for $\frac{da_n(t)}{dt}$ and solve for $a_n(t)$
- Substitute Eq. (15) into Eq. (3) will do the job!

Two-state (two-level) System [make life simpler]



pick two states (any two)

"Atom"

state "2" —— ψ_2, E_2

state "1" —— ψ_1, E_1

$$\underbrace{\text{“Atom”}}_{\hat{H}_0 \text{ or } \hat{H}_{atom}}$$

Could be:

"1" —— ψ_1, E_1

"2" —— ψ_2, E_2

Initially ($t=0$), $\left.\begin{array}{l} a_1(0)=1 \\ a_2(0)=0 \end{array}\right\}$ definitely in state "1"

$\boxed{\text{What is } a_2(t) \text{ due to } \hat{H}'(t)?}$

Could also have picked

"3" —— ψ_3, E_3

"1" —— ψ_1, E_1

OR

"7" —— ψ_7, E_7

"1" —— ψ_1, E_1

...

∴ Handling two-level atom first gives result that can be applied to many-level!

- For two-level case, Eq. (15) reads

$$\Psi(\vec{r},t) = a_1(t) \underbrace{\psi_1(\vec{r}) e^{-\frac{iE_1 t}{\hbar}}} + a_2(t) \underbrace{\psi_2(\vec{r}) e^{-\frac{iE_2 t}{\hbar}}}$$

$$= a_1(t) \underbrace{\Psi_1(\vec{r},t)}_{\substack{\text{due to } \hat{H}_0 \\ \text{(known)}}} + \underbrace{a_2(t)}_{\text{want to get } a_2(t)} \underbrace{\Psi_2(\vec{r},t)}_{\substack{\text{due to } \hat{H}_0 \\ \text{(known)}}} \qquad (15')$$

$$\underbrace{(\hat{H}_0 + \hat{H}')\left[a_1(t)\Psi_1(\vec{r},t) + a_2(t)\Psi_2(\vec{r},t)\right]} = \underbrace{i\hbar\frac{\partial}{\partial t}\left[a_1(t)\Psi_1(\vec{r},t) + a_2(t)\Psi_2(\vec{r},t)\right]}$$

$$\cancel{a_1(t)\hat{H}_0\Psi_1(\vec{r},t)} + \cancel{a_2(t)\hat{H}_0\Psi_2(\vec{r},t)} + a_1(t)\hat{H}'\Psi_1(\vec{r},t) + a_2(t)\hat{H}'\Psi_2(\vec{r},t) = \cancel{a_1(t)\, i\hbar\frac{\partial\Psi_1}{\partial t}} + \cancel{a_2(t)\, i\hbar\frac{\partial\Psi_2}{\partial t}} + i\hbar\Psi_1(\vec{r},t)\frac{da_1(t)}{dt} + i\hbar\Psi_2(\vec{r},t)\frac{da_2(t)}{dt}$$

[Because Ψ_1 & Ψ_2 satisfy $\hat{H}_0\Psi_1 = i\hbar\frac{\partial\Psi_1}{\partial t}$ & $\hat{H}_0\Psi_2 = i\hbar\frac{\partial\Psi_2}{\partial t}$]

$\therefore$ TDSE gives

$$\boxed{a_1(t)\hat{H}'\Psi_1 + a_2(t)\hat{H}'\Psi_2 = i\hbar\Psi_1\frac{da_1(t)}{dt} + i\hbar\Psi_2\frac{da_2(t)}{dt}} \quad (16)$$

- Can obtain an equation for $\frac{da_2}{dt}$ (and $\frac{da_1(t)}{dt}$, if needed)
- Left multiply $\Psi_2^*(\vec{r},t)$ and $\int \cdots d^3r$ will give $\frac{da_2(t)}{dt}$

$$a_1(t)\, e^{\frac{i(E_2-E_1)t}{\hbar}} \int \psi_2^*(\vec{r})\,\hat{H}'\,\psi_1(\vec{r})\, d^3r + a_2(t)\int \psi_2^*(\vec{r})\,\hat{H}'\,\psi_2(\vec{r})\, d^3r$$

$$= \quad 0 \quad + \quad i\hbar \frac{da_2(t)}{dt} \qquad\qquad (Ex.)$$

$$\therefore \quad \boxed{i\hbar \frac{da_2(t)}{dt} = a_1(t)\, e^{\frac{i(E_2-E_1)t}{\hbar}} \int \psi_2^*(\vec{r})\,\hat{H}'\,\psi_1(\vec{r})\, d^3r + a_2(t)\int \underline{\psi_2^*(\vec{r})\,\hat{H}'\,\psi_2(\vec{r})\, d^3r}} \quad (17)$$

- $\hat{H}' = \hat{H}'(\vec{r},t)$ (see Eq. (12), Eq. (14))
- Can obtain a similar equation for $i\hbar \frac{da_1(t)}{dt}$ (even without work)
- Generalize readily to many-state case [more terms like the 1st term]
- In general, coupled eqs. for $a_1(t)$ & $a_2(t)$ [or more]

- Very humble task — Only want lowest order $a_2(t)$ due to $\hat{H}'$
  - Initial condition: $a_1(0) = 1$, $a_2(0) = 0$
  - Some time t later (with $\hat{H}'$): $a_1(t) \approx 1$, $a_2(t) \ll 1$ (≈ 0)

<u>Meaning</u>: Take Eq.(17) as

$$\boxed{i\hbar \frac{da_2(t)}{dt} = e^{\frac{i(E_2-E_1)t}{\hbar}} \int \psi_2^*(\vec{r})\, \hat{H}'\, \psi_1(\vec{r})\, d^3r} \qquad (18)$$

- Key equation (all results follow) [<u>used initial condition</u>]
- Eq.(18) works for any $\hat{H}'$ & it is 1st order in $\hat{H}'$
- State "2" is arbitrary, could either be $E_2 > E_1$ or $E_2 < E_1$
- Eq.(18) governs physics of transitions from state 1 to (arbitrary) state 2

"Analyzing" Eq. (18) : It makes good sense

$$i\hbar \frac{da_2(t)}{dt} = e^{\frac{i(E_2-E_1)t}{\hbar}} \int \psi_2^*(\vec{r}) \underbrace{\hat{H}' \psi_1(\vec{r})} d^3r \qquad (18)$$

$\hat{H}_0$ can't take system away from ψ_1, only $\hat{H}'$ can

$\therefore$ $\underbrace{\hat{H}'\psi_1(\vec{r})}$ = Some state that $\hat{H}'$ evolves the system away from ψ_1

some part in ψ_2, some part in ψ_3, etc. [if not two-level system]

Amplitude in ψ_2 = "Project $[\hat{H}'\psi_1(\vec{r})]$ on $\psi_2(\vec{r})$" (inner product)

$$= \int \psi_2^*(\vec{r})\, \hat{H}'\, \psi_1(\vec{r})\, d^3r$$

Prefactor $e^{i(E_2-E_1)t/\hbar}$ comes from evolution due to $\hat{H}_0$