Atomic Transitions, Emission and Absorption of Light

- Why are there absorption & emission of light when an atom (matter) meets an incident light†?
- Rules governing transitions between atomic (molecular) states in atoms (molecules)? [in solids as well]
  - frequency must be right (why?)
  - selection rules (why?)
- Why an excited atom de-excites and emits light† (apparently) by itself?

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† "Light" here covers EM radiation beyond visible range

Our discussion is based on $\underbrace{\text{Schrödinger QM}}_{\text{Time-dependent Schrödinger Equation}^{\dagger}}$ only

- but complete theory needs photons (quantizing EM fields, etc.)
- will see how far we can get based on TDSE

$\therefore$ only an introduction to the big topic on
"Light-Matter Interaction"

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† $i\hbar \dfrac{\partial \Psi}{\partial t} = \hat{H}\Psi$ (TDSE) governs time evolution of a system

A. Get to know the Phenomena

- Optical Properties of Atoms (Molecules, solids)

  Convenient and important way of studying physical systems

- Physics: To probe a system, must do something on it!

- Optical Properties / Spectroscopy: Incident light upon atom

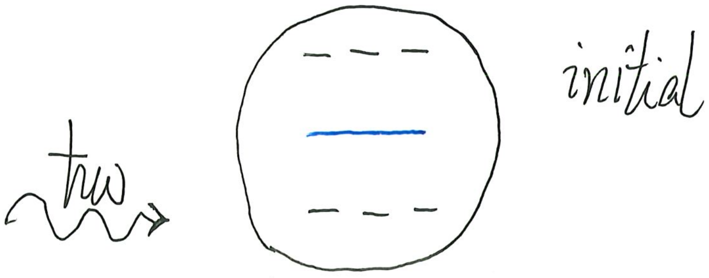
Atom at a lower energy state and a photon comes in

Atom at a higher energy state and no photon

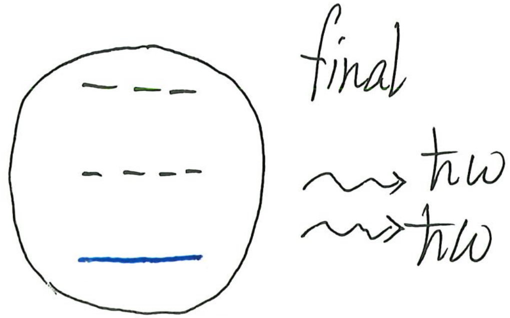
Absorption OR "Stimulated Absorption"

["final": at a later time]

Stimulated Emission



Atom at higher energy state and a photon comes in

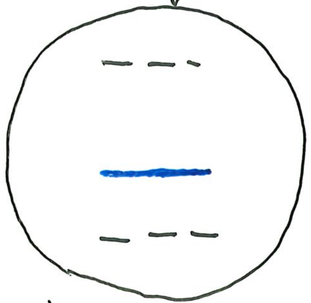


Atom at lower energy state and emits one more photon

[Why is it necessary to have stimulated emission process?]

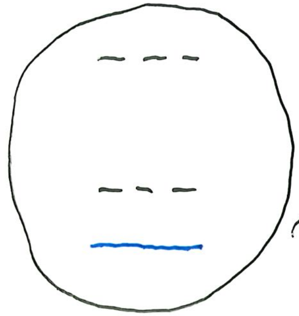
- Conditions for stimulated absorption/emission to occur?

- Something happens to an excited atom even we do "nothing" on it



"do nothing to it"
(leave alone)

Atom in an excited (higher) state "isolated" from everything



$\rightsquigarrow \hbar\omega$

Spontaneous Emission

Atom de-excited and emits a photon

- Spontaneous emission is essential for light-emitting devices (except laser)
- But spontaneous emission†, though looks natural, is the hardest to understand (needs the physics of vacuum, thus QED)

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† This is puzzling within Schrödinger QM because excited states are energy eigenstates and thus once there ($t=0$ in n^{th} state), the atom should stay in n^{th} state forever!

B. Any contradiction? Should $\hat{H}_{atom}$ eigenstates have infinite lifetime?

- Solved $\hat{H}_{H\text{-atom}}$ for $\mathcal{E}_n$ and $\psi_{n\ell m_\ell}(\vec{r}) = R_{n\ell}(r)\,Y_{\ell m_\ell}(\theta,\phi)$
- Solved $\hat{H}_{atom}$ using IPA + Pauli Principle for other atoms
- But (say, H-atom) for $\psi(\vec{r}, \underbrace{t=0}_{\text{time } 0}) = \psi_{n\ell m_\ell}(r,\theta,\phi)$ [an energy eigenstate],

we know that $\psi(\vec{r},t) = \psi_{n\ell m_\ell}(r,\theta,\phi)\, e^{\frac{-i\mathcal{E}_n t}{\hbar}}$ (1) [Why?]$^{+}$

$\therefore$ Prob. of finding atom in state $\psi_{n\ell m_\ell}(\vec{r})$ at later time $= \left|e^{-\frac{i\mathcal{E}_n t}{\hbar}}\right|^2 = 1$

[How could there be transitions? Any contradiction?]

$^{+}$ See QMI

- Calm down (冷静) Think like a physicist!

(1) is right <u>only</u> when $\hat{H}_{H\text{-atom}}$ is the Hamiltonian that governs the time evolution of ψ from $t=0$ to time t

- But with light incident upon an atom (even for a short duration)

$$\hat{H} \neq \hat{H}_{atom} \text{ only}$$

$$\hat{H} = \underbrace{\hat{H}_{atom}}_{\text{atom alone}} + \hat{H}'_{\substack{\text{interaction} \\ \text{(light-atom)}}} + \overbrace{\hat{H}_{photon}}^{\text{photon (light) alone}} \qquad (2)$$

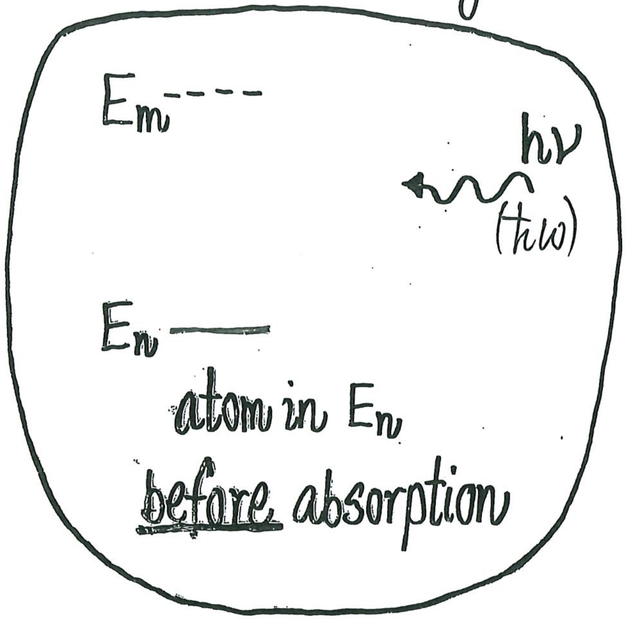
When we consider absorption/emission, we are <u>NOT</u> considering <u>isolated</u> atom.

Absorption:

Stimulated (受激) or induced Absorption

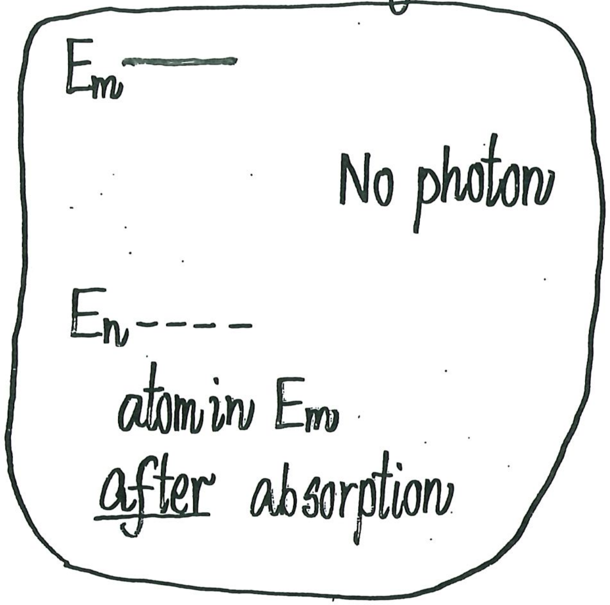
Conceptually

Atom Light



Whole system

Atom Light



Whole system

- We focused on $\hat{H}_{atom}\psi = E\psi$ before
- $\hat{H}'_{interaction}$ leads to transitions [Not $\hat{H}_{atom}$ only all the time!] Key idea
- QM is OK! No contradiction.

- "Atom in state n and one photon $h\nu$" is a description of a state of $(\hat{H}_{atom} + \hat{H}_{photon})$

key concept

- $\hat{H}'_{interaction}$ leads to transitions to

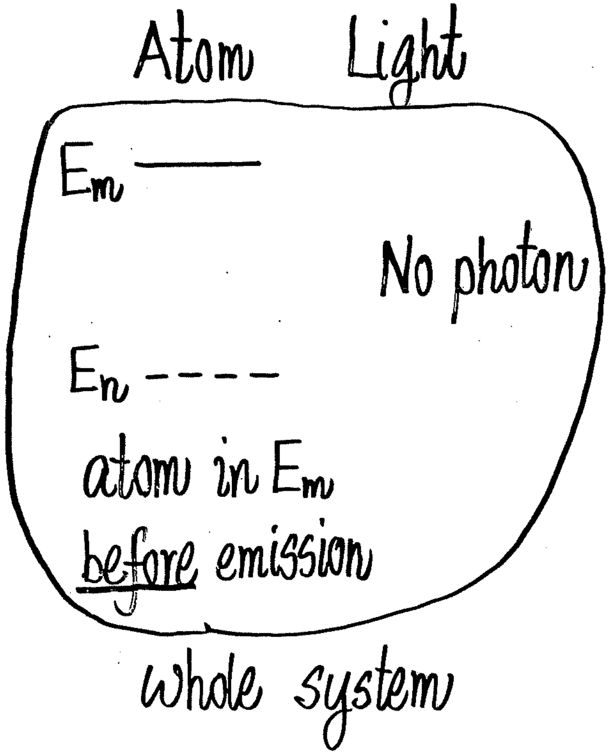
  "Atom in state m and no photon" (which is another state of $\hat{H}_{atom} + \hat{H}_{photon}$)

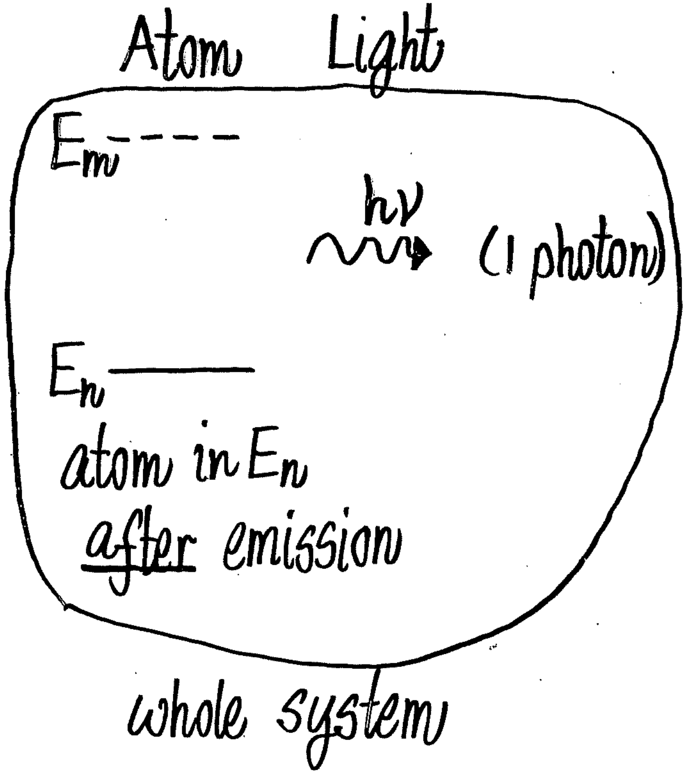
- Similar consideration for $\underbrace{\text{stimulated emission}}_{\text{not mysterious once we realize that } \hat{H}'_{interaction} \text{ is there}}$

How about spontaneous emission?

Is "No photon" really nothing?

No! In QM, "Vacuum" is Something!





- Photons come from quantizing EM fields
- Frequency ω, energy density $= \frac{1}{2}\varepsilon_0 E^2 + \frac{1}{2\mu_0} B^2$ $\left(\text{c.f. } \frac{p^2}{2m} + \frac{1}{2} k x^2 \right)$

$\Rightarrow$ allowed energy $= (n_\omega + \frac{1}{2})\hbar\omega$ [n_ω = # photons]

Ground state ("nothing") energy $= \frac{1}{2}\hbar\omega$ [something]

$\therefore$ It is the interaction between excited atom and vacuum via $\hat{H}'_{\text{interaction}}$ that leads to spontaneous emission.

[Needs QED for complete treatment]

This is the picture. [What we learned is OK!]

We will see how far we can go with Schrödinger QM (without quantizing the EM fields).

C. Initial Value Problem with time-dependent Hamiltonian

- Get the big picture first
- $t \leq 0$, Atom in some atomic eigenstate ψ_i referring to $\hat{H}_{atom}$ [this is the initial condition]
- $t > 0$, light comes in $\Rightarrow$ $\hat{H}'_{interaction}$ is ON

$$\hat{H}'_{interaction} \propto \vec{\mathcal{E}} \sim \vec{\mathcal{E}}_0 \cos\omega t$$

time-dependent

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

$t \leq 0 \quad \hat{H} = \hat{H}_{atom}$

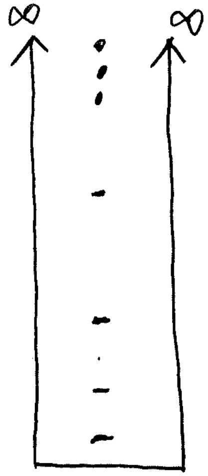
$t > 0 \quad \hat{H} = \hat{H}_{atom} + \hat{H}'_{interaction}$

thus $\hat{H}$ is time-dependent

Question: Probability of finding atom in another state ψ_f $(\neq \psi_i)$ at some time t?

Note: Question refers back to state (ψ_f) of $\hat{H}_{atom}$

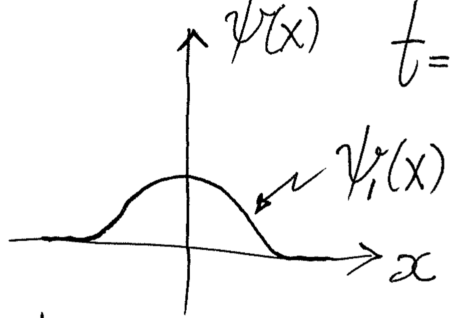
An analogy



1D Box as "Atom"

[Not bad! $\underbrace{\text{Discrete energies}}_{\text{as atomic states}}$]

Initial Condition (say, ground state)

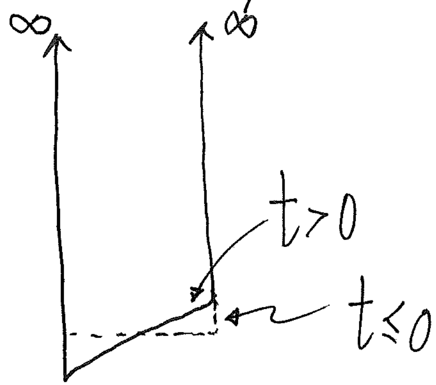


$t=0$

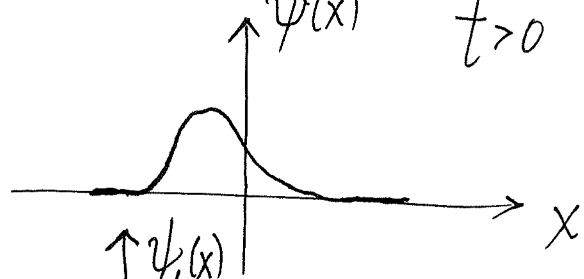
$$\psi(x, t=0) = 1 \cdot \psi_1(x)$$

1 ⇐ certain to be $\psi_1(x)$

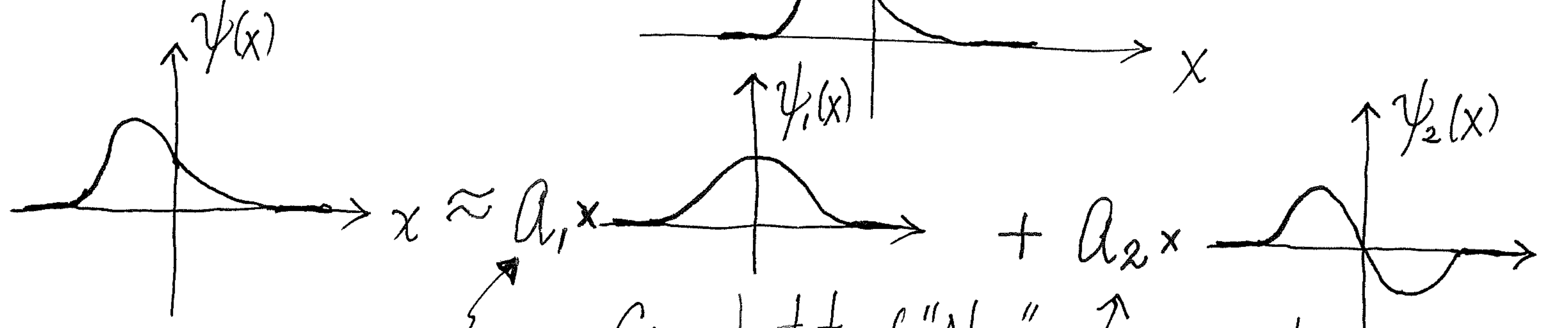
Simplest analogy: tilted floor at $t \geq 0$ [more realistic will be oscillating floor]



Particle adapts to tilted well after some time



But



Ground state of "Atom"

1st excited state of "Atom"

Not "1" any more

Not "0" any more

$\therefore$ Prob. of finding "Atom" in 1st excited state $= |a_2|^2 \neq 0$

Possible to have a transition!

Poorman's[+] Time-dependent Perturbation Theory

TDSE $$i\hbar \frac{\partial \Psi}{\partial \underline{t}} = \hat{H}\Psi \quad (3)$$ governs time evolution of Ψ

referring to $\hat{H}(\underline{t})$

[good for time-independent AND time-dependent $\hat{H}$]

- With $\Psi(x,0)$, what is $\Psi(x,\underline{\Delta t})$?

slightly later

$$\Psi(x,\Delta t) \approx \Psi(x,0) + \left.\frac{\partial \Psi}{\partial t}\right|_{t=0} \cdot \Delta t \qquad \text{(Taylor expansion)}$$

$$= \Psi(x,0) + \frac{1}{i\hbar}\left(\hat{H}\Psi\right)_{t=0} \cdot \Delta t \quad (4) \quad \text{(Using TDSE)}$$

$t=0$ meaning $\hat{H}(t=0)\Psi(x,0)$

[+] Quickly getting at the key result, despite not in complete form

Let's say $\begin{cases} \hat{H} = \hat{H}_{atom} \text{ for } t<0 \quad \underline{\text{AND}} \quad \Psi(x,0) = \underbrace{\psi_i(x)}_{\text{an eigenstate of } \hat{H}_{atom} \text{ with energy } \varepsilon_i} \\ \hat{H} = \hat{H}_{atom} + \underbrace{\hat{H}'}_{\text{interaction enters (switched on)}} \text{ for } \underline{t \geq 0} \end{cases}$

- From (4), $\Psi(x,\Delta t) \approx \psi_i(x) + \frac{1}{i\hbar}\left(\hat{H}_{atom} + \underbrace{\hat{H}'}_{}\right)\psi_i(x)\cdot\Delta t \quad (5)$

↑ takes part in evolving state (in addition to $\hat{H}_{atom}$)

<u>Probability of finding atom in state ψ_f?</u>

$$\text{Prob. amplitude} = \int_{-\infty}^{\infty}\psi_f^*(x)\,\Psi(x,\Delta t)\,dx$$

$$= \cancelto{0}{\int_{-\infty}^{\infty}\psi_f^*(x)\psi_i(x)\,dx} + \frac{1}{i\hbar}\varepsilon_i\cancelto{0}{\int_{-\infty}^{\infty}\psi_f^*(x)\psi_i(x)\,dx}\cdot\Delta t + \frac{\Delta t}{i\hbar}\int_{-\infty}^{\infty}\psi_f^*(x)\hat{H}'\psi_i(x)\,dx$$

$$= \Delta t\cdot\frac{1}{i\hbar}\int_{-\infty}^{\infty}\psi_f^*(x)\,\hat{H}'\,\psi_i(x)\,dx \qquad (6)$$

$$\boxed{\therefore \text{Probability} \propto \left| \underbrace{\int_{-\infty}^{\infty} \psi_f^*(x)\, \hat{H}'\, \psi_i(x)\, dx}_{\text{depends on an integral } I_{fi}} \right|^2 \qquad (7)}$$

Key Result!

- $I_{fi} = 0 \Rightarrow \text{Prob.} = 0 \Rightarrow$ forbidden transition
- $\underbrace{I_{fi} \neq 0 \Rightarrow \text{Prob.} \neq 0}$ $\Rightarrow$ Allowed transition

Gives Selection rules

Bigger $|I_{fi}|^2 \Rightarrow$ Transition occurs readily [brighter line in spectrum]

Smaller $|I_{fi}|^2 \Rightarrow$ Transition occurs but less readily [dimmer line]

This is the key physical picture!

<u>Aside</u>: Eq. (4): $\Psi(x,\Delta t) \approx \Psi(x,0) + \frac{1}{i\hbar}(\hat{H}\Psi)_{t=0}\cdot\Delta t$

- It gives known results for <u>time-independent $\hat{H}$</u>
- If $\Psi(x,0) = \sum_n a_n \psi_n$ where $\hat{H}\psi_n = \varepsilon_n \psi_n$

$$\Psi(x,\Delta t) \underset{\text{(See QMI)}}{=} \sum_n a_n \psi_n e^{-i\frac{\varepsilon_n \Delta t}{\hbar}} \approx \sum_n a_n \left(1 - \frac{i}{\hbar}\varepsilon_n \Delta t\right)\psi_n$$

$$= \Psi(x,0) - \frac{i}{\hbar}\sum_n a_n \varepsilon_n \psi_n \cdot \Delta t$$

- From Eq. (4), $\Psi(x,\Delta t) \cong \Psi(x,0) - \frac{i}{\hbar}\hat{H}\left(\sum_n a_n \psi_n\right)\cdot\Delta t$

$$= \Psi(x,0) - \frac{i}{\hbar}\sum_n a_n \varepsilon_n \psi_n \cdot \Delta t$$

Same result

In transition problems, what's new is $\hat{H}(t)$ [<u>time-dependent</u>]

Key Physical Sense

$$\hat{H}_{atom}: \quad \begin{matrix} \psi_1 & \cdots & \psi_i & \cdots & \psi_f & \cdots \\ \updownarrow & & \updownarrow & & \updownarrow & \\ E_1 & & E_i & & E_f & \end{matrix}$$

Light comes in: $\hat{H} = \hat{H}_{atom} + \hat{H}'$ ← atom-light interaction

- $\hat{H}_{atom}$ can't take ψ_i to ψ_f ($\because$ ψ_i is an eigenstate of $\hat{H}_{atom}$)

$$\int \psi_f^* \underbrace{\hat{H}_{atom}\psi_i}_{E_i\psi_i} d\tau \sim \int \psi_f^* \psi_i \, d\tau = 0 \quad (i \neq f)$$

- Only $\hat{H}'$ can "take ψ_i to ψ_f"
- thus integral $\underbrace{\int \psi_f^* \hat{H}' \psi_i \, d\tau}$ enters
  - conditions for $I_{fi} \neq 0 \Rightarrow$ Selection rules!
  - I_{fi} "How well can $\hat{H}'$ take system from ψ_i to ψ_f?"