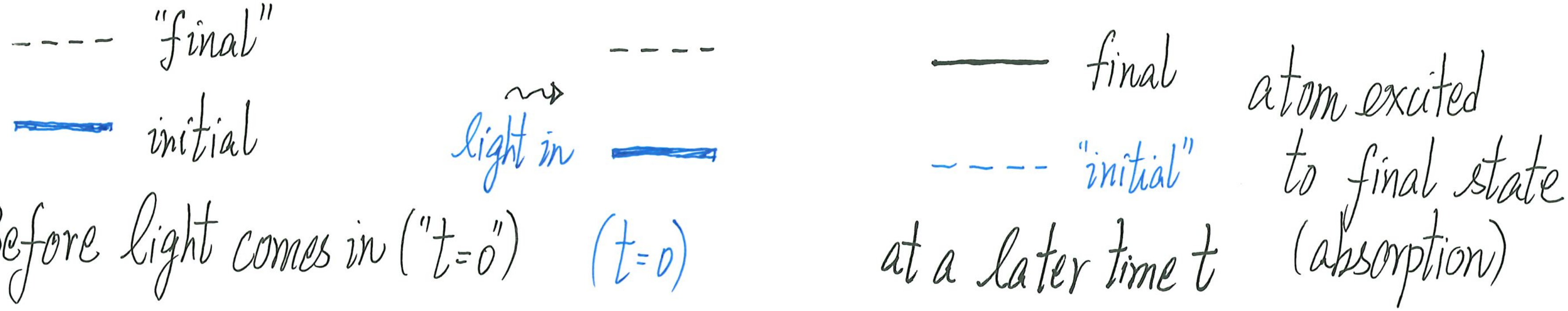
Emission and Absorption of Light

- A brief introduction to the big-topic of "Light-Matter Interaction"
- Concepts applicable to atomic transitions, and molecules & solids



Criteria?

- Selection rules?
- light's $\hbar\omega$ matches energy difference
- rate of transition?

Governing Equation $\hat{H}\Psi = i\hbar\frac{\partial\Psi}{\partial t}$

A. Get to know the Phenomena

- $\underbrace{\text{Optical Properties}}$ of Atoms (Molecules, solids)

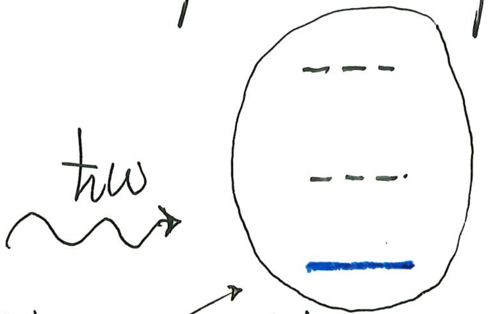
  Convenient and important way of studying physical systems

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

- Optical Properties / Spectroscopy: Incident light upon atom

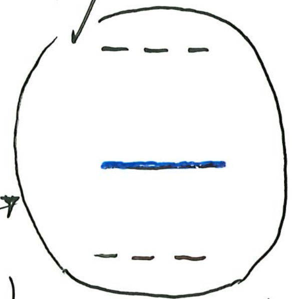
$\hbar\omega$

[stimulation]



initial

Atom at a lower energy state and a photon comes in

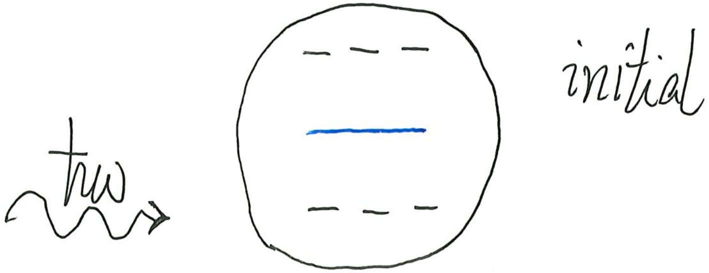


final

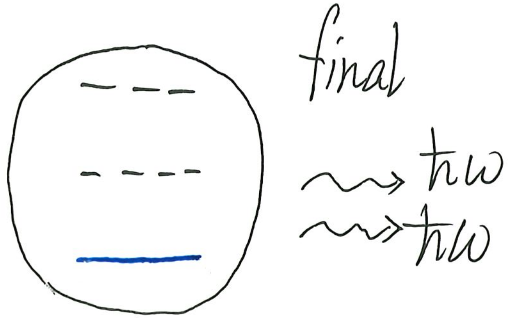
Atom at a higher energy state and no photon

Absorption OR "Stimulated Absorption"

["final": at a later time]



Atom at higher energy state and a photon comes in



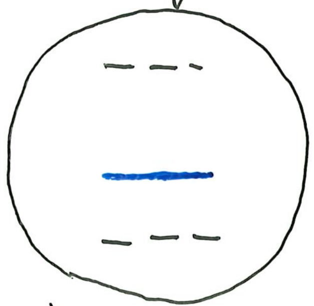
Atom at lower energy state and emits one more photon

Stimulated Emission

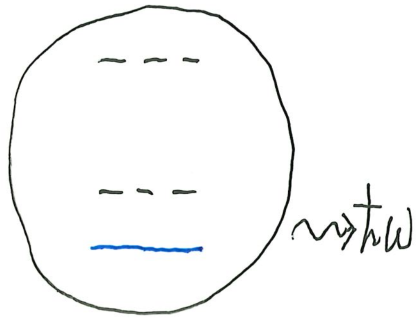
[Why is it necessary to have stimulated emission process?]

- Conditions for stimulated absorption/emission to occur?

- Something happens to an excited atom even we <u>do "nothing" on it</u>



"do nothing to it"
(leave alone)



$\boxed{\text{Spontaneous Emission}}$

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

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. Transitions are due to Light-Atom Interaction

$\hat{H}_{atom}$ alone, $t=0$ $\Psi(\vec{r}, t=0) = \psi_{n\ell m_\ell}(r,\theta,\phi)$ of energy $E_{n\ell}$

later time t $\Psi(\vec{r},t) = \psi_{n\ell m_\ell}(\vec{r}) \underbrace{e^{-iE_{n\ell}t/\hbar}}_{|\text{coefficient}|^2 = 1}$

$\therefore$ Atom remains in state $\psi_{n\ell m_\ell}(\vec{r})$ at time t (any t, forever)

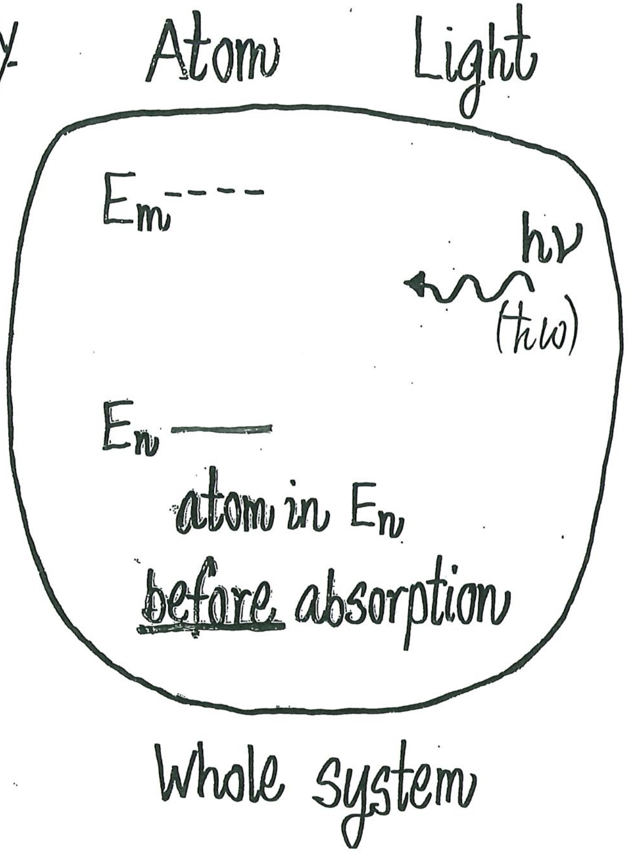
- Light incident upon atom: $\hat{H} \neq \hat{H}_{atom}$ only

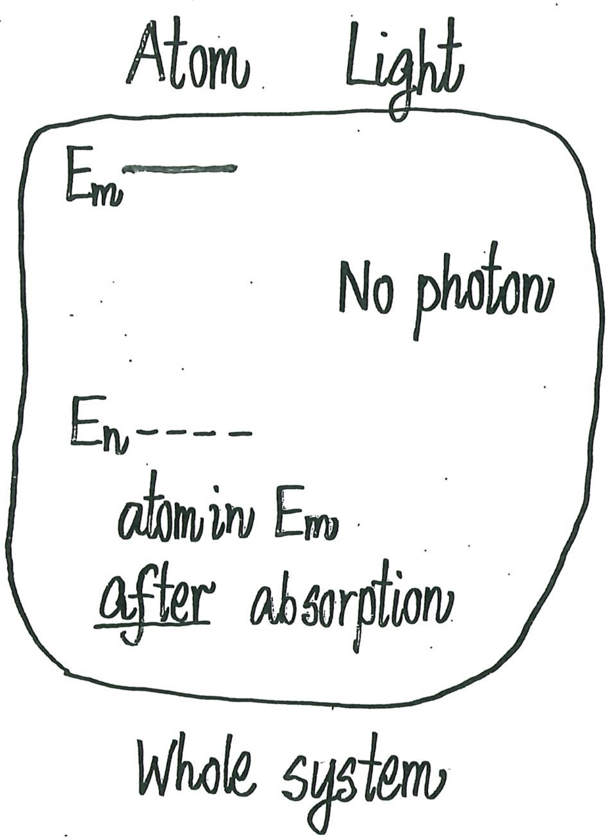
Formally, $\hat{H} = \underbrace{\hat{H}_{atom}}_{\text{isolated atom}} + \underbrace{\hat{H}'_{interaction}}_{\substack{\text{(light-atom)} \\ \text{leads to transitions between atomic states}}} + \hat{H}_{photon}$ (1)

Absorption:

Stimulated (受激) or induced Absorption

Conceptually





- 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.

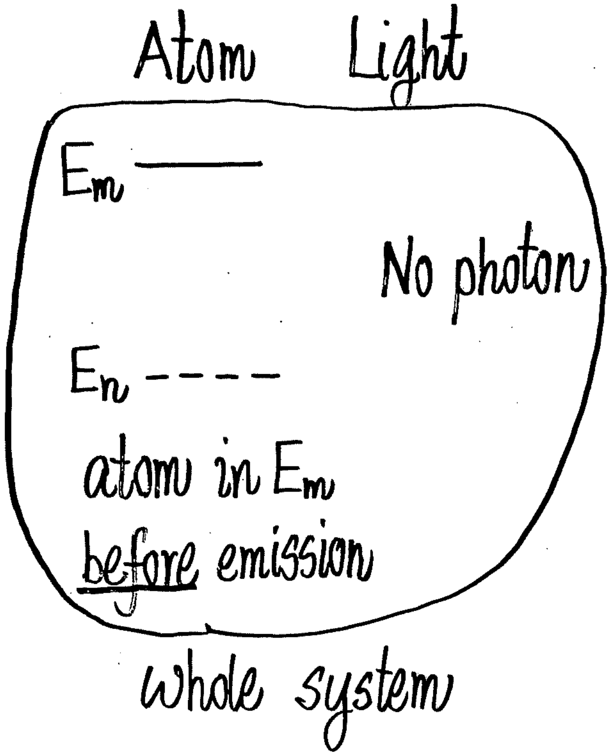
- "Atom in state n and one photon $h\nu$" is a description of a state of $(\hat{H}_{atom} + \hat{H}_{photon})$
- $\hat{H}'_{interaction}$ leads to transitions to "Atom in state m and no photon" (which is another state of $\hat{H}_{atom} + \hat{H}_{photon}$)

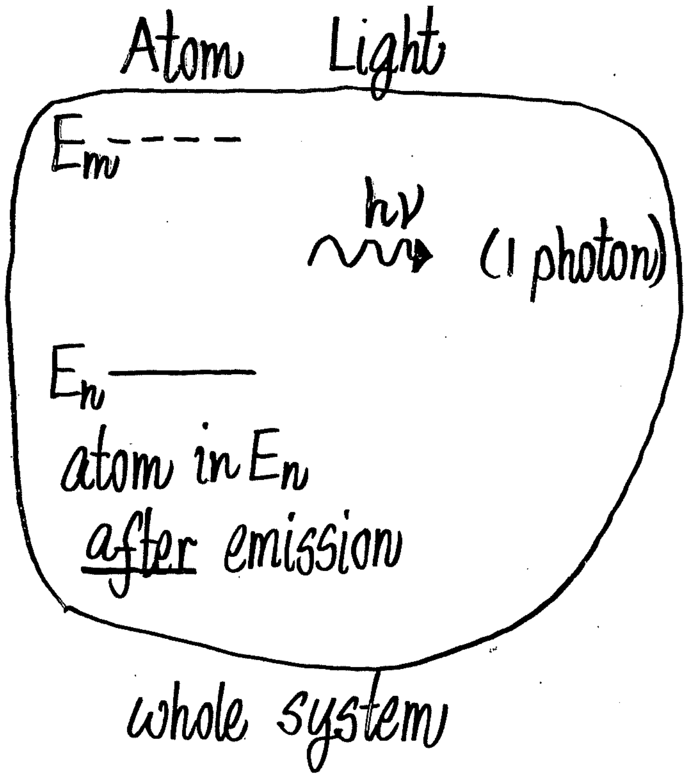
  key concept
- Similar consideration for $\underbrace{\text{stimulated emission}}_{\text{not mysterious once we realize that } \hat{H}'_{interaction} \text{ is there}}$

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 <u>excited atom</u> and <u>vacuum</u> via $\hat{H}'_{interaction}$ 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

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

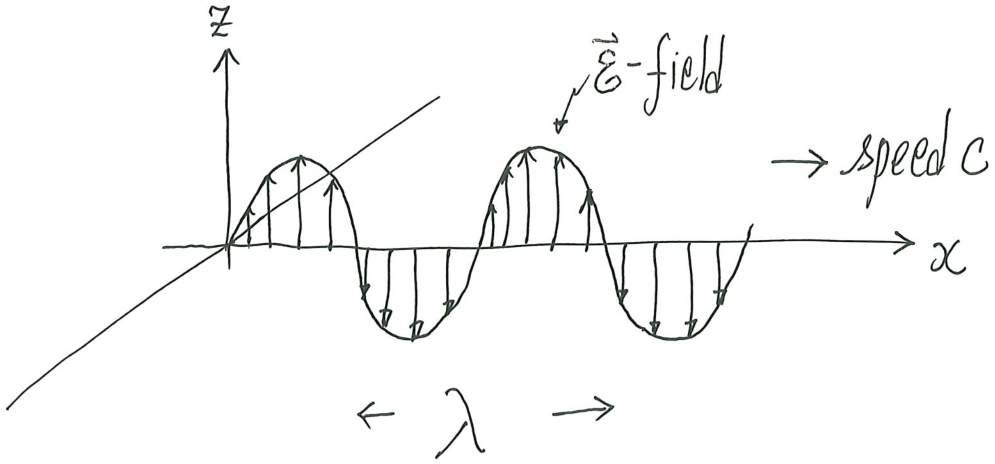
$$\hat{H}'_{interaction} \propto \vec{\mathcal{E}} \sim \vec{\mathcal{E}}_0 \cos\omega t$$

time-dependent

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

$$\left.\begin{aligned} t \leq 0 \quad & \hat{H} = \hat{H}_{atom} \\ t > 0 \quad & \hat{H} = \hat{H}_{atom} + \hat{H}'_{interaction} \end{aligned}\right\} \text{thus } \hat{H} \text{ is time-dependent}$$

$\hat{H}'_{\text{interaction}}$ (simply $\hat{H}'$) due to "Electric Dipole Mechanism"



hundreds of nm

This example has $\underbrace{\vec{\mathcal{E}} \parallel \hat{z}}_{\text{linearly polarized}}$

(could be circularly polarized)

$\hat{H}_{atom}$

Atom

→ ← $\sim$ Å

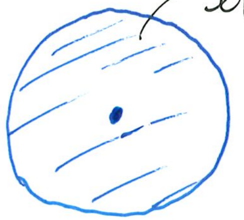
(0.1 nm)

Note: $\lambda \gg$ size of atom

What is $\hat{H}'$?

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

- Classical EM thinking



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

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

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

electric dipole

time →

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

- can radiate EM wave [emission]
- 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 $\vec{r}$

$$\vec{\mu} = -e\,\vec{r} \quad \text{(electric dipole moment) (EM theory)} \qquad (2)$$

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

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

$$\hat{H}' = -\vec{\mu}\cdot\vec{\mathcal{E}} \qquad (3) \quad \text{["electric dipole" approximation]}$$

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

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

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

$$\left[\text{OR } \vec{\mathcal{E}} = \mathcal{E}_0 \hat{z} \cos(kx - \omega t)\right]$$ (see figure)

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

- At the atom, i.e. $x \sim \underbrace{1\,nm}_{a\,=\,\text{typical size of atom}}$ (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]

$$\therefore \boxed{\vec{\mathcal{E}} = \vec{\mathcal{E}}_0 \cos\omega t} \quad (4)$$ (this is how time-dependence enters)

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

$$\boxed{\vec{\mathcal{E}} = \mathcal{E}_0 \hat{z} \cos\omega t} \quad (5)$$

It follows from Eq. (3) and Eq. (4) that

$$\boxed{\hat{H}' = -\vec{\mu}\cdot\vec{\mathcal{E}}_0 \cos\omega t} \quad (6) \qquad \text{OR} \qquad \boxed{\hat{H}' = e\,\vec{r}\cdot\vec{\mathcal{E}}_0 \cos\omega t} \quad (7)$$

(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. (7) becomes[+]

$$\boxed{\hat{H}' = \overbrace{e\,\mathcal{E}_0}^{\text{constant}}\; z\; \underbrace{\cos\omega t}_{\text{time-dependent perturbation}}} \quad (8)$$

position operator of electron

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

[+] 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:

$$\boxed{\hat{H} = \hat{H}_{atom} + \hat{H}'(t) = \hat{H}_{atom} + \overbrace{\underbrace{ez}_{\text{atom (matter)}}\ \underbrace{\mathcal{E}_0 \cos\omega t}_{\mathcal{E}\text{-field (light)}}}^{\text{switching on from time } 0}} \quad (9)$$

atom (matter) $\mathcal{E}$-field (light): time-dependent perturbation $\hat{H}'(t)$

> For a given initial condition, e.g. atom in $\psi_{initial}$ (ψ_i), what is the probability of finding the atom in some final state ψ_{final} (ψ_f) after $\hat{H}'(t)$ is turned on for a time t?

> $\hat{H}'(t)$ is responsible for taking (evolving) the system from ψ_i to have a chance to be in ψ_f

we want to get a sense of how this happens

We tend to focus on the Atom in transition problems

$t \leq 0$ $\qquad$ $t > 0$ $\underbrace{\left[\hat{H}_{atom} + \hat{H}'(t)\right]}_{\text{full Hamiltonian}}$

ψ_i

$\hat{H} = \hat{H}_{atom}$

$\hat{H}_{atom} \psi_i = E_i \psi_i$

E_i ← energy of initial state

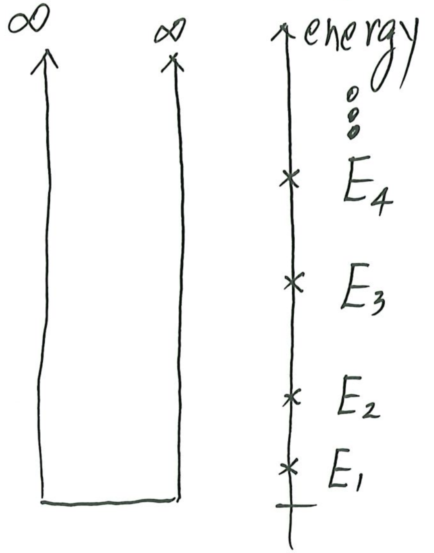
but we ask (refer to $\hat{H}_{atom}$ eigenstates) if atom has made a transition to ψ_f (where is an eigenstate of $\hat{H}_{atom}$)

ψ_f ?

ψ_f ← refers to $\hat{H}_{atom}$ (thus atom)

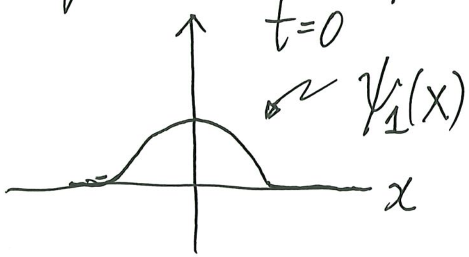
An analogy of the physics and what happens

"Atom" (1D infinite well)

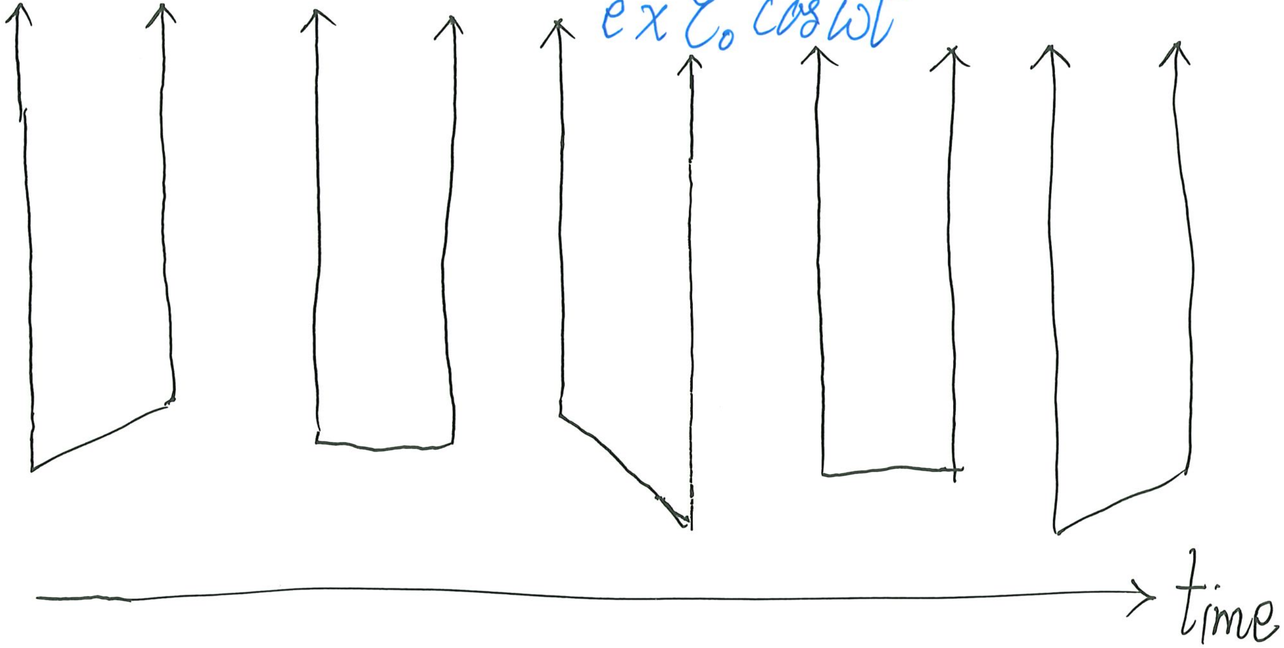


initial condition

e.g. ground state ψ_1

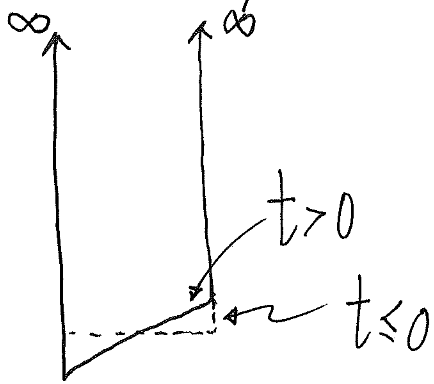


"Atom" + $\underbrace{\hat{H}'(t)}_{e\,x\,\mathcal{E}_0 \cos\omega t}$

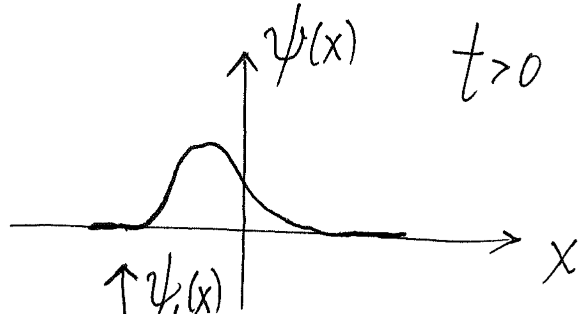


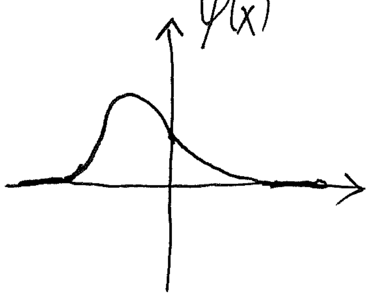
But we ask if the "Atom" (1D flat-bottom well) has a chance to be excited to an excited state (say) ψ_2?

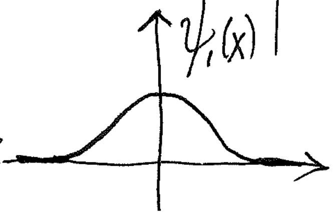
Simplest analogy: tilted floor

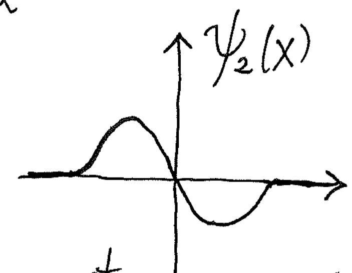


Particle adapts to tilted well



But 

$\approx a_1 \times$ 

$+ \, a_2 \times$ 

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 <u>a transition</u>!