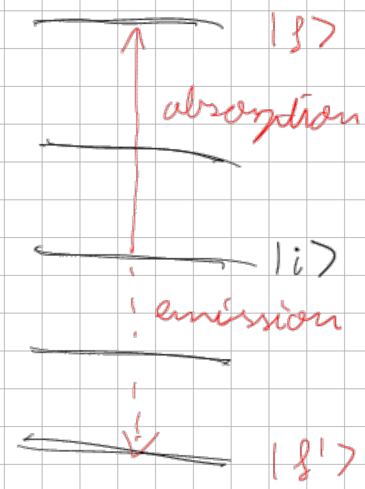
Time-Dependent Perturbation Theory

Motivation:



- deal with time dependences in the standard approach
- application: electric field, periodically modulated
  → hydrogen atom
- electric field is classically treated:
  absorption ⟷ emission (with equal probabilities)
- 2 of 3 elementary processes of interaction of light and matter
  (spontaneous emission is excluded: only occurs when electric field is treated quantum mechanically → quantum optics)

General Theory:

$$i\hbar \frac{\partial}{\partial t}|\Psi(t)\rangle = \hat{H}\underbrace{(t)}_{\text{explicit time dependence}}|\Psi(t)\rangle \quad (1) \Rightarrow |\Psi_n(t)\rangle \neq e^{-\frac{i}{\hbar}E_n t}|\Psi_n\rangle$$

Note: How can time-independent perturbation theory be considered as a special case of time-dependent " " ?

$$\hat{H}(t) = \underbrace{\hat{H}^{(0)}}_{\text{time-independent}} + \underbrace{\hat{V}(t)}_{\text{time-dependent}} \quad ; \quad \hat{H}^{(0)}|\Psi_n^{(0)}\rangle = E_n^{(0)}|\Psi_n^{(0)}\rangle$$

unperturbed $\qquad$ perturbation

basis of states:

$$|\Psi(t)\rangle = \sum_n c_n(t) \underbrace{|\psi_n^{(0)}\rangle e^{-\frac{i}{\hbar}E_n^{(0)} t}}_{= |\psi_n^{(0)}(t)\rangle} \qquad (2)$$

stationary state

$$\langle \psi_n^{(0)}(t) | \psi_n^{(0)}(t)\rangle = \langle \psi_n^{(0)} | \psi_n^{(0)}\rangle = 1$$

probability amplitude to find the state $|\psi_n^{(0)}\rangle$ in $|\Psi(t)\rangle$ at time t

$$\Rightarrow \quad \sum_n |c_n(t)|^2 = 1$$ due to normalization of $|\Psi(t)\rangle$

(2) in (1):

$$i\hbar \frac{\partial}{\partial t}|\Psi(t)\rangle = i\hbar \sum_n \left\{ \dot{c}_n(t) \cancel{- \frac{i}{\hbar} E_n^{(0)} c_n(t)} \right\} e^{-\frac{i}{\hbar}E_n^{(0)} t} |\psi_n^{(0)}\rangle$$

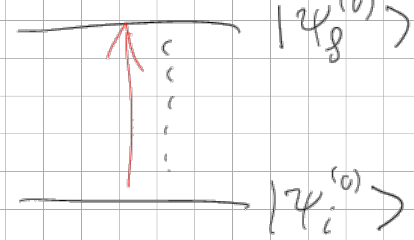
$$= \cancel{\sum_n E_n^{(0)} c_n(t) e^{-\frac{i}{\hbar}E_n^{(0)} t} |\psi_n^{(0)}\rangle} + \sum_n c_n(t) e^{-\frac{i}{\hbar}E_n^{(0)} t} \hat{V}(t) |\psi_n^{(0)}\rangle$$

project onto $\langle \psi_m^{(0)}|$: $\quad \langle \psi_m^{(0)} | e^{\frac{i}{\hbar}E_m^{(0)} t}$

$$i\hbar \dot{c}_m(t) = \sum_n e^{\frac{i}{\hbar}(E_n^{(0)} - E_m^{(0)})t} \underbrace{\langle \psi_n^{(0)} | \hat{V}(t) | \psi_m^{(0)} \rangle}_{= V_{nm}(t)} c_n(t)$$

$c_f(t)$

$c_i(t)$



initial condition: $c_i(t_0) = 1$

$c_n(t_0) = 0, \quad n \neq i$

probability for a transition from i to $f \neq i$

$$P_{i\to f}(t) = |c_f(t)|^2$$

Task: Solve this infinitely large coupled system of first order ordinary differential equations ⇒ usually no analytic solution

⇒ But perturbatively this is possible

Iterative solution:

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

$$\frac{\partial c_n^{(0)}(t)}{\partial t} = 0 \Rightarrow c_n^{(0)}(t) = \text{const} = c_n^{(0)}(t_0) = \delta_{ni}$$

$$\frac{\partial c_n^{(1)}(t)}{\partial t} = -\frac{i}{\hbar} \sum_m e^{i \underbrace{\frac{E_n^{(0)} - E_m^{(0)}}{\hbar}}_{= \omega_{nm}^{(0)}} t} V_{nm}(t) \underbrace{c_m^{(0)}(t)}_{\delta_{mi}}$$

$$= -\frac{i}{\hbar} e^{i \omega_{ni}^{(0)} t} V_{ni}(t)$$

$$c_n^{(1)}(t) = \underbrace{c_n^{(1)}(t_0)}_{\equiv 0} - \frac{i}{\hbar} \int_{t_0}^{t} dt'' e^{i \omega_{ni}^{(0)} t'} V_{ni}(t')$$

$$\frac{\partial c_n^{(2)}(t)}{\partial t} = -\frac{i}{\hbar} \sum_m e^{i \omega_{nm}^{(0)} t} V_{nm}(t) c_m^{(1)}(t)$$

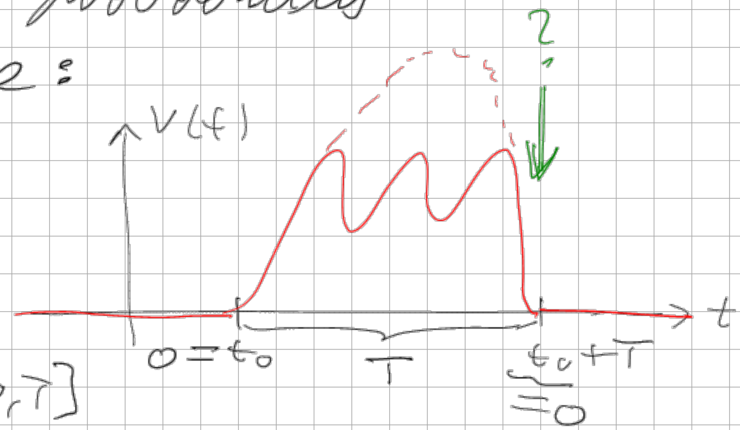
$$c_n^{(2)}(t) = \underbrace{c_n^{(2)}(t_0)}_{= 0} - \frac{i}{\hbar} \int_{t_0}^{t} dt' \sum_m e^{i \omega_{nm}^{(0)} t'} V_{nm}(t') c_m^{(1)}(t')$$

$$= \left(-\frac{i}{\hbar}\right)^2 \int_{t_0}^{t} dt' \int_{t_0}^{t'} dt'' \sum_m e^{i \omega_{nm}^{(0)} t'} V_{nm}(t') e^{i \omega_{mi}^{(0)} t''} V_{mi}(t'')$$

$\vdots$

$$P_{i\to f}(t) = \Big|\underbrace{c_f^{(0)}(t)}_{f\neq i\;\; =0} + c_f^{(1)}(t) + c_f^{(2)}(t) + \dots\Big|^2 = \underbrace{\big|c_f^{(1)}(t)\big|^2}_{\text{lowest order for transition probability}} + \dots$$

differents ways how $\hat V(t)$ may depend on time:



a) $\hat V(t) \neq 0$ only in interval $t_0 \le t \le t_0 + T$

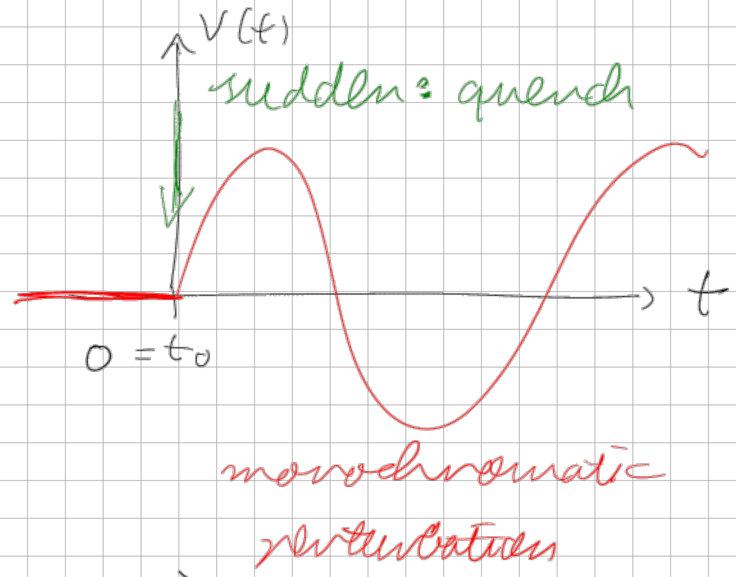
$$P_{i\to f}(T) = \frac{1}{\hbar^2}\Big|\int_0^T dt\, e^{i\omega_{fi}^{(0)} t}\, V_{fi}(t) + \dots\Big|^2$$

Note: $V_{ni}(t) \xrightarrow[\text{transformation}]{\text{Fourier}}$ $\qquad V_{ni}(t) = 0$ outside $[0,T]$

$$V_{ni}(\omega) = \int_{-\infty}^{+\infty} dt\, e^{i\omega t}\, V_{ni}(t) \overset{\downarrow}{=} \int_0^T dt\, e^{i\omega t}\, V_{ni}(t)$$

$$\Rightarrow P_{i\to f}(T) = \frac{1}{\hbar^2}\big|V_{fi}(\omega_{fi}^{(0)})\big|^2$$

Quench of monochromatic perturbation:



$\hat V(t) = \hat A\, e^{-i\omega t} + \hat A^{\dagger} e^{i\omega t}$; $\hat A$ some operator

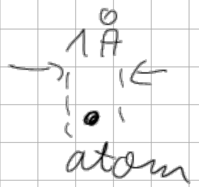
example: hydrogen atom in presence of electromagnetic wave

$\hat V(t) = -\vec d \cdot \vec E(\cancel{\vec x}, t)$, $\quad \vec d = -\underbrace{e}_{>0}\vec x$,

$= \frac{\vec E_0}{2}\, e^{i(\cancel{\vec k \vec x} - \omega t)} + c.c.$, $\quad$ transversality: $\vec E_0 \perp \vec k$

comparison $\hat{A} = -\frac{1}{2}\vec{E}_0 \cdot \vec{d}\; \underbrace{e^{i\vec{k}\vec{x}}}_{\approx 1}$

optical range $\lambda \hat{=} (200-400)\,nm$



odd in $\vec{x}$

$V_{nn}(t) = 0$ due to $V_{nn} = \langle \psi_n^{(0)} | \hat{V} | \psi_n^{(0)} \rangle = 0$

even in $\vec{x}$

$$c_i^{(1)}(t) = -\frac{i}{\hbar}\int_0^t dt'\, V_{ii}(t') \equiv 0$$

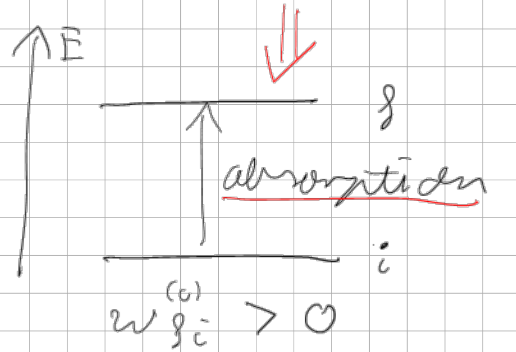
$$c_f^{(1)}(t) = -\frac{i}{\hbar}\int_0^t dt'\, e^{i\omega_{fi}^{(0)}t'}\, V_{fi}(t')$$

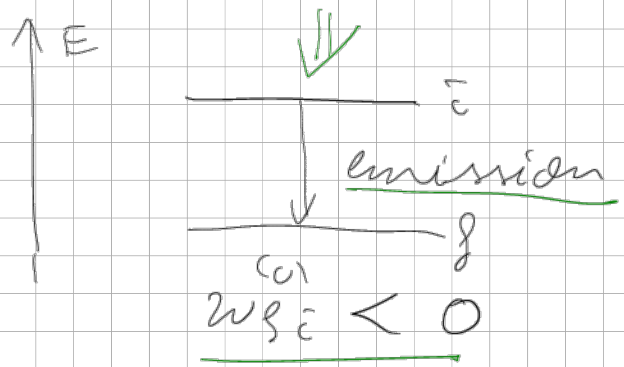
$f \neq i$

$$= \frac{1}{2\hbar}\left\{ (\vec{d}_{fi}\cdot\vec{E}_0)\cdot \frac{e^{i(\omega_{fi}^{(0)}-\omega)t}-1}{\omega_{fi}^{(0)}-\omega} + (\vec{d}_{fi}\cdot\vec{E}_0)^* \frac{e^{i(\omega_{fi}^{(0)}+\omega)t}}{\omega_{fi}^{(0)}+\omega} \right\}$$

$\vec{d}_{fi} = \langle \psi_f^{(0)} | \vec{d} | \psi_i^{(0)} \rangle$

(selection rules!)





let us focus on absorption: $\omega_{fi}^{(0)} > 0$

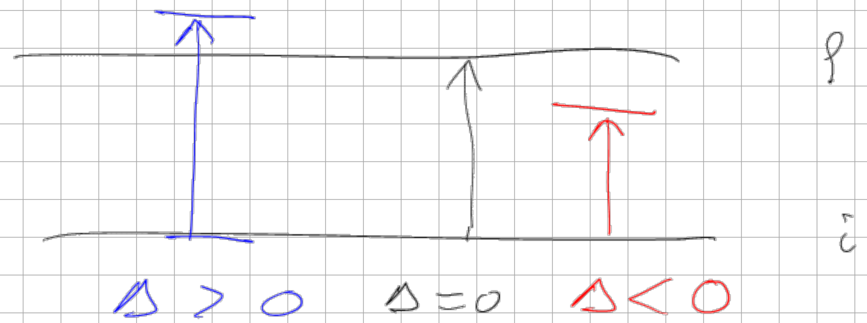
$$c_{fi}^{(1)}(t) = \frac{-1}{2\hbar}\vec{d}_{fi}\cdot\vec{E}_0 \cdot \frac{e^{i\Delta t}-1}{\Delta}$$

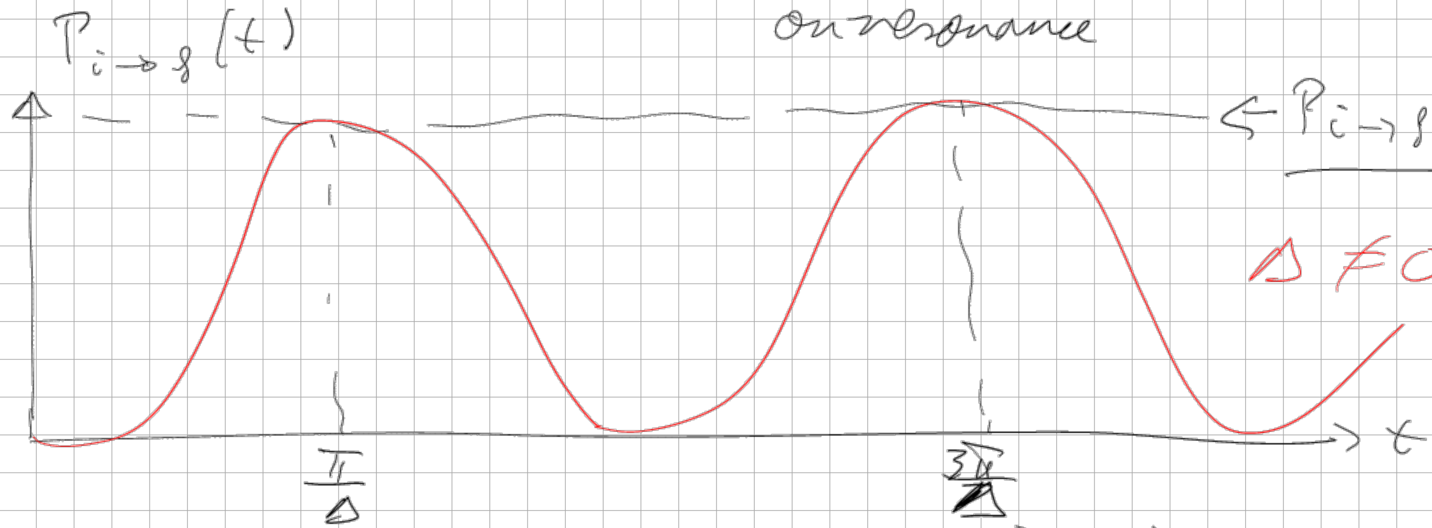
detuning: $\Delta = \omega - \omega_{fi}^{(0)}$

photonic frequency $\nearrow$ $\qquad$ $\nwarrow$ atomic transition frequency

$\Delta > 0 \;\hat{=}\; \omega > \omega_{fi}^{(0)}$ $\qquad\qquad$ $\Delta < 0 \;\hat{=}\; \omega < \omega_{fi}^{(0)}$

blue detuning $\qquad\qquad$ red detuning





$\Leftarrow P_{i\to f}\left(\frac{\pi}{\Delta}\right) = \dfrac{|\vec{d}_{fi}\cdot\vec{E}_0|^2}{\hbar^2\Delta^2}$

$\Delta \neq 0$ (not resonant)

on resonance ($\Delta = 0$): $P_{i\to f}(t) = \dfrac{|\vec{d}_{fi}\cdot\vec{E}_0|^2}{4\hbar^2}t^2 \quad \Leftarrow$

When is this perturbative result valid?

1) $\Delta \neq 0$:

$$\max_t P_{i\to f}(t) \ll 1 \Rightarrow \frac{|\vec{d}_{fi}\cdot\vec{E}_0|}{\hbar} \ll |\Delta|$$

2) $\Delta = 0$:

$$P_{i\to f}(t) \ll 1 \Rightarrow t \ll \frac{2\hbar}{|\vec{d}_{fi}\cdot\vec{E}_0|}$$