5 Time-Dependent Perturbation:

Motivation:

- canonical approach, up to first
- application: electric field, periodically modulated → hydrogen atom
  absorption $\overset{\uparrow}{=}$ induced emission provided electric field
  equal probability treated classically
  ⇒ 2 of 3 elementary processes for interactions of light and matter
  (Albert Einstein: 1916)

5.1 General Theory:

$$i\hbar \frac{\partial}{\partial t} |\Psi(t)\rangle = \hat{H}(t) |\Psi(t)\rangle \Rightarrow |\Psi_n(t)\rangle \neq e^{-\frac{i}{\hbar}E_n t} |\Psi_n\rangle$$

no longer stationary states due to explicit time dependence of $\hat{H}(t)$

$$\hat{H}(t) = \underbrace{\hat{H}_0}_{\text{time-independent}} + \underbrace{\hat{V}(t)}_{\text{time-dependent}} \qquad \hat{H}^{(0)} |\Psi_n^{(0)}\rangle = E_n^{(0)} |\Psi_n^{(0)}\rangle$$

time-independent ↓ basis of states → $|\Psi(t)\rangle = \sum_n c_n(t)\, e^{-\frac{i}{\hbar}E_n^{(0)} t} |\Psi_n^{(0)}\rangle$

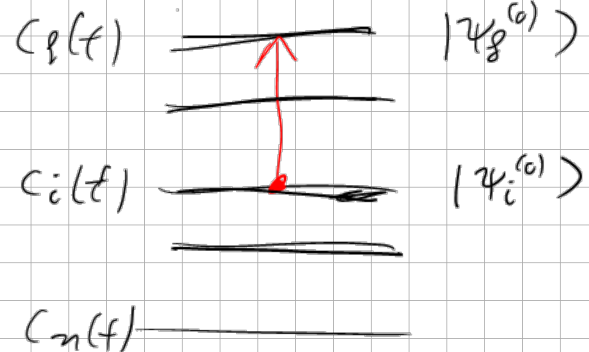
normalization: $\sum_n |c_n(t)|^2 = 1$

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

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

project upon $\langle \psi_n^{(0)}|$:

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



initial condition: $c_i(0) = 1$, $c_n(0) = 0$, $n \neq i$

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

propability for a transition from i to f.

Task: solve this infinitely large coupled system of 1st differential equations $\Rightarrow$ usually no analytic solution

5.2 Iterative Solution:

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

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

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

$$\Rightarrow c_n^{(1)}(t) = -\frac{i}{\hbar}\int_0^t dt'\, e^{i\omega_{ni}t'} V_{ni}(t')$$ $\Rightarrow$ we discuss this in Chapter 5

$$\Rightarrow c_n^{(2)}(t) = - - - - -$$ $\Rightarrow$ in Chapter 6

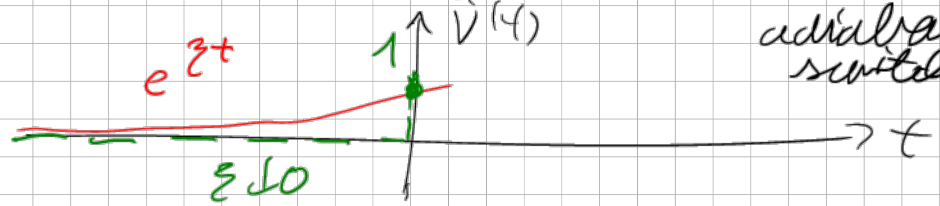
$$P_{i\to f}(t) = \Big|\underbrace{c_f^{(0)}(t)}_{f\neq i \;=\; 0} + c_f^{(1)}(t) + c_f^{(2)}(t) + \dots\Big|^2 = \Big|c_f^{(1)}(t) + \dots\Big|^2$$

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

a) $\hat V(t) \neq 0$ only for $0 \le t \le T$ $\Rightarrow$ now

b) $\hat V(t)$: time-periodic (absorption, emission) after quench $\rightarrow$ chapter 5

c) $\hat V(t)$:



adiabatic switch $\rightarrow$ chapter 6

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

$$V_{ni}(t) \xrightarrow[\text{transform}]{\text{Fourier}} V_{ni}(\omega) = \int_{-\infty}^{+\infty} dt\, e^{i\omega t}\, V_{ni}(t) = \int_0^T dt\, e^{i\omega t}\, V_{ni}(t)$$

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

5.3 Quench of Monochromatic Perturbation:

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

hydrogen atom in presence of electromagnetic wave

- focus electric field

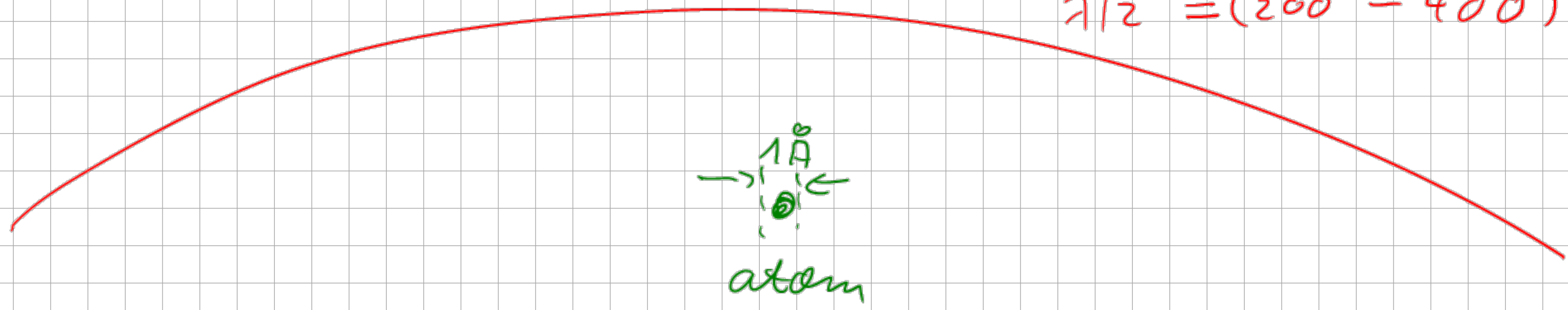
• $\hat{V}(t) = -\vec{d}\cdot\vec{E}(t)$, $\vec{d} = -e\,\vec{x}$

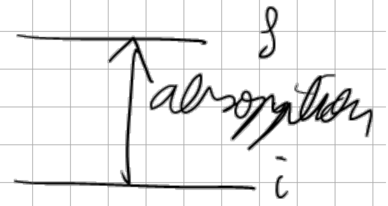
$\vec{E}(t) = \frac{\vec{E}_0}{2}\, e^{i(\vec{k}\vec{x}-\omega t)} + c.c.$ $\qquad \vec{E}_0 \perp \vec{k}$

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

optical range

$\lambda/2 \hat{=} (200-400)\,\mathrm{nm}$





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

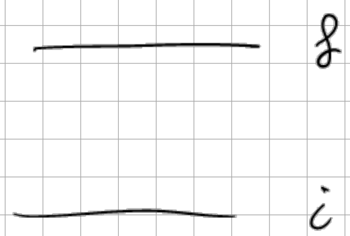
$$c_f^{(1)}(t) = -\frac{i}{\hbar}\int_0^t dt'\, e^{i\omega_{fi}t'}\, V_{fi}(t')$$

neglect due rotating wave approximation

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

much smaller than first term

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



selection rules!

assume: $\omega_{fi} = \frac{E_f^{(0)}-E_i^{(0)}}{\hbar} > 0$

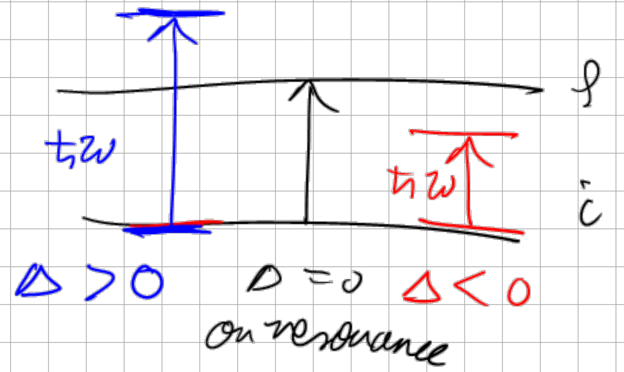
$$c_f^{(1)}(t) = \frac{1}{2\hbar}\,\vec{d}_{fi}\cdot\vec{E}_0\,\frac{e^{i\Delta t}-1}{\Delta}$$

detuning $\Delta = \omega - \omega_{fi}$

atomic transition frequency

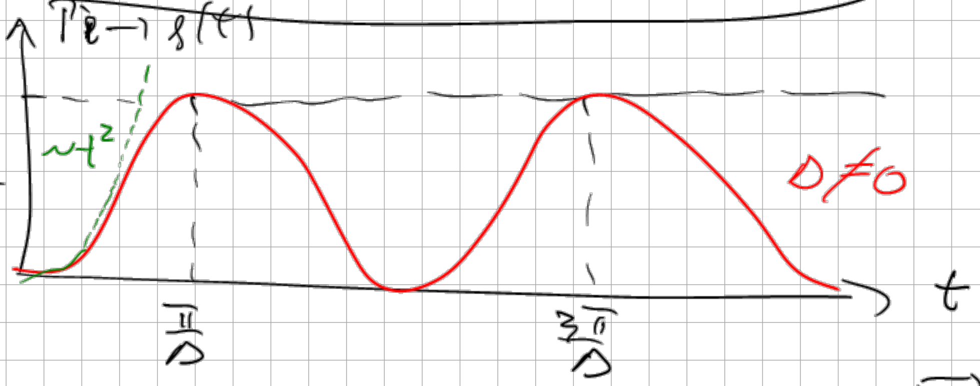
photonic frequencies

$\Delta > 0$ $\quad\omega > \omega_{fi}$ blue $\qquad\qquad$ $\Delta < 0$ $\quad\omega < \omega_{fi}$ red



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

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

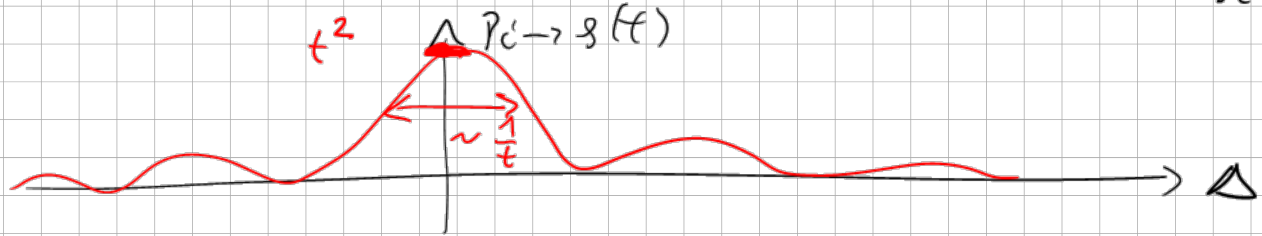


on resonance : $\Delta = 0$ $\qquad P_{i\to f}(t) = \frac{|\vec{d}_{fi}\cdot\vec{E}_0|^2}{4\hbar^2}\,t^2$

When is this perturbative result valid?

$$\max_t P_{i\to f}(t) \ll 1 \Rightarrow \frac{|\vec{d}_{fi}\cdot\vec{E}_0|}{\hbar} \ll \Delta \qquad \Delta \neq 0$$

$$P_{i\to f}(t) \ll 1 \Rightarrow t \ll \frac{2\hbar}{|\vec{d}_{fi}\cdot\vec{E}_0|} \qquad \Delta = 0$$



diffraction function

$$\int_{-\infty}^{+\infty} d\Delta \, \frac{\sin^2 \Delta t/2}{\Delta^2} = \frac{t}{2} \underbrace{\int_{-\infty}^{+\infty} dx \, \frac{\sin^2 x}{x^2}}_{=\pi} = \frac{t\pi}{2}$$

$$\frac{\sin^2 \Delta t/2}{\Delta^2} \xrightarrow[t \to \infty]{} \frac{\pi}{2} t \, \delta(\Delta)$$

$$P_{i \to f}(t) \Longrightarrow \frac{\pi t}{2} \frac{|\vec{d}_{fi} \cdot \vec{E}_0|^2}{\hbar^2} \delta(\omega - \omega_{fi}) \quad t \to \infty$$

transition rate

$$W_{i \to f} = \lim_{t \to \infty} \frac{P_{i \to f}(t)}{t} = \frac{\pi}{2} \frac{|\vec{d}_{fi} \cdot \vec{E}_0|^2}{\hbar^2} \delta(\omega - \omega_{fi})$$

$$W_{i \to [f]} = \frac{\pi}{2} \sum_{[f]} \frac{|\vec{d}_{fi} \cdot \vec{E}_0|^2}{\hbar^2} \delta(\omega - \omega_{fi})$$

Fermi's golden rule

Incoming light consists of many frequency:

$$\frac{P_{i \to f}(t)}{t} = \frac{1}{\hbar^2} \int_{-\infty}^{+\infty} d\omega \, |\vec{d}_{fi} \cdot \underbrace{\vec{E}_0(\omega)}|^2 \frac{\sin^2 (\omega - \omega_{fi}) t/2}{(\omega - \omega_{fi})^2 t}$$

varies slowly
in ~~the~~ frequency around ω_{fi}

$$= \frac{\pi}{2\hbar} |\vec{d}_{fi} \cdot \vec{E}_0(\omega_{fi})|^2$$