Foundations of quantum chemistry
4. Interaction between matter and radiation

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October 2007 - Revised on April 28th, 2018

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Taylor expansion of $E_{m\text{-}F}$

- Static electric field $\vec{F} = -\vec{\nabla} V(\vec{r})$:

a detailed information about the charge distribution is needed

$$E_{m-F} = \sum_{j=1}^{n} q_j V(\vec{r}_j) = \boxed{\sum_{j=1}^{n} q_j} \left[V_0 + \left(\frac{\partial V}{\partial x}\right)_0 x_j + \left(\frac{\partial V}{\partial y}\right)_0 y_j + \left(\frac{\partial V}{\partial z}\right)_0 z_j \right.$$

$$\left. + \frac{1}{2}\left(\frac{\partial^2 V}{\partial x^2}\right)_0 x_j^2 + \frac{1}{2}\left(\frac{\partial^2 V}{\partial x \partial y}\right)_0 x_j y_j + \ldots + \frac{1}{2}\left(\frac{\partial^2 V}{\partial z^2}\right)_0 z_j^2 + \ldots \right]$$

Electric multipoles

- Static electric field $\vec{F} = -\vec{\nabla} V(\vec{r})$:

a detailed information about the charge distribution is needed

$$E_{m-F} = \sum_{j=1}^{n} q_j V(\vec{r}_j) = \boxed{\sum_{j=1}^{n} q_j} \Bigg[V_0 + \left(\frac{\partial V}{\partial x}\right)_0 x_j + \left(\frac{\partial V}{\partial y}\right)_0 y_j + \left(\frac{\partial V}{\partial z}\right)_0 z_j$$

$$+ \frac{1}{2}\left(\frac{\partial^2 V}{\partial x^2}\right)_0 x_j^2 + \frac{1}{2}\left(\frac{\partial^2 V}{\partial x \partial y}\right)_0 x_j y_j + \ldots + \frac{1}{2}\left(\frac{\partial^2 V}{\partial z^2}\right)_0 z_j^2 + \ldots \Bigg]$$

$$= V_0 \boxed{\sum_{j=1}^{n} q_j} - (F_x)_0 \boxed{\sum_{j=1}^{n} q_j x_j} - (F_y)_0 \boxed{\sum_{j=1}^{n} q_j y_j} - (F_z)_0 \boxed{\sum_{j=1}^{n} q_j z_j}$$

$$- \frac{1}{2}\left(\frac{\partial F_x}{\partial x}\right)_0 \boxed{\sum_{j=1}^{n} q_j x_j^2} - \frac{1}{2}\left(\frac{\partial F_x}{\partial y}\right)_0 \boxed{\sum_{j=1}^{n} q_j x_j y_j} \ldots - \frac{1}{2}\left(\frac{\partial F_z}{\partial z}\right)_0 \boxed{\sum_{j=1}^{n} q_j z_j^2} \ldots$$

Electric multipole moments

Static electric field:

$$E_{m-F} = V_0 q - \vec{F}_0 \cdot \vec{d} - \frac{1}{2}\left[\left(\frac{\partial F_x}{\partial x}\right)_0 Q_{xx} + \left(\frac{\partial F_x}{\partial y}\right)_0 Q_{xy} + \ldots + \left(\frac{\partial F_z}{\partial z}\right)_0 Q_{zz}\right] - \ldots$$

zero-th order electric moment (electric monopole)

$$q \equiv \sum_{j=1}^{n} q_j$$

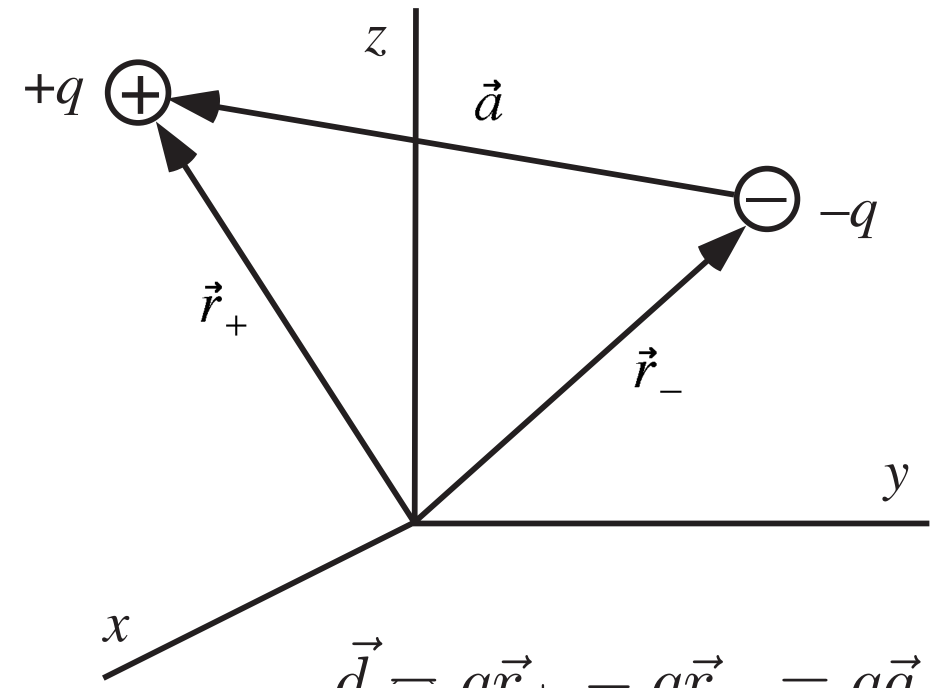
first-order electric moment (electric dipole)

$$\begin{cases} d_x \equiv \sum_{j=1}^{n} q_j x_j \\ d_y \equiv \sum_{j=1}^{n} q_j y_j \\ d_z \equiv \sum_{j=1}^{n} q_j z_j \end{cases}$$

second-order electric moment (electric quadrupole)

$$\begin{cases} Q_{xx} \equiv \sum_{j=1}^{n} q_j x_j^2 \\ Q_{xy} \equiv \sum_{j=1}^{n} q_j x_j y_j \\ \ldots \\ Q_{zz} \equiv \sum_{j=1}^{n} q_j z_j^2 \end{cases}$$

$\cdots$ *n-th order electric moment (electric 2^n-pole)*



$$\vec{d} = q\vec{r}_+ - q\vec{r}_- = q\vec{a}$$

Continuous charge distributions

$$\vec{d} = \sum_{j=1}^{n} \vec{r}_j q_j \longrightarrow \int_{\mathcal{R}^3} \vec{r} dq \longrightarrow \int_{\mathcal{R}^3} \vec{r} \sigma_q(\vec{r}) d\vec{r}$$

$$\sum_{j=1}^{n} (\ldots) q_j \longrightarrow \int_{\mathcal{R}^3} (\ldots) \sigma_q(\vec{r}) d\vec{r}$$

Exemple: hydrogen atom

last eq. of slide 3.12 with $f(\vec{r}) = -ex = d_x$

$$d_x = \int_{\mathcal{R}^3} x \sigma_q(\vec{r}) d\vec{r} = \int_{\mathcal{R}^3} \underbrace{(-ex)}_{f(\vec{r})} \sigma(\vec{r}) d\vec{r} = \langle d_x \rangle$$

which is equivalent to the more familiar expression:

$$\langle d_x \rangle = \left\langle \phi \middle| \widehat{d_x} \phi \right\rangle = \int_{\mathcal{R}^3} \phi^*(\vec{r}) d_x \phi(\vec{r}) d\vec{r} = \int_{\mathcal{R}^3} (-ex) \sigma(\vec{r}) d\vec{r}$$

The classical calculation for a continuous charge density leads to the correct quantum result for spin-independent monoelectronic observables diagonal in position representation.

Magnetic multipoles

- Moving charges in a time-dependent EM field:

$$\boxed{E_{m-r}(t) = V_0 q - \vec{F}_0 \cdot \vec{d} \qquad\qquad - \vec{B}_0 \cdot \vec{\mu}} - \frac{1}{2}\left[\left(\frac{\partial F_x}{\partial x}\right)_0 Q_{xx} + \ldots\right] - \ldots - \ldots$$

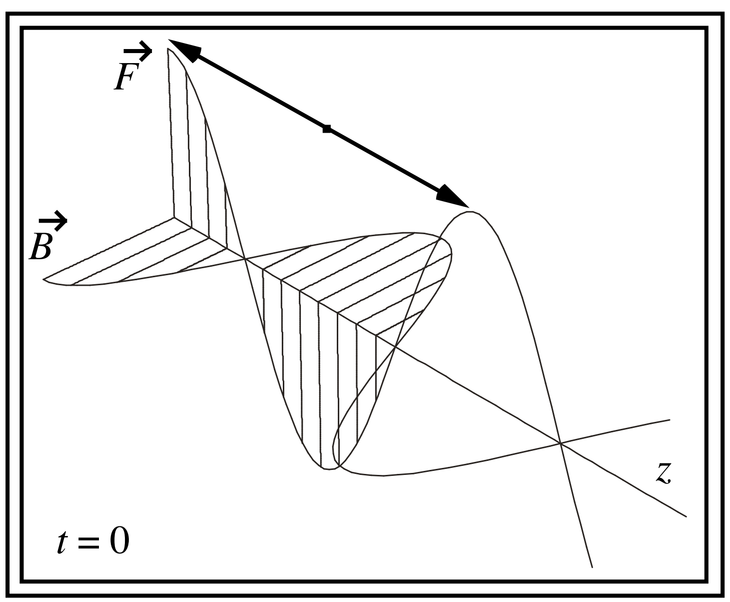
Dipole approximation

$$\vec{\mu} = \vec{\mu}_L + \vec{\mu}_S + \vec{\mu}_J + \vec{\mu}_I \quad \begin{cases} \vec{\mu}_L = \sum_{i=1}^{n} \frac{-e}{2m_e}\vec{l}_i = \frac{-e}{2m_e}\vec{L} \\ \vec{\mu}_S = \sum_{i=1}^{n} g_e \frac{-e}{2m_e}\vec{s}_i = g_e \frac{-e}{2m_e}\vec{S} \\ \vec{\mu}_J = \sum_{A=1}^{N} \frac{Z_A e}{2m_A}\vec{j}_A \\ \vec{\mu}_I = \sum_{A=1}^{N} (g_N)_A \frac{e}{2m_p}\vec{I}_A \end{cases}$$

PLM electromagnetic waves

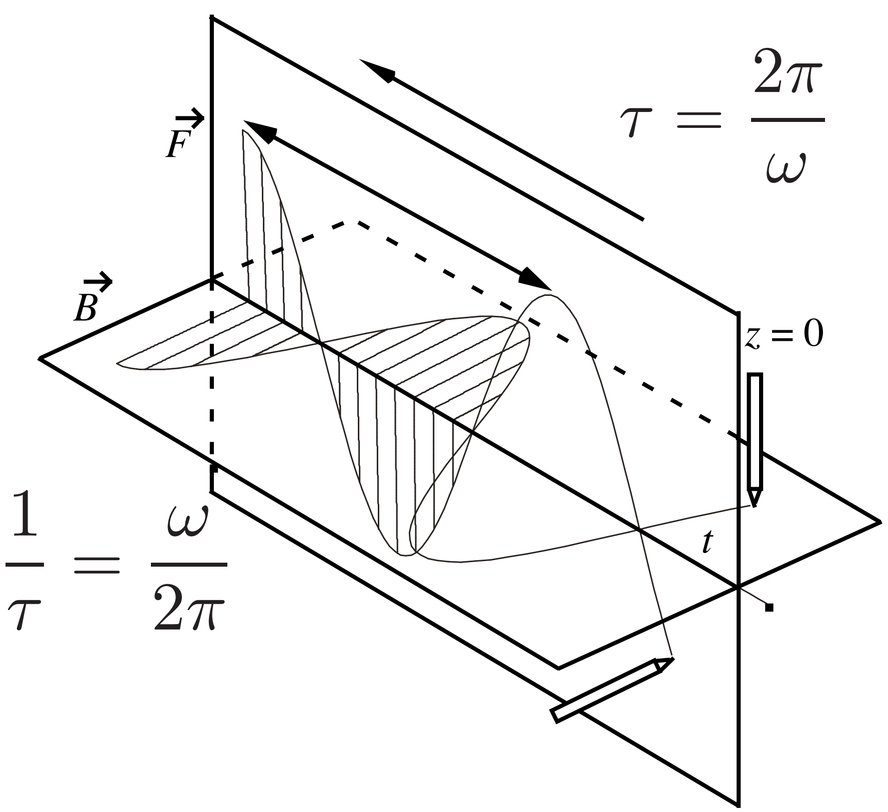
- (Particular) solution of Maxwell equations in vacuum (PLM):

$$\boxed{\begin{aligned}\vec{F} &= \vec{u}_x F \cos(\omega t - kz + \varphi)\\ \vec{B} &= \vec{u}_y B \cos(\omega t - kz + \varphi)\end{aligned}} \qquad c = \frac{\omega}{k} \qquad F = cB \qquad c = \frac{1}{\sqrt{\varepsilon_0 \mu_0}} = 2,99792458 \times 10^8 \mathrm{ms}^{-1}$$



$$\lambda = \frac{2\pi}{k}$$

$$\overline{\nu} = \frac{1}{\lambda} = \frac{k}{2\pi}$$



$$\tau = \frac{2\pi}{\omega}$$

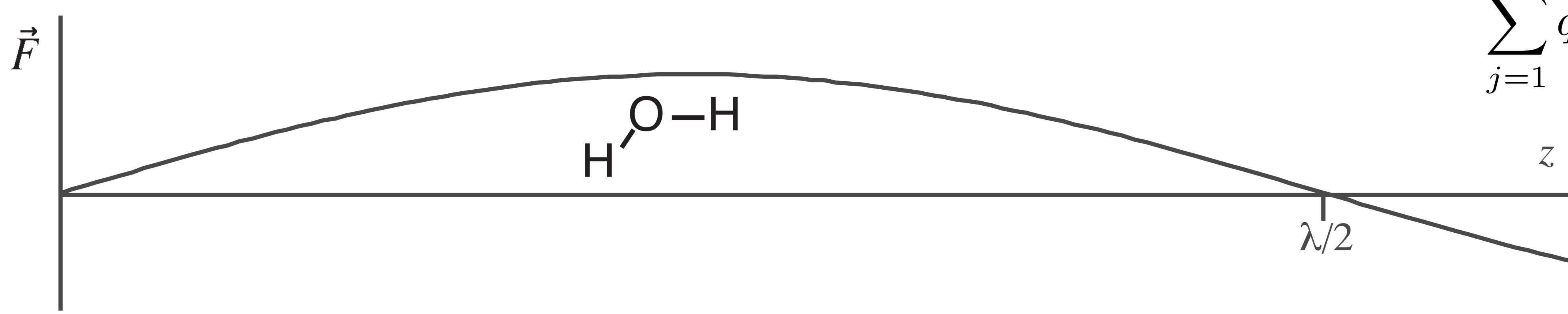
$$\nu = \frac{1}{\tau} = \frac{\omega}{2\pi}$$

Dipole approximation

- Dipole approximation ($\lambda >> r_i$):

$$E_{m-r}(t) = V_0(t)q - \vec{F}_0(t)\cdot\vec{d} - \vec{B}_0(t)\cdot\vec{\mu} \cancel{- \frac{1}{2}\left[\left(\frac{\partial F_x(t)}{\partial x}\right)_0 Q_{xx} + \ldots\ldots\right]} + \ldots$$

$$\sum_{j=1}^{n} q_j x_j^2$$



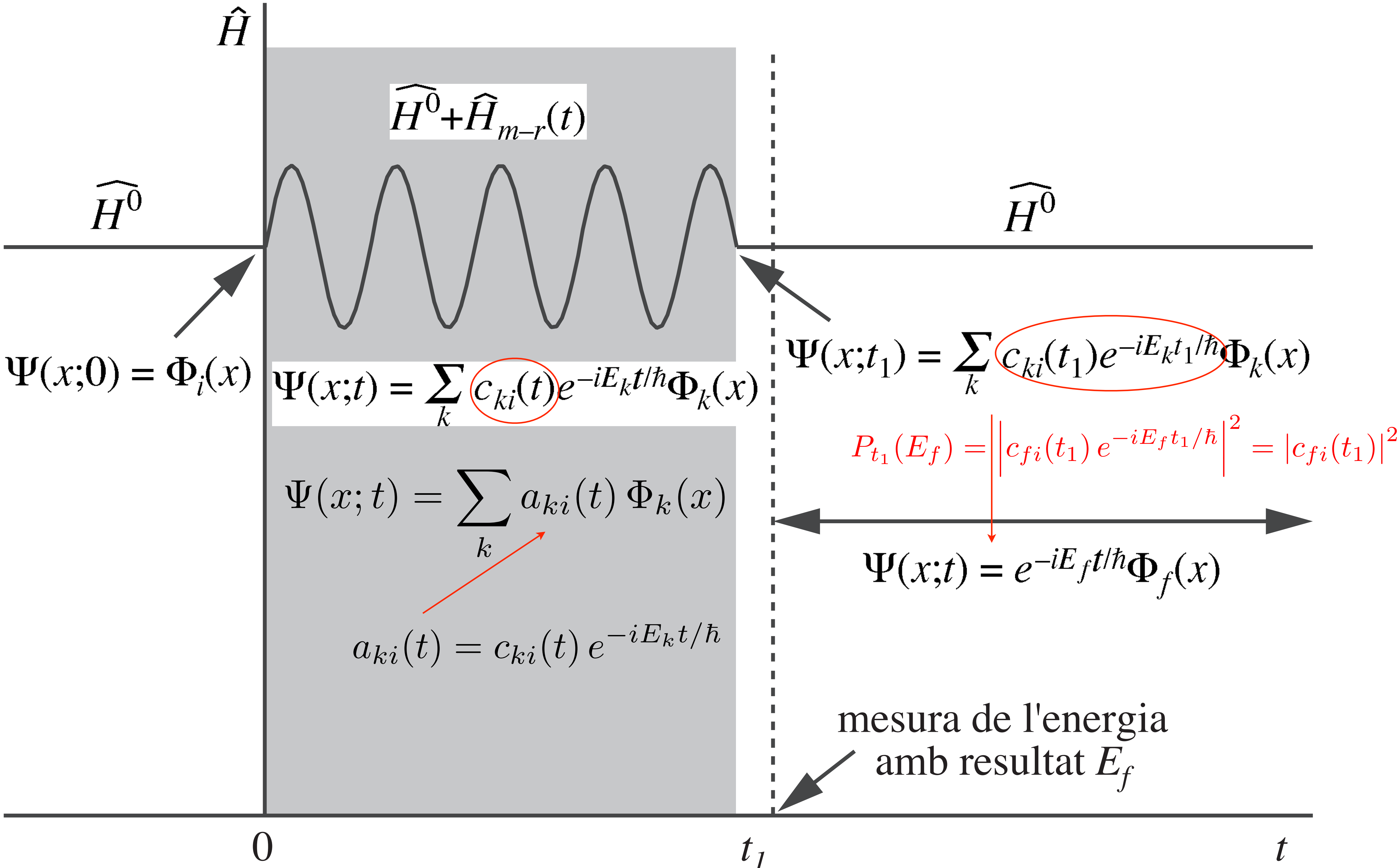
- Lorentz:

$$F = cB$$

$$q\left(\vec{F} + \vec{v}\times\vec{B}\right) = -eB\left(c\vec{u}_x + \vec{v}\times\vec{u}_y\right)\cos(\omega t - kz + \varphi)$$

$$\frac{\text{magnetic force}}{\text{electric force}} \leq \frac{\cancel{-e B} v \cancel{\cos(\omega t - kz + \varphi)}}{\cancel{-e B} c \cancel{\cos(\omega t - kz + \varphi)}} = \frac{v}{c}$$

Evolution of a stationary state



Evolution of a stationary state

- During irradiation $(0,\ t_1)$:

$$\Psi(x;t) = \sum_k c_{ki}(t)\, e^{-iE_k t/\hbar}\, \Phi_k(x)$$

$$i\hbar \frac{\partial \Psi}{\partial t} = \left(\widehat{H^0} + \widehat{H_{m-r}}(t) \right) \Psi$$

$$\boxed{\frac{dc_{fi}(t)}{dt} = \frac{1}{i\hbar} \sum_k c_{ki}(t)\, e^{i\omega_{fk} t} \left\langle \Phi_f \middle| \widehat{H_{m-r}}(t)\, \Phi_k \right\rangle} \qquad t \in (0, t_1)$$

$$\omega_{fk} \equiv \frac{E_f - E_k}{\hbar}$$

Time-dependent perturbation meth.

- 1st order: $c_{ki}(t) \approx c_{ki}(0) = \delta_{ki} \qquad \forall k$

$$\frac{dc_{fi}^{(1)}(t)}{dt} = \frac{1}{i\hbar} e^{i\omega_{fi}t} \left\langle \Phi_f \middle| \widehat{H_{m-r}}(t)\, \Phi_i \right\rangle \qquad t \in (0, t_1)$$

$$c_{fi}^{(1)}(t) = \frac{1}{i\hbar} \int_0^t e^{i\omega_{fi}t'} \left\langle \Phi_f \middle| \widehat{H_{m-r}}(t')\, \Phi_i \right\rangle dt'$$

For any $\Phi_f \neq \Phi_i$ ($c_{ii}(t)$ can be obtained by normalizing Ψ)

- Dipole approximation:

$$\widehat{H_{m-r}}(t) = V_0(t)q - F\cos(\omega t)\widehat{d_x} - B\cos(\omega t)\widehat{\mu_y} \qquad \text{(ona PML)}$$

$$\widehat{\vec{d}} = \sum_{j=1}^{n} q_j \widehat{\vec{r}_j} \qquad \widehat{\vec{\mu}_L} = \frac{-e}{2m_e}\widehat{\vec{L}} \qquad \text{etc.}$$

1-photon transitions

$$P_{t_1}(E_f) = P(s \leftrightarrow i) = \frac{F^2}{\hbar^2} \left| \underbrace{\left\langle \Phi_s \middle| \left(\widehat{d_x} + \frac{1}{c}\widehat{\mu_y} \right) \Phi_i \right\rangle}_{\textit{Selection rules}} \right|^2 \frac{\sin^2\left[(\omega_{si} - \omega)t_1/2\right]}{(\omega_{si} - \omega)^2} \qquad \text{(ona PML)}$$

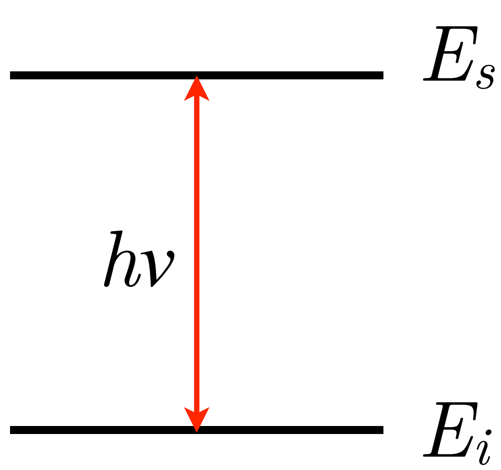
absorption: $\leftarrow$

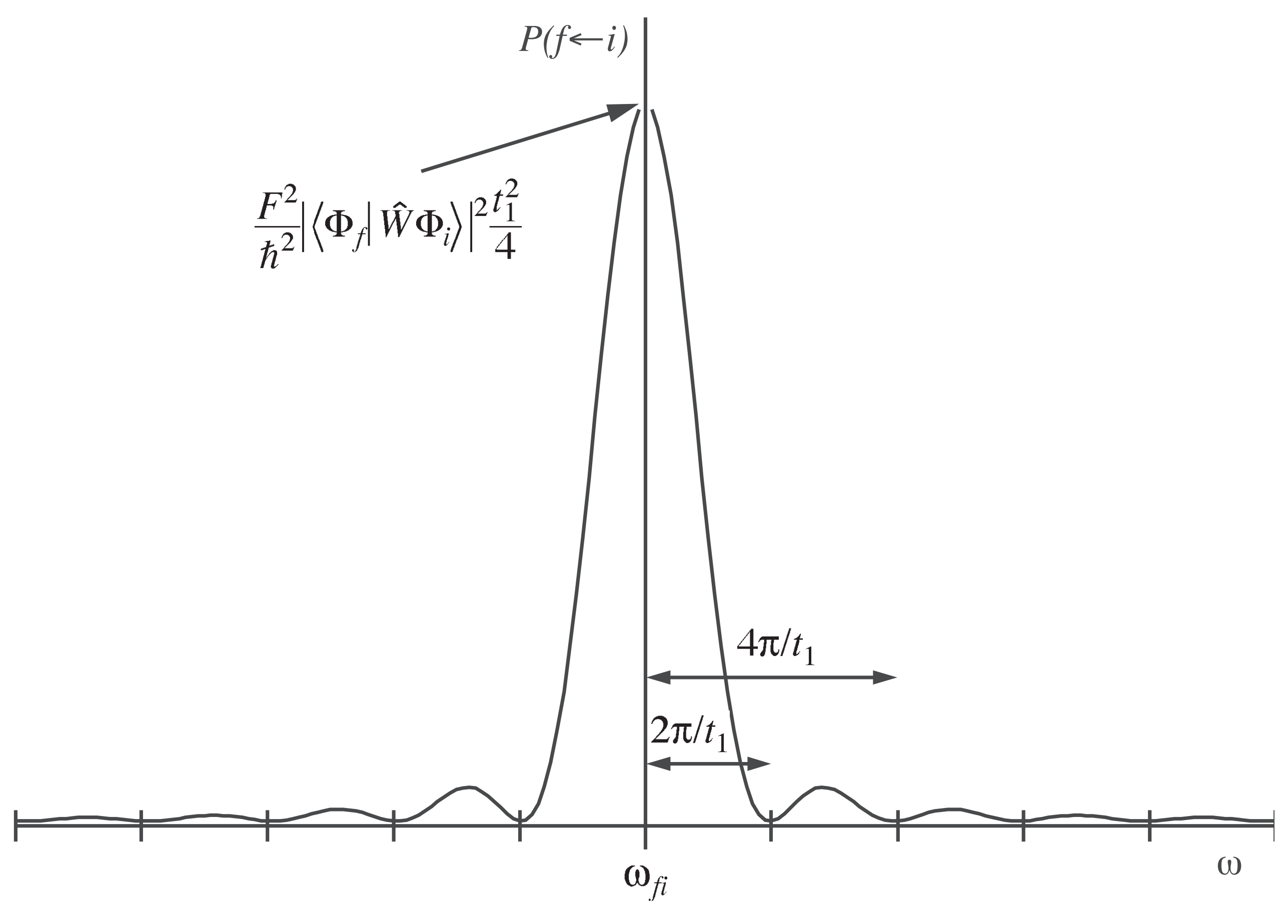
induced emission: $\rightarrow$

(LASERs!)

(dipolar and 1st order or monophotonic)

$$\boxed{E_s - E_i \approx \hbar\omega = h\nu}$$





(monophotonic) absorption: $\uparrow$

(monophotonic) induced emission: $\downarrow$

Charged harmonic oscillator

- Transition $1 \leftrightarrow 0$:

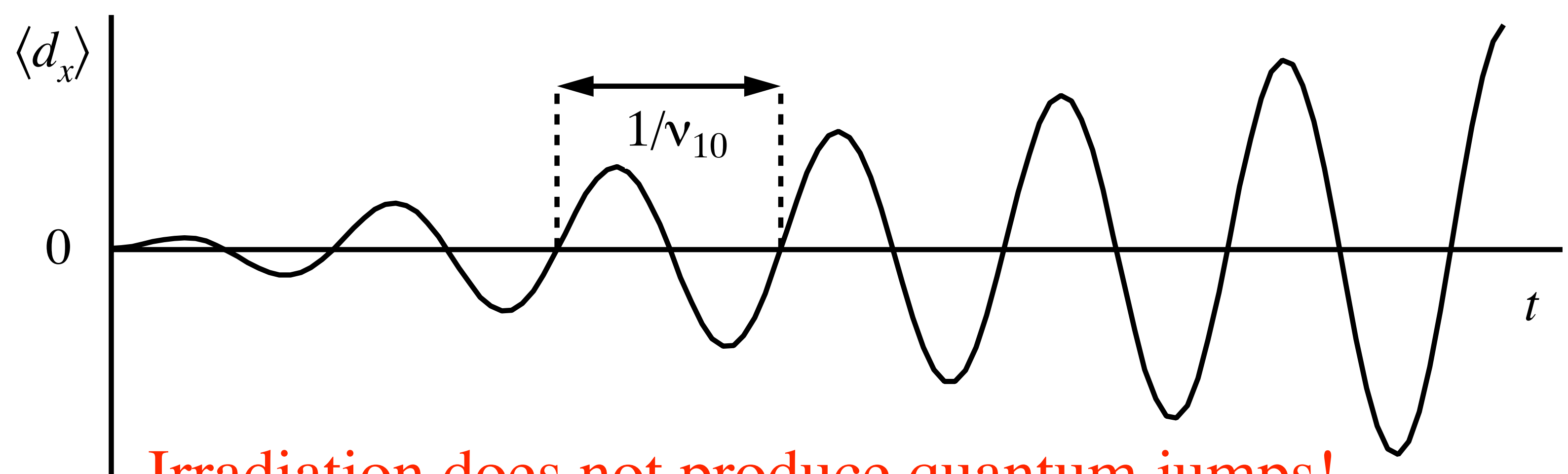
$$\left\langle \Phi_1 \middle| \widehat{d_x}\Phi_0 \right\rangle = \int_{-\infty}^{\infty} \Phi_1^*(x)\, qx\, \Phi_0(x)\, dx = \int_{-\infty}^{\infty} \left(\frac{4\alpha^3}{\pi}\right)^{1/4} xe^{-\alpha x^2/2}\, qx \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2/2}\, dx$$

$$= \left(\frac{2\alpha^2}{\pi}\right)^{1/2} 2q \int_0^{\infty} x^2 e^{-\alpha x^2} dx = \frac{q}{\sqrt{2\alpha}} \neq 0$$ (electric dipole) allowed

If we irradiate at $\nu = \nu_{10} = (E_1 - E_0)/h$ then

$$\Psi(x;t) = c_{00}(t)\, e^{-iE_0 t/\hbar}\, \Phi_0(x) + c_{10}(t)\, e^{-iE_1 t/\hbar}\, \Phi_1(x) \qquad t \in (0, t_1)$$

$$\langle d_x \rangle (t) \approx \frac{Fq^2}{2\hbar\alpha} t \sin 2\pi\nu_{10} t$$



Irradiation does not produce quantum jumps!

- Transition $n \leftrightarrow n'$: $\Delta n = \pm 1$

Gradual evolution

Exercise 4.1

Verify the equation for $\langle d_x \rangle$(t) in slide 4.13.

Hints:

- Use the expression for the first-order coefficient $c_{fi}^{(1)}(t)$ of slide 11 to calculate $c_{10}^{(1)}(t)$. In the interaction hamiltonian (slide 11) you can neglect the magnetic dipolar term, since the transition is electric-dipole allowed.
- Take into account that the frequency is >>1 (which applies in all standard spectroscopic techniques).
- Since we are using first-order time-dependent perturbation theory the coefficients $c_{fi}^{(1)}(t)$ should differ little from to their initial values, which allows to make the approximation $c_{00}^{(1)}(t)$=1 (of course we cannot take $c_{10}^{(1)}(t)$=0 if we want to find any time-evolution).

Solution of the exercise 4.1

Slide 11:

$$C_{10}^{(1)}(t) = \frac{1}{i\hbar}\int_0^t e^{i\omega_{10}t'} \left\langle \Phi_1 \middle| \left\{ V_0(t')\, q - F\cos(\omega t')\,\hat{d}_x \right\} \Phi_0 \right\rangle dt' =$$

$$= \frac{1}{i\hbar}\int_0^t e^{i\omega_{10}t'}\, V_0(t')\, q \underbrace{\langle \Phi_1 | \Phi_0 \rangle}_{0}\, dt' - \frac{Fq}{i\hbar}\int_0^t e^{i\omega_{10}t'} \underbrace{\cos\omega_{10}t'}_{\frac{1}{2}\left(e^{i\omega_{10}t'}+e^{-i\omega_{10}t'}\right)} \langle \Phi_1 | \hat{x}\,\Phi_0 \rangle\, dt' =$$

$$= -\frac{Fq}{2i\hbar}\int_0^t \left(e^{2i\omega_{10}t'}+1\right)\frac{1}{\sqrt{2\alpha}}\, dt' \underset{\times\frac{i}{i}}{=} i\,\frac{Fq}{2\hbar}\,\frac{1}{\sqrt{2\alpha}}\left[\frac{e^{2i\omega_{10}t'}}{2i\omega_{10}} + t'\right]_0^t =$$

$$= i\,\frac{Fq}{2\sqrt{2\alpha}\,\hbar}\left(\frac{\overbrace{e^{2i\omega_{10}t}-1}^{|\;|\leq 2}}{2i\underbrace{\omega_{10}}_{>10^8\ (\mathrm{NMR})}} + t\right) \approx i\,\frac{Fq}{2\sqrt{2\alpha}\,\hbar}\, t$$

Solution of the exercise 4.1 (cont)

$$C_{00}^{(1)}(t) \approx C_{00}^{(1)}(0) = 1$$

$$\begin{cases} E_n = \left(n+\frac{1}{2}\right)\hbar\omega \\ \omega = \sqrt{\frac{k}{m}} = \omega_{10} \end{cases}$$

$$\Psi(x;t) = C_{00}(t)\, e^{-i\frac{E_0}{\hbar}t}\,\Phi_0(x) + C_{10}(t)\, e^{-i\frac{E_1}{\hbar}t}\,\Phi_1(x) + \cdots$$

$$\simeq e^{-i\frac{\omega_{10}}{2}t}\,\Phi_0(x) + i\,\frac{Fq}{\sqrt{8\alpha}\,\hbar}\,t\, e^{-i\frac{3\omega_{10}}{2}t}\,\Phi_1(x)$$

$$\langle d_x \rangle_\Psi = \langle \Psi | qx\Psi \rangle \simeq \underbrace{\left\langle e^{-i\frac{\omega_{10}}{2}t}\Phi_0(x) \,\middle|\, qx\, e^{-i\frac{\omega_{10}}{2}t}\Phi_0(x)\right\rangle}_{=0 \text{ (ungerade integrand)}} + (\cdots)\underbrace{\langle \Phi_1 | x\Phi_1 \rangle}_{0}$$

$$+\, e^{i\frac{\omega_{10}}{2}t}\, i\,\frac{Fqt}{\sqrt{8\alpha}\,\hbar}\, e^{-i\frac{3\omega_{10}}{2}t}\underbrace{\langle \Phi_0 | qx\Phi_1 \rangle}_{q/\sqrt{2\alpha}} - i\,\frac{Fqt}{\sqrt{8\alpha}\,\hbar}\, e^{i\frac{3\omega_{10}}{2}t}\, e^{-i\frac{\omega_{10}}{2}t}\underbrace{\langle \Phi_1 | qx\Phi_0 \rangle}_{q/\sqrt{2\alpha}} =$$

$$= i\,\frac{Fq^2t}{4\alpha\hbar}\underbrace{\left(e^{-i\omega_{10}t} - e^{i\omega_{10}t}\right)}_{-2i\sin\omega_{10}t} = \frac{Fq^2}{2\alpha\hbar}\,t\sin\omega_{10}t \underset{\omega_{10}=2\pi\nu_{10}}{=} \frac{Fq^2}{2\alpha\hbar}\,t\sin 2\pi\nu_{10}t$$

Polychromatic isotropic radiation

- ... or rotating molecules:

energy density of radiation with frequency ν_{si}

$$\boxed{w_{si}} = \frac{dP(s\leftrightarrow i)}{dt_1} = \boxed{\frac{1}{6\hbar^2\varepsilon_0}\left|\left\langle \Phi_s \middle| \widehat{\vec{d}}\,\Phi_i \right\rangle\right|^2} u(\nu_{si}) = B_{si}u(\nu_{si})$$

transition rate

B_{si}

$$\left|\left\langle \Phi_s \middle| \widehat{\vec{d}}\,\Phi_i \right\rangle\right|^2 = \left|\left\langle \Phi_s \middle| \widehat{d_x}\Phi_i \right\rangle\right|^2 + \left|\left\langle \Phi_s \middle| \widehat{d_y}\Phi_i \right\rangle\right|^2 + \left|\left\langle \Phi_s \middle| \widehat{d_z}\Phi_i \right\rangle\right|^2$$

$$\boxed{B_{si} \equiv \frac{1}{6\hbar^2\varepsilon_0 c^2}\left|\left\langle \Phi_s \middle| \widehat{\vec{\mu}}\,\Phi_i \right\rangle\right|^2}$$

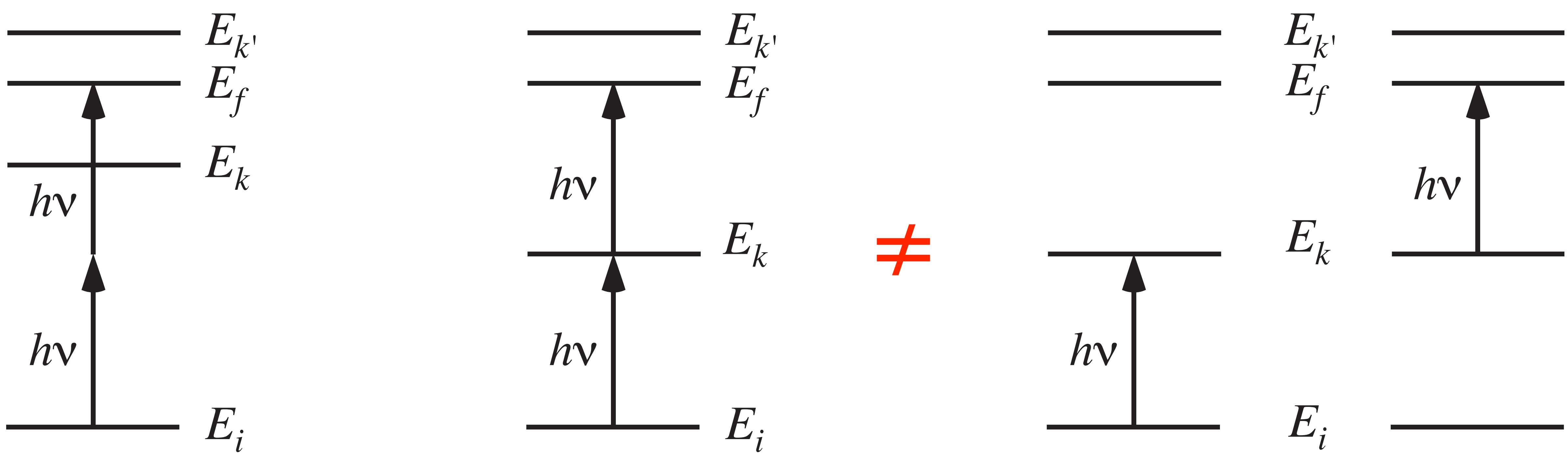
$\Bigg\{$ trans. per dipol magnètic, radiació isòtropa o molèc. en rotació

- Number of molecules passing from Φ_i to Φ_s per unit time:

$$N_i w_{si}^{abs} = N_i B_{si} u(\nu_{si})$$

2-photon processes

- *2nd-order time-dependent perturbation method* ($F\uparrow$):
  - 2-photon absorption / emission

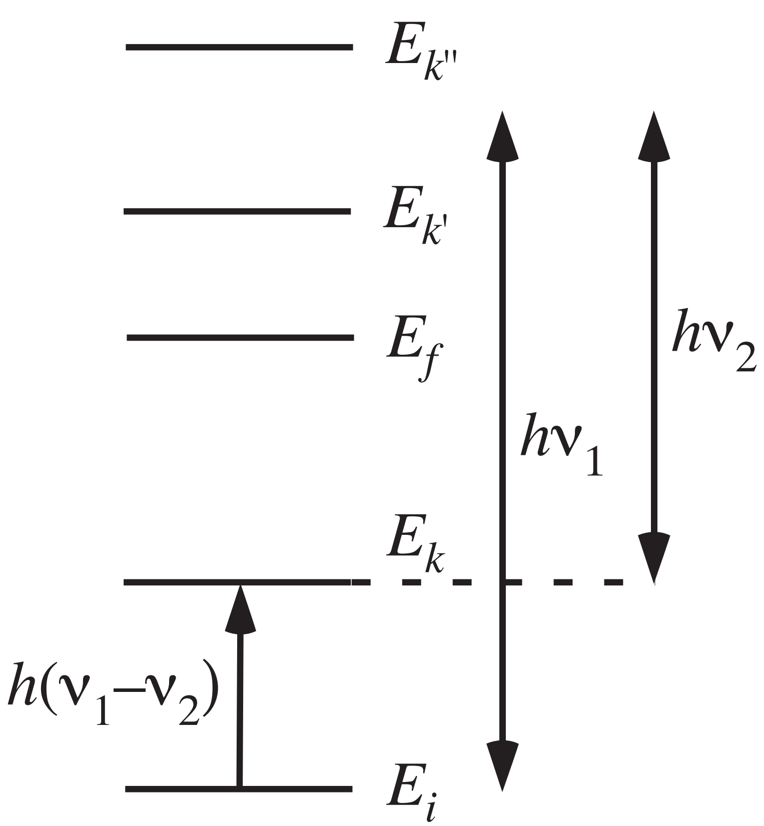


$$\frac{F\left\langle \Phi_f \middle| \widehat{d_x} \Phi_i \right\rangle}{2\hbar} \longrightarrow \sum_k \frac{F^2\left\langle \Phi_f \middle| \widehat{d_x} \Phi_k \right\rangle\left\langle \Phi_k \middle| \widehat{d_x} \Phi_i \right\rangle}{4\hbar^2(\omega_{ki} \pm \omega)}$$

ressonances *non-linear spectroscopy*

Multi-photon processes

- *Raman*

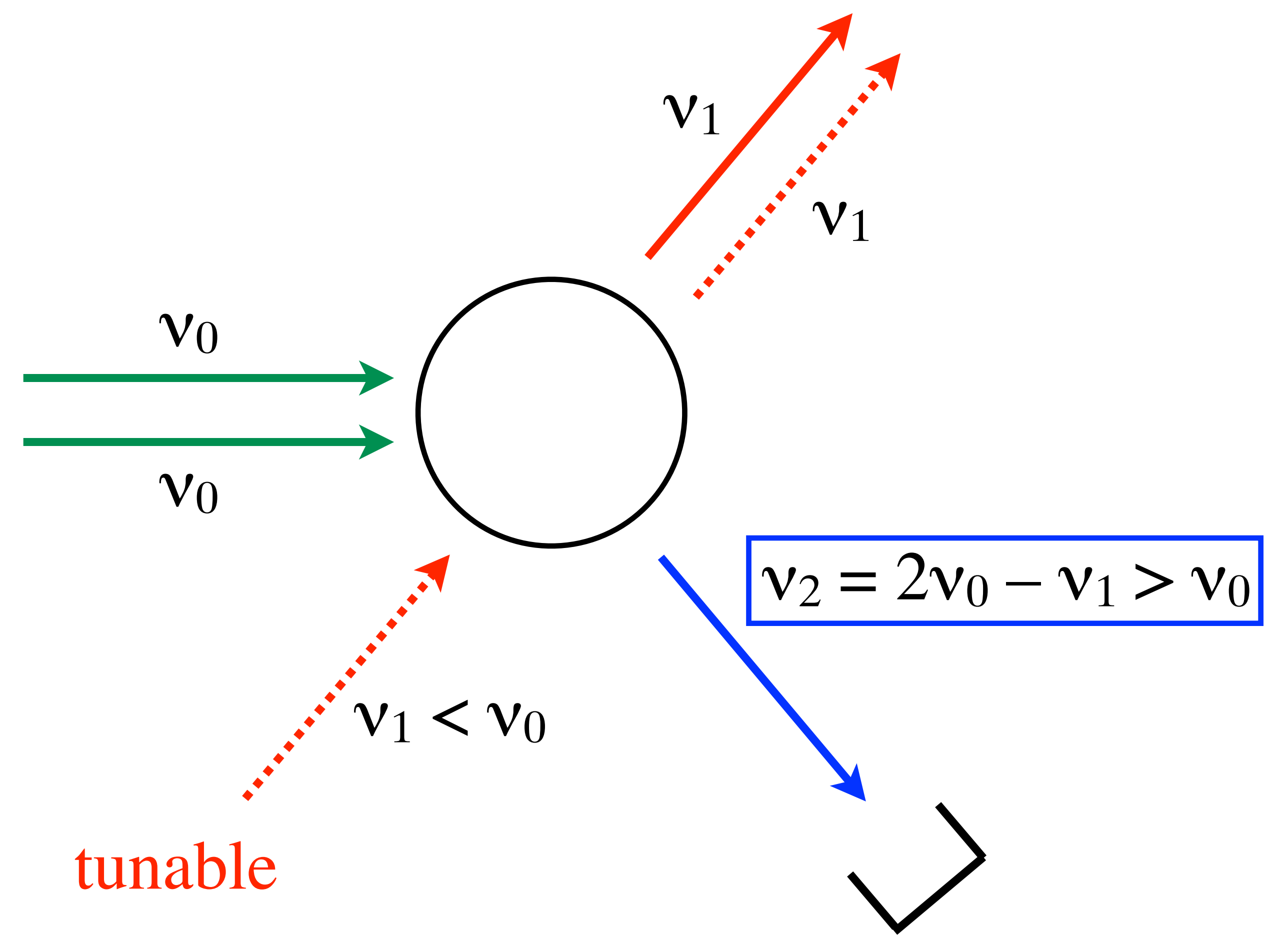


$$\boxed{E_f - E_i = h\nu_{exc} - h\nu}$$

$$\langle \Psi'_{vib} \,|[\alpha_{ab}(\nu_{exc})]_i \; \Psi''_{vib} \rangle$$

dynamic (dipole) polarizability

- *CARS*



Elastic tetraphotonic scattering is greatly enhanced at resonances ($\nu_0 - \nu_1 \approx \nu_{vib}$).

Spontaneous emission

- Stationary states: $\Psi(x;t) = e^{-iE_i t/\hbar}\Phi_i(x)$

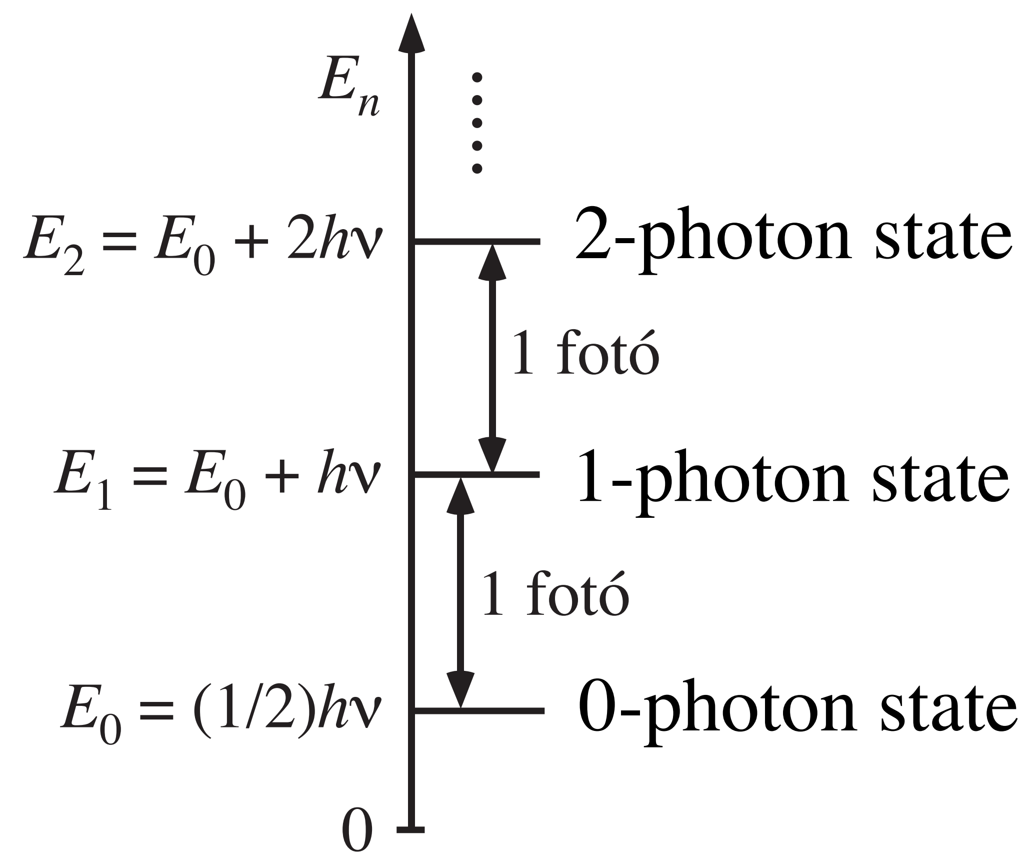
$$|\Psi(x;t)|^2 = \left(e^{-iE_i t/\hbar}\Phi_i(x)\right)^* \times \left(e^{-iE_i t/\hbar}\Phi_i(x)\right) = |\Phi_i(x)|^2$$

- *Spontaneous* emission?
  - *quantum theory of radiation*

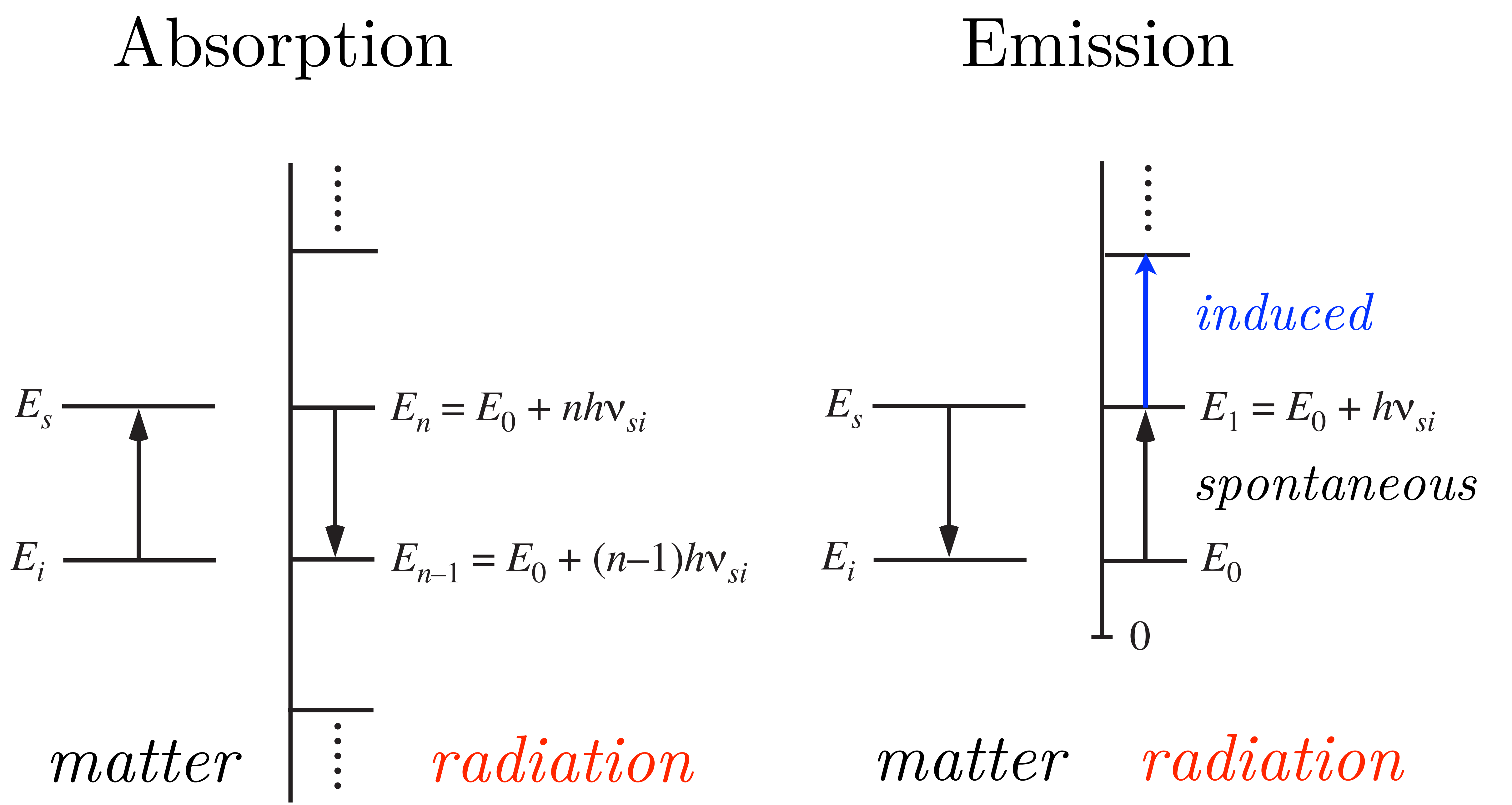
    (x-$p \leftrightarrow E$-B)

$$m_{phot,\nu} = \frac{E_{phot,\nu}}{c^2} = \frac{h\nu}{c^2} = \frac{p_{phot,\nu}}{c}$$

$$p_{phot,\nu} = \frac{h\nu}{c} = \frac{h}{\lambda}$$



Quantum theory of radiation



Spontaneous emission

!!

$$\boxed{A_{si} = \frac{8\pi^2 \nu_{si}^3}{3\hbar\varepsilon_0 c^3} \left| \left\langle \Phi_s \middle| \hat{\vec{d}} \Phi_i \right\rangle \right|^2}$$

same selection rules

spontaneous emission rate

- If $u(\nu) = 0$

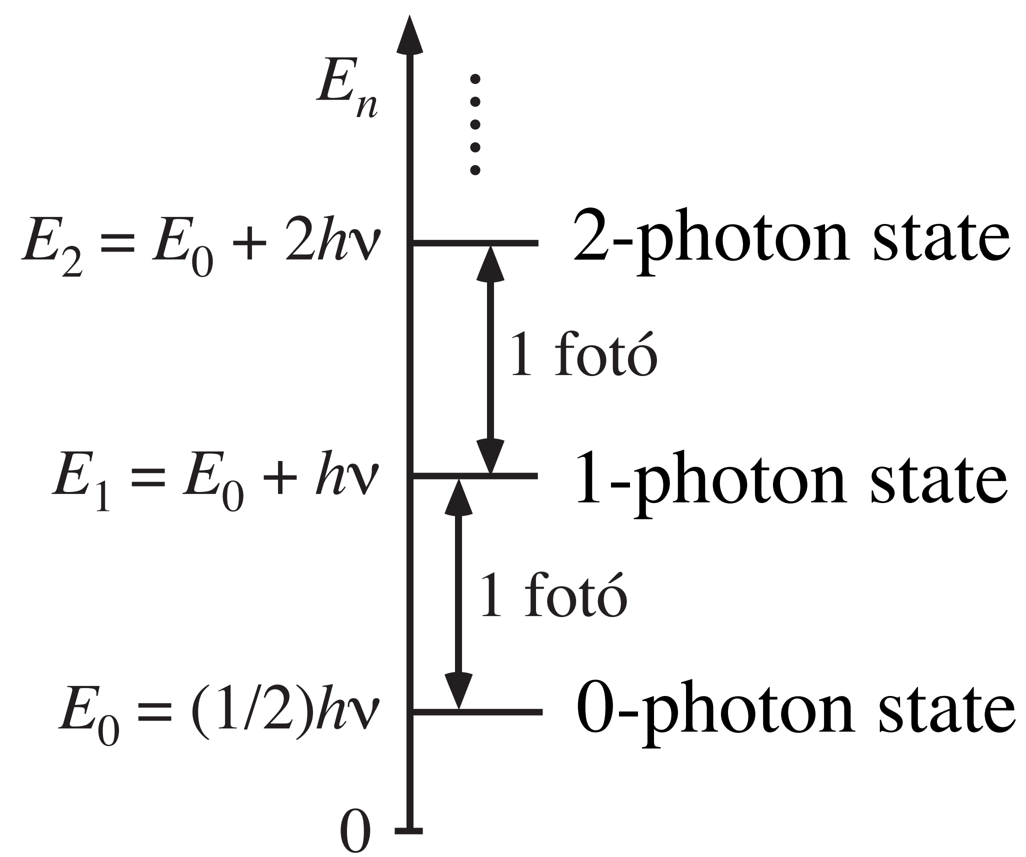
$$\frac{dN_s}{dt} = -N_s A_{si} \quad \rightarrow \quad N_s(t) = N_s(0) e^{-A_{si} t} \quad \rightarrow \quad \boxed{\tau_{si} = \frac{1}{A_{si}}}$$

Transition	$\left\| \left\langle \Phi_s \middle\| \hat{\vec{d}} \Phi_i \right\rangle \right\|$ / Cm	ν_{si}	τ_{si}
$2p_z \rightarrow 1s$	$6{,}3 \times 10^{-30}$	2467 THz	10^{-9} s
$(2s)\,^2S_{1/2} \rightarrow (2p)\,^2P_{1/2}$	25×10^{-30}	1058 MHz	20 years

Ratio: $/10^6$ $\times\ 10^{18}$

Ground state of radiation

$E_0 \neq 0$!!

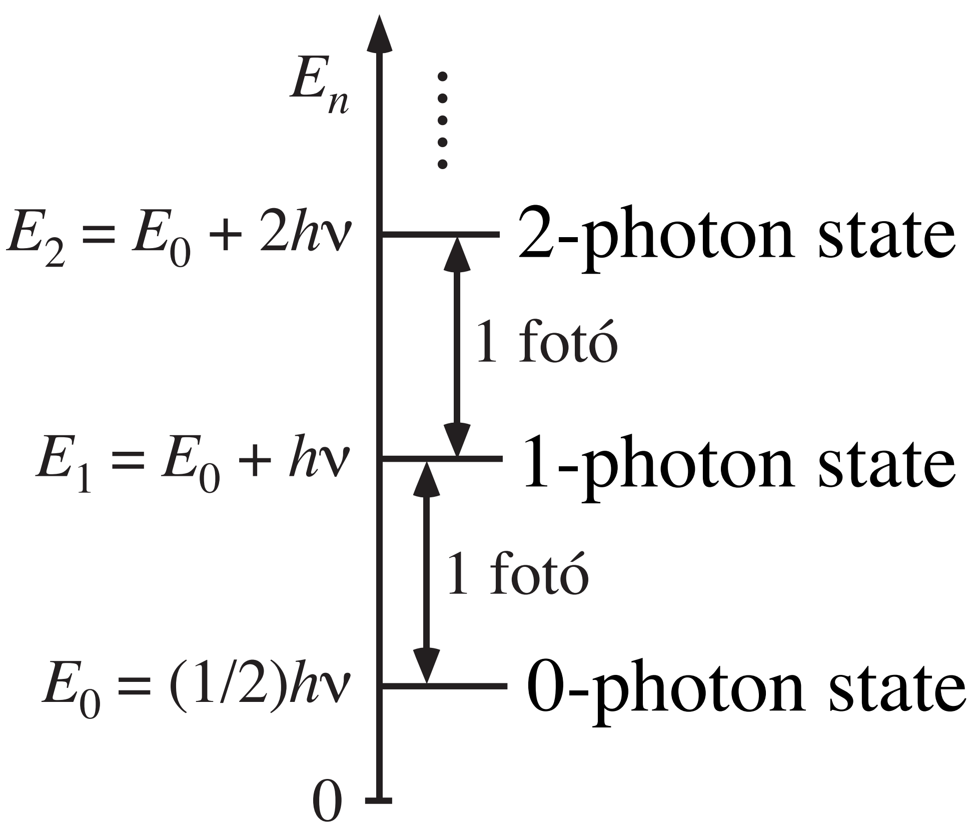


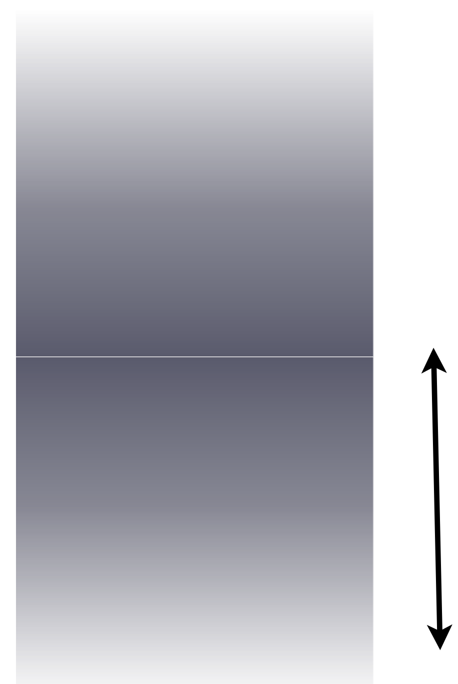
$$E_{vacuum} = \int_0^\infty \frac{1}{2} h d\nu \qquad E_n = \int_{\mathcal{R}^3} \left(\frac{\varepsilon_0}{2} \overset{?}{\left\langle F^2 \right\rangle} + \frac{1}{2\mu_0} \overset{?}{\left\langle B^2 \right\rangle} \right) d\vec{r}$$

Physical *vs* classical vacuum

$E = mc^2$ ⇒ electron-positron pairs can be created from photons with $h\nu \geq 2m_e c^2$

$$\tau_\Psi \Delta_\Psi H \geq \hbar/2$$

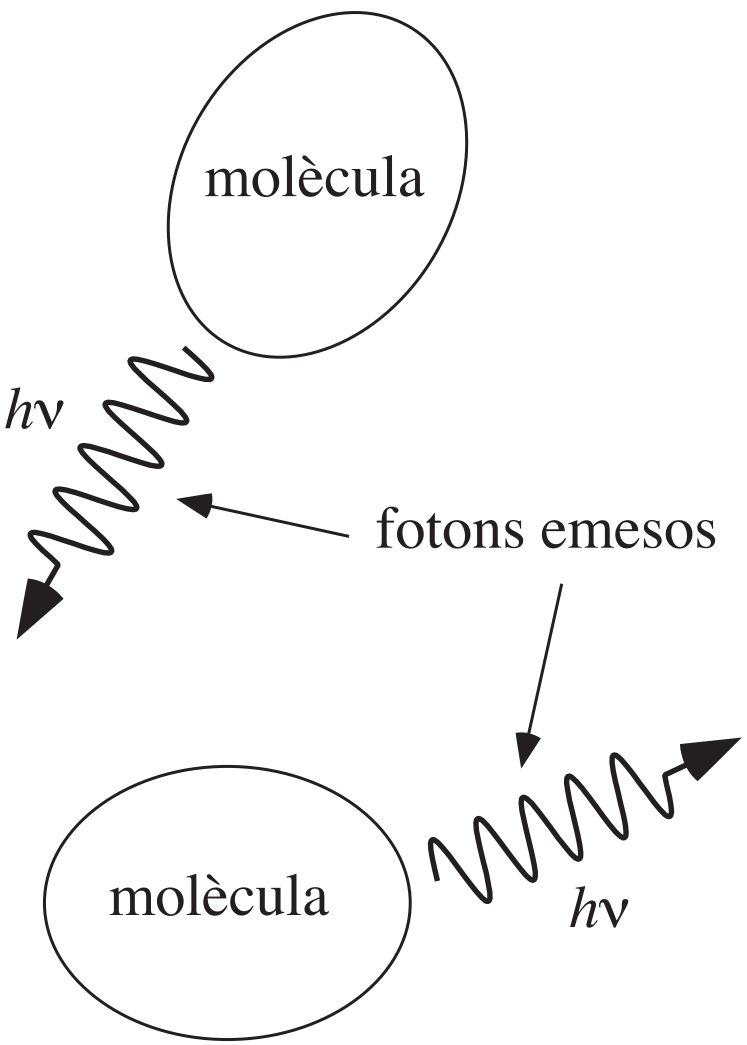


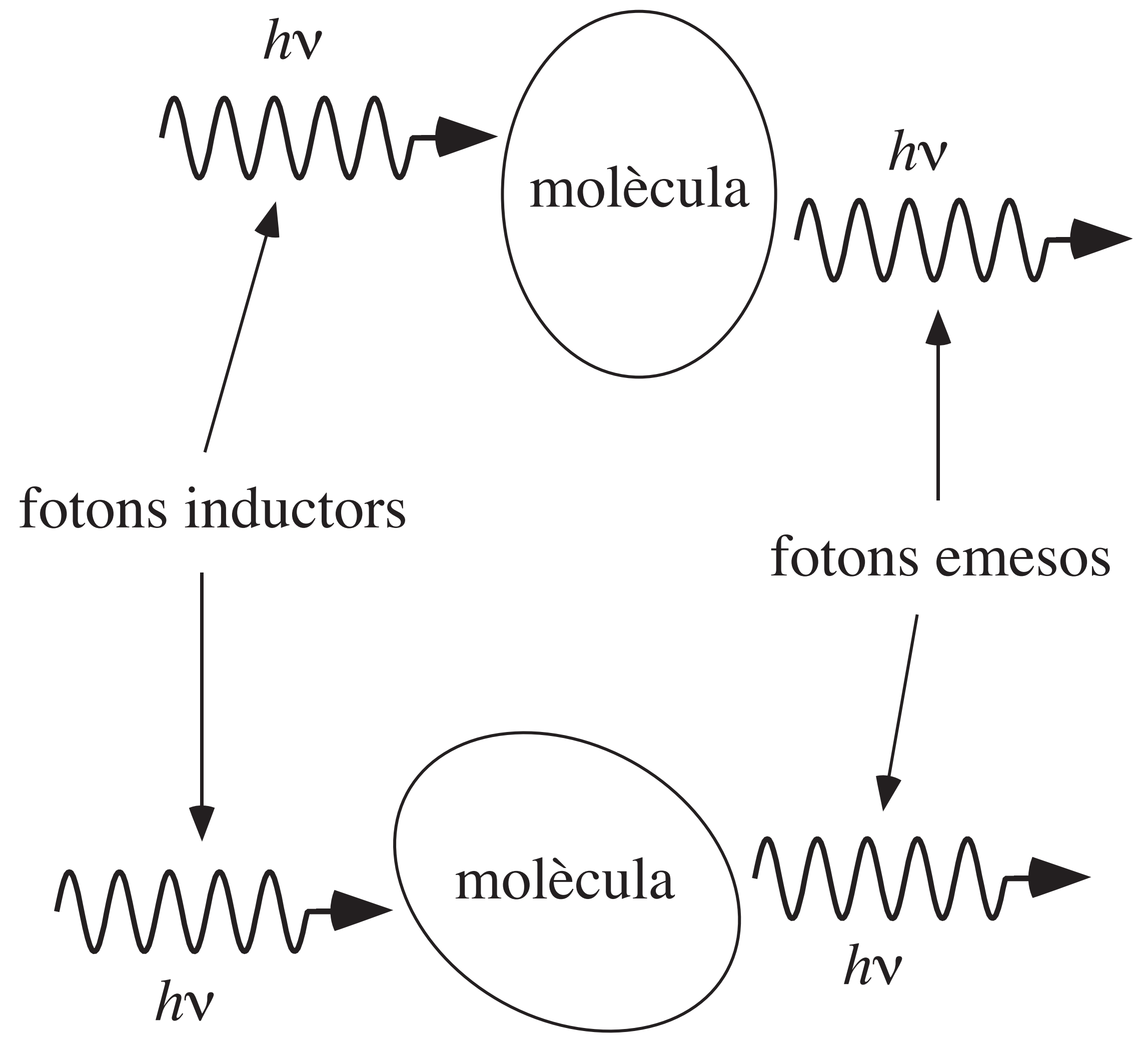


$$\Delta_\Psi H > h\nu = 2m_e c^2$$

$g_e = -2.002\ 319\ 304\ 361\ 82\ (2017)$

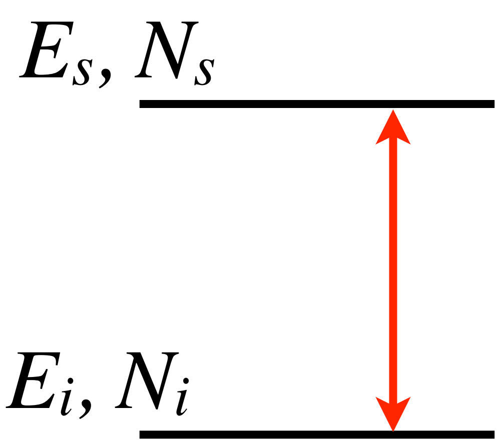
Spontaneous *vs* induced emission





LASER

Relaxation



$$\left.\begin{array}{c}\text{therm. equil.}\\ u(\nu_{si}) = 0\end{array}\right\}$$

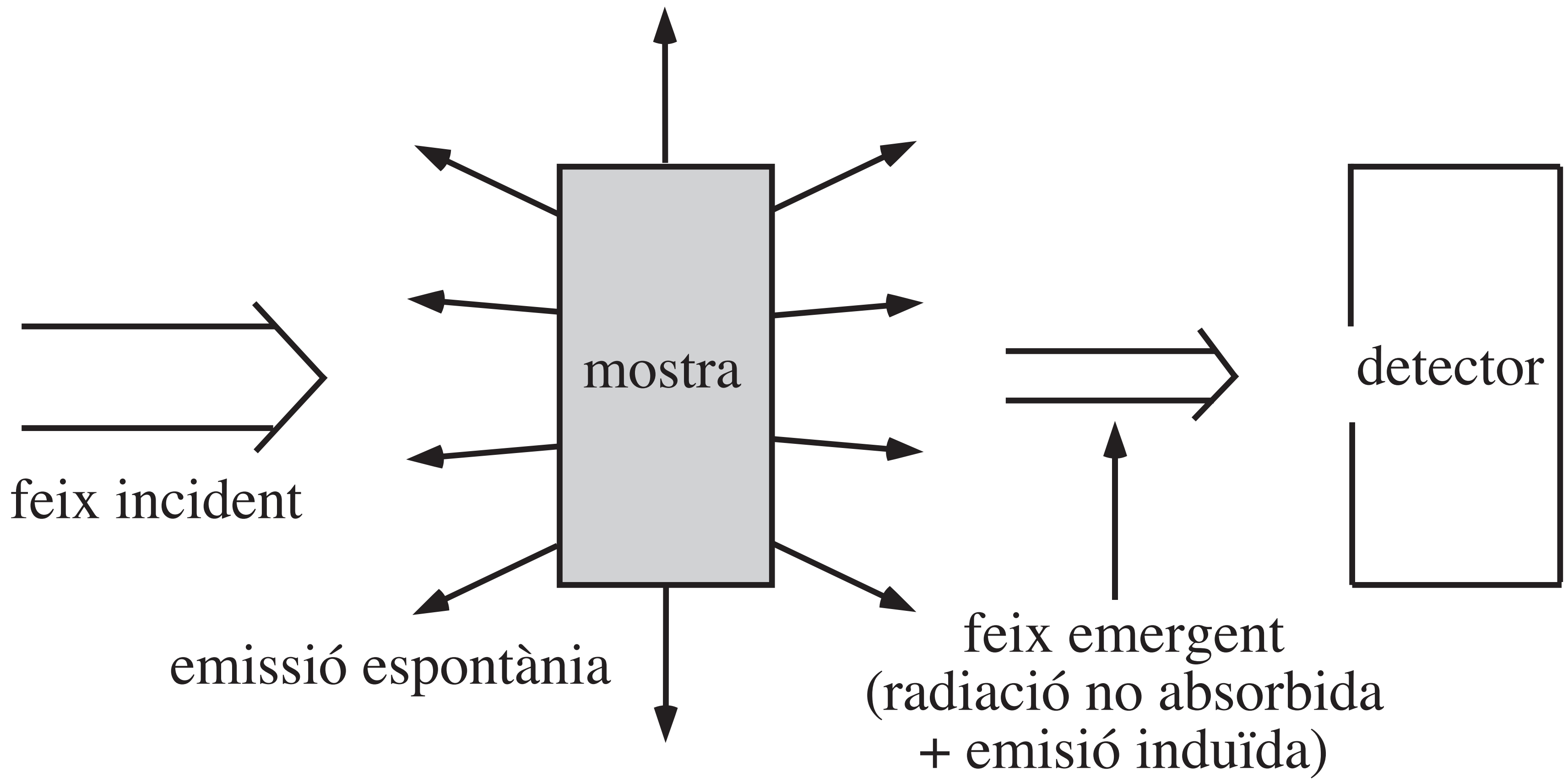
$$\overbrace{N_{i,eq}R_{s\leftarrow i}} = \overbrace{N_{s,eq}(A_{si} + R_{s\rightarrow i})}$$

$$\boxed{\frac{N_{s,eq}}{N_{i,eq}} = \frac{R_{s\leftarrow i}}{A_{si} + R_{s\rightarrow i}} = e^{-h\nu_{si}/k_B T}}$$

Boltzmann law

ν_{si}	10^4 THz (*UV*)	500 THz (*vis*)	200 THz (*NIR*)	30 THz (*MIR*)	3 THz (*FIR*)	100 GHz (*MW*)	500 MHz (*RF*)
25ºC	10^{-699}	10^{-35}	10^{-14}	10^{-2}	0,6	0,98	0,99992
–150ºC	≈ 0	10^{-85}	10^{-34}	10^{-5}	0,3	0,96	0,99989

Absorbed energy



$$\frac{dE_{abs}}{dt} = \overbrace{N_i B_{si} u(\nu_{si})(E_s - E_i)} - \overbrace{N_s B_{si} u(\nu_{si})(E_s - E_i)}$$

$$= (N_i - N_s)\, B_{si} u(\nu_{si}) h\nu_{si}$$

High frequencies (> FIR)

$$\frac{N_{s,eq}}{N_{i,eq}} = \frac{R_{s\leftarrow i}}{A_{si} + R_{s\rightarrow i}} = e^{-h\nu_{si}/k_B T} \ll 1 \quad \Rightarrow \quad A_{si} + R_{s\rightarrow i} \gg R_{s\leftarrow i}$$

- A small increment of N_s produced by absorption is quickly compensated by relaxation (spont. emission half-live $< 10^{-2}$ s).
- $N_i \approxeq N_{i,eq} \approxeq N$

$$\frac{dE_{abs}}{dt} = (N_i - N_s)\, B_{si} u(\nu_{si}) h\nu_{si} \approx N B_{si} u(\nu_{si}) h\nu_{si}$$

- Good sensitivity; good for *quantitative analysis* (simple relationship between N and absorption intensity); qualitative analysis, structural determination, material characterization, etc. (UV-vis, IR...)

Low frequencies (< FIR)

$$\frac{N_{s,eq}}{N_{i,eq}} = \frac{R_{s\leftarrow i}}{A_{si} + R_{s\rightarrow i}} = e^{-h\nu_{si}/k_B T} \approx 1 \qquad \text{and} \qquad A_{si} \approx 0$$

$$\frac{dE_{abs}}{dt} = (N_i - N_s)\, B_{si} u(\nu_{si}) h\nu_{si}$$

$(N_i - N_s) << N$ and depends on $T \Rightarrow dE_{abs}/dt \propto N$ only under controlled conditions.

- Absorption tends to equate N_i and N_s $(R_{s\rightarrow i} \eqsim R_{s\rightarrow i}) \Rightarrow (N_i - N_s)$ and dE_{abs}/dt decrease with the irradiation time (*saturation*).

- Low sensitivity; quantitative analysis requires careful calibration; good for qualitative analysis, structural determination, materials characterization, etc. (ESR, NMR, NQR, MW, ...)