Some topics of physical chemistry

Density functional theory

Termodinámica estadística

Intermolecular interactions

Bases de l'espectroscòpia

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Density functional theory (method)

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Bibliografía: J. C. Paniagua & P. Alemany, *Química Quàntica*, § 6.5.17

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Hohenberg-Kohn theorems

One-electron density:

$$\rho(\vec{r}) = n \int_{\omega_1} \int_{\vec{r}_2} \int_{\omega_2} \ldots \int_{\vec{r}_n} \int_{\omega_n} |\Psi_{el}(\vec{r}, \omega_1, \vec{r}_2, \omega_2, \ldots \vec{r}_n, \omega_n)|^2 \, d\omega_1 d\vec{r}_2 d\omega_2 \ldots d\vec{r}_n d\omega_n$$

many Ψ's $\rightarrow$ same ρ

$$\int_{\mathcal{R}^3} \rho(\vec{r}) d\vec{r} = n$$

1st HK theorem: $\boxed{\rho_0 \longrightarrow \widehat{H_{el}} \longrightarrow \text{any stationary-state electronic wf}}$

2nd HK theorem: $\boxed{E_0 = \min_{\rho} E[\rho]}$ (similar to $E_0 = \min_{\psi} W[\psi] = \min_{\psi} \langle \psi | \widehat{H_{el}} \psi \rangle$)

The energy functional

$$\widehat{H_{el}} = \widehat{T_{el}} + \widehat{V_{el}} + \widehat{V_{nuc-el}} \qquad \widehat{T_{el}} = \sum_{i=1}^{n} -\frac{\nabla_i}{2} \qquad \widehat{V_{el}} = \sum_{i=1}^{n-1}\sum_{j>i}^{n} \frac{1}{r_{ij}} \qquad \widehat{V_{nuc-el}} = \sum_{i=1}^{n} v_{ne}(\vec{r}_i)$$

External potential (energy): $v_{ne}(\vec{r}_i) = \sum_{A=1}^{N} -\frac{Z_A}{r_{iA}}$ (any local, multiplicative, spin-independent operator)

$$E[\rho] = F[\rho] + V_{nuc-el}[\rho]$$

$$F[\rho] \equiv \min_{\Psi_\rho} \left\langle \Psi_\rho \middle| \left(\widehat{T_{el}} + \widehat{V_{el}}\right) \Psi_\rho \right\rangle = T[\rho] + V_{el}[\rho]$$

a UNIVERSAL functional (the same for *any* n-electron system)

$$\langle V_{nuc-el} \rangle = \int_{\vec{r}} v_{ne}(\vec{r})\rho(\vec{r})d\vec{r}$$

straightforward to calculate

$\rho(x,y,z)$ is a much simpler object than $\Psi(x_1,y_1,z_1,\omega_1,\ldots\ x_n,y_n,z_n,\omega_n)$ (the number of variables does not increase with the size of the system)

Kohn-Sham method

$$\boxed{\Phi^{KS}(\vec{w}_1, \ldots \vec{w}_n) = \frac{1}{\sqrt{n!}} \left| \psi_1^{KS}(\vec{w}_1) \ldots \psi_n^{KS}(\vec{w}_n) \right|} \quad \text{with} \quad \rho^{KS} = \rho_0$$

$$\psi_i^{KS}(\vec{w}) = \phi_i^{KS}(\vec{r}) g_i(\omega) \qquad \boxed{\widehat{h^{KS}}(\vec{r}) \phi_i^{KS}(\vec{r}) = \epsilon_i^{KS} \phi_i^{KS}(\vec{r})}$$

$$\widehat{h^{KS}}(\vec{r}) = -\frac{\nabla^2}{2} + v_{ne}(\vec{r}) + v_{re}^{KS}(\rho_0, \vec{r}) + v_{xc}(\rho_0, \vec{r}) \quad \text{SCF}$$

$$E[\rho] = F[\rho] + V_{nuc-el}[\rho]$$

$$\downarrow$$

$$F[\rho] = T[\rho] + V_{el}[\rho] = T^{KS}[\rho] + J[\rho] + E_{xc}[\rho]$$

Many exchange-correlation functionals $E_{xc}[\rho]$: BP86, PBE, B3LYP, PBE0, ...

Termodinámica estadística

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Bibliografía: I. N. Levine: *Fisicoquímica*, cap. 22

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Termodinámica estadística

- *Mecánica estadística*: deducir las propiedades macroscópicas de la materia a partir de propiedades de las moléculas o partículas que la componen y las interacciones entre ellas.

- *Termod. estad.* = ME de sistemas en equilibrio termodinámico.

- Sistema macroscópico:
  - ★ *Estado termodinámico* o *macroestado*: queda determinado fijando los valores de un número suficiente de propiedades termodinámicas (P, T, V, comp., ...).
  - ★ *Estado cuántico* o *microestado*: queda determinado mediante la función de onda del sistema macrosc. (máxima información posible).

Hipótesis ergódica

- El valor que se obtiene al medir una propiedad macroscópica en un sistema en equilibrio termod. es un promedio a lo largo del tiempo que dura la medida. Calcular teóricamente tales promedios es difícil, por lo que supondremos que, *para las propiedades mecánicas**, se obtiene el mismo resultado calculando un promedio *ponderado* sobre un conjunto de microestados (un *colectivo*) que tengan ciertas propiedades iguales a las del sistema (**hipótesis ergódica**).

  - ★ Para calcular los promedios ponderados sobre el colectivo de microestados necesitamos conocer el *peso* que debemos dar a cada uno, también llamado *probabilidad* (p_j) del microestado.

  - ★ *Por ej.*: Energía interna termodinámica (no SEP): $U = \langle E_j \rangle_{colectivo} = \sum_{j}^{microest} p_j E_j$

*Las propiedades *mecánicas* son las que definen el sistema cuántico o pueden calcularse a partir de sus funciones de onda: N, V, E, P, $H{=}U{+}PV$... Las demás propiedades son *térmicas*: T, S, A, G, μ, C_P, C_V ..., y se determinan a partir de las mecánicas utilizando relaciones termodinámicas.

Máxima entropía

- **Principio de máxima entropía estadística**: de entre todas las posibles distribuciones de probabilidad de los microestados del colectivo (p_1, p_2,...) se ha de escoger la de mayor *entropía estadística* (la menos sesgada). Ésta entropía de define como $S = -k \sum_j p_j \ln p_j$ ($k = k_B = 1{,}38066$ x 10^{-23} JK^{-1}).

★ *Dado*: si sólo sé que la media de muchas tiradas es 3,5 la distribución de probabilidades podría ser, por ejemplo, $\{1/2, 0, 0, 0, 0, 1/2\}$ ($S \approx k \ln 2 \approx 0{,}7k$), pero la más plausible (la menos sesgada) será la que asigne la misma probabilidad a cada cara: $\{1/6, 1/6, 1/6, 1/6, 1/6, 1/6\}$ ($S_{max} \approx k \ln 6 \approx 1{,}8k$).

★ Distribución de velocidades de la moléculas de un gas a una temperatura.

Colectivo canónico

- Consideremos un sistema macroscópico en un estado de equilibrio termodinámico caracterizado por V, N_B, N_C, ... (composición) y T.

- Calcularemos las propiedades mecánicas del macroestado como promedios ponderados sobre el colectivo "*canónico*", formado por todos los *microestados estacionarios* del sistema:

$$\{\Psi_j\} \quad \text{tales que} \quad \widehat{H}\Psi_j = E_j\Psi_j \qquad E_j(V, N_B, N_C, \cdots)$$

del sistema macroscópico

- *Ejemplo*: $$U = \langle E_j \rangle_{colect.\ can\acute{o}nico} = \sum_{j}^{microest.\ estac.} p_j E_j$$

Probab. de un microestado

- Aplicando el principio de máxima S se demuestra que la probabilidad de un microestado estacionario de energía E_j es:

$$\boxed{p_j = \frac{e^{-\frac{E_j}{kT}}}{Z}}$$

★ *Función de partición canónica*:

(papel ≈ Ψ en mec. cuántica)

$$\boxed{Z = \sum_{j}^{microest} e^{-\frac{E_j}{kT}}}$$

★ Probabilidad del *nivel* de energía E_j :

$$p(E_j) = \frac{d_j e^{-\frac{E_j}{kT}}}{Z} \qquad (d_j = \text{degeneración de } E_j)$$

(pico muy pronunciado en torno a $E_j = U$)

- Basta conocer los valores propios del hamiltoniano i T para obtener Z.

Demostración

Tenemos que maximizar $S = -k\sum_j p_j \ln p_j$ respecto de cada p_j con las restricciones $\sum_j p_j = 1$ y $\sum_j p_j E_j = U$

$$\frac{\partial}{\partial p_j}\left[-k\sum_j p_j \ln p_j + \alpha\left(\sum_j p_j - 1\right) + \beta\left(\sum_j p_j E_j - U\right)\right] = 0$$

$$-k(\ln p_j + 1) + \alpha + \beta E_j = 0 \quad \Rightarrow \quad \ln p_j = \frac{\alpha + \beta E_j}{k} - 1 \quad \Rightarrow \quad p_j = e^{\frac{\alpha}{k} + \frac{\beta E_j}{k} - 1} = cte\, e^{\frac{\beta E_j}{k}}$$

$$1 = \sum_j p_j = cte \sum_j e^{\frac{\beta E_j}{k}} \quad \Rightarrow \quad cte = \frac{1}{\sum_j e^{\frac{\beta E_j}{k}}} \equiv \frac{1}{Z} \quad \Rightarrow \quad p_j = \frac{e^{\frac{\beta E_j}{k}}}{Z}$$

$$S = -k\sum_j p_j \ln p_j = -k\sum_j p_j\left(\frac{\beta E_j}{k} - \ln Z\right) = k\ln Z - \beta U \quad \Rightarrow \quad -\beta = \left(\frac{\partial S}{\partial U}\right)_{V,N}$$

Termodinámica: $\left.\begin{array}{l} dU = TdS - PdV \\ dS = \frac{1}{T}dU + \frac{P}{T}dV \end{array}\right\} \Rightarrow \left(\frac{\partial S}{\partial U}\right)_{V,N} = \frac{1}{T} \quad \Rightarrow \quad \beta = -\frac{1}{T} \quad \Rightarrow \quad \boxed{p_j = \frac{e^{-\frac{E_j}{kT}}}{Z}}$

Energía interna

- 1 fase y 1 componente (se puede generalizar): $\boxed{Z = \sum_{j}^{microest} e^{-\frac{E_j}{kT}}}$

$$\left(\frac{\partial Z}{\partial T}\right)_{V,N} = \sum_{j}^{microest} e^{-\frac{E_j}{kT}} \frac{E_j}{kT^2} \frac{Z}{Z} = \frac{Z}{kT^2} \sum_{j}^{microest} p_j E_j = \frac{Z}{kT^2} U$$

$$\boxed{U = \frac{kT^2}{Z}\left(\frac{\partial Z}{\partial T}\right)_{V,N} = kT^2\left(\frac{\partial \ln Z}{\partial T}\right)_{V,N}}$$

Presión

- Si cambiamos V reversiblemente a N cte. cambiarán las E_j

★ *Ejemplo*: moléculas no interact. en una caja tridimensional cúbica:

$$\boxed{Z = \sum_{j}^{microest} e^{-\frac{E_j}{kT}}}$$

$$E_{n_x,n_y,n_z} = \frac{h^2}{8ma^2}(n_x^2+n_y^2+n_z^2) = \frac{h^2}{8mV^{2/3}}(n_x^2+n_y^2+n_z^2)$$

★

$$\left(\frac{\partial Z}{\partial V}\right)_{T,N} = \sum_{j}^{micr}\left(\frac{\partial e^{-\frac{E_j}{kT}}}{\partial E_j}\right)_{T,N}\left(\frac{\partial E_j}{\partial V}\right)_N = -\frac{1}{kT}\sum_{j}^{micr} e^{-\frac{E_j}{kT}}\frac{Z}{Z}\underbrace{\left(\frac{\partial E_j}{\partial V}\right)_N}$$

★ Si solo hay trabajo de expansión:

$$dE_j = dw_{rev} = -P_j dV \quad \Rightarrow \quad P_j = -\left(\frac{\partial E_j}{\partial V}\right)_N$$

$$\left(\frac{\partial Z}{\partial V}\right)_{T,N} = \frac{Z}{kT}\sum_{j}^{micr} p_j P_j = \frac{Z}{kT}P$$

$$\boxed{P = \frac{kT}{Z}\left(\frac{\partial Z}{\partial V}\right)_{T,N} = kT\left(\frac{\partial \ln Z}{\partial V}\right)_{T,N}}$$

Otras propiedades termod.

- *Entropía*: $S = -k\sum_j p_j \ln p_j = -k\sum_j p_j \ln \frac{e^{-\frac{E_j}{kT}}}{Z} = -k\sum_j p_j \left(-\frac{E_j}{kT} - \ln Z\right)$

$$= \frac{U}{T} + k\ln Z = kT\left(\frac{\partial \ln Z}{\partial T}\right)_{V,N} + k\ln Z$$

- *Energía de Helmholtz*: $A = U - TS = -kT\ln Z$

- *Entalpía*: $H = U + PV$

- *Energía de Gibbs*: $G = A + PV = H - TS$

- *Potencial químico*:

$$\mu_B = \left(\frac{\partial A}{\partial n_B}\right)_{T,V,n_{C\neq B}} = -kT\left(\frac{\partial \ln Z}{\partial n_B}\right)_{T,V,n_{C\neq B}} = -\overset{kN_A}{R}T\left(\frac{\partial \ln Z}{\partial N_B}\right)_{T,V,N_{C\neq B}}$$

N_B/N_A

Moléculas indep. disting.

- *Por ejemplo*: las moléculas de un *sólido molecular*.

$$\widehat{H} = \widehat{H_1} + \widehat{H_2} + \cdots \widehat{H_N} \qquad E_j = \varepsilon_{1s} + \varepsilon_{2t} + \cdots \varepsilon_{Nw}$$

$$Z = \sum_{j}^{microest} e^{-\frac{\varepsilon_{1s}+\varepsilon_{2t}+\cdots\varepsilon_{Nw}}{kT}} = \sum_{s}^{estMol1} \sum_{t}^{estMol2} \cdots \sum_{w}^{estMolN} e^{-\frac{\varepsilon_{1s}}{kT}} e^{-\frac{\varepsilon_{2t}}{kT}} \cdots e^{-\frac{\varepsilon_{Nw}}{kT}}$$

Def.: *Función de partición molecular* de la moléc. 1: $z_1 = \sum_{s}^{estMol1} e^{-\frac{\varepsilon_{1s}}{kT}}$

$$Z = z_1 z_2 \cdots z_N$$

- Si todas las moléculas son del mismo tipo: $Z = z^N$
- Si hay N_B moléculas del tipo B, N_C moléculas del tipo C, ...: $Z = {z_B}^{N_B}\ {z_C}^{N_C} \ldots$

Moléculas indep. indisting.

- *Gas ideal puro* (1 componente):

★ *Supondremos que núm. estados moleculares accesibles* $\gg N$ ($\langle N_s \rangle \ll 1$, trasl.) $\Rightarrow$ es enormemente improbable que haya >1 moléc. en un mismo estado.

- *Estadística clásica*: válido excepto a T muy baja ($He_{(l)}$) y/o ρ muy alta (estrellas de n) y/o m muy pequeña (e^- de conducción de un metal) $\Rightarrow$ *estadística cuántica* (bosones $\neq$ fermiones).

★ Moléc. 1 en s y moléc. 2 en t es indistinguible de moléc. 1 en t y moléc. 2 en s $\Rightarrow$ mismo microestado. Para N moléculas $N!$ permutaciones $\Rightarrow$ *núm. microest. partíc. indisting.* = *núm. microest. partíc. disting.* / $N!$

$$Z = \sum_{s}^{estMol1} \sum_{t}^{estMol2} \cdots \sum_{w}^{estMolN} e^{-\frac{\varepsilon_{1s}}{kT}} e^{-\frac{\varepsilon_{2t}}{kT}} \cdots e^{-\frac{\varepsilon_{Nw}}{kT}} / N! = \frac{z^N}{N!}$$

Moléculas indep. indisting.

$$\varepsilon_s = \varepsilon_{tr,t} + \varepsilon_{rot,r} + \varepsilon_{vib,v} + \varepsilon_{el,u}$$

$$\boxed{z = \sum_{s}^{estMol} e^{-\frac{\varepsilon_s}{kT}}} = \sum_{t}^{estTr} \sum_{r}^{estRot} \sum_{v}^{estVib} \sum_{u}^{estEl} e^{-\frac{\varepsilon_{tr,t}+\varepsilon_{rot,r}+\varepsilon_{vib,v}+\varepsilon_{el,u}}{kT}}$$

$$= \boxed{\sum_{t}^{estTr} e^{-\frac{\varepsilon_{tr,t}}{kT}}} \boxed{\sum_{r}^{estRot} e^{-\frac{\varepsilon_{rot,r}}{kT}}} \boxed{\sum_{v}^{estVib} e^{-\frac{\varepsilon_{vib,v}}{kT}}} \boxed{\sum_{u}^{estEl} e^{-\frac{\varepsilon_{el,u}}{kT}}}$$

$$= z_{tr}\, z_{rot}\, z_{vib}\, z_{el}$$

$$\ln Z = \ln \frac{z^N}{N!} = N \ln z - \ln N! = N(\ln z_{tr} + \ln z_{rot} + \ln z_{vib} + \ln z_{el}) - \ln N!$$

$$U = kT^2 \left(\frac{\partial \ln Z}{\partial T}\right)_{V,N} = NkT^2 \left(\frac{\partial \ln z_{tr}}{\partial T}\right)_{V,N} + NkT^2 \left(\frac{\partial \ln z_{rot}}{\partial T}\right)_{V,N} + \cdots - \underbrace{\left(\frac{\partial \ln N!}{\partial T}\right)_{V,N}}_{0}$$

$$= U_{tr} + U_{rot} + U_{vib} + U_{el}$$

Moléculas indep. indisting.

$$S = \frac{U}{T} + k \ln Z$$

$$= \frac{U_{tr}}{T} + \frac{U_{rot}}{T} + \frac{U_{vib}}{T} + \frac{U_{el}}{T} + kN(\ln z_{tr} + \ln z_{rot} + \ln z_{vib} + \ln z_{el}) - k \ln N!$$

Moléculas indep. indisting.

$$S = \frac{U}{T} + k \ln Z$$

$$= \frac{U_{tr}}{T} + \frac{U_{rot}}{T} + \frac{U_{vib}}{T} + \frac{U_{el}}{T} + kN(\ln z_{tr} + \ln z_{rot} + \ln z_{vib} + \ln z_{el}) - k \ln N!$$

$$= S_{tr} + S_{rot} + S_{vib} + S_{el}$$

consecuencia del movimiento traslacional

donde

$$S_{tr} = \frac{U_{tr}}{T} + k(N \ln z_{tr} - \ln N!)$$

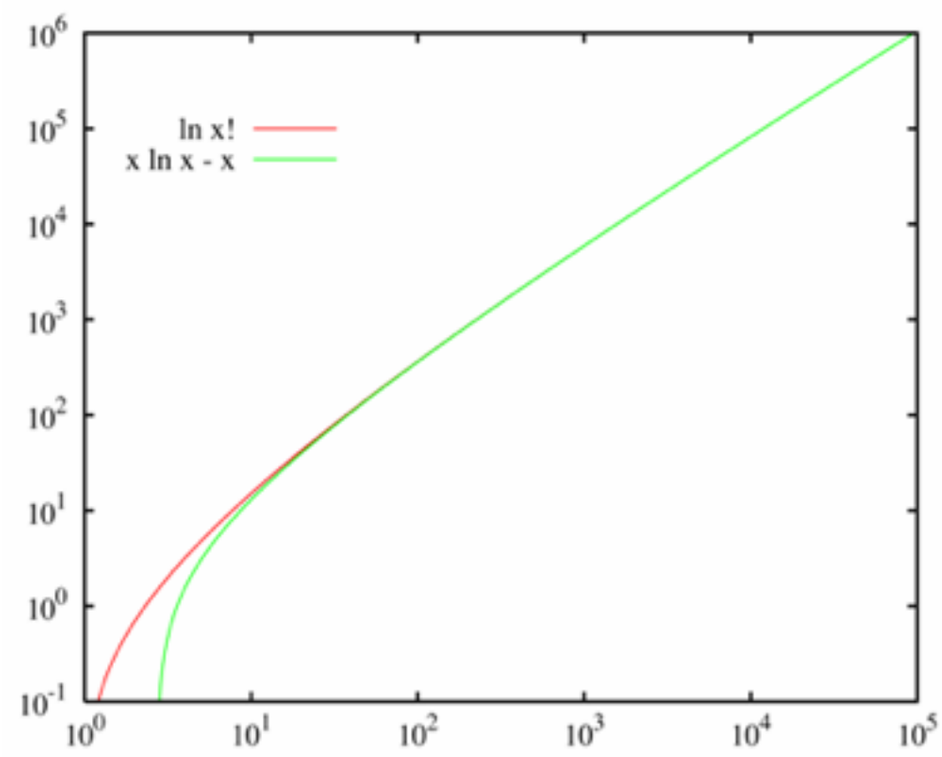
$$S_{rot} = \frac{U_{rot}}{T} + kN \ln z_{rot}$$

$$S_{vib} = \frac{U_{vib}}{T} + kN \ln z_{vib}$$

$$S_{el} = \frac{U_{el}}{T} + kN \ln z_{el}$$

Fórmula de Stirling (N↑↑):

$\ln N! \approx N \ln N - N$



Población de un est. molecular

- *Gas ideal puro* (moléculas independientes indistinguibles)

★ Energía de un microestado: $E_j = N_{sj}\,\boldsymbol{\varepsilon}_s + N_{tj}\,\boldsymbol{\varepsilon}_t + \ldots$

★ $$\langle N_s \rangle = \sum_j^{microest} p_j N_{sj} = \frac{\sum_j N_{sj} e^{-(N_{sj}\varepsilon_s + N_{tj}\varepsilon_t + \cdots)/kT}}{Z}$$

$$\left(\frac{\partial Z}{\partial \varepsilon_s}\right)_{T,N} = \frac{\partial}{\partial \varepsilon_s} \sum_j e^{-(N_{sj}\varepsilon_s + N_{tj}\varepsilon_t + \cdots)/kT}$$

$$= -\frac{1}{kT} \sum_j N_{sj} e^{-(N_{sj}\varepsilon_s + N_{tj}\varepsilon_t + \cdots)/kT}$$

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$$= -\frac{1}{kT} \boxed{\sum_j N_{sj} e^{-(N_{sj}\varepsilon_s + N_{tj}\varepsilon_t + \cdots)/kT}}$$

$$\langle N_s \rangle = -kT \frac{1}{Z} \left(\frac{\partial Z}{\partial \varepsilon_s}\right)_{T,N} = -kT \left(\frac{\partial \ln Z}{\partial \varepsilon_s}\right)_{T,N}$$

Ley de distr. de poblaciones

$$\langle N_s \rangle = -kT \left(\frac{\partial \ln Z}{\partial \varepsilon_s} \right)_{T,N}$$

no depende de $\boldsymbol{\varepsilon}_s$

$$\ln Z = \ln \frac{z^N}{N!} = N \ln z - \ln N!$$

$$\left(\frac{\partial \ln Z}{\partial \varepsilon_s} \right)_{T,N} = N \frac{\partial \ln z}{\partial \varepsilon_s} = \frac{N}{z} \frac{\partial z}{\partial \varepsilon_s} = \frac{N}{z} \frac{\partial \sum_t^{estMol} e^{-\frac{\varepsilon_t}{kT}}}{\partial \varepsilon_s} = -\frac{N}{zkT} e^{-\frac{\varepsilon_s}{kT}}$$

Ley de Boltzmann:
(pobl. estados molec.)

$$\boxed{\frac{\langle N_s \rangle}{N} = \frac{e^{-\frac{\varepsilon_s}{kT}}}{z}} \qquad \boxed{\frac{\langle N_s \rangle}{\langle N_t \rangle} = e^{-\frac{\varepsilon_s - \varepsilon_t}{kT}}} \qquad (\langle N_s \rangle \ll 1)$$

Ley de Boltzmann:
(pobl. niveles molec.)

$$\boxed{\frac{\langle N(\varepsilon_s) \rangle}{N} = \frac{d_s e^{-\frac{\varepsilon_s}{kT}}}{z}} = \frac{d_s e^{-\frac{\varepsilon_s}{kT}}}{\sum_t^{nivMol} d_t e^{-\frac{\varepsilon_t}{kT}}} \qquad \boxed{\frac{\langle N(\epsilon_s) \rangle}{\langle N(\epsilon_t) \rangle} = \frac{d_s}{d_t} e^{-\frac{\varepsilon_s - \varepsilon_t}{kT}}}$$

Gas ideal diatómico

- FP traslacional: caja de potencial de lados a, b y c

$$z_{tr} = \left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}} V \qquad \Delta\varepsilon_{tr} \ll kT$$

(válida para cualquier gas ideal puro)

- FP rotacional: rotor rígido (*núm. de simetría* $\sigma = 1$ para heteronuc. y 2 para homonuc.)

$$z_{rot} = \frac{T}{\sigma\Theta_{rot}} \qquad \Theta_{rot} \equiv \frac{\hbar^2}{2I_e k} = \frac{hB_e}{k} \ll T \quad (\Theta_{rot}\text{: temp. rot. caract.})$$

(válida para moléculas lineales)

- FP vibracional: $$z_{vib} = \frac{e^{-h\nu_e/2kT}}{1 - e^{-h\nu_e/kT}} = \frac{e^{-\Theta_{vib}/2T}}{1 - e^{-\Theta_{vib}/T}} \qquad \left(\Theta_{vib} = \frac{h\nu_e}{k}\right)$$

- FP electrónica: $$z_{el} = d_{el,0} \qquad (\varepsilon_{el,0} = 0 \quad \text{y} \quad \varepsilon_{el,1} - \varepsilon_{el,0} \gg kT)$$

(válida para cualquier gas ideal puro)

Gas ideal diatómico

- Energia interna:

(diapo 13)

$$U_{tr} = NkT^2 \left(\frac{\partial \ln z_{tr}}{\partial T} \right)_{V,N} = \frac{3}{2} nRT$$ (válida para cualquier gas ideal puro*)

$$U_{rot} = nRT$$ (válida para moléculas lineales*; $(3/2)nRT$ para moléculas no lineales*)

$$U_{vib} = nR\frac{h\nu}{k} \left(\frac{1}{2} + \frac{1}{e^{h\nu_e/kT} - 1} \right) = nR\Theta_{vib} \left(\frac{1}{2} + \frac{1}{e^{\Theta_{vib}/T} - 1} \right)$$

$$U_{el} = 0$$ (válida para cualquier gas ideal puro*)

*en las condiciones indicadas en la diapositiva anterior

Intermolecular interactions

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Bibliografía: J. C. Paniagua & P. Alemany, *Química Quàntica*, § 7.3
I. N. Levine: *Fisicoquímica*, § 22.10

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Electric multipoles

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

a detailed information about the charge distribution is needed

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

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

Electric multipoles

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

a detailed information about the charge distribution is needed

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

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

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

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

Electric multipoles

- 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)

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

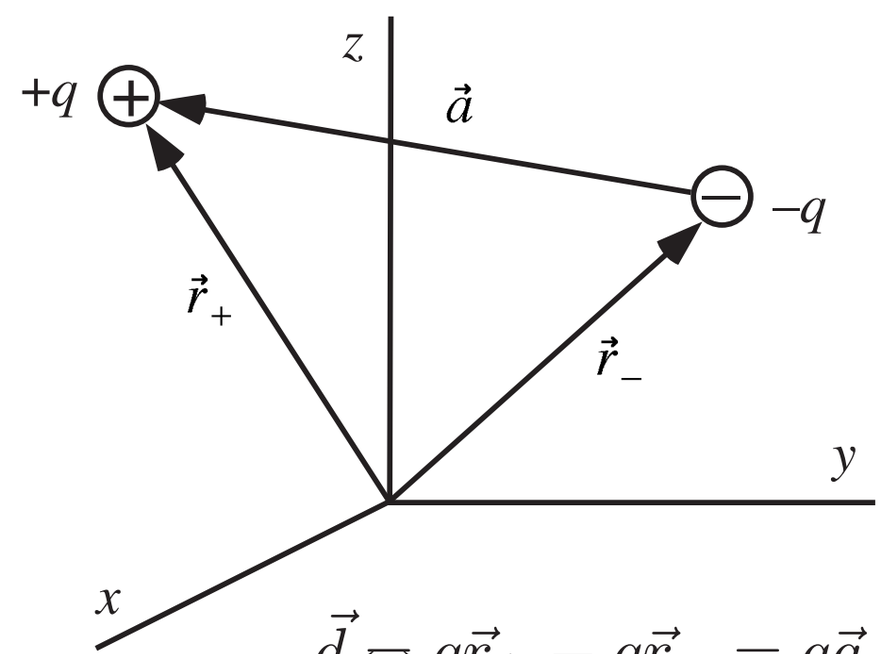
first-order electric moment (electric dipole)

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

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)*



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

Magnetic multipoles

- Moving charges in a time-dependent EM field:

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

Dipolar approximation

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

Polarizability

- *Static* electric field:
  - *static* polarizability

$$\begin{pmatrix} d_x(\vec{F}) \\ d_y(\vec{F}) \\ d_z(\vec{F}) \end{pmatrix} = \begin{pmatrix} d_x(\vec{0}) \\ d_y(\vec{0}) \\ d_z(\vec{0}) \end{pmatrix} + \boxed{\begin{pmatrix} \alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\ \alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\ \alpha_{zx} & \alpha_{zy} & \alpha_{zz} \end{pmatrix}} \begin{pmatrix} F_x \\ F_y \\ F_z \end{pmatrix} + \cdots$$

permanent electric dipole moment

induced electric dipole moment

- *Time-dependent* electric field:
  - *dynamic* or *frequency-dependent* polarizability

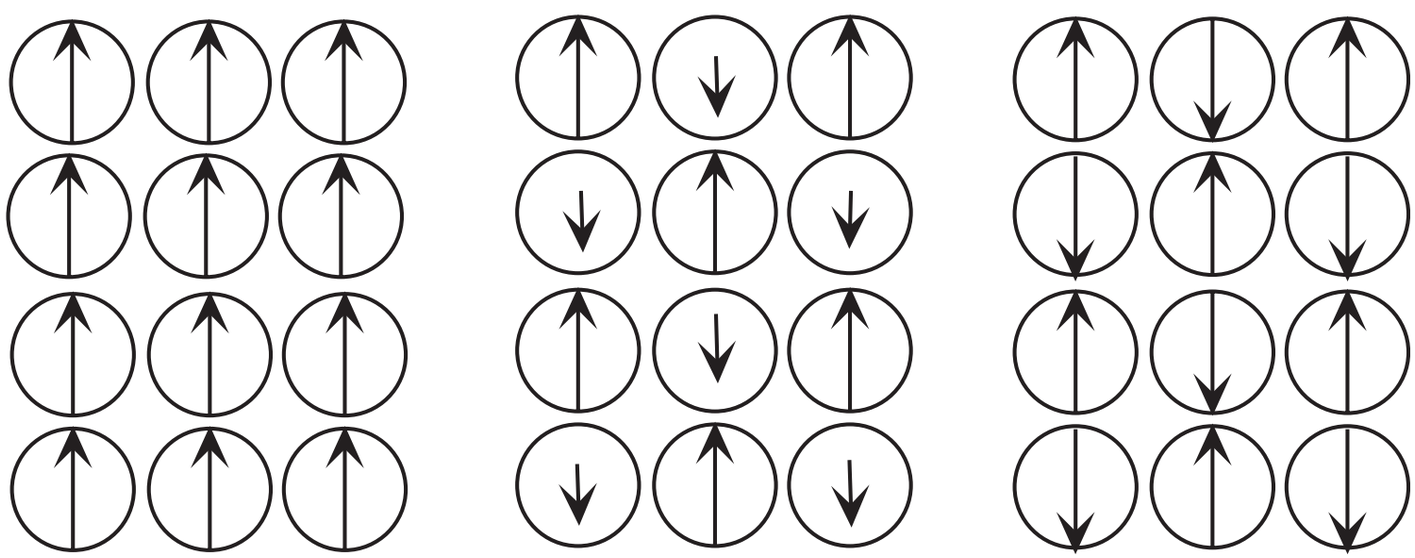
Polarization & magnetization

$$\vec{P} = \chi_e \varepsilon_0 \vec{F}$$

$$\chi_e = \varepsilon_r - 1$$

$$\vec{M} = \chi_m \frac{1}{\mu} \vec{B}$$

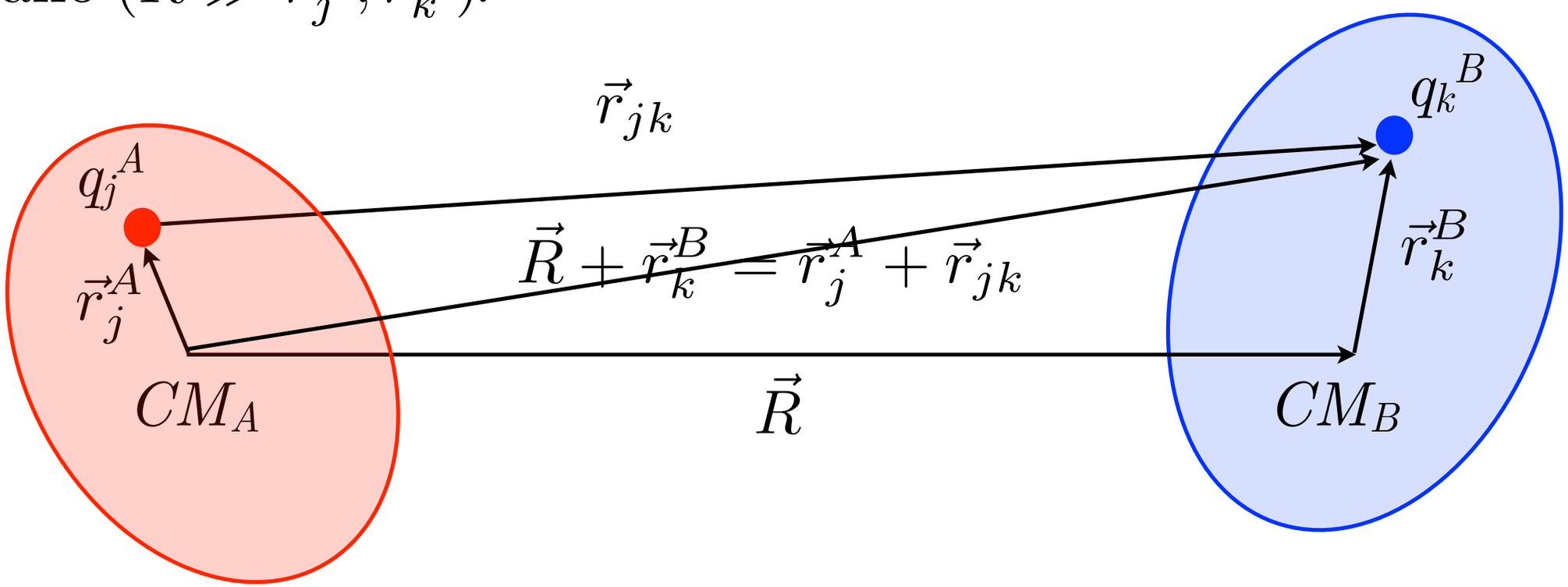
$$\chi_m = \mu_r - 1$$



Ferromagnetic Ferrimagnetic Antiferromagnetic

Interac. intermoleculares

- 2 moléculas separadas una distancia grande en relación con su tamaño ($R \gg r_j^A, r_k^B$):



$$E_{intAB} = \sum_{j=1}^{n_A}\sum_{k=1}^{n_B} \frac{1}{4\pi\varepsilon_0}\frac{q_j^A q_k^B}{r_{jk}} = \sum_{j=1}^{n_A}\sum_{k=1}^{n_B} \frac{1}{4\pi\varepsilon_0}\frac{q_j^A q_k^B}{\left|\vec{R} + \vec{r}_k^B - \vec{r}_j^A\right|} = \cdots$$

Cargas estáticas

- Distribuciones de carga estáticas (sin considerar la polarización de una molécula por el campo producido por la otra, ni el movimiento de las moléculas, ni interacciones a 3 cuerpos):

★ int. carga-carga: $E_{qq} = \dfrac{q_A q_B}{4\pi\varepsilon_0}\dfrac{1}{R}$

★ int. carga-dipolo: $E_{qd} = \dfrac{q_A d_B + q_B d_A}{4\pi\varepsilon_0}\dfrac{1}{R^2}$

★ int. carga-cuadrupolo y dipolo-dipolo: $E_{qQ} = \dfrac{q_A Q_B + Q_B q_A}{4\pi\varepsilon_0}\dfrac{1}{R^3}$

★ ... $E_{dd} = \dfrac{d_A d_B + d_B d_A}{4\pi\varepsilon_0}\dfrac{1}{R^3}$

★ int. entre multipolos de órdenes n y m: $\propto R^{-(n+m+1)}$

Atracción de van der Waals

- Los movimientos moleculares (rotaciones, ...) hacen que debamos promediar las interacciones ponderando de acuerdo con la ley de Boltzmann: $$\langle E_{dip-dip}\rangle_{rot} = -\frac{d_A^2 d_B^2}{6\pi\varepsilon_0 kT}\frac{1}{R^6}$$

- Interacciones entre momentos inducidos por el campo de la otra molécula; por ej. dipolo permanente - dipolo inducido: $$\langle E_{dip-dipInd}\rangle = -\frac{d_A^2\alpha_B + d_B^2\alpha_A}{(4\pi\varepsilon_0)^2}\frac{1}{R^6}$$

- Interacciones entre momentos instantáneos debidos a fluctuaciones de carga en una molécula y los momentos que éstos inducen en la otra (*energía de dispersión o de London*); por ej. dipolo instantáneo - dipolo inducido:

$$\langle E_{dipInst-dipInd}\rangle = -\frac{3EI_A EI_B \alpha_A \alpha_B}{2(4\pi\varepsilon_0)^2(EI_A + EI_B)}\frac{1}{R^6}$$

★ término dominante en la atracción de vdW salvo para moléculas pequeñas muy polares.

Energía total de interacción

- Van der Waals: ≈ 0,1 - 2 kcal/mol (moléculas pequeñas)
  - ★ En ausencia de enlaces covalentes o de H:

$$E_{intAB} \approx 4D_e \left[\left(\frac{R_0}{R}\right)^{12} - \left(\frac{R_0}{R}\right)^{6} \right]$$

Potencial de Lennard-Jones o *6-12* ($R_e = 2^{1/6}R_0 \approx 1{,}12R_0$)

repulsión de Pauli

$R_0 \approx$ suma de radios medios moleculares (3 - 6 Å para moléculas pequeñas)

- Enlaces (puentes) de H: ≈ 2 a 10 kcal/mol; 2 - 3 Å.

- Enlaces covalentes: ≈ 30 a 230 kcal/mol; 1 - 3 Å.

Bases de l'espectroscòpia

Maig de 2014 - Revisat el 9 de desembre de 2019

Bibliografía: J. C. Paniagua & P. Alemany, *Química Quàntica*, cap. 7

Universitat de Barcelona

Dos Campus d'Excel·lència Internacional:
B:KC Barcelona Knowledge Campus
HUBC Health Universitat de Barcelona Campus

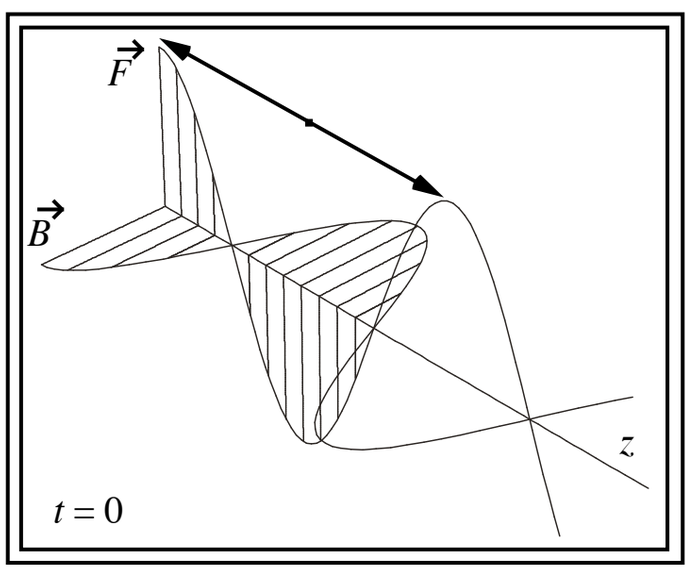
iqtc Institut de Química Teòrica i Computacional

Electromagnetic waves

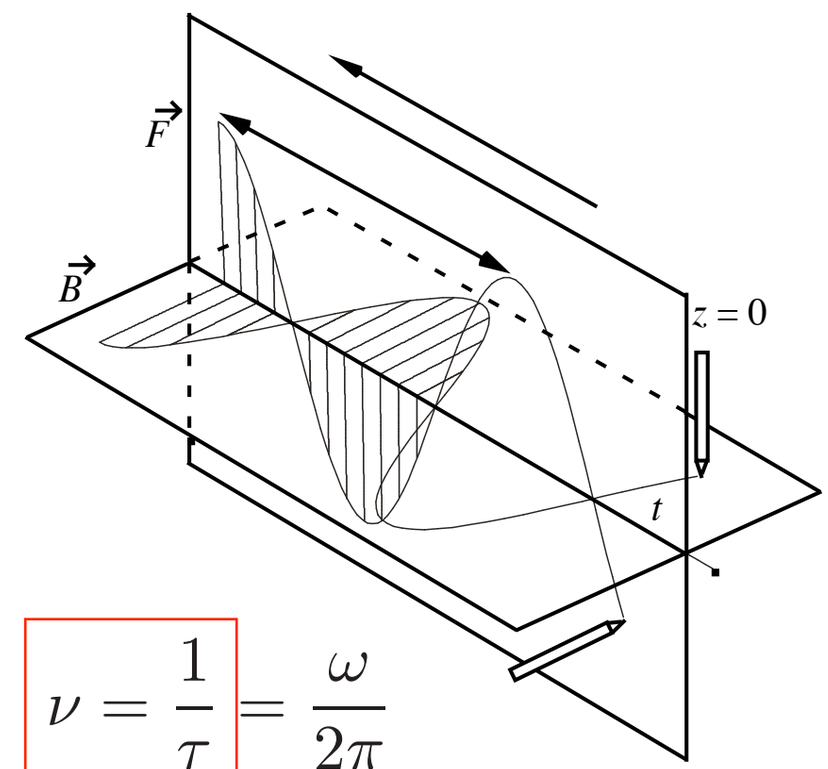
(Particular) solution of Maxwell equations in vacuum:

$$\boxed{\begin{aligned}\vec{F} &= \vec{u}_x F\cos(\omega t - kz + \varphi)\\ \vec{B} &= \vec{u}_y B\cos(\omega t - kz + \varphi)\end{aligned}}$$

$$c = \frac{\omega}{k} \qquad F = cB \qquad c = \frac{1}{\sqrt{\varepsilon_0\mu_0}} = 2,99792458\times 10^8 \mathrm{ms}^{-1}$$



PML waves



$$\lambda = \frac{2\pi}{k} \qquad \boxed{\bar{\nu} = \frac{1}{\lambda}} = \frac{k}{2\pi}$$

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

$$\boxed{c = \lambda\nu} \qquad \boxed{E_{phot} = h\nu = hc\bar{\nu}}$$

EM spectrum

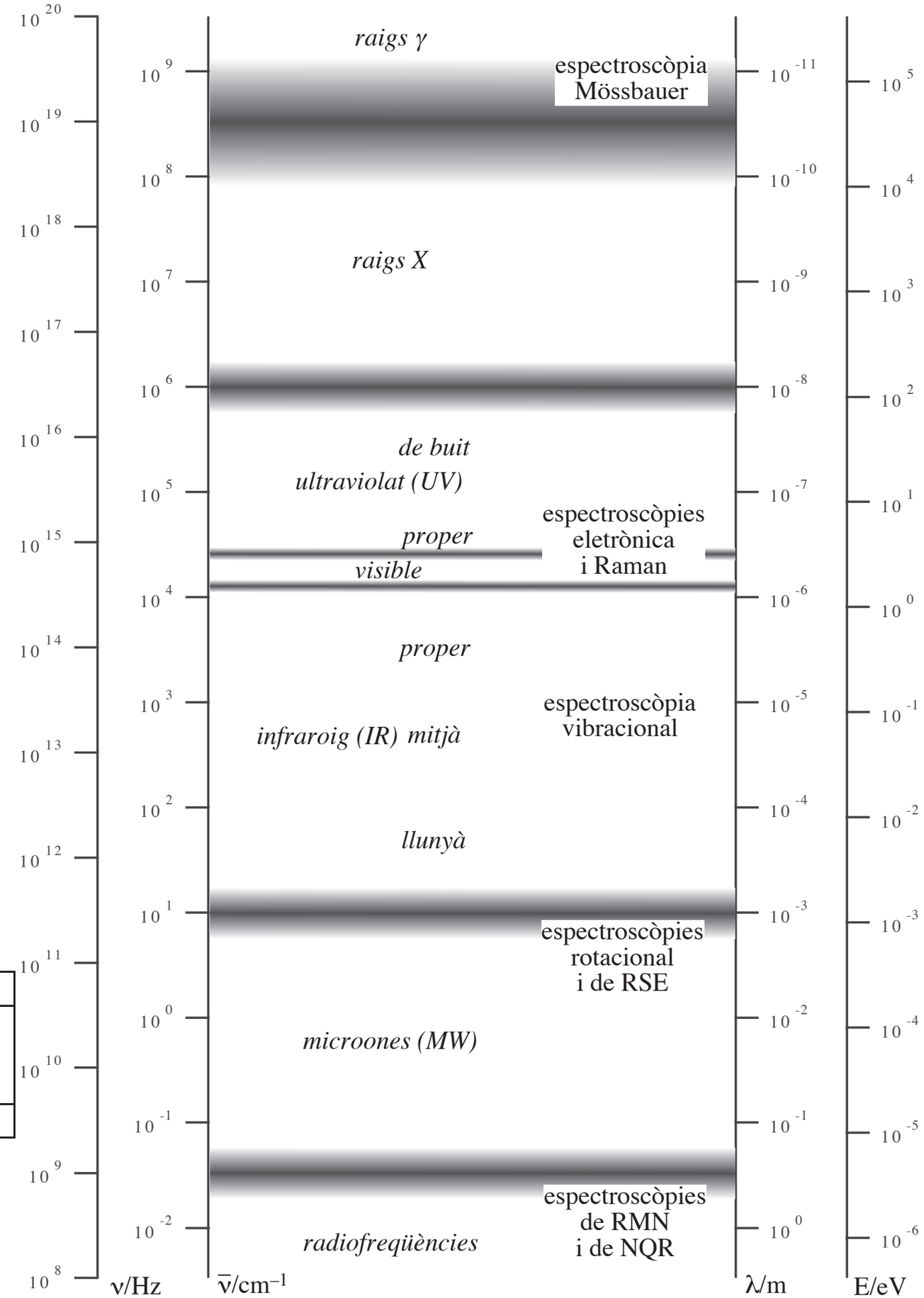
$$\nu = \frac{c_{med}}{\lambda_{med}} = \frac{c}{\lambda_{vac}}$$

$$\lambda_{vac} = \frac{c\ \lambda_{med}}{c_{med}} = n_{med}\ \lambda_{med}$$

$$n_{med} \equiv \frac{c}{c_{med}} = \frac{\sqrt{\varepsilon_{med}\ \mu_{med}}}{\sqrt{\varepsilon_0\ \mu_0}} = \sqrt{\varepsilon_r\ \mu_r}$$

Zona	UV	UV proper	Visible	NIR	MIR - RF
ν/THz	1500	1000	500	200	$\leq$30
$\overline{\nu}$/cm^{-1}	50000	33360	16680	6670	$\leq$1000
λ	200 nm	300 nm	600 nm	1,5 μm	$\geq$10 μm
n_{aire}	1,0003241	1,0002916	1,0002770	1,0002733	1,0002726

- PES: eV

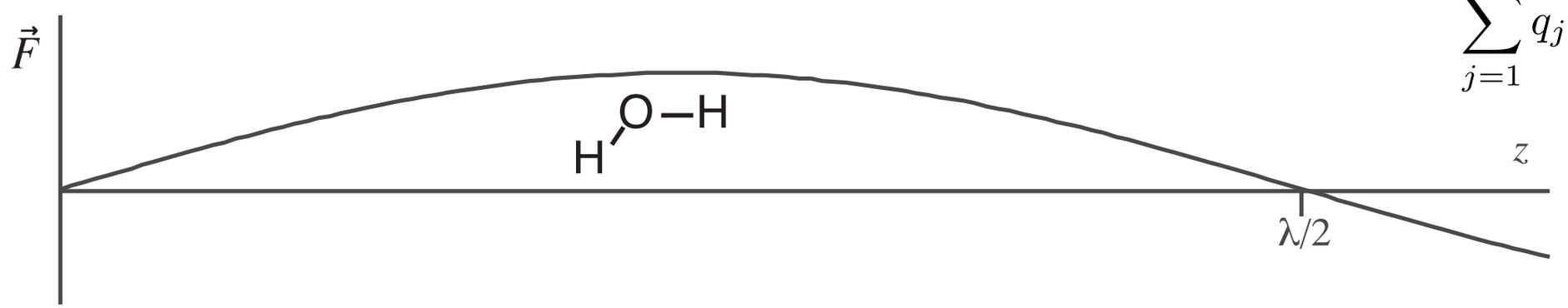


Interaction energy

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

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

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



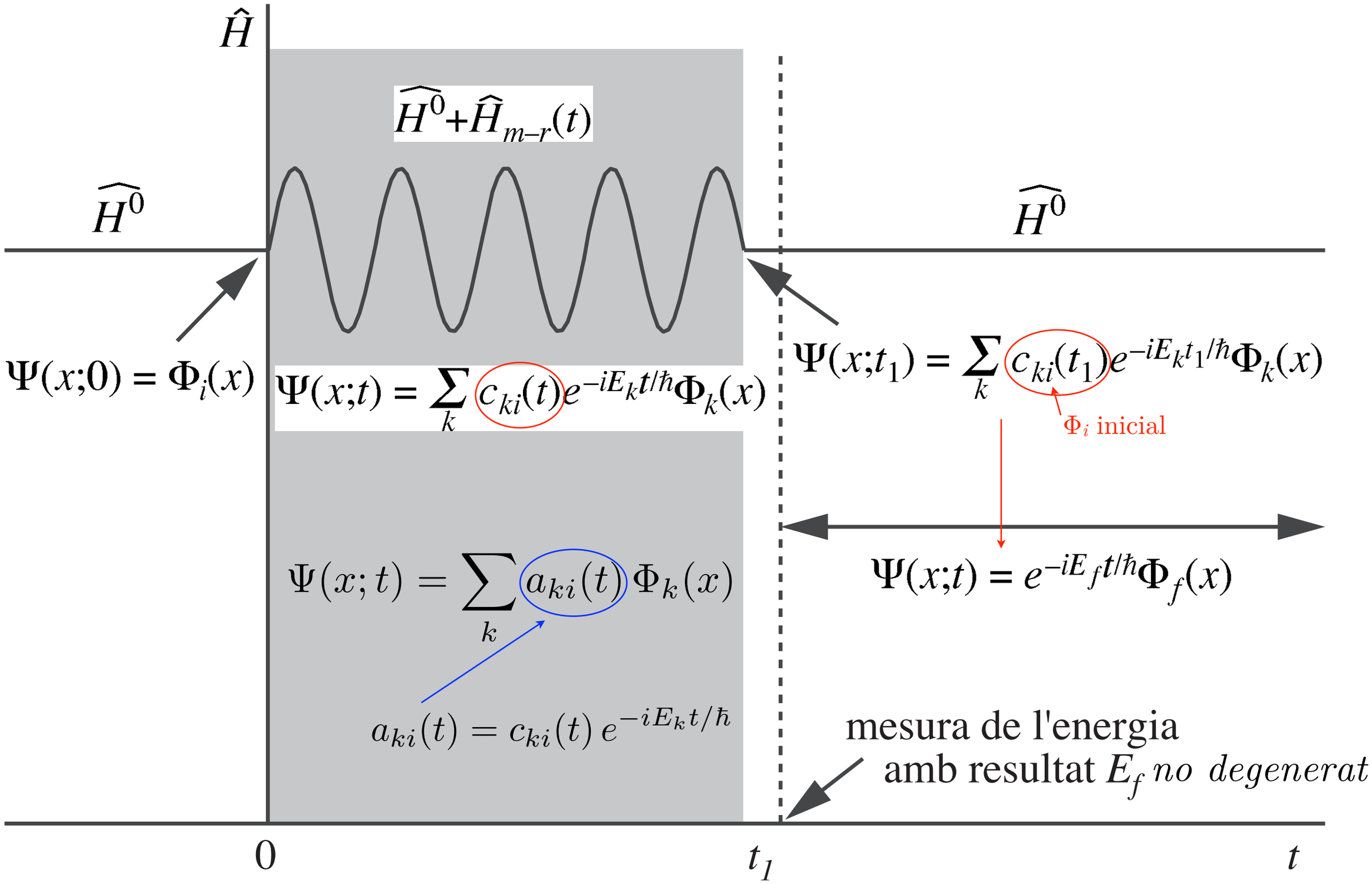
- Lorentz:

$$F = cB$$

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

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

Evolució de un estat estac.



Evolució d'un estat estac.

- Durant la irradiació $(0,\ t_1)$:

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

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

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

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

Time-dependent perturb.

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

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

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

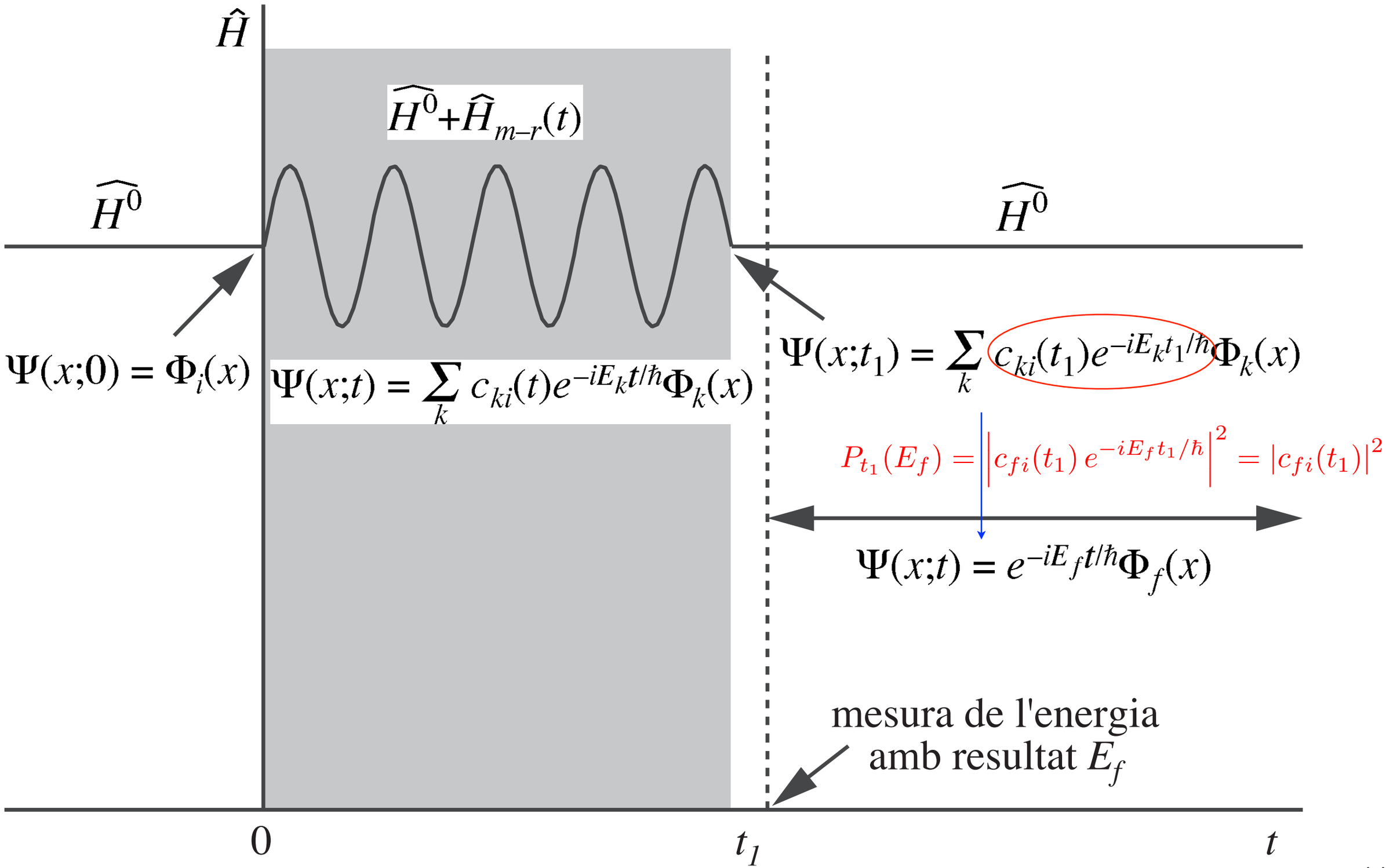
For any $\Phi_f \neq \Phi_i$ ($c_{ii}(t)$ can be obtained by normalizing Ψ)

- Dipole approximation:

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

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

Probabilitat de transició



1-photon transitions

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

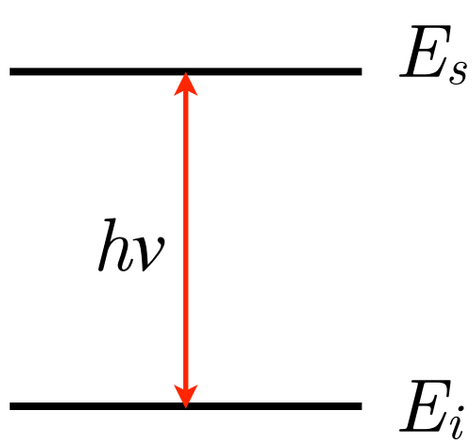
absorption: $\leftarrow$

induced emission: $\rightarrow$

Selection rules

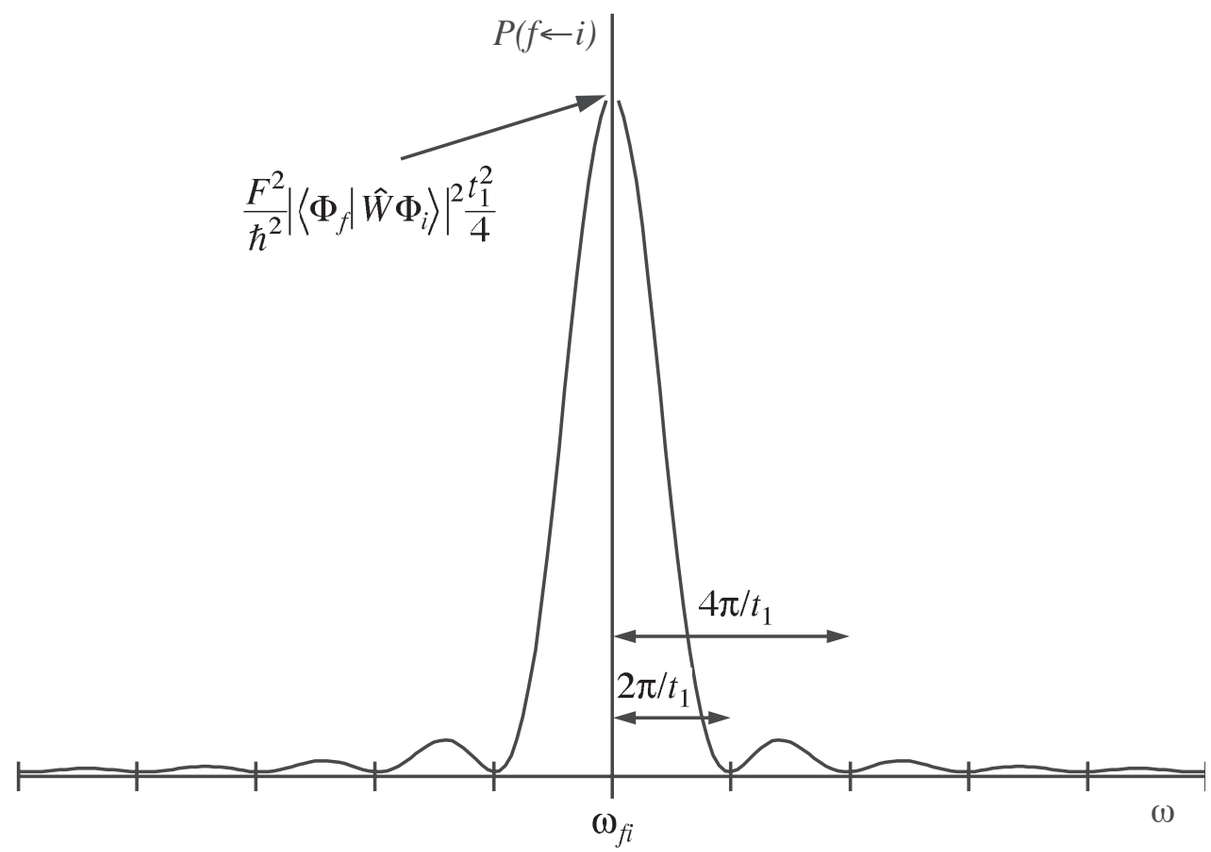
(dipolar and 1st order or monophotonic)

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



(*monophotonic*) *absorption*: $\uparrow$

(*monophotonic*) *induced emission*: $\downarrow$



Rad. policrom. isòtropa

constant de velocitat de la transició

densitat d'energia per unitat de freqüència

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

trans. per dipol elèctric, radiació isòtropa o molèc. en rotació

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

$$\boxed{w_{si} = B_{si} u(\nu_{si})}$$

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

trans. per dipol magnètic, radiació isòtropa o molèc. en rotació

Molècules que passen de Φ_i a Φ_s en la unitat de temps : $N_i w_{si}^{abs} = N_i B_{si} u(\nu_{si})$

Quantum theory of radiation

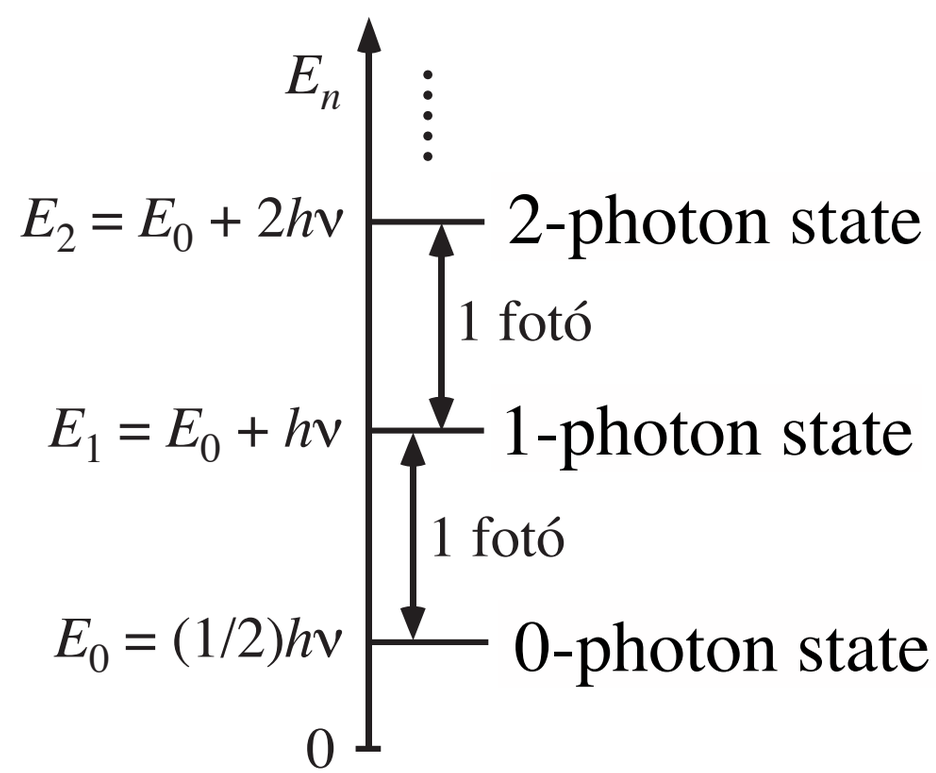
- Stationary states do not evolve: $\Psi(x;t) = e^{-iE_i t/\hbar}\Phi_i(x)$

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

- Spontaneous emission?
  - *quantum theory of radiation*

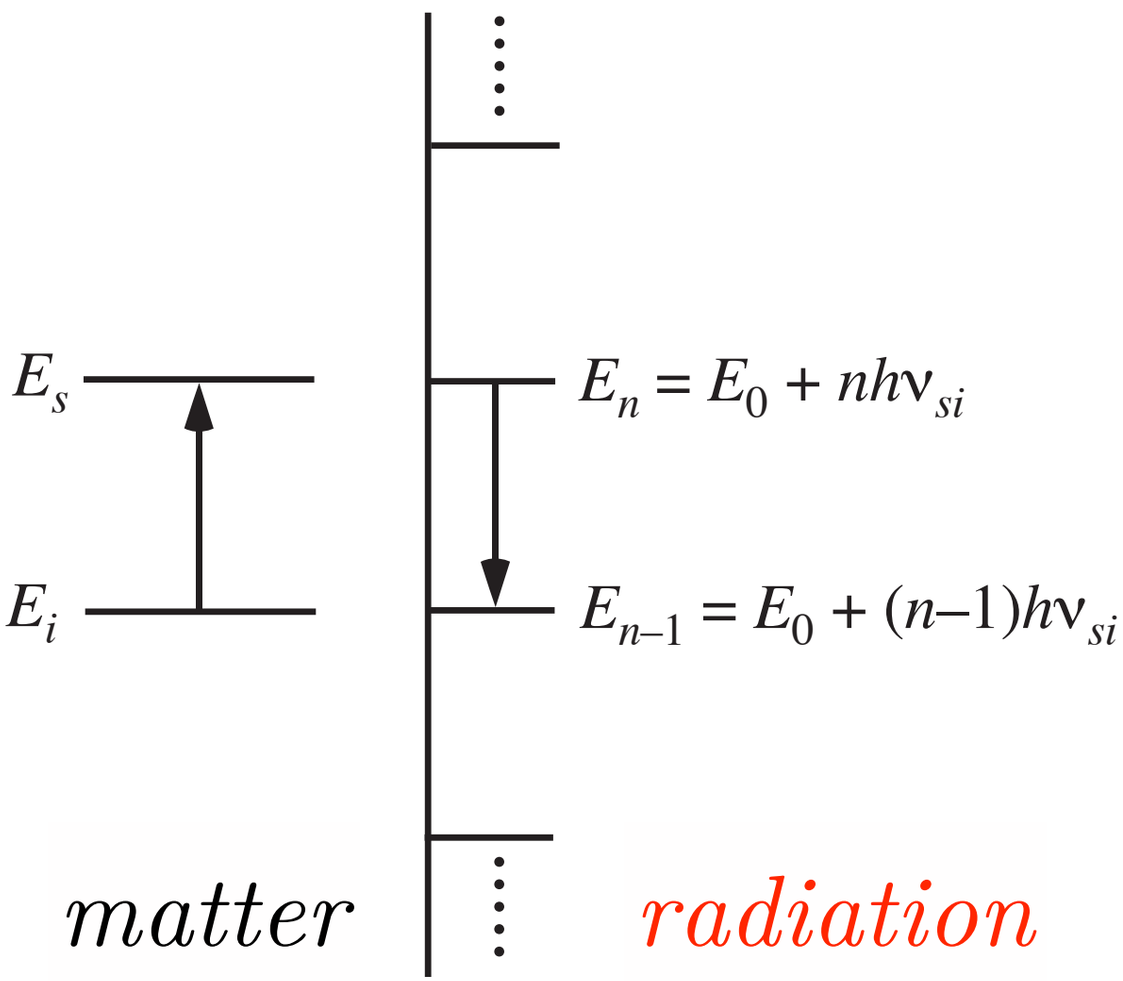
$$m_{phot,\nu} = \frac{E_{phot,\nu}}{c^2} = \frac{h\nu}{c^2} = \frac{p_{phot,\nu}}{c}$$

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

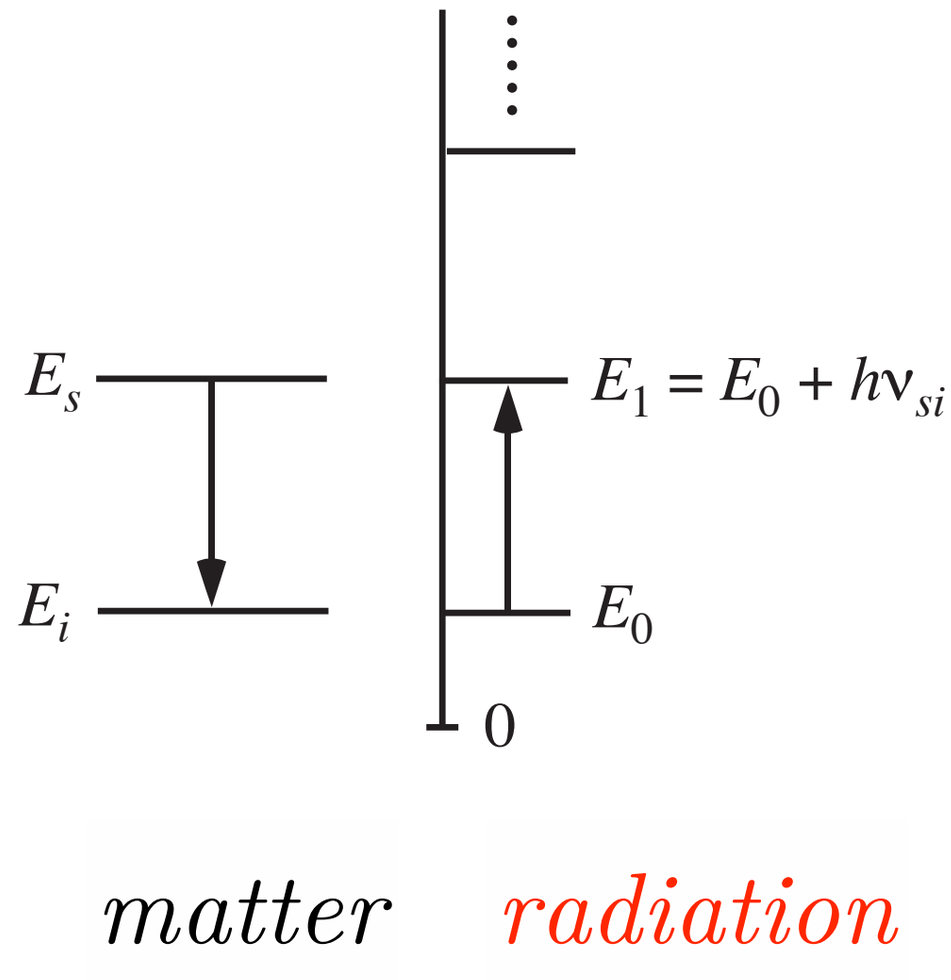


Spontaneous emission

Absorption



Spontaneous emission



Spontaneous emission

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

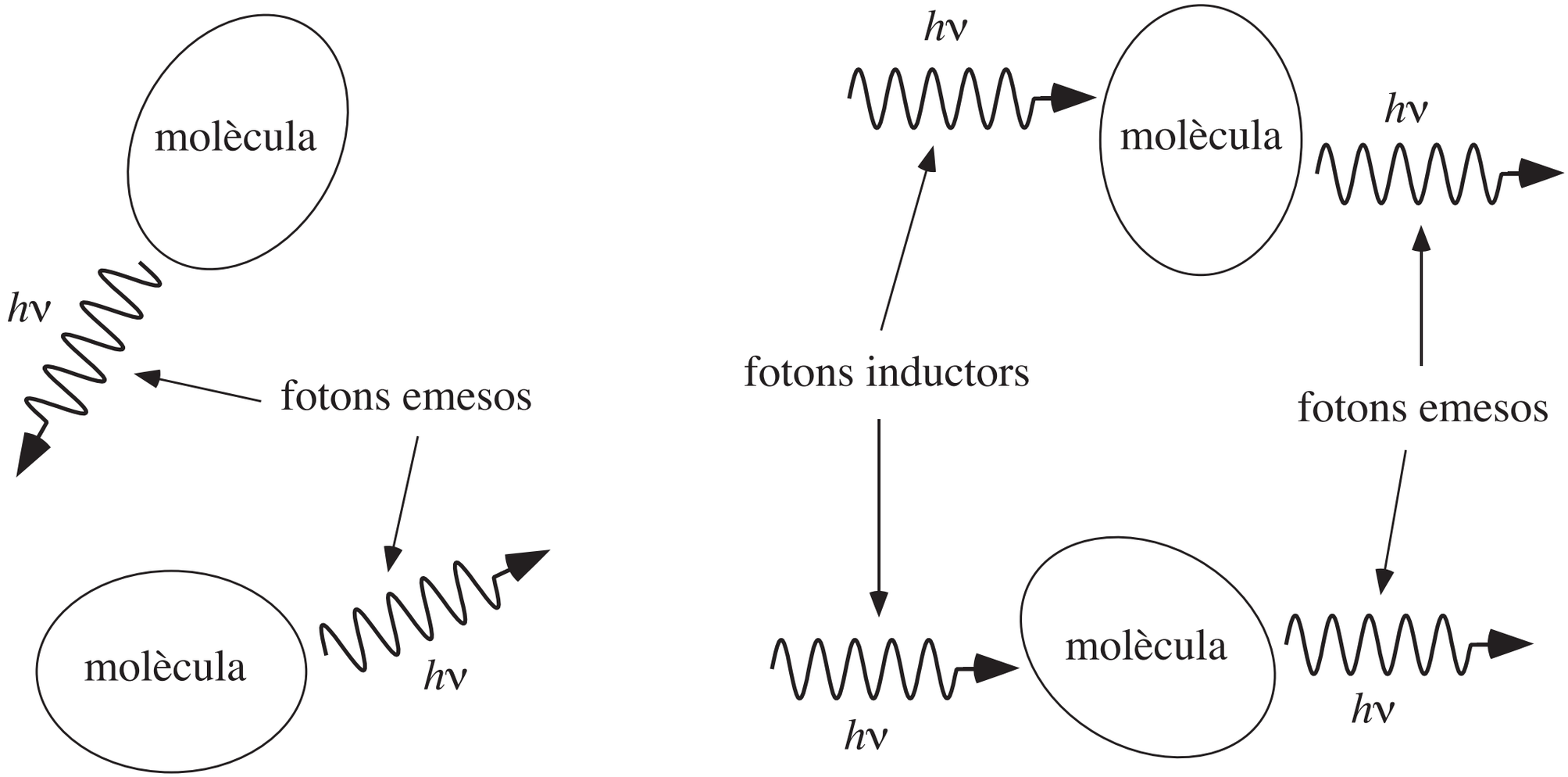
same selection rules

- If $u(\nu) = 0$

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

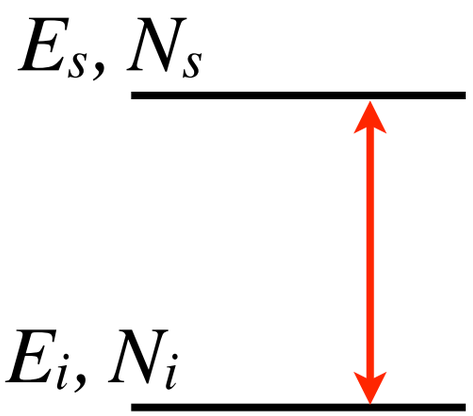
Transition	$\left\| \left\langle \Phi_s \left\| \widehat{\vec{d}} \Phi_i \right. \right\rangle \right\|$ / Cm	ν_{si}	τ_{si}
$2p_z \rightarrow 1s$	6,3 × 10^{-30}	2467 THz	10^{-9} s
$(2s)\,^2S_{1/2} \rightarrow (2p)\,^2P_{1/2}$	25 × 10^{-30}	1058 MHz	20 years
		$/10^6$	x 10^{18}

Emissió espontània vs induïda



LASER

Relaxation



$$\left.\begin{array}{c}\text{therm. equil.}\\ u(\nu_{si})=0\end{array}\right\}\quad \overbrace{N_{i,eq}R_{s\leftarrow i}}^{N_i} = \overbrace{N_{s,eq}(A_{si}+R_{s\rightarrow i})}^{N_s}$$

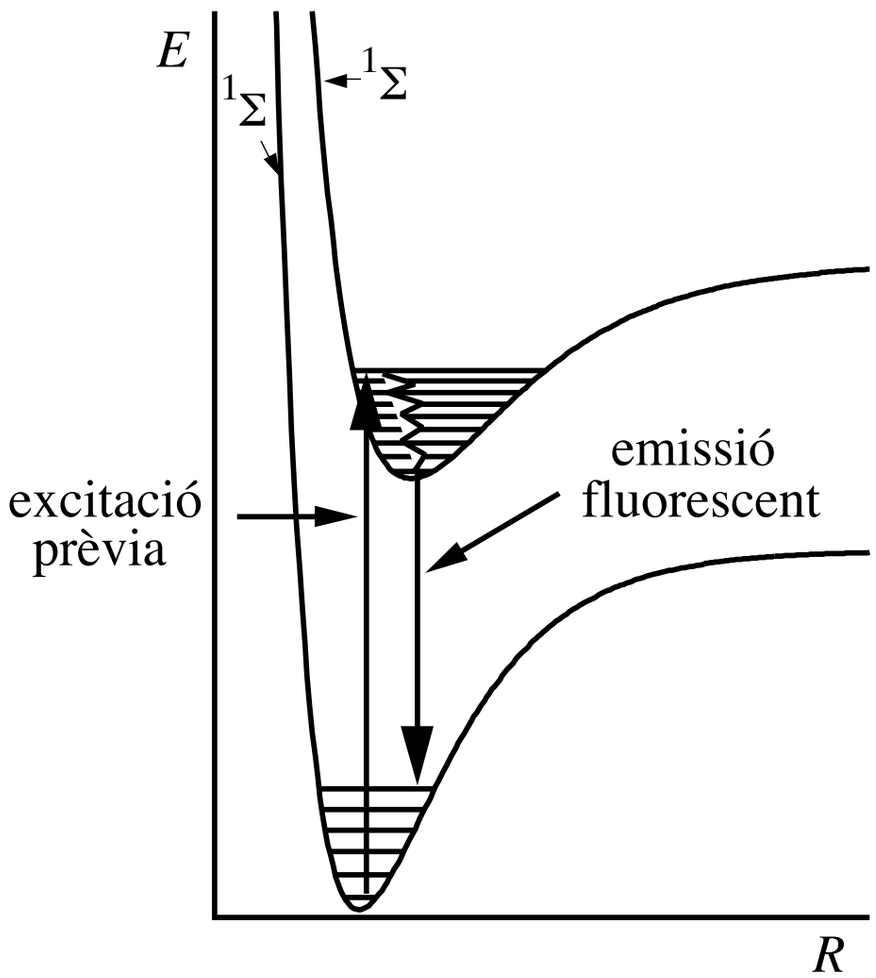
$$\boxed{\frac{N_{s,eq}}{N_{i,eq}} = \frac{R_{s\leftarrow i}}{A_{si}+R_{s\rightarrow i}} = e^{-h\nu_{si}/k_BT}}$$

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

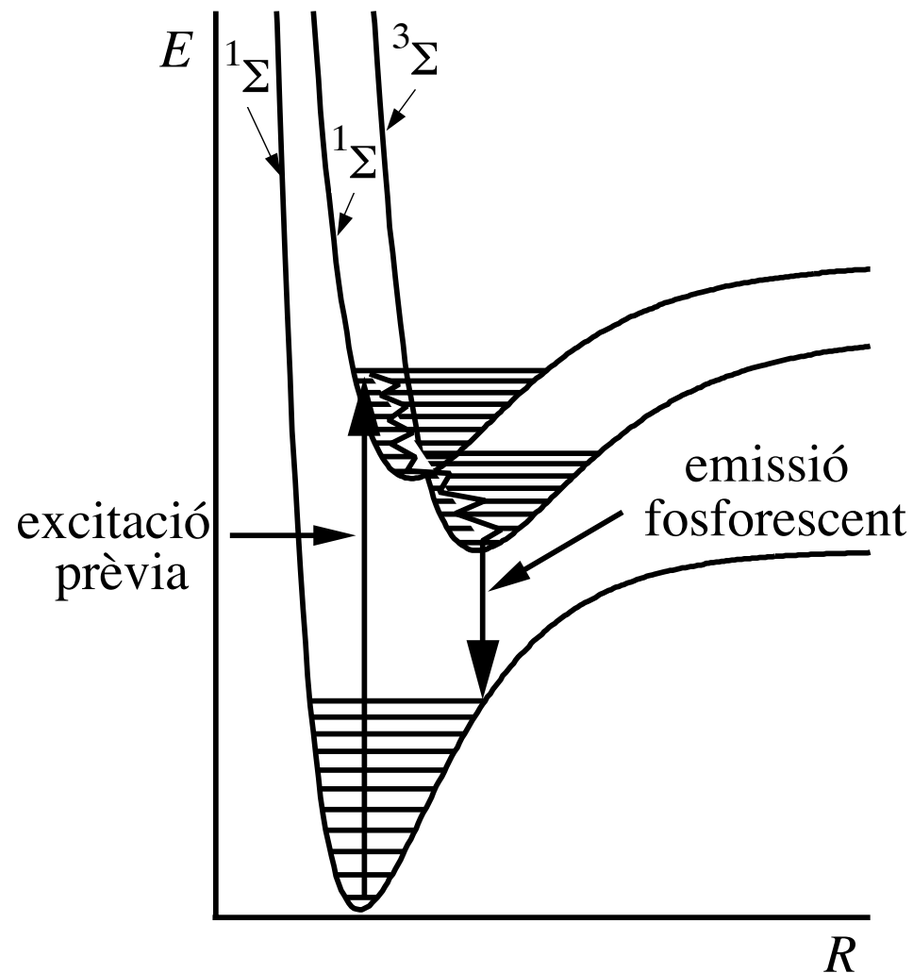
Fluorescència i fosforescència

Fluorescence



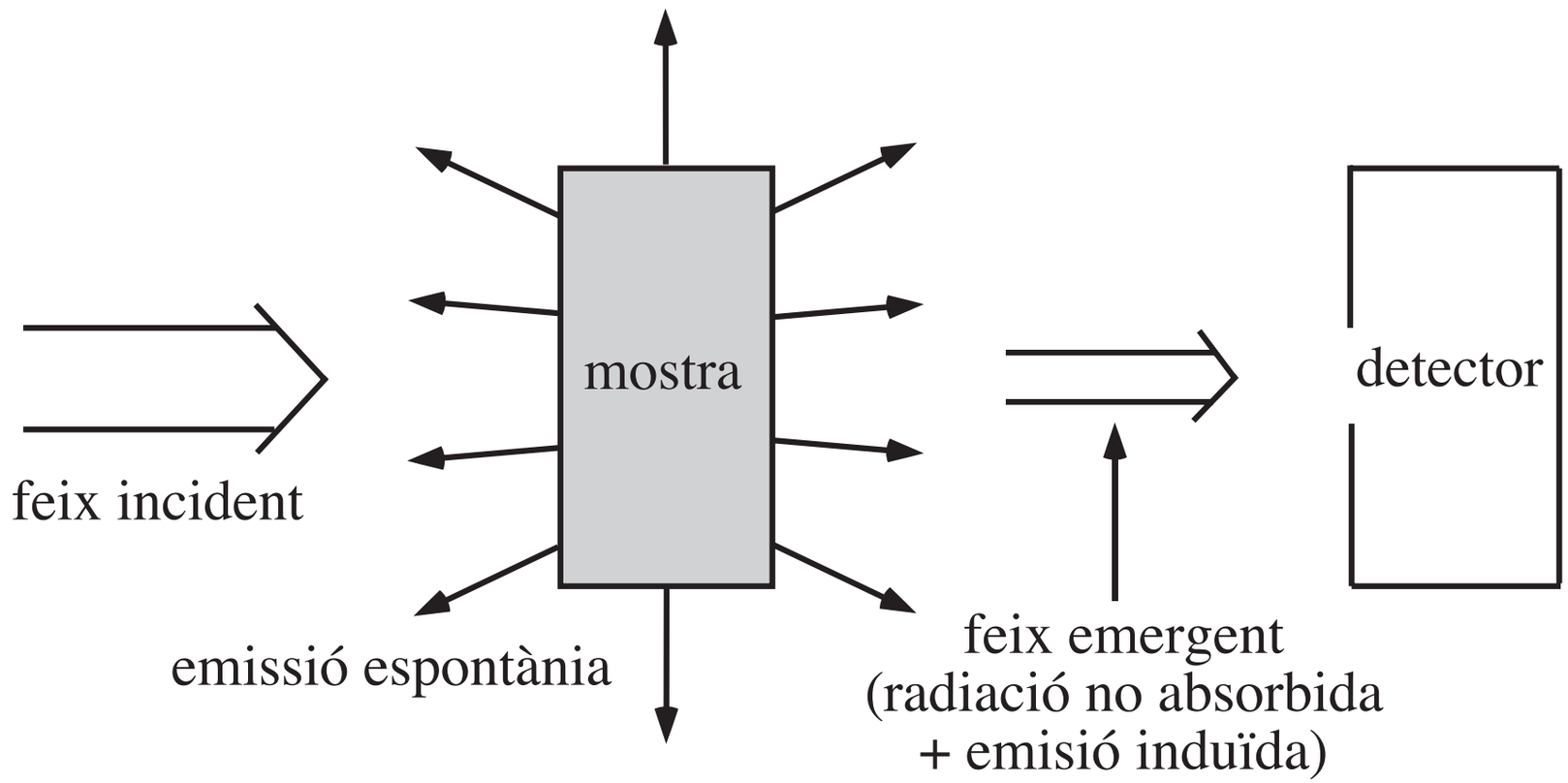
$\tau < 10^{-5}$ s

Phosphorescence



$\tau > 10^{-3}$ s

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. em. half live $< 10^{-2}$).
- $N_i \backsimeq N_{i,eq} \backsimeq N$

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

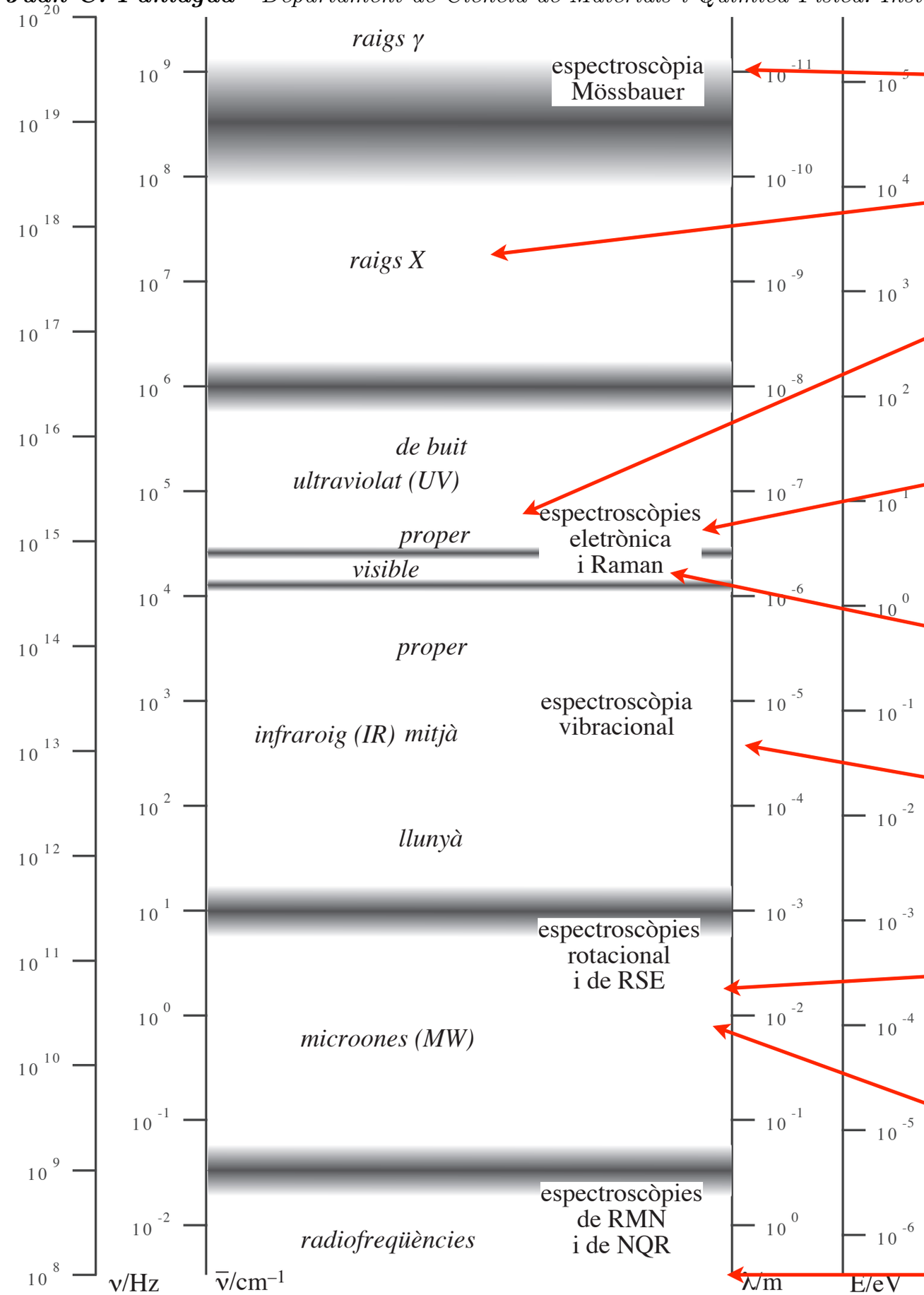
- Good sensitivity; good for *quantitative analysis* (simple relationship between N and absorption intensity); qualitative analysis, structural determination, material characterization, etc. (UV-vis, IR...)

Low frequencies (< FIR)

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

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

- $dE_{abs}/dt \propto (N_i - N_s) << N \;\Rightarrow$ low sensitivity.
- $(N_i - N_s)$ and dE_{abs}/dt decrease upon absorption (*saturation*) $\Rightarrow$
- quantitative analysis is not accurate and requires careful calibration of a standard
- good for qualitative analysis, structural determination, materials characterization, etc. (ESR, NMR, NQR, MW, ...)



^{57}Fe (^{129}I, ^{119}Sn, ^{121}Sb, …)

X-PES/ESCA, elemental analysis, …

U-PES, ionization potentials, surfaces, …

qualitative and quantitative analysis, excited state energies, …

qualitative and quantitative analysis, force constants, …

qualitative and quantitative analysis, force constants, …

molecular geometry, interstellar space molecule identification, …

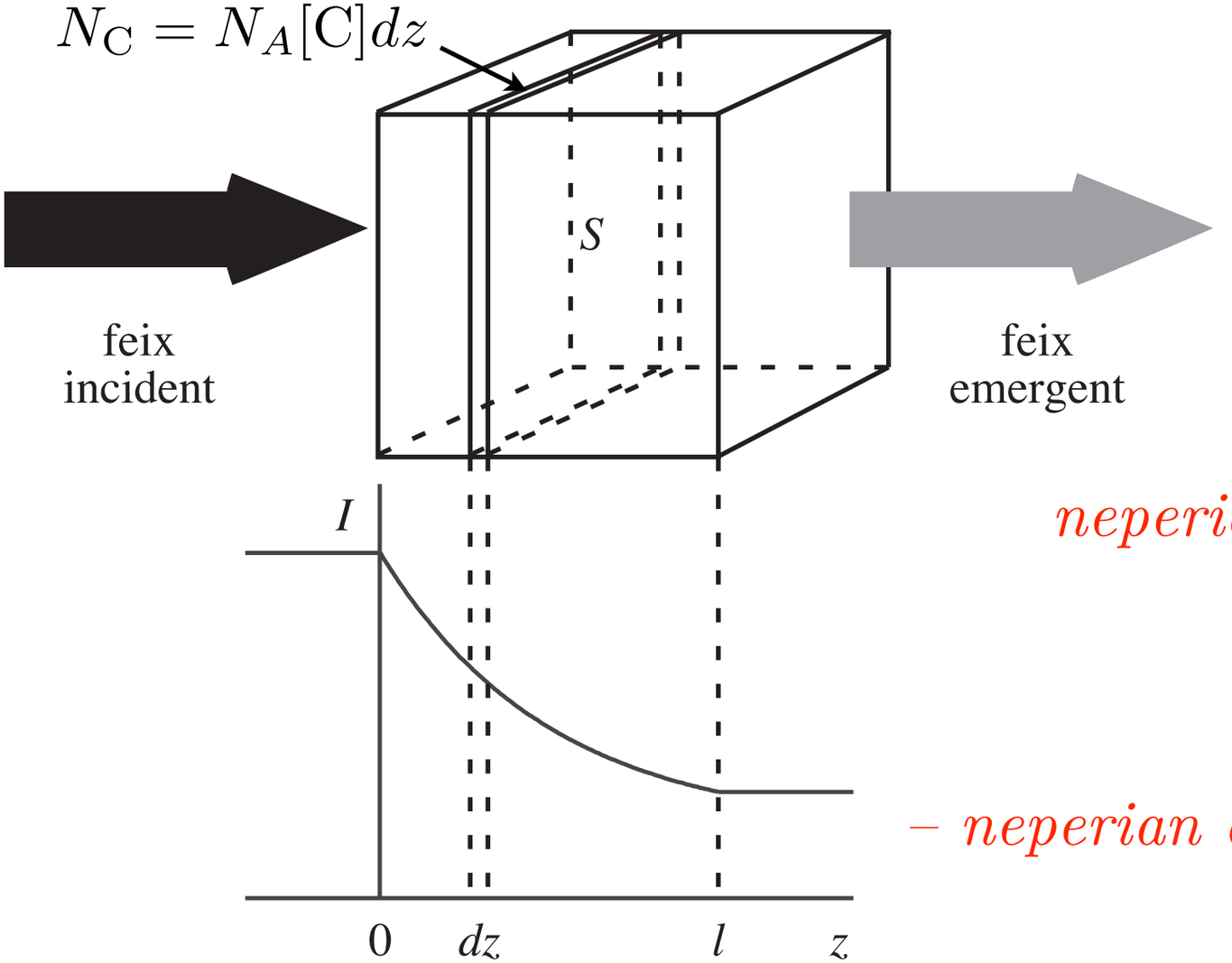
structure of radicals, transition metal complex, …

molecular structure

Lambert-Beer law

$$\frac{dE_{abs}}{dt} = \underbrace{(N_A[\mathrm{C}]dz)}\, B_{si}u(\nu_{si})h\nu_{si}$$

$N_\mathrm{C} = N_A[\mathrm{C}]dz$



Radiant intensity (irradiance) of frequency ν:

$$I(\nu) = \frac{u(\nu)dz}{dz/c} = c\,u(\nu)$$

$$dI(\nu_{si}) = -(N_A[\mathrm{C}]dz)B_{si}u(\nu_{si})h\nu_{si}$$

$$= -\frac{N_A B_{si} h\nu_{si}}{c} I(\nu_{si})[\mathrm{C}]dz$$

neperian molar absorption coefficient (κ_{si})

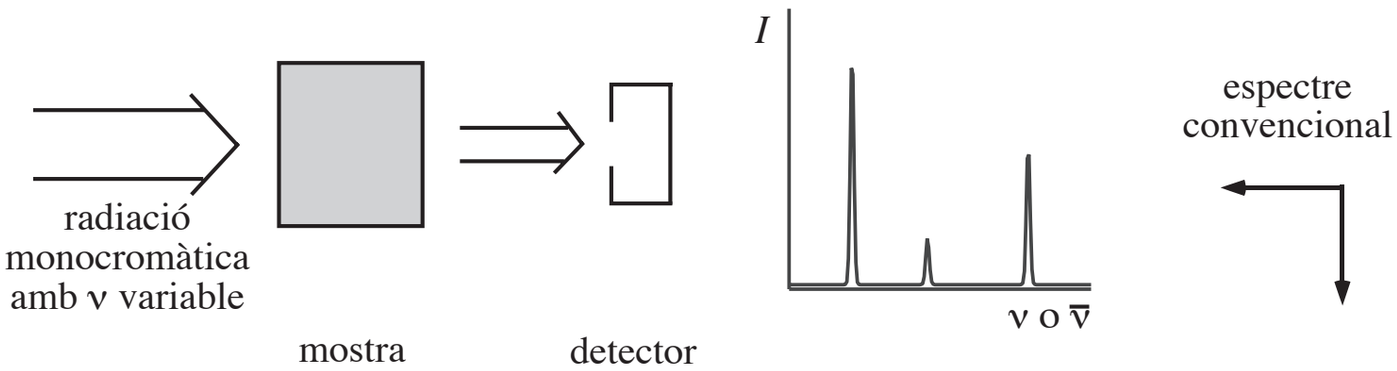
transmittance (T)

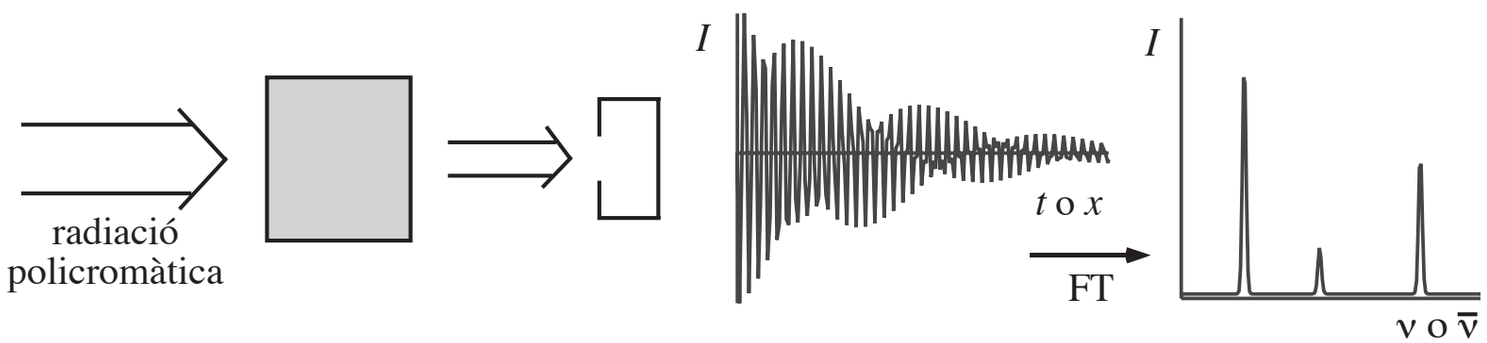
$$\ln\frac{I_l(\nu_{si})}{I_0(\nu_{si})} = -\kappa_{si}[\mathrm{C}]l$$

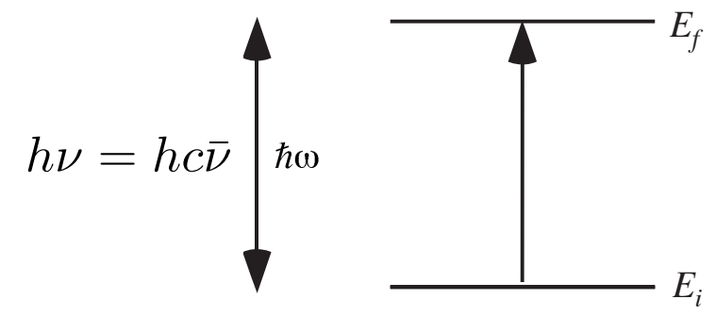
– *neperian absorbance* ($-A_e$)

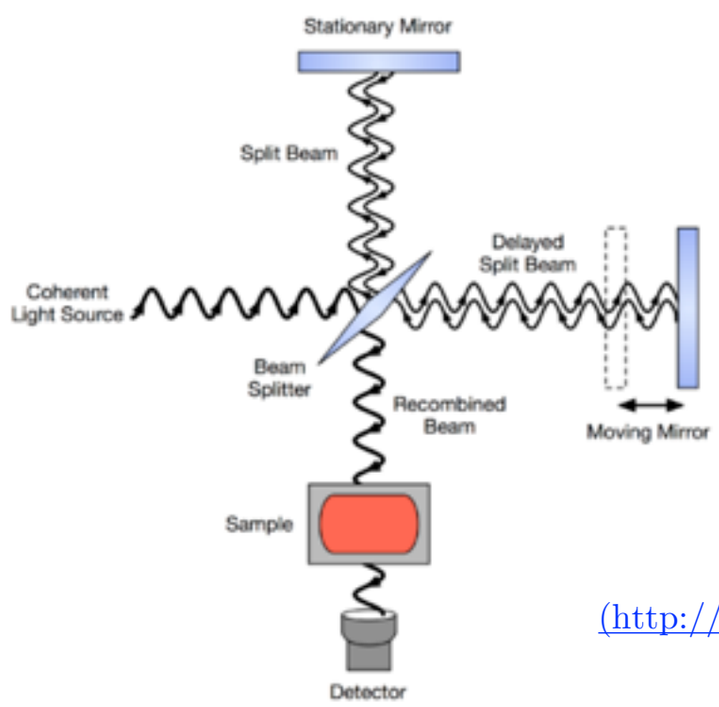
$$I_l(\nu_{si}) = I_0(\nu_{si})e^{-\kappa_{si}[\mathrm{C}]l}$$

Scan *vs* Fourier transform







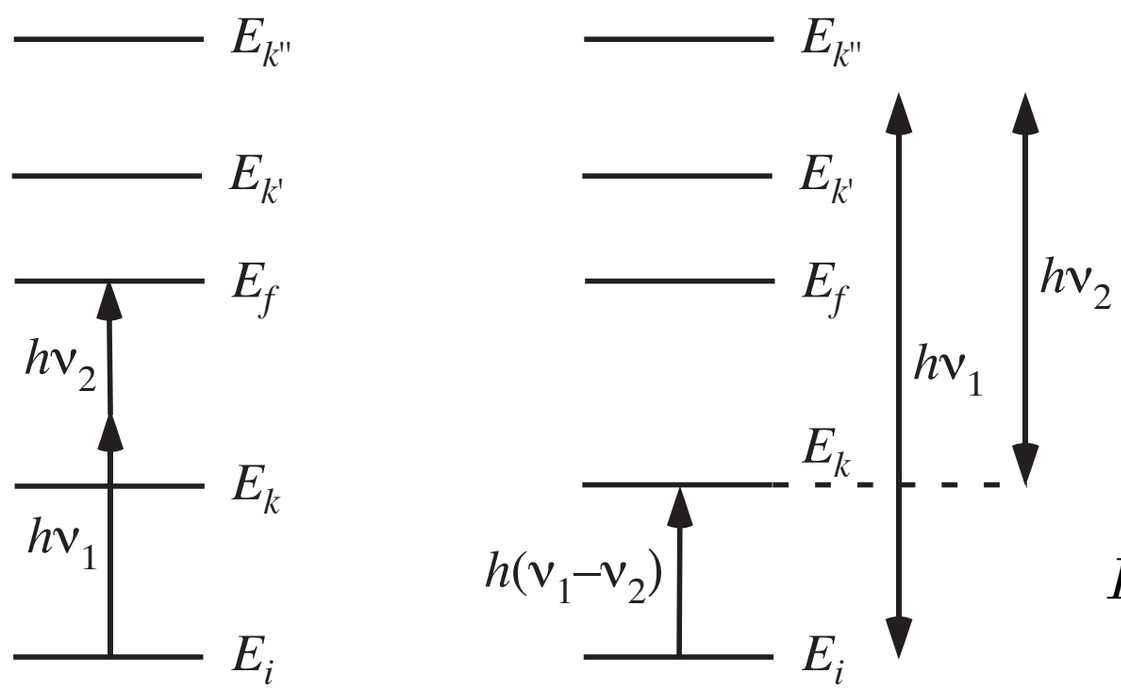


(http://en.wikipedia.org/wiki/User:Sanchonx)

Higher orders of TD perturb.

- *2nd order*: biphotonic processes (biphotonic absorption, biphotonic emission, Raman dispersion),

$$E_f - E_i = h\nu_1 + h\nu_2$$



$$E_f - E_i = h\nu_1 - h\nu_2$$

- *3rd order*: triphotonic processes (harmonic generation, ...),
- *4th order*: tetraphotonic processes (CARS & CSRS, ...)
- etc.