

LAST TIME: transition prob. for atom in EM field



Hamiltonian for charged particle in EM field:

$$H = \frac{p^2}{2m} - \frac{q}{m} \vec{p} \cdot \vec{A}(\vec{x}, t) + \frac{q^2}{2m} \vec{A}^2(\vec{x}, t) + q\phi(\vec{x}, t)$$

Choose \vec{A}, ϕ so: $\nabla \times \vec{A} = \vec{B}$, $-\nabla\phi - \frac{\partial \vec{A}}{\partial t} = \vec{E}$

Have: $\vec{E} = \vec{E}_0 \cos(\vec{k} \cdot \vec{x} - \omega t)$ $\vec{B} = \vec{B}_0 \cos(\vec{k} \cdot \vec{x} - \omega t)$

Can pick: $\phi = 0$, $\vec{A} = -\frac{1}{\omega} \vec{E}_0 \sin(\vec{k} \cdot \vec{x} - \omega t)$

for light:

$\lambda \sim 500 \text{ nm} \gg \text{atom size}$

$\therefore \vec{k} \cdot \vec{x}$ small $|\vec{k}| = \frac{2\pi}{\lambda}$

$$\phi = 0 \quad \vec{A} \approx \frac{1}{\omega} \vec{E}_0 \sin(\omega t)$$

Simplify via gauge transformation $\phi \rightarrow \phi - \partial_t \lambda$
 $\vec{A} \rightarrow \vec{A} - \nabla \lambda$

with $\lambda = \frac{\vec{E}_0 \cdot \vec{x}}{\omega} \sin(\omega t)$.

Get: $\phi_{\text{new}} = -\vec{E}_0 \cdot \vec{x} \cos(\omega t)$ $\vec{A}_{\text{new}} \approx 0$

+ small terms we ignored.

Then: $H_{EM} \approx e \vec{E}_0 \cdot \vec{x} \cos(\omega t)$
 $= -\vec{E}_0 \cdot \vec{p} \cos(\omega t)$

DIPOLE
APPROXIMATION.

↑ \vec{x} $-e$
 ● $+e$ electric dipole moment operator
 for atom: $\vec{p} = -e\vec{x}$

General molecule: same H with $\vec{p} = \sum_i q_i \vec{x}_i$

Use this in our transition rate formula for sinusoidal time dependence:

$$P_{a \rightarrow b} = \frac{E_0^2}{\hbar^2} \left| \langle p_{ab} | \hat{E}_0 \rangle \right|^2 \frac{\sin^2((\omega - \omega_0)t/2)}{(\omega - \omega_0)^2}$$

Proportional to energy density:

$$u = \frac{\epsilon_0}{2} E_0^2$$

matrix element of dipole moment operator in \vec{E}_0 direction

Realistic application: always have some combination of frequencies:

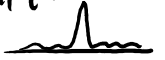
Define $\rho(\omega)d\omega =$ energy density in range $[\omega, \omega + d\omega]$

Assuming incoherent radiation (no phase correlations)

$$P_{b \rightarrow a} = \frac{2}{\epsilon_0 \hbar^2} \left| \vec{P}_{ab} \cdot \hat{E}_0 \right|^2 \int_0^\infty d\omega \rho(\omega) \left\{ \frac{\sin^2((\omega_0 - \omega)t/2)}{(\omega_0 - \omega)^2} \right\}$$

highly peaked at $\omega = \omega_0$ at large times

small t:



large t:



$$\text{Integral} \approx \rho(\omega_0) \cdot \frac{t}{2} \cdot \pi$$

$$P_{b \rightarrow a}(t) \approx \frac{\pi \left| \vec{P}_{ab} \cdot \hat{E}_0 \right|^2}{\epsilon_0 \hbar^2} \rho(\omega_0) \cdot t$$

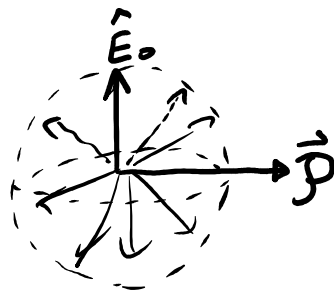
⇒ Constant transition rate

↑ prob. increases linearly w. time.

$$R_{b \rightarrow a} = \frac{\pi}{\epsilon_0 \hbar^2} \left| \vec{P}_{ab} \cdot \hat{E}_0 \right|^2 \rho(\omega_0)$$

Uniform bath of radiation: average over directions & polarizations

avg of $|\vec{P}_{ab} \cdot \hat{E}_0|^2$



$$\frac{1}{4\pi} \int d\Omega |\vec{P} \cdot \hat{n}|^2$$

$$= \frac{1}{4\pi} \int d\phi \sin\theta d\theta |\vec{P} \cdot \vec{P}| \cos^2\theta$$

$$= \frac{1}{3} \vec{P} \cdot \vec{P}^*$$

FINAL TRANSITION RATE (dipole approximation)

$$R_{b \rightarrow a} = \frac{\pi}{3\epsilon_0 \hbar^2} \vec{P}_{ab} \cdot \vec{P}_{ab}^* \rho(\omega_{ab})$$

$\langle \psi_a | \sum q_n \vec{x}_n | \psi_b \rangle$ energy density at freq. ω_{ab}

valid for any atom/molecule, for ABSORPTION or STIMULATED EMISSION.