Optical Properties of Semiconductors

You must have seen similar figures like this one (but probably better looking). You may have used them to answer questions like these:

Can we make decent light emitters (LEDs) based on band-to-band transitions from an indirect gap semiconductor (e.g. Si)?
Can we make decent light detectors (photodiodes) from an indirect gap semiconductor? Why?
Light absorption and emission of a semiconductor

“Vertical” transition (momentum conservation). But why the photon’s momentum is negligible?

But why decent light detectors (photodiodes) can be made from an indirect gap semiconductor?
Energy of the photon

\[ E = h \nu = \hbar \omega = \hbar k c = \frac{hc}{\lambda} = \frac{2\pi \hbar c}{\lambda} \]

For \( \lambda \sim 1\mu m \), \( E \sim 1\text{eV} \).

Momentum of the photon

\[ p = \hbar k \]

\[ k = \frac{2\pi}{\lambda} \]

\( \lambda \sim 1\mu m \)

band gaps of many semiconductors are in this range.

Compare the \( k \) of a photon to the dimension of the Brillouin zone:

For an indirect-gap semiconductor,

\[ \Delta k_{\text{valley}} \sim \frac{2\pi}{a} \]

\[ a \sim 5\text{\AA} \]

Therefore,

\( k \ll \Delta k_{\text{valley}} \) (photon)

\( k \sim 0 \) (photon)
Light absorption & emission processes in a system of discrete levels

Spontaneous emission: Into all possible photon modes. How LEDs work. Stimulated emission: Duplicate the incoming photon. Amplification. Amplification + positive feedback $\Rightarrow$ oscillation – lasers!

The positive feedback and frequency selection mechanism:

Optical cavity

$$2L = n\lambda = n\frac{c}{\nu}$$

$$\nu = n\frac{c}{2L}$$
Light absorption and emission of a semiconductor

$$E_2 = \frac{\hbar^2 k^2}{2m^*_n} + E_g$$

$$E_1 = -\frac{\hbar^2 k^2}{2m^*_p}$$

$$E_2 - E_1 = \hbar \omega = h \nu$$

(How do we get $E_{Fn} \neq E_{Fp}$?)
Forward biased

\[ E_{Fn} > E_{Fp} \]

More carriers than in equilibrium

Like an npn BJT with BC junction forward biased
Strong field in depletion region sweeps electrons to n side, holes to p side.

$E_{Fn} < E_{Fp}$, fewer carriers than in equilibrium. E-h pairs are generated everywhere, but...

Subscript "0" means no light. (not equilibrium)
$E_2$ and $E_1$ are related by the photon energy

$$E_2 - E_1 = \frac{\hbar^2 k^2}{2m^*} + \frac{\hbar^2 k^2}{2m_p^*} + E_g = \hbar \nu = h \nu$$

$$\frac{\hbar^2}{2} \left( \frac{1}{m_n^*} + \frac{1}{m_p^*} \right) k^2 = h \nu - E_g$$

Let \( \frac{1}{m} = \frac{1}{m_n^*} + \frac{1}{m_p^*} \)

\( m_r \): the reduced effective mass of the e-h pair

$$\frac{\hbar^2 k^2}{2m_r} = h \nu - E_g \quad \rightarrow \quad k^2 = \frac{2m_r}{\hbar^2} (h \nu - E_g)$$

$$D_n(E_2) \, dE_2 = \rho(\nu) \, d\nu$$

Density of states of conduction band e’s

Joint density of states

$$\rho(\nu) = \frac{(2m_r)^{3/2}}{\pi \hbar^2} (h \nu - E_g)^{1/2} \propto \sqrt{h \nu - E_g}$$
Probability of emission (e at $E_2$, and there’s a hole at $E_2$ for it to fall into):

$$f_e(\nu) = f_n(E_2) \left[1 - f_p(E_1)\right]$$

Probability of absorption:

$$f_a(\nu) = \left[1 - f_n(E_2)\right] f_p(E_1)$$

Probability of net gain in number of photons:

$$f_e(\nu) - f_a(\nu) = f_n(E_2) - f_p(E_1)$$
The LED works by spontaneous emission.

Spontaneous emission rate:
(Emissions per time per volume per frequency interval)

\[ r_{sp}(\nu) = \frac{1}{\tau_r} \rho(\nu) f_e(\nu) \]

Radiative recombination lifetime

At equilibrium,

\[ f_e(\nu) = e^{-\frac{E_g - E_F}{k_BT}} e^{-\frac{E_g - E_F}{k_BT}} = e^{-\frac{E_g - E_F}{k_BT}} = e^{-\frac{\nu}{k_BT}} \]

Joint density of states (per volume per frequency interval)

\[ r_{sp}(\nu) = \frac{1}{\tau_r} \rho(\nu) f_e(\nu) \]

\[ = \frac{1}{\tau_r} \left( \frac{2m_r}{\pi \hbar^2} \right)^{3/2} \sqrt{\hbar \nu - E_g} \cdot e^{-\frac{\nu}{k_BT}} \]

You can calculate the optical power emitted by a slab of semiconductor.
At room temperature, a 2 micron layer of GaAs emits \(1.5 \times 10^{-20}\) W/cm².
You have to either heat it up (incandescence) or “pump” e-h pairs into it (electroluminescence).

This and some other figures are adapted from Saleh & Teich, *Fundamentals of Photonics*
We are not interested in making incandescent light bulbs from semiconductors. Let’s look at LEDs. Or, photoluminescence, if we want to avoid talking about devices now.

\[
f_e(\nu) = f_n(E_2) \left[1 - f_p(E_1)\right]
\]

LED: (weak injection)

\[
f_e(\nu) = e^{\frac{E_2 - E_{Fn}}{k_B T}} e^{\frac{E_1 - E_{Fn}}{k_B T}}
\]

\[
= e^{\frac{E_{Fn} - E_{FP}}{k_B T}} e^{-\frac{\nu}{k_B T}}
\]

\[
\rho_{sp}(\nu) = \frac{1}{\tau_r} \rho(\nu) f_e(\nu)
\]

\[
= e^{\frac{E_{Fn} - E_{FP}}{k_B T}} \rho_{sp0}(\nu)
\]

Compare to the equilibrium case:

\[
\rho_{sp0}(\nu) = \frac{1}{\tau_r} \rho(\nu) f_e(\nu)
\]

\[
= \frac{1}{\tau_r} \frac{(2m_r)^{\frac{3}{2}}}{\pi h^2} \sqrt{\nu - E_g} \cdot e^{-\frac{\nu}{k_B T}}
\]
Weak injection:

\[ r_{sp}(\nu) = \frac{1}{\tau_r} \rho(\nu) f_e(\nu) = e^{\frac{E_{F_n} - E_{FP}}{k_B T}} \]

Equilibrium:

\[ r_{sp0}(\nu) = \frac{1}{\tau_r} \rho(\nu) f_e(\nu) = \frac{1}{\tau_r} \frac{(2m_r)^{3/2}}{\pi^1/2} \sqrt{h \nu - E_g} \cdot e^{-\frac{h \nu}{k_B T}} \]

Peak at \( E_g + \frac{1}{2} k_B T \)

Same peak, same width, enhanced by an exponential factor

Compare with "incandescence"

Photons can escape before getting absorbed. Therefore we consider \( f_e \), instead of net \( f_e - f_a \).

Photons are emitted into all modes.
Now let’s talk about semiconductor optical amplifiers and lasers

Stimulated emission rate:
(Emmissions per time per volume per frequency interval)

\[ r_{st} (\nu) = \phi_{\nu} \frac{\lambda^2}{8\pi \tau_r} \rho(\nu) f_e(\nu) \]

Absorption rate:
(Photons absorbed per time per volume per frequency interval)

\[ r_{ab} (\nu) = \phi_{\nu} \frac{\lambda^2}{8\pi \tau_r} \rho(\nu) f_a(\nu) \]

Incoming photon flux
(photons per time per area per frequency interval)

Compare with the spontaneous emission rate:

\[ r_{sp} (\nu) = \frac{1}{\tau_r} \rho(\nu) f_e(\nu) \]

The origin of the \( \lambda^2 \) dependence: density of modes

\[ M(\nu) = \frac{8\pi \nu^2}{c^3} \]

The photon density of modes is similar to the electron density of states \( D(E) \).
The difference: \( E = \hbar^2 k^2/(2m^*) \) for e’s, \( E = h\nu = c\hbar k \) for photons.
Simply put, the larger the \( E \), the more \( k \) states in an interval \( dE \).
For spontaneous emission, photons are emitted into all modes.

\[ \gamma_{sp}(\nu) = \frac{1}{\tau_r} \rho(\nu) f_e(\nu) \]

For stimulated emission, photons are emitted into the one mode of the incoming photon.

\[ \gamma_{st}(\nu) = \phi_\nu \frac{\lambda^2}{8\pi \tau_r} \rho(\nu) f_e(\nu) \]

\[ \gamma_{ab}(\nu) = \phi_\nu \frac{\lambda^2}{8\pi \tau_r} \rho(\nu) f_a(\nu) \]

For absorption, the absorbed photon is of a specific mode. Thus the modal density should be in the denominator

\[ M(\nu) = \frac{8\pi \nu^2}{c^3} \]

Thus the \( \lambda^2 \) dependence.
A medium absorbs at equilibrium. 

\[ I(x) = I(0) e^{-\alpha(\nu)x} \]

If “pumped”, net gain is possible: 

\[ I(x) = I(0) e^{\gamma x} \]

\[
\gamma(\nu) = \frac{\lambda^2}{8\pi \tau_r} \rho(\nu) \left[ f_e(\nu) - f_a(\nu) \right] 
\]

\[
= \frac{\lambda^2}{8\pi \tau_r} \rho(\nu) \left[ f_n(E_z) - f_p(E_i) \right] 
\]

\[
= \frac{1}{8\pi} \frac{(2m_e)^\frac{3}{2}}{\pi \hbar^2} \frac{\lambda^2}{\tau_r} \sqrt{(\hbar \nu - E_g)} \left[ f_n(E_z) - f_p(E_i) \right] 
\]
\[ Y(\nu) = \frac{\lambda^2}{8 \pi \tau r} \rho(\nu) [f_e(\nu) - f_a(\nu)] \]
\[ = \frac{\lambda^2}{8 \pi \tau r} \rho(\nu) [f_n(E_2) - f_p(E_1)] \]
\[ = \frac{l}{8 \pi} \left( \frac{2m_r}{\pi \hbar^2} \right)^{\frac{3}{2}} \frac{\lambda^2}{\tau r} \left[ (\hbar \nu - E_g) \right] [f_n(E_2) - f_p(E_1)] \]

Notations used in figures:

\[ f_g = f_e - f_a \]
\[ f_c(E_2) \equiv f_n(E_2) \]
\[ f_v(E_1) \equiv f_p(E_1) \]
\[ Y(\nu) = \frac{\lambda^2}{8\pi c \tau_r} \rho(\nu) [f_e(\nu) - f_a(\nu)] \]
\[ = \frac{\lambda^2}{8\pi c \tau_r} \rho(\nu) [f_n(E_2) - f_p(E_1)] \]
\[ = \frac{1}{8\pi} \left( \frac{2m_e}{\pi\hbar^2} \right)^{\frac{3}{2}} \frac{\lambda^2}{\tau_r} \left( h\nu - E_g \right) [f_n(E_2) - f_p(E_1)] \]

Notations used in figures:

\[ f_g = f_e - f_a \quad E_{fc} \equiv E_{Fn} \]
\[ f_c(E_2) \equiv f_n(E_2) \quad E_{fv} \equiv E_{Fp} \]
\[ f_v(E_1) \equiv f_p(E_1) \]

Net gain: amplification.

To have net gain (for some frequencies), you must have \( E_{Fn} - E_{Fp} > E_g \).

(the "population inversion" in semiconductors)
To have net gain (for some frequencies), you must have $E_{Fn} - E_{Fp} > E_g$.

(the “population inversion” in semiconductors)

(Filled CB bottom and empty VB top)
Quantum wells

https://www.researchgate.net/publication/301742238_Many-body_electron_correlations_in_graphene/figures?lo=1

https://link.springer.com/chapter/10.1007/978-3-319-50651-7_22

https://www.researchgate.net/publication/301742238_Many-body_electron_correlations_in_graphene/figures?lo=1
Quantum wells

What is the density of states of the quantum well?

https://www.iue.tuwien.ac.at/phd/moradinasab/dissse2.html
Fundamentals of optical transitions (for your offline reading)

Here we show how transition rates are calculated, using a simple 2-state model system.

Real physical systems are usually many-state, therefore the complete basis set must include all eigenstates of the Hamiltonian. This makes the notation to account for all states to be complicated, thus student may simply be scared off. Here, the 2-state model shows the essence. Once you understand the simple 2-state model, it will be straightforward to follow a quantum mechanics text book on a many-state formulation – the notation will not be overwhelming.

Refer to Slide 13 of Set 3 (Quantum Mechanics).

Without the incoming radiation (light), the model system Hamiltonian \( H_{(0)} \) has two eigenstates: ground state \( |0\rangle \) and excited state \( |1\rangle \). \( H_{(0)} \) is time-independent, thus \( |0\rangle \) and \( |1\rangle \) are stationary.

\[
H_{(0)} = \begin{pmatrix} E_0 & 0 \\ 0 & E_1 \end{pmatrix}
\]

The time evolution of the system follows

\[
\frac{i\hbar}{dt} \begin{pmatrix} c_0 \\ c_1 \end{pmatrix} = H_{(0)} \begin{pmatrix} c_0(t) \\ c_1(t) \end{pmatrix} = \begin{pmatrix} E_0 & 0 \\ 0 & E_1 \end{pmatrix} \begin{pmatrix} c_0(t) \\ c_1(t) \end{pmatrix}
\]
This is just two simple differential equations: \[ i \hbar \frac{d}{dt} c_0 = E_0 c_0 \] and \[ i \hbar \frac{d}{dt} c_1 = E_0 c_1 \]

Obviously, \( (c_0(t)) = (e^{-i \omega_0 t} c_0(0)) \) with \( \omega_0 = \frac{E_0}{\hbar} \) and \( \omega_1 = \frac{E_1}{\hbar} \)

You see, \( |c_0(t)|^2 \) and \( |c_1(t)|^2 \), probabilities that the system is found in the two states, will never change. No transition without external disturbance.

Now, let’s “turn on” the external field, signified by an additional term \( H' \) in the Hamiltonian.

\[ H' = \begin{pmatrix} H'_{00} & H'_{01} \\ H'_{10} & H'_{11} \end{pmatrix} \]

\[ H'_{00} = \langle 0 | H' | 0 \rangle \quad H'_{01} = \langle 0 | H' | 1 \rangle \]
\[ H'_{10} = \langle 1 | H' | 0 \rangle \quad H'_{11} = \langle 1 | H' | 1 \rangle \]

Don’t worry. We will express these matrix elements later.

\[ H = H_{(0)} + H' = \begin{pmatrix} E_0 + H'_{00} & H'_{01} \\ H'_{10} & E_1 + H'_{11} \end{pmatrix} \]

External fields are usually much weaker than the internal.
We will keep this in mind, and treat the radiation field as perturbation to \( H_{(0)} \).

\[ i \hbar \frac{d}{dt} \begin{pmatrix} c_0 \\ c_1 \end{pmatrix} = \begin{pmatrix} E_0 + H'_{00} & H'_{01} \\ H'_{10} & E_1 + H'_{11} \end{pmatrix} \begin{pmatrix} c_0(t) \\ c_1(t) \end{pmatrix} \]
\[ i\hbar \frac{d}{dt} c_0 = (E_0 + H'_{00})c_0 + H'_{01}c_1 \]

and

\[ i\hbar \frac{d}{dt} c_1 = H'_{10}c_0 + (E_1 + H'_{11})c_1 \]

Consider the case where \( c_0(0) = 1 \) and \( c_1(0) = 0 \) for absorption.

Keep in mind that \( H' \) is a perturbation. \( c_1(t) \ll c_0(t) \) for all \( t \). Neglect small quantities in the above two differential equations, then we have

\[ i\hbar \frac{d}{dt} c_0 = E_0 c_0 \quad \text{Same as the unperturbed} \quad \Rightarrow \quad c_0(t) = e^{-i\omega_0 t} c_0(0) = e^{-i\omega_0 t} \]

\[ i\hbar \frac{d}{dt} c_1 = H'_{10}c_0 + E_1 c_1 \quad \Rightarrow \quad i\hbar \frac{d}{dt} c_1 - E_1 c_1 = H'_{10}c_0 \]

\[ \Rightarrow \quad i\hbar \frac{d}{dt} c_1 - E_1 c_1 = H'_{10}e^{-i\omega_0 t} \]

Let \( c_1(t) = A(t)e^{-i\omega_1 t} \). This is a math trick, as you’ll see, but physical intuition tells us that it’s a good thing to do.

Then,

\[ i\hbar \frac{dA}{dt} e^{-i\omega_1 t} + A(t)E_1 e^{-i\omega_1 t} - A(t)E_1 e^{-i\omega_1 t} = H'_{10}e^{-i\omega_0 t} \]
\[ i\hbar \frac{dA}{dt} e^{-i\omega_1 t} = H'_{10} e^{-i\omega_0 t} \]

\[ i\hbar \frac{dA}{dt} = H'_{10} e^{i(\omega_1 - \omega_0) t} \]

Do not forget that matrix elements of \( H' \) are \textit{time-dependent}.

\[ A(t) = \frac{1}{i\hbar} \int_0^t H'_{10}(t') e^{i(\omega_1 - \omega_0) t'} dt' \]

The \textit{probability} of finding the system in state \(|1\rangle\), i.e., the absorption already happened, is

\[ |c_1(t)|^2 = |A(t)|^2 \quad \text{Recall that we let} \quad c_1(t) = A(t)e^{-i\omega_1 t}. \]

Now, let’s look at the \( H' \) corresponding to the field of the radiation.

Our model is a 2-level molecule or atom, whose size \(<<\) the radiation wavelength. Thus only local field \( \mathcal{E} = \mathcal{E}_0 \cos \omega t \) needs to be considered, without spatial variation. This field leads to an additional term in the electron’s potential, which is \(-qr \cdot \mathcal{E}\).

If we define \( r \) as from the charge centroid of the system, \(-qr\) is the \textit{dipole moment}.

You see, the system (molecule or atom) interacts with the radiation field through its \textit{dipole moment}.

Therefore, \( H' = -qr \cdot \mathcal{E} \). \( \Rightarrow \)
\[ H'_{10} = \langle 1 | H' | 0 \rangle = -\langle 1 | q r \cdot \mathcal{E}_0 \cos \omega t | 0 \rangle = -\langle 1 | q r | 0 \rangle \cdot \mathcal{E}_0 \cos \omega t = d_{11} \cdot \mathcal{E}_0 \cos \omega t \]

Here, \( d_{10} \equiv -\langle 1 | q r | 0 \rangle \) is a dipole moment matrix element.

Other matrix elements \( H' \) can be found in the same way, although we don’t need them.

Now, the probability of finding the system in state \( |1\rangle \), i.e., the absorption already happened, is

\[ |A(t)|^2 = \left| \frac{1}{i \hbar} \int_0^t H'_{10}(t')e^{i(\omega_1 - \omega_0)t'} dt' \right|^2 = \frac{(d_{10} \cdot \mathcal{E}_0)^2}{\hbar^2} \left| \int_0^t \cos^2 \omega t e^{i(\omega_1 - \omega_0)t'} dt' \right|^2 \]

You can already see something interesting:

1. Absorption will never happen if \( d_{10} \perp \mathcal{E}_0 \Rightarrow d_{10} \cdot \mathcal{E}_0 = 0 \).
   Thus transition probability depends on polarization.

2. Absorption will never happen if \( d_{10} = 0 \).

   If the wave function of \( |0\rangle \) is spherically symmetric, \( \psi_0(r) = \psi_0(-r) \), but \( |0\rangle \) is antisymmetric, \( \psi_0(r) = -\psi_0(-r) \), then \( d_{10} \equiv -\langle 1 | q r | 0 \rangle = 0 \).

This is the reason behind selection rules.
We are interested in the transition probability at times much longer $\frac{\pi}{\omega}$. 

$$|A(t)|^2 = \frac{(d_{10} \cdot \mathcal{E}_0)^2}{\hbar^2} \left| \int_0^t \cos^2 \omega t e^{i(\omega_1 - \omega_0)t'} dt' \right|^2$$

Define $\omega_{10} \equiv \omega_1 - \omega_0$, then

$$|A(t)|^2 = \frac{(d_{10} \cdot \mathcal{E}_0)^2 \sin^2 \frac{\omega_{10} - \omega}{2} t}{4\hbar^2} = \frac{(d_{10} \cdot \mathcal{E}_0)^2}{4\hbar^2} t^2 \sin^2 \left( \frac{\omega_{10} - \omega}{2} t \right)$$

Here, we use the sinc function, defined as

$$\text{sinc } x = \frac{\sin x}{x}.$$ 

We are interested in the transition probability at times much longer $2\pi/\omega$.

$$\lim_{t \to \infty} \left[ t^2 \sin^2 \left( \frac{\omega_{10} - \omega}{2} t \right) \right] = \pi t \delta \left( \frac{\omega_{10} - \omega}{2} \right)$$

See next slide for the math of sinc squared and this limit.

https://upload.wikimedia.org/wikipedia/commons/2/2c/Sinc_squared_function.svg
Math digression: the sinc squared function

The Fourier transform of the triangular pulse is a sinc squared function.

\[ f(x) = -\frac{A}{T_1} |x| + A \]
\[ f(x) = 0 \quad |x| < T_1 \quad \text{and} \quad |x| > T_1 \]

The Fourier transform is given by:

\[ F(p) = A T_1 \left[ \frac{\sin(\pi T_1 p)}{\pi T_1 p} \right]^2 = A T_1 \mathrm{sinc}^2(\pi T_1 p) \]

In the convention used here, \( p \) is frequency, not angular frequency.

If we keep \( A = 1 \) and let \( T_1 \to \infty \), the Fourier transform will approach the delta function.

\[ \lim_{T_1 \to \infty} [T_1 \, \mathrm{sinc}^2(T_1 \pi p)] = \delta(p) = \pi \delta(\pi p) \quad \Rightarrow \quad \lim_{T_1 \to \infty} [(T_1)^2 \, \mathrm{sinc}^2(T_1 \pi p)] = \pi T_1 \delta(\pi p) \]

(We know this is bad mathematical notation, but keeping writing this way for convenience.)

Simply by substitution, we get:

\[ \lim_{t \to \infty} \left[ t^2 \, \mathrm{sinc}^2 \left( \frac{\omega_{10} - \omega}{2} t \right) \right] = \pi t \delta \left( \frac{\omega_{10} - \omega}{2} \right) \]
With \( \lim_{t \to \infty} \left[ t^2 \text{sinc}^2 \left( \frac{\omega_{10} - \omega}{2} t \right) \right] = \pi t \delta \left( \frac{\omega_{10} - \omega}{2} \right) \) inserted into

\[
|A(t)|^2 = \frac{(\mathbf{d}_{10} \cdot \mathbf{E}_0)^2}{4\hbar^2} t^2 \text{sinc}^2 \left( \frac{\omega_{10} - \omega}{2} t \right)
\]

we get the transition probability for large time \( t \):

\[
|A(t)|^2 = \frac{(\mathbf{d}_{10} \cdot \mathbf{E}_0)^2}{4\hbar^2} \pi t \delta \left( \frac{\omega_{10} - \omega}{2} \right) = \frac{(\mathbf{d}_{10} \cdot \mathbf{E}_0)^2}{2\hbar^2} \pi t \delta(\omega_{10} - \omega)
\]

Notice linear dependence on \( t \)

Thus the transition rate is

\[
\frac{d}{dt} |A(t)|^2 = \frac{(\mathbf{d}_{10} \cdot \mathbf{E}_0)^2}{2\hbar^2} \pi \delta(\omega_{10} - \omega)
\]

This means transition happens only when \( \omega_{10} = \omega \), i.e., \( E_1 - E_0 = \hbar \omega \).

**Stimulated emission**

Use the same general formulation in Slides 21-23 but consider the model system initially in \( |1\rangle \), i.e., \( c_0(0) = 0 \) and \( c_1(0) = 1 \) for stimulated emission.

We will get the same transition rate as absorption, using

\[
|\mathbf{d}_{01}|^2 = |\mathbf{d}_{10}|^2,
\]

for one single atom or molecule (the model).
In the above for a single atom/molecule, we don’t need to consider spatial variation of the radiation field, since the wavelength is much larger than the atom/molecule size.

A semiconductor crystal is larger than or at least comparable to optical wavelengths. Considering radiation wave propagation leads to conservation of momentum, in addition to conservation of energy.

The transition rate is the same for absorption and stimulated emission, for one single atom or molecule.

Extend to solid state: The rate is the same for absorption and stimulated emission, for a pair of VB and CB state.

And, the rate is $\propto$ radiation intensity through the factor $|\mathcal{E}_0|^2$, therefore $\propto$ photon flux.

Naturally, we have

Stimulated emission rate

$$r_{st}(\nu) = \phi_{\nu} \frac{\lambda^2}{8\pi \tau_r} \rho(\nu) f_{ce}(\nu)$$

# of emitting pair of states

Absorption rate

$$\gamma_{ab}(\nu) = \phi_{\nu} \frac{\lambda^2}{8\pi \tau_r} \rho(\nu) f_{ca}(\nu)$$

# of absorbing pair of states

Factor originating from photon density of modes
Spontaneous emission

According to the version of quantum mechanics we know, a system in $|1\rangle$ will stay in the excited state forever, since it is a stationary state. But that’s not true.

The explanation of spontaneous emission requires quantum electrodynamics (QED).

Here we give a heuristic explanation:

We learned that, in a system of coupled harmonic oscillators, the energy of a normal mode characterized by angular frequency $\omega$ is

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega, \quad n = 0, 1, 2, \ldots$$

The vibration energy is never zero.

The electromagnetic field is similar, having a ground state, called the QED vacuum. **Spontaneous emission** is the result of the excited stationary states of a quantum system (e.g. our 2-state model) interacting with the QED vacuum.

The system can emit into an infinite number of modes that satisfy $\hbar\omega = E_1 - E_0$. 
Spontaneous emission can thus be thought of as “stimulated” by modes of the QED vacuum.

Thus, the spontaneous emission rate is $\propto |\mathbf{d}_{10}|^2$, same as for absorption and stimulated emission. Therefore the same selection rules apply.

For solid state,

$$\gamma_{sp}(\nu) = \frac{l}{c_r} \rho(\nu) f_e(\nu)$$

# of emitting pair of states