

Chapter 3

Optical Transitions in Bulk Semiconductors

3.1 Introduction

In this chapter we will discuss optical transitions in semiconductors, optical loss, and optical gain. The basic rule for obtaining the transition rates is given by Fermi's golden rule.

3.2 Fermi's Golden Rule

Consider a quantum mechanical system with a Hamiltonian \hat{H}_0 . The set of eigenstates $|\phi_n\rangle$ of the Hamiltonian satisfy,

$$\hat{H}_0 |\phi_n\rangle = \varepsilon_n |\phi_n\rangle$$

Suppose now at $t=0$ a time dependent perturbation, described by $\{\hat{H}_+ e^{-i\alpha t} + \hat{H}_- e^{i\alpha t}\}$ is "switched on". The total Hamiltonian for $t \geq 0$ is,

$$\hat{H} = \hat{H}_0 + \hat{H}_+ e^{-i\alpha t} + \hat{H}_- e^{i\alpha t}$$

The time dependent part causes transitions between states, and the rates for these transitions is given by Fermi's Golden Rule. For the Hamiltonian to be Hermitian, we must have,

$$\hat{H}_+ = (\hat{H}_-)^{\dagger}$$

Suppose at $t=0$ the an electron was sitting in energy eigenstate $|\phi_k\rangle$. For $t \geq 0$, the state of the electron can be written most generally as,

$$|\psi(t)\rangle = \sum_n c_n(t) e^{-i \frac{\varepsilon_n t}{\hbar}} |\phi_n\rangle$$

where,

$$c_n(t=0) = \begin{cases} 1 & \text{if } n = k \\ 0 & \text{if } n \neq k \end{cases}$$

The quantity $|c_n(t)|^2$ gives the probability of the electron being in state $|\phi_n\rangle$. We plug the above expression for $|\psi(t)\rangle$ in the time-dependent Schrodinger equation,

$$i\hbar \frac{\partial |\psi(t)\rangle}{\partial t} = \hat{H} |\psi(t)\rangle$$

and take the bra on both sides with $\langle \phi_k |$ to get,

$$\begin{aligned}
 \frac{\partial}{\partial t} c_k(t) &= -\frac{i}{\hbar} \sum_{n \neq k} \langle \phi_k | \hat{H}_+ e^{-i\omega t} + \hat{H}_- e^{i\omega t} | \phi_n \rangle c_n(t) e^{-i \frac{(\varepsilon_n - \varepsilon_k)t}{\hbar}} \\
 &= -\frac{i}{\hbar} \sum_{n \neq k} \langle \phi_k | \hat{H}_+ | \phi_n \rangle c_n(t) e^{-i \frac{(\varepsilon_n - \varepsilon_k + \hbar\omega)t}{\hbar}} \\
 &\quad - \frac{i}{\hbar} \sum_{n \neq k} \langle \phi_k | \hat{H}_- | \phi_n \rangle c_n(t) e^{-i \frac{(\varepsilon_n - \varepsilon_k - \hbar\omega)t}{\hbar}} \quad (1)
 \end{aligned}$$

The right hand side of the above equation contains terms some of which are resonant and important and some which are not resonant and unimportant. The resonant terms are those for which the time dependent exponentials are close to zero and for which the energy ε_n differs from the energy ε_k by values close $\hbar\omega$. These terms don't oscillate rapidly as a function of time and therefore give much larger contribution to the sum than the non-resonant terms. We discard all the non-resonant terms and assume that the summation on the right hand side is only over the resonant terms. This means that for each n at most only one term on the right hand side will contribute (but never both). Next we write a similar equation for $c_n(t)$ ($n \neq k$) assuming it is a coefficient of one of the resonant terms,

$$i\hbar \frac{\partial}{\partial t} c_n(t) = \langle \phi_n | \hat{H}_+ e^{-i\omega t} + \hat{H}_- e^{i\omega t} | \phi_k \rangle c_k(t) e^{-i \frac{(\varepsilon_k - \varepsilon_n)t}{\hbar}} \quad (2)$$

Note that on the right hand side we have retained only one term because $c_k(t \approx 0) \approx 1$ and all other coefficients are approximately zero for $t \approx 0$. We directly integrate Equation (2) to get,

$$\begin{aligned}
 c_n(t) &= -\frac{i}{\hbar} \langle \phi_n | \hat{H}_+ | \phi_k \rangle \int_0^t c_k(t') e^{-i \frac{(\varepsilon_k - \varepsilon_n + \hbar\omega)t'}{\hbar}} dt' \\
 &\quad - \frac{i}{\hbar} \langle \phi_n | \hat{H}_- | \phi_k \rangle \int_0^t c_k(t') e^{-i \frac{(\varepsilon_k - \varepsilon_n - \hbar\omega)t'}{\hbar}} dt'
 \end{aligned}$$

Since the time exponentials are rapidly varying functions of time compared to $c_k(t')$ we can pull $c_k(t')$ out of the integral and then integrate to get,

$$\begin{aligned}
 c_n(t) &= -\frac{i}{\hbar} \langle \phi_n | \hat{H}_+ | \phi_k \rangle \left[e^{-i \frac{(\varepsilon_k - \varepsilon_n + \hbar\omega)t}{\hbar}} - 1 \right] \frac{c_k(t)}{-i \frac{(\varepsilon_k - \varepsilon_n + \hbar\omega)}{\hbar}} \\
 &\quad - \frac{i}{\hbar} \langle \phi_n | \hat{H}_- | \phi_k \rangle \left[e^{-i \frac{(\varepsilon_k - \varepsilon_n - \hbar\omega)t}{\hbar}} - 1 \right] \frac{c_k(t)}{-i \frac{(\varepsilon_k - \varepsilon_n - \hbar\omega)}{\hbar}} \quad (3)
 \end{aligned}$$

Depending on the relative energy alignment of levels n and k only one term (which is resonant) on the right hand side will contribute in a significant way (but never both). We keep only that term and then substitute the result into Equation (1) taking care to keep only the resonant terms. This gives,

$$\begin{aligned} \frac{\partial}{\partial t} c_k(t) = & -\frac{i}{\hbar^2} \sum_{n \neq k} \left| \langle \phi_n | \hat{H}_- | \phi_k \rangle \right|^2 \left[1 - e^{-i \frac{(\varepsilon_n - \varepsilon_k + \hbar\omega)t}{\hbar}} \right] \frac{c_k(t)}{\frac{(\varepsilon_k - \varepsilon_n - \hbar\omega)}{\hbar}} \\ & - \frac{i}{\hbar^2} \sum_{n \neq k} \left| \langle \phi_n | \hat{H}_+ | \phi_k \rangle \right|^2 \left[1 - e^{-i \frac{(\varepsilon_n - \varepsilon_k - \hbar\omega)t}{\hbar}} \right] \frac{c_k(t)}{\frac{(\varepsilon_k - \varepsilon_n + \hbar\omega)}{\hbar}} \end{aligned}$$

Now to figure out the transition rate we need to evaluate $\partial |c_k(t)|^2 / \partial t$. This can be obtained by taking the above equation, multiplying on both sides by $c_k^*(t)$, and then adding its complex conjugate to it to obtain,

$$\frac{\partial}{\partial t} |c_k(t)|^2 = \left[\begin{aligned} & -\frac{2}{\hbar^2} \sum_{n \neq k} \left| \langle \phi_n | \hat{H}_- | \phi_k \rangle \right|^2 \frac{\sin \left[\frac{(\varepsilon_k - \varepsilon_n - \hbar\omega)t}{\hbar} \right]}{\frac{(\varepsilon_k - \varepsilon_n - \hbar\omega)}{\hbar}} \\ & -\frac{2}{\hbar^2} \sum_{n \neq k} \left| \langle \phi_n | \hat{H}_+ | \phi_k \rangle \right|^2 \frac{\sin \left[\frac{(\varepsilon_k - \varepsilon_n + \hbar\omega)t}{\hbar} \right]}{\frac{(\varepsilon_k - \varepsilon_n + \hbar\omega)}{\hbar}} \end{aligned} \right] |c_k(t)|^2$$

For times that are large the two sinc functions, as a functions of $\hbar\omega$, become very sharply peaked at the energy differences $\varepsilon_k - \varepsilon_n$ and $\varepsilon_n - \varepsilon_k$, and may be approximated as delta functions with a total integrated weight equal to π . We finally have,

$$\frac{\partial}{\partial t} |c_k(t)|^2 = -\Gamma |c_k(t)|^2$$

The above equation shows that the probability of the electron being in the initial state decays exponentially with time because the electron is likely to make a transition to another state. The probability decay rate Γ is given by,

$$\Gamma = \frac{2\pi}{\hbar} \sum_{n \neq k} \left| \langle \phi_n | \hat{H}_- | \phi_k \rangle \right|^2 \delta(\varepsilon_k - \varepsilon_n - \hbar\omega) + \frac{2\pi}{\hbar} \sum_{n \neq k} \left| \langle \phi_n | \hat{H}_+ | \phi_k \rangle \right|^2 \delta(\varepsilon_k - \varepsilon_n + \hbar\omega)$$

Note that the probability decay rate consists of two parts. The first part is due to transitions from the initial state $|\phi_k\rangle$ to all final states whose energy is smaller than the energy of the initial state by $\hbar\omega$. The second part is due to transitions from the initial state $|\phi_k\rangle$ to all final states whose energy is larger than the energy of the initial state by $\hbar\omega$. Fermi's golden rule states that,

- a. Transition rate (or transition probability per second) to states of higher energy is given as,

$$\frac{2\pi}{\hbar} \sum_{n \neq k} \left| \langle \phi_n | \hat{H}_+ | \phi_k \rangle \right|^2 \delta(\varepsilon_k - \varepsilon_n + \hbar\omega)$$

- b. Transition rate to states of lower energy is given as,

$$\frac{2\pi}{\hbar} \sum_{n \neq k} \left| \langle \phi_n | \hat{H}_- | \phi_k \rangle \right|^2 \delta(\varepsilon_k - \varepsilon_n - \hbar\omega)$$

In each case, upward or downward transitions, the final states are those that are connected to initial state by the matrix elements, $\langle \phi_n | \hat{H}_+ | \phi_k \rangle$ or $\langle \phi_n | \hat{H}_- | \phi_k \rangle$, respectively. In these transitions, the energy conservation is enforced by the delta functions. Additional selection rules, as we will see, come from the matrix elements.

3.3 Light-Matter Interaction in Quantum Mechanics

3.3.1 Light-Matter Hamiltonian I:

Electromagnetic radiation can be described by its electric and magnetic fields, $\vec{E}(\vec{r}, t)$ and $\vec{H}(\vec{r}, t)$ equivalently by the vector potential $\vec{A}(\vec{r}, t)$, where,

$$\vec{E}(\vec{r}, t) = -\frac{\partial}{\partial t} \vec{A}(\vec{r}, t)$$

$$\vec{H}(\vec{r}, t) = \frac{1}{\mu_0} \nabla \times \vec{A}(\vec{r}, t).$$

In the presence of electromagnetic radiation the Hamiltonian for a particle of charge q is given as,

$$\frac{\hat{p}^2}{2m} + V(\vec{r}) \rightarrow \frac{[\hat{p} - q\vec{A}(\vec{r}, t)]^2}{2m} + V(\vec{r})$$

Since electron charge is negative for electrons one should write the Hamiltonian as,

$$\frac{[\hat{p} + q\vec{A}(\vec{r}, t)]^2}{2m} + V(\vec{r}) = \left\{ \frac{\hat{p}^2}{2m} + V(\vec{r}) \right\} + \frac{q}{2m} \left\{ \vec{A}(\vec{r}, t) \cdot \hat{p} + \hat{p} \cdot \vec{A}(\vec{r}, t) \right\} + \frac{q^2}{2m} |\vec{A}(\vec{r}, t)|^2$$

From basic quantum mechanics,

$$\left[f(\vec{r}), \hat{P} \right] = i\hbar \vec{\nabla} f(\vec{r})$$

$$\Rightarrow \vec{A}(\vec{r}, t) \cdot \hat{p} - \hat{p} \cdot \vec{A}(\vec{r}, t) = i\hbar \nabla \cdot \vec{A}(\vec{r}, t) \propto \text{divergence of } \vec{A}(\vec{r}, t)$$

Since,

$$\vec{E}(\vec{r}, t) = -\frac{\partial}{\partial t} \vec{A}(\vec{r}, t)$$

and $\nabla \cdot \vec{E}(\vec{r}, t) = 0$ for radiation fields, this means $\nabla \cdot \vec{A}(\vec{r}, t) = 0$ for radiation fields. Therefore, $\hat{p} \cdot \vec{A}(\vec{r}, t)$ can be replaced by $\vec{A}(\vec{r}, t) \cdot \hat{p}$ in the Hamiltonian. One may ignore the term $\frac{e^2}{2m} |\vec{A}(\vec{r}, t)|^2$ in the Hamiltonian because it is not important for optical transitions. The final form of the Hamiltonian becomes,

$$\hat{H} = \left\{ \frac{\hat{p}^2}{2m} + V(\vec{r}) \right\} + \frac{q}{m} \vec{A}(\vec{r}, t) \cdot \hat{p}$$

3.3.2 Plane Wave Classical Electromagnetics:

For a plane wave, $\vec{A}(\vec{r}, t)$ can be expressed as,

$$\vec{A}(\vec{r}, t) = \vec{A}_0 \cos[\vec{q} \cdot \vec{r} - \omega t] = \frac{\vec{A}_0}{2} e^{i\vec{q} \cdot \vec{r}} e^{-i\omega t} + \frac{\vec{A}_0}{2} e^{-i\vec{q} \cdot \vec{r}} e^{i\omega t}$$

where,

$$q = \frac{\omega n}{c}$$

And n is the refractive index of the medium in which the wave is travelling. For a plane wave,

$$\nabla \cdot \vec{A}(\vec{r}, t) = 0$$

$$\Rightarrow \vec{q} \cdot \vec{A}(\vec{r}, t) = 0$$

A plane wave is always polarized perpendicular to direction of propagation. Energy carried by plane wave per unit area per second is given by the Poynting vector,

$$\vec{S}(\vec{r}, t) = \vec{E}(\vec{r}, t) \times \vec{H}(\vec{r}, t)$$

$$\vec{E}(\vec{r}, t) = -\frac{\partial \vec{A}(\vec{r}, t)}{\partial t} = -\omega \vec{A}_0 \sin[\vec{q} \cdot \vec{r} - \omega t] = \vec{E}_0 \sin[\vec{q} \cdot \vec{r} - \omega t]$$

$$\vec{H}(\vec{r}, t) = -\frac{\vec{q} \times \vec{A}_0}{\mu_0} \sin[\vec{q} \cdot \vec{r} - \omega t] = \vec{H}_0 \sin[\vec{q} \cdot \vec{r} - \omega t]$$

$$\vec{S}(\vec{r}, t) = \frac{\omega \vec{q}}{\mu_0} |\vec{A}_0|^2 \sin^2[\vec{q} \cdot \vec{r} - \omega t]$$

One is generally interested in the time averaged power,

$$\langle \vec{S}(\vec{r}, t) \rangle = \frac{\omega \vec{q}}{2\mu_0} |\vec{A}_0|^2$$

Direction of energy flow is given by the wavevector \vec{q} . Magnitude of $\langle \vec{S}(\vec{r}, t) \rangle$ equals $\frac{n\omega^2}{2\mu_0 c} |\vec{A}_0|^2$

which is the energy flow per unit area per second or power per unit area. Power flow per unit area is also called the intensity I ,

$$I = \frac{n\omega^2}{2\mu_0 c} |\vec{A}_0|^2 = \frac{n |\vec{E}_0|^2}{2\mu_0 c}$$

3.3.3 Photons and Photon Density:

Energy in radiation fields can be added or subtracted in discrete units only, called photons. Each photon has energy $\hbar\omega$. So far a plane wave, whose power per unit area equals $\frac{n\omega^2}{2\mu_0 c} |\vec{A}_0|^2$, the photon flow

per unit area per second is $\frac{n\omega}{2\hbar\mu_0 c} |\vec{A}_0|^2$. Consequently, the photon density n_p (number of photons per unit volume) for a plane wave equals,

$$n_p = \frac{\text{Photon flow per unit area per second}}{\text{velocity of photons}} = \frac{\frac{n\omega}{2\hbar\mu_0 c} |\vec{A}_0|^2}{\frac{c}{n}}$$

$$= \frac{1}{2} \frac{\omega^2}{\hbar\omega} n^2 \epsilon_0 |\vec{A}_0|^2 = \frac{1}{2} \frac{\omega^2}{\hbar\omega} \epsilon_r \epsilon_0 |\vec{A}_0|^2$$

Here, the relative permittivity ϵ_r equals the square of the refractive index. The photon density can also be written as,

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$$n_p = \frac{1}{2} \frac{\epsilon_r \epsilon_0}{\hbar \omega} |\vec{E}_o|^2$$

In this course photon density will be represented by n_p . In dispersive media, where the refractive index is frequency dependent, a distinction needs to be made between the phase velocity v_p of a wave and the group velocity v_g^M of a wave,

$$v_p = \frac{c}{n}$$

$$v_g^M = \frac{c}{n + \omega \frac{dn}{d\omega}} = \frac{c}{n_g^M}$$

The group velocity is the velocity at which the energy, and therefore the photons, travel. The superscript “ M ” stands for material group velocity. Later in the course we will need to distinguish between the material group velocity and the group velocity of a guided wave in a waveguide. The photon density n_p (number of photons per unit volume) for a plane wave equals,

$$\begin{aligned} n_p &= \frac{\text{Photon flow per unit area per second}}{\text{velocity of photons}} = \frac{\frac{n\omega}{2\hbar\mu_0 c} |\vec{A}_o|^2}{\frac{c}{n_g^M}} \\ &= \frac{1}{2} \frac{\omega^2}{\hbar \omega} n n_g^M \epsilon_0 |\vec{A}_o|^2 \end{aligned}$$

The photon density can also be written in terms of the electric field,

$$n_p = \frac{1}{2} \frac{n n_g^M \epsilon_0}{\hbar \omega} |\vec{E}_o|^2 = \frac{1}{2} \frac{\partial(\omega \epsilon_r)}{\partial \omega} \frac{\epsilon_0}{\hbar \omega} |\vec{E}_o|^2$$

3.3.4 Light-Matter Hamiltonian II:

We start from the Hamiltonian.

$$\hat{H} = \left\{ \frac{\hat{p}^2}{2m} + V(\hat{r}) \right\} + \frac{q}{m} \vec{A}(\hat{r}, t) \cdot \hat{p}$$

We assume the Hamiltonian describes the interaction of an electron inside a semiconductor with an electromagnetic wave. The wave is given as,

$$\vec{A}(\vec{r}, t) = \vec{A}_o \cos[\vec{q} \cdot \vec{r} - \omega t] = \hat{n} \frac{A_o}{2} e^{i\vec{q} \cdot \vec{r}} e^{-i\omega t} + \hat{n} \frac{A_o}{2} e^{-i\vec{q} \cdot \vec{r}} e^{i\omega t}$$

The unit vector \hat{n} indicates the polarization direction of the field, $\vec{A}_o = \hat{n} A_o$. Using the above expression we can put the Hamiltonian in the form,

$$\hat{H} = \hat{H}_0 + \left\{ \hat{H}_+ e^{-i\omega t} + \hat{H}_- e^{i\omega t} \right\}$$

where,

$$\hat{H}_0 = \frac{\hat{p}^2}{2m} + V(\hat{r})$$

$$\hat{H}_+ = \frac{e}{2m} \bar{A}_0 e^{i\vec{q}\cdot\hat{r}} \cdot \hat{p} = \frac{q}{2m} A_0 e^{i\vec{q}\cdot\hat{r}} (\hat{n}\cdot\hat{p})$$

$$\hat{H}_- = \frac{e}{2m} \bar{A}_0 e^{-i\vec{q}\cdot\hat{r}} \cdot \hat{p} = \frac{q}{2m} A_0 e^{-i\vec{q}\cdot\hat{r}} (\hat{n}\cdot\hat{p})$$

3.5 Optical Transitions in Semiconductors

We consider a semiconductor in which the conduction band and valence band energy dispersions are given by,

$$E_c(\vec{k}) = E_c + \frac{\hbar^2 k^2}{2m_e}$$

$$E_v(\vec{k}) = E_v - \frac{\hbar^2 k^2}{2m_h}$$

The energy eigenstates are Bloch functions that can be written as,

$$\psi_{n,\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} u_{n,\vec{k}}(\vec{r})$$

3.5.1 Selection Rules for Optical Transitions:

Suppose an electromagnetic wave is propagating through the semiconductor. The first question to ask is what are the possible ways in which an electron in the semiconductor can absorb a photon from the electromagnetic wave. The possible transitions are shown in the Figure below. There are two kinds of photonic transitions; interband transitions (in which the electron makes a transition to a state in a different band) and intraband transitions (in which the electron makes a transition to a state in the same band). Consider an electron with an initial crystal momentum \vec{k}_i and energy $E_n(\vec{k}_i)$. The electron absorbs a photon and transitions to a state with crystal momentum \vec{k}_f and energy $E_m(\vec{k}_f)$. Energy conservation implies,

$$E_m(\vec{k}_f) = E_n(\vec{k}_i) + \hbar\omega$$

Final energy Initial energy Photon energy

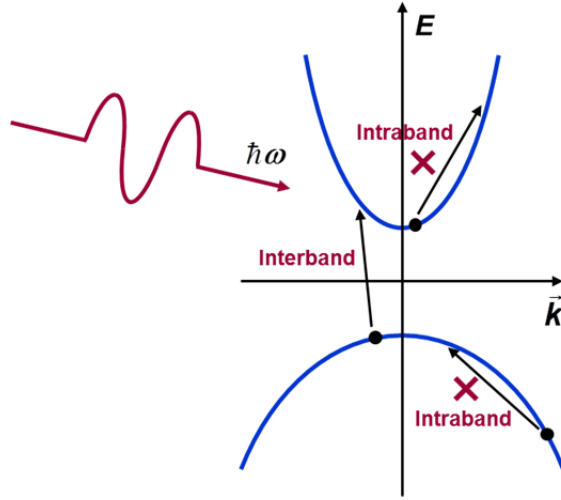
In addition to the energy conservation rule there is another selection rule, conservation of momentum, which states,

$$\vec{k}_f = \vec{k}_i + \vec{q}$$

Final crystal Initial crystal Photon
momentum momentum momentum

We will derive the momentum selection rule later. The two conservation rules allow only those optical transitions in which the initial and final states of the electron belong to different bands. These transitions are called interband transitions. Optical transitions in which the initial and final states of the electron belong to the same band are not allowed as they cannot satisfy both the conservation rules. Such transitions, called intraband transitions, are therefore forbidden. We will therefore focus on only interband optical transitions. There is a third selection rule that has to do with the electron angular momentum and spin but its full discussion is beyond the scope of this course. We will assume here, for simplicity, that the electron spin is conserved during optical transitions as this assumption will let us arrive at many results

without incurring any errors.



3.5.2 Optical Transition Rates:

Consider an electron with an initial state in the valence band given by,

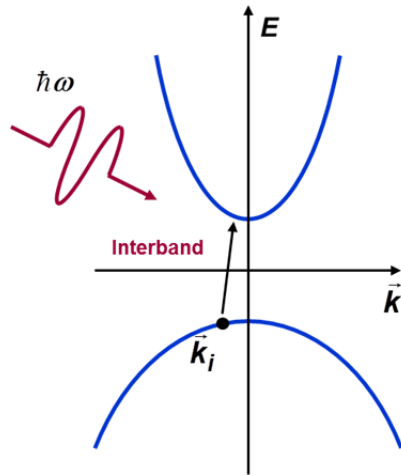
$$|\psi(t=0)\rangle = |\psi_{v,\vec{k}_i}\rangle$$

The transition rate from the initial state to a state in the conduction band in the presence of electromagnetic radiation is given by Fermi's golden rule,

$$W_{\uparrow}(\vec{k}_i) = \frac{2\pi}{\hbar} \sum_{\vec{k}_f} \left| \langle \psi_{c,\vec{k}_f} | \hat{H}_+ | \psi_{v,\vec{k}_i} \rangle \right|^2 \delta(E_c(\vec{k}_f) - E_v(\vec{k}_i) - \hbar\omega)$$

Note that the summation is over all possible final states in the conduction band that have the same spin as the initial state. Energy conservation is enforced by the delta function.

$$\begin{aligned} W_{\uparrow}(\vec{k}_i) &= \frac{2\pi}{\hbar} \sum_{\vec{k}_f} \left| \langle \psi_{c,\vec{k}_f} | \hat{H}_+ | \psi_{v,\vec{k}_i} \rangle \right|^2 \delta(E_c(\vec{k}_f) - E_v(\vec{k}_i) - \hbar\omega) \\ &= \frac{2\pi}{\hbar} \left(\frac{eA_0}{2m} \right)^2 \sum_{\vec{k}_f} \left| \langle \psi_{c,\vec{k}_f} | e^{i\vec{q} \cdot \hat{r}} \hat{P} \cdot \hat{n} | \psi_{v,\vec{k}_i} \rangle \right|^2 \delta(E_c(\vec{k}_f) - E_v(\vec{k}_i) - \hbar\omega) \end{aligned}$$



To proceed further we need the momentum matrix element between the initial and final states,

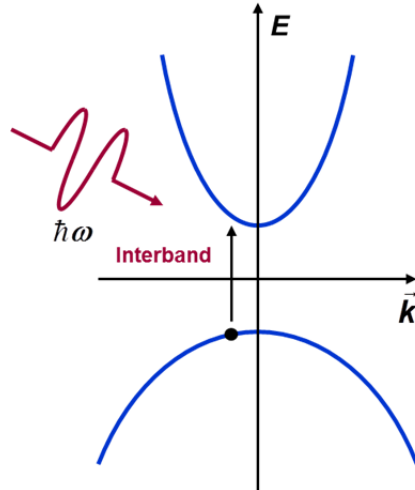
$$\begin{aligned}
 & \left\langle \psi_{c, \bar{k}_f} \left| e^{i\bar{q} \cdot \bar{r}} \hat{\mathbf{p}} \cdot \hat{\mathbf{n}} \right| \psi_{v, \bar{k}_i} \right\rangle \\
 &= \int d^3\bar{r} \psi_{c, \bar{k}_f}^*(\bar{r}) e^{i\bar{q} \cdot \bar{r}} \hat{\mathbf{p}} \cdot \hat{\mathbf{n}} \psi_{v, \bar{k}_i}(\bar{r}) \\
 &= \int d^3\bar{r} e^{-i\bar{k}_f \cdot \bar{r}} u_{c, \bar{k}_f}^*(\bar{r}) e^{i\bar{q} \cdot \bar{r}} \hat{\mathbf{p}} \cdot \hat{\mathbf{n}} e^{i\bar{k}_i \cdot \bar{r}} u_{v, \bar{k}_i}(\bar{r}) \\
 &= \int d^3\bar{r} e^{-i\bar{k}_f \cdot \bar{r}} u_{c, \bar{k}_f}^*(\bar{r}) e^{i\bar{q} \cdot \bar{r}} e^{i\bar{k}_i \cdot \bar{r}} (\hat{\mathbf{p}} + \hbar\bar{k}_i) \cdot \hat{\mathbf{n}} u_{v, \bar{k}_i}(\bar{r}) \\
 &= \int d^3\bar{r} e^{-i\bar{k}_f \cdot \bar{r}} u_{c, \bar{k}_f}^*(\bar{r}) e^{i\bar{q} \cdot \bar{r}} e^{i\bar{k}_i \cdot \bar{r}} \hat{\mathbf{p}} \cdot \hat{\mathbf{n}} u_{v, \bar{k}_i}(\bar{r})
 \end{aligned}$$

In the integrand, the lattice periodic functions, $u_{v, \bar{k}_i}(\bar{r})$ and $u_{c, \bar{k}_f}(\bar{r})$, are rapidly varying in space whereas the exponentials are slowly varying in space. Therefore, we can break up the integral over the entire crystal into integrals over all the primitive cells and then replace the exponentials by their average values in each primitive cell and then pull them out of the integrals to get,

$$\begin{aligned}
 & \left\langle \psi_{c, \bar{k}_f} \left| e^{i\bar{q} \cdot \bar{r}} \hat{\mathbf{p}} \cdot \hat{\mathbf{n}} \right| \psi_{v, \bar{k}_i} \right\rangle \\
 &= \int d^3\bar{r} e^{-i\bar{k}_f \cdot \bar{r}} u_{c, \bar{k}_f}^*(\bar{r}) e^{i\bar{q} \cdot \bar{r}} e^{i\bar{k}_i \cdot \bar{r}} \hat{\mathbf{p}} \cdot \hat{\mathbf{n}} u_{v, \bar{k}_i}(\bar{r}) \\
 &= \sum_{\bar{R}_j \text{ one primitive cell}} \int d^3\bar{r} e^{-i\bar{k}_f \cdot \bar{r}} u_{c, \bar{k}_f}^*(\bar{r}) e^{i\bar{q} \cdot \bar{r}} e^{i\bar{k}_i \cdot \bar{r}} \hat{\mathbf{p}} \cdot \hat{\mathbf{n}} u_{v, \bar{k}_i}(\bar{r}) \\
 &= \sum_{\bar{R}_j} e^{i(\bar{k}_i + \bar{q} - \bar{k}_f) \cdot \bar{R}_j} \int_{\text{one primitive cell}} d^3\bar{r} u_{c, \bar{k}_f}^*(\bar{r}) \hat{\mathbf{p}} \cdot \hat{\mathbf{n}} u_{v, \bar{k}_i}(\bar{r}) \\
 &= N \delta_{\bar{k}_i + \bar{q}, \bar{k}_f} \int_{\text{one primitive cell}} d^3\bar{r} u_{c, \bar{k}_f}^*(\bar{r}) \hat{\mathbf{p}} \cdot \hat{\mathbf{n}} u_{v, \bar{k}_i}(\bar{r}) \\
 &= \delta_{\bar{k}_i + \bar{q}, \bar{k}_f} \hat{\mathbf{p}}_{cv} \cdot \hat{\mathbf{n}}
 \end{aligned}$$

Note that the momentum conservation rule comes out of the momentum matrix element. With these results, we can finally write the transition rate as,

$$\begin{aligned}
 W_{\uparrow}(\bar{k}_i) &= \frac{2\pi}{\hbar} \left(\frac{eA_0}{2m} \right)^2 \sum_{\bar{k}_f} \left| \left\langle \psi_{c, \bar{k}_f} \left| e^{i\bar{q} \cdot \bar{r}} \hat{\mathbf{p}} \cdot \hat{\mathbf{n}} \right| \psi_{v, \bar{k}_i} \right\rangle \right|^2 \delta(E_c(\bar{k}_f) - E_v(\bar{k}_i) - \hbar\omega) \\
 &= \frac{2\pi}{\hbar} \left(\frac{eA_0}{2m} \right)^2 \sum_{\bar{k}_f} \left| \hat{\mathbf{p}}_{cv} \cdot \hat{\mathbf{n}} \right|^2 \delta_{\bar{k}_i + \bar{q}, \bar{k}_f} \delta(E_c(\bar{k}_f) - E_v(\bar{k}_i) - \hbar\omega) \\
 &= \frac{2\pi}{\hbar} \left(\frac{eA_0}{2m} \right)^2 \left| \hat{\mathbf{p}}_{cv} \cdot \hat{\mathbf{n}} \right|^2 \delta(E_c(\bar{k}_i + \bar{q}) - E_v(\bar{k}_i) - \hbar\omega)
 \end{aligned}$$



The momentum conservation rule states that,

$$\vec{k}_f = \vec{k}_i + \vec{q}$$

The photon momentum \vec{q} is generally so much smaller than the electron crystal momentum that to a very good approximation it can be ignored and the momentum conservation rule can be approximated as,

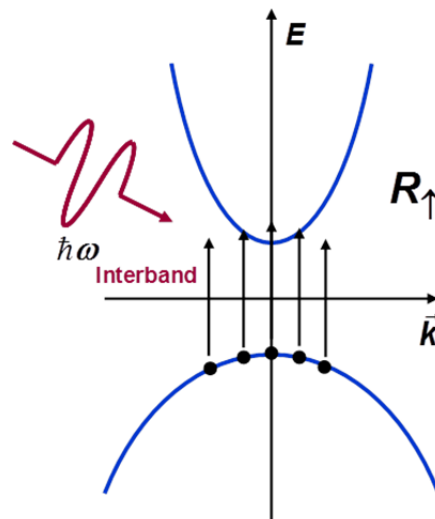
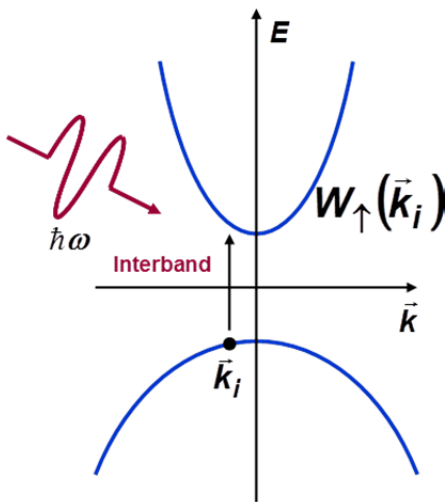
$$\vec{k}_f = \vec{k}_i$$

The above rule says that the optical transitions are vertical in k-space, as shown in the Figure above. We can therefore write the transition rate as,

$$W_{\uparrow}(\vec{k}_i) = \frac{2\pi}{\hbar} \left(\frac{qA_0}{2m} \right)^2 |\hat{p}_{cv} \cdot \hat{n}|^2 \delta(E_c(\vec{k}_i) - E_v(\vec{k}_i) - \hbar\omega)$$

Generally one is not interested in the transition rate for any one particular initial electron state but in the number of transitions happening per unit volume of the material per second. The upward transition rate per unit volume R_{\uparrow} is obtained by summing over all the possible initial states per unit volume weighed by the occupation probability of the initial state and by the probability that the final state is empty,

$$R_{\uparrow}(\omega) = \frac{2}{V} \times \sum_{\vec{k}_i} W_{\uparrow}(\vec{k}_i) f_v(\vec{k}_i) [1 - f_c(\vec{k}_i)]$$



If we assume, as in an intrinsic semiconductor, in which the valence band is almost full and the

conduction band is almost empty of electrons, then,

$$\begin{aligned}
 R_{\uparrow}(\omega) &\approx \frac{2}{V} \times \sum_{\vec{k}_i} W_{\uparrow}(\vec{k}_i) \\
 &= \frac{2}{V} \times \sum_{\vec{k}_i} \frac{2\pi}{\hbar} \left(\frac{qA_0}{2m} \right)^2 \left| \hat{\vec{p}}_{cv} \cdot \hat{n} \right|^2 \delta(E_c(\vec{k}_i) - E_v(\vec{k}_i) - \hbar\omega) \\
 &= 2 \times \int_{\text{FBZ}} \frac{d^3\vec{k}_i}{(2\pi)^3} \frac{2\pi}{\hbar} \left(\frac{qA_0}{2m} \right)^2 \left| \hat{\vec{p}}_{cv} \cdot \hat{n} \right|^2 \delta(E_c(\vec{k}_i) - E_v(\vec{k}_i) - \hbar\omega) \\
 &= \frac{2\pi}{\hbar} \left(\frac{qA_0}{2m} \right)^2 \left\langle \left| \hat{\vec{p}}_{cv} \cdot \hat{n} \right|^2 \right\rangle 2 \times \int_{\text{FBZ}} \frac{d^3\vec{k}_i}{(2\pi)^3} \delta(E_c(\vec{k}_i) - E_v(\vec{k}_i) - \hbar\omega) \\
 &= \frac{2\pi}{\hbar} \left(\frac{qA_0}{2m} \right)^2 \left\langle \left| \hat{\vec{p}}_{cv} \cdot \hat{n} \right|^2 \right\rangle 2 \times \int_{\text{FBZ}} \frac{d^3\vec{k}}{(2\pi)^3} \delta(E_c(\vec{k}) - E_v(\vec{k}) - \hbar\omega)
 \end{aligned}$$

The squared momentum matrix element $\left| \hat{\vec{p}}_{cv} \cdot \hat{n} \right|^2$ depends on the electron wavevector \vec{k} and also the polarization direction of the electromagnetic wave. The dependence on the electron wavevector is usually weak and one may replace $\left| \hat{\vec{p}}_{cv} \cdot \hat{n} \right|^2$ by its average value $\left\langle \left| \hat{\vec{p}}_{cv} \cdot \hat{n} \right|^2 \right\rangle$ and pull it out of the integral. In most bulk III-V semiconductors with cubic symmetry the average value $\left\langle \left| \hat{\vec{p}}_{cv} \cdot \hat{n} \right|^2 \right\rangle$ does not depend on the polarization direction of the electromagnetic wave.

The integral on the right hand side is not difficult to do. In fact, we have already seen a similar integral. Consider the conduction band energy dispersion,

$$E_c(\vec{k}) = E_c + \frac{\hbar^2 k^2}{2m_e} \quad (1)$$

The density of states function for the conduction band can be written as,

$$g_c(E) = 2 \times \int_{\text{FBZ}} \frac{d^3\vec{k}}{(2\pi)^3} \delta(E_c(\vec{k}) - E) = \frac{1}{2\pi^2} \left(\frac{2m_e}{\hbar^2} \right)^{3/2} \sqrt{E - E_c} \quad (2)$$

If one compares the above integral to the one appearing in the expression for R_{\uparrow} it can be seen that they are similar. To see this explicitly consider,

$$E_c(\vec{k}) - E_v(\vec{k}) = E_c - E_v + \frac{\hbar^2 k^2}{2} \left(\frac{1}{m_e} + \frac{1}{m_h} \right) = E_g + \frac{\hbar^2 k^2}{2m_r} \quad (3)$$

where the reduced mass m_r is defined as,

$$\frac{1}{m_r} = \frac{1}{m_e} + \frac{1}{m_h}$$

Comparing Equations (1) and (2) with Equation (3) and the expression for R_{\uparrow} , one can write the final result,

$$R_{\uparrow}(\omega) = \frac{2\pi}{\hbar} \left(\frac{qA_0}{2m} \right)^2 \left\langle \left| \hat{\mathbf{p}}_{cv} \cdot \hat{\mathbf{n}} \right|^2 \right\rangle \frac{1}{2\pi^2} \left(\frac{2m_r}{\hbar^2} \right)^{3/2} \sqrt{\hbar\omega - E_g}$$

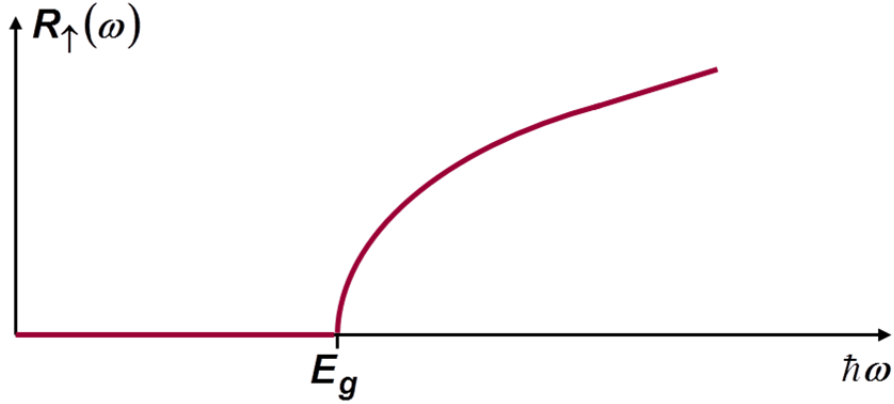
3.5.3 Joint Density of States:

The integral,

$$2 \times \int_{\text{FBZ}} \frac{d^3\vec{k}}{(2\pi)^3} \delta(E_c(\vec{k}) - E_v(\vec{k}) - \hbar\omega) = \frac{1}{2\pi^2} \left(\frac{2m_r}{\hbar^2} \right)^{3/2} \sqrt{\hbar\omega - E_g}$$

appearing in the expression for R_{\uparrow} is called the joint density of states. It gives the number of pairs of states (one in the valence band and one in the conduction band) per unit volume per unit photon energy interval whose energy difference equals $\hbar\omega$.

In the Figure below the transition rate is plotted as a function of the photon energy. There are no interband transitions if the photon energy is smaller than the bandgap. The transition rate increases as the joint density of states for photon energies larger than the bandgap.



We can write the expression for $R_{\uparrow}(\omega)$ in terms of the optical intensity I or the photon density N_p . Recall that,

$$I = \frac{n\omega^2}{2\mu_0 c} |\bar{A}_0|^2$$

$$n_p = \frac{1}{2} \frac{\omega^2}{\hbar\omega} n n_g^M \epsilon_0 |\bar{A}_0|^2$$

It follows that,

$$R_{\uparrow}(\omega) = \left(\frac{q}{m} \right)^2 \left(\frac{\pi n_p}{\omega n n_g^M \epsilon_0} \right) \left\langle \left| \hat{\mathbf{p}}_{cv} \cdot \hat{\mathbf{n}} \right|^2 \right\rangle \frac{1}{2\pi^2} \left(\frac{2m_r}{\hbar^2} \right)^{3/2} \sqrt{\hbar\omega - E_g}$$

$$R_{\uparrow}(\omega) = \left(\frac{q}{m} \right)^2 \left(\frac{\pi \mu_0 c I}{\hbar\omega^2 n} \right) \left\langle \left| \hat{\mathbf{p}}_{cv} \cdot \hat{\mathbf{n}} \right|^2 \right\rangle \frac{1}{2\pi^2} \left(\frac{2m_r}{\hbar^2} \right)^{3/2} \sqrt{\hbar\omega - E_g}$$

Note that the transition is proportional to the photon density or the intensity of radiation but not to the power of the radiation.

3.5.4 Momentum Matrix Elements:

In bulk III-V semiconductors with cubic symmetry, the average value of the momentum matrix element

$\left\langle \left| \hat{\mathbf{p}}_{cv} \cdot \hat{\mathbf{n}} \right|^2 \right\rangle$ is usually expressed in terms of the energy E_p as,

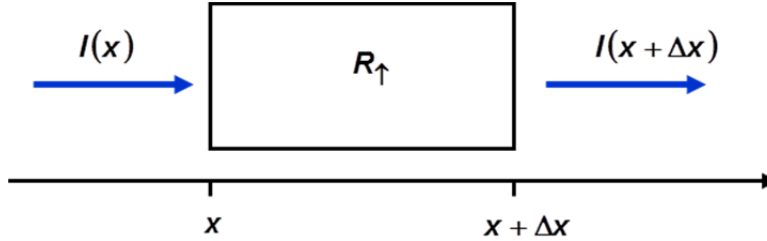
$$\left\langle \left| \hat{\mathbf{p}}_{cv} \cdot \hat{\mathbf{n}} \right|^2 \right\rangle = \frac{mE_p}{6}$$

The values of the momentum matrix element between the heavy hole and the conduction band states and between the light hole and the conduction band states are identical and are given in terms of the energy E_p in the Table below.

Parameters at 300K	GaAs	AlAs	InAs	InP	GaP
E_p (eV)	25.7	21.1	22.2	20.7	22.2

3.5.5 Loss Coefficient of Semiconductors:

Consider a semiconductor through which an electromagnetic wave is propagating. If the semiconductor is absorbing photons from the wave then the energy carried by the wave must decrease as the wave propagates. This energy loss can be related to the rate of optical transitions in the semiconductor.



Suppose the power $I(x)$ carried by the wave decays exponentially,

$$\frac{dI(x)}{dx} = -\alpha I(x)$$

$$\Rightarrow I(x + \Delta x) - I(x) = -\alpha I(x) \Delta x$$

Therefore, the energy loss per unit area per second in distance Δx is $\alpha I(x) \Delta x$. This energy loss must also equal $\hbar\omega R_{\uparrow}(\omega) \Delta x$. Equating these two expressions gives us the loss coefficient (or the absorption coefficient) $\alpha(\omega)$ of the semiconductor,

$$\alpha(\omega) = \left(\frac{q}{m} \right)^2 \left(\frac{\pi}{\epsilon_0 n \omega c} \right) \left\langle \left| \hat{\mathbf{p}}_{cv} \cdot \hat{\mathbf{n}} \right|^2 \right\rangle \frac{1}{2\pi^2} \left(\frac{2m_r}{\hbar^2} \right)^{3/2} \sqrt{\hbar\omega - E_g}$$

The above expression for $\alpha(\omega)$ is valid only for the case when the valence band is full of electrons and the conduction is empty. Throwing back in the electron occupation factors we get,

$$R_{\uparrow}(\omega) = \left(\frac{q}{m} \right)^2 \left(\frac{\pi n_p}{\omega n n_g^M \epsilon_0} \right) \left\langle \left| \hat{\mathbf{p}}_{cv} \cdot \hat{\mathbf{n}} \right|^2 \right\rangle 2 \times \int_{\text{FBZ}} \frac{d^3 \vec{k}}{(2\pi)^3} f_v(\vec{k}) [1 - f_c(\vec{k})] \delta(E_c(\vec{k}) - E_v(\vec{k}) - \hbar\omega)$$

and the absorption coefficient becomes,

$$\alpha(\omega) = \left(\frac{q}{m} \right)^2 \left(\frac{\pi}{\epsilon_0 n \omega c} \right) \left\langle \left| \hat{\mathbf{p}}_{cv} \cdot \hat{\mathbf{n}} \right|^2 \right\rangle 2 \times \int_{\text{FBZ}} \frac{d^3 \vec{k}}{(2\pi)^3} f_v(\vec{k}) [1 - f_c(\vec{k})] \delta(E_c(\vec{k}) - E_v(\vec{k}) - \hbar\omega)$$

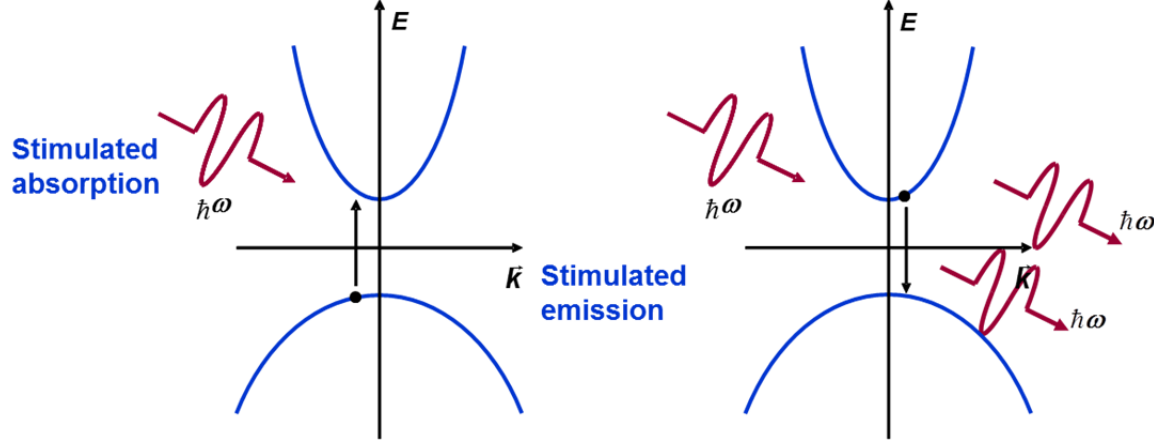
3.5.6 Stimulated Absorption and Stimulated Emission:

The process of photon absorption is called stimulated absorption (because, quite obviously, the process is initiated by the incoming radiation or photons some of which eventually end up getting absorbed). The

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photon absorption rate is therefore proportional to the photon density of the electromagnetic wave.

We have seen that Fermi's golden rule also allows electrons to make transitions to states whose energy is lower than their initial energy by $\hbar\omega$. For example, an electron sitting in the conduction band can make a transition to a valence band state by losing energy equal to $\hbar\omega$. The energy lost by the electron goes to the electromagnetic wave which initiated or stimulated the transition. Quantum mechanically we say that the electron in the conduction band emits a photon and makes a transition to the valence band. This process, depicted in the Figure below, is called stimulated emission.



The rate of stimulated emission is also given by the Fermi's golden rule and following the same procedure as was done to obtain to stimulated absorption rate, the stimulated emission rate can be written as,

$$R_{\downarrow}(\omega) = \left(\frac{q}{m}\right)^2 \left(\frac{\pi n_p}{\omega n n_g^M \epsilon_0}\right) \left\langle \left| \hat{p}_{cv} \cdot \hat{n} \right|^2 \right\rangle 2 \times \int_{\text{FBZ}} \frac{d^3 \vec{k}}{(2\pi)^3} f_c(\vec{k}) [1 - f_v(\vec{k})] \delta(E_c(\vec{k}) - E_v(\vec{k}) - \hbar\omega)$$

The net photon absorption rate is the difference between the stimulated absorption rate and the stimulated emission rate, The absorption coefficient of the semiconductor can then be related to the net photon absorption rate as follows,

$$\alpha(\omega) = \frac{R_{\uparrow}(\omega) - R_{\downarrow}(\omega)}{n_p \frac{c}{n_g^M}}$$

$$= \left(\frac{q}{m}\right)^2 \left(\frac{\pi}{\epsilon_0 n \omega c}\right) \left\langle \left| \hat{p}_{cv} \cdot \hat{n} \right|^2 \right\rangle 2 \times \int_{\text{FBZ}} \frac{d^3 \vec{k}}{(2\pi)^3} [f_v(\vec{k}) - f_c(\vec{k})] \delta(E_c(\vec{k}) - E_v(\vec{k}) - \hbar\omega)$$

The above expression is the most general form for the absorption of loss coefficient. Values of $\alpha(\omega)$ for most semiconductors can range from a few hundred cm^{-1} to hundred thousand cm^{-1} . In the Figure below, $\alpha(\omega)$ is plotted for different semiconductors.

If we consider a semiconductor in which the conduction band and valence band energy dispersions are given by,

$$E_c(\vec{k}) = E_c + \frac{\hbar^2 k^2}{2m_e} \quad E_v(\vec{k}) = E_v - \frac{\hbar^2 k^2}{2m_h}$$

then the integral for $\alpha(\omega)$ can be evaluated exactly,

$$\alpha(\omega) = \left(\frac{q}{m}\right)^2 \left(\frac{\pi}{\epsilon_0 n \omega c}\right) \left\langle \left| \hat{p}_{cv} \cdot \hat{n} \right|^2 \right\rangle 2 \times \int_{\text{FBZ}} \frac{d^3 \bar{k}}{(2\pi)^3} [f_v(\bar{k}) - f_c(\bar{k})] \delta(E_c(\bar{k}) - E_v(\bar{k}) - \hbar\omega)$$

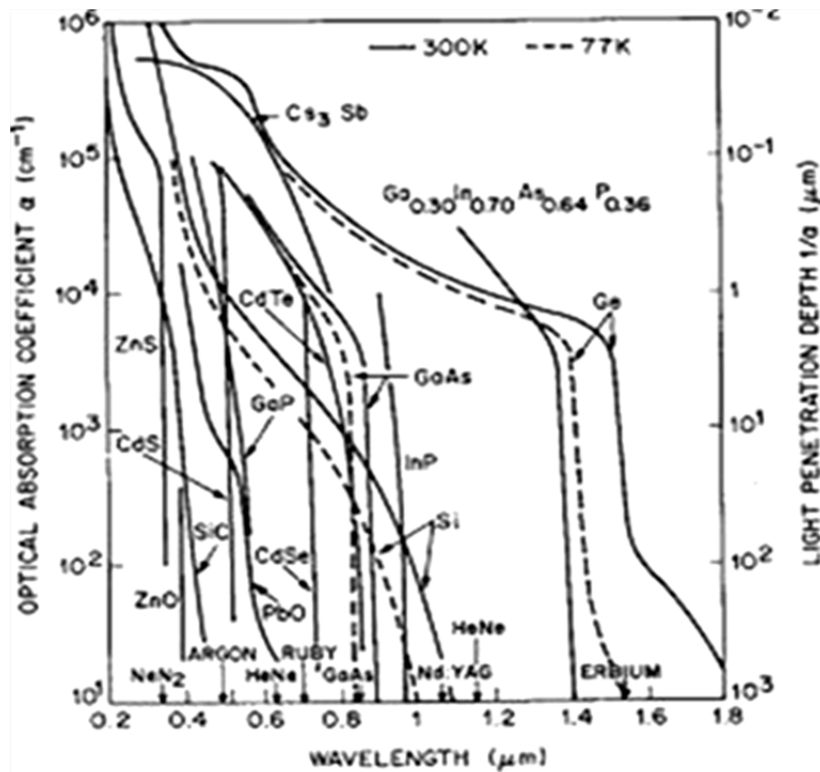
$$= \left(\frac{q}{m}\right)^2 \left(\frac{\pi}{\epsilon_0 n \omega c}\right) \left\langle \left| \hat{p}_{cv} \cdot \hat{n} \right|^2 \right\rangle \frac{1}{2\pi^2} \left(\frac{2m_r}{\hbar^2}\right)^{3/2} \sqrt{\hbar\omega - E_g}$$

$$\times \left[f_v \left(E_v - (\hbar\omega - E_g) \frac{m_r}{m_h} \right) - f_c \left(E_c + (\hbar\omega - E_g) \frac{m_r}{m_e} \right) \right]$$

There is a very convenient and compact expression for the net photon absorption rate.

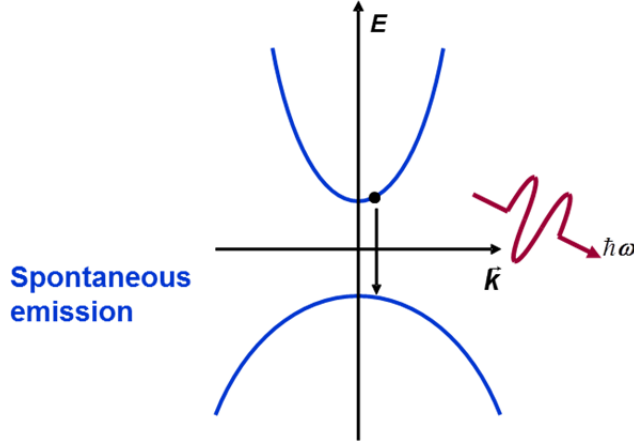
$$R_{\uparrow}(\omega) - R_{\downarrow}(\omega) = \frac{c}{n_g^M} \alpha(\omega) n_p = v_g^M \alpha(\omega) n_p$$

The above expression will be used throughout this course.



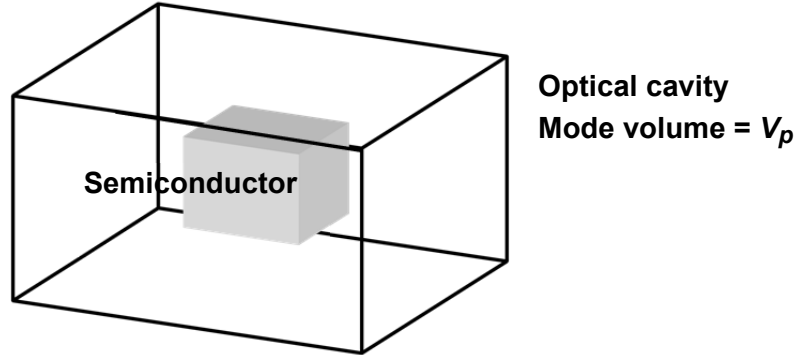
3.5.7 Spontaneous Emission:

In addition to the stimulated emission process, an electron in a higher energy level can spontaneously (i.e. in the absence of an external electromagnetic field) emit a photon and transition to a lower energy level. This process is called spontaneous emission. The Figure below depicts the spontaneous emission process for an electron initially in the conduction band. A complete description of the spontaneous emission process requires a quantum theory of radiation which is beyond the scope of this course. Here we follow an elegant thermodynamic argument by Albert Einstein to derive the rate of spontaneous emission.



Consider an optical cavity that has single mode of radiation with mode volume V_p . A more rigorous definition of the mode volume would be given in later Chapters. The cavity contains a small piece of an intrinsic semiconductor. Let the total number of photons in the cavity be N_p and let the photon energy be $\hbar\omega$. The radiation mode is assumed to be in perfect thermal equilibrium with the cavity and also with the semiconductor both of which are maintained at temperature T . In thermal equilibrium, the number of photons in the radiation mode is given by the Bose-Einstein factor,

$$N_p = \frac{1}{e^{\hbar\omega/KT} - 1}$$



The stimulated emission rate in the semiconductor is given as,

$$R_{\downarrow}(\omega) = \left(\frac{q}{m}\right)^2 \left(\frac{\pi}{\omega n n_g^M \epsilon_0}\right) \left(\frac{N_p}{V_p}\right) \left\langle \left| \hat{p}_{cv} \cdot \hat{n} \right|^2 \right\rangle 2 \times \int_{\text{FBZ}} \frac{d^3 \bar{k}}{(2\pi)^3} f_c(\bar{k}) [1 - f_v(\bar{k})] \delta(E_c(\bar{k}) - E_v(\bar{k}) - \hbar\omega)$$

And the stimulated absorption rate is given the expression,

$$R_{\uparrow}(\omega) = \left(\frac{q}{m}\right)^2 \left(\frac{\pi}{\omega n n_g^M \epsilon_0}\right) \left(\frac{N_p}{V_p}\right) \left\langle \left| \hat{p}_{cv} \cdot \hat{n} \right|^2 \right\rangle 2 \times \int_{\text{FBZ}} \frac{d^3 \bar{k}}{(2\pi)^3} f_v(\bar{k}) [1 - f_c(\bar{k})] \delta(E_c(\bar{k}) - E_v(\bar{k}) - \hbar\omega)$$

Suppose we were unaware of the spontaneous emission process. In thermal equilibrium the upward and downward transitions must completely balance each other out so we can write,

$$R_{\downarrow}(\omega) - R_{\uparrow}(\omega) = 0$$

$$\Rightarrow \left(\frac{q}{m}\right)^2 \left(\frac{\pi}{\omega n n_g^M \epsilon_0}\right) \left(\frac{N_p}{V_p}\right) \left\langle \left| \hat{p}_{cv} \cdot \hat{n} \right|^2 \right\rangle 2 \times \int_{\text{FBZ}} \frac{d^3 \bar{k}}{(2\pi)^3} [f_c(\bar{k}) - f_v(\bar{k})] \delta(E_c(\bar{k}) - E_v(\bar{k}) - \hbar\omega) = 0$$

$$\Rightarrow f_c(\bar{k}) - f_v(\bar{k}) = 0 \quad \text{for} \quad E_c(\bar{k}) - E_v(\bar{k}) = \hbar\omega$$

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The last result is clearly wrong if one assumes Fermi-Dirac occupation statistics for electrons in the semiconductor in thermal equilibrium. In fact, $R_{\downarrow}(\omega) \ll R_{\uparrow}(\omega)$. In order for the thermodynamics to work out Einstein assumed that there must be an additional mechanism by which electrons can make a downward transition and emit a photon and the rate for this mechanism should not depend on the number of photons in the cavity in order to allow an electron somehow excited from the valence band into the conduction to relax back into the valence band even in the absence of any other photons inside the cavity. Suppose the rate of this mechanism is $R_{sp}(\omega)$. One can argue further that in order to satisfy energy conservation and Pauli's exclusion principle $R_{sp}(\omega)$ must be proportional to,

$$R_{sp}(\omega) \propto 2 \times \int_{\text{FBZ}} \frac{d^3 \bar{k}}{(2\pi)^3} f_c(\bar{k}) [1 - f_v(\bar{k})] \delta(E_c(\bar{k}) - E_v(\bar{k}) - \hbar\omega)$$

Without losing generality, one may assume,

$$R_{sp}(\omega) \propto \left(\frac{q}{m}\right)^2 \left(\frac{\pi}{\omega n n_g^M \epsilon_0}\right) \left\langle \left| \hat{p}_{cv} \cdot \hat{n} \right|^2 \right\rangle 2 \times \int_{\text{FBZ}} \frac{d^3 \bar{k}}{(2\pi)^3} f_c(\bar{k}) [1 - f_v(\bar{k})] \delta(E_c(\bar{k}) - E_v(\bar{k}) - \hbar\omega)$$

$$\Rightarrow R_{sp}(\omega) = C \left(\frac{q}{m}\right)^2 \left(\frac{\pi}{\omega n n_g^M \epsilon_0}\right) \left\langle \left| \hat{p}_{cv} \cdot \hat{n} \right|^2 \right\rangle 2 \times \int_{\text{FBZ}} \frac{d^3 \bar{k}}{(2\pi)^3} f_c(\bar{k}) [1 - f_v(\bar{k})] \delta(E_c(\bar{k}) - E_v(\bar{k}) - \hbar\omega)$$

The constant of proportionality C remains to be determined. In thermal equilibrium one must have,

$$R_{\downarrow}(\omega) + R_{sp}(\omega) - R_{\uparrow}(\omega) = 0$$

$$\Rightarrow 2 \times \int_{\text{FBZ}} \frac{d^3 \bar{k}}{(2\pi)^3} \left\{ \left(\frac{N_p}{V_p}\right) [f_c(\bar{k}) - f_v(\bar{k})] + C f_c(\bar{k}) [1 - f_v(\bar{k})] \right\} \delta(E_c(\bar{k}) - E_v(\bar{k}) - \hbar\omega) = 0$$

$$\Rightarrow \left(\frac{N_p}{V_p}\right) [f_c(\bar{k}) - f_v(\bar{k})] + C f_c(\bar{k}) [1 - f_v(\bar{k})] = 0 \quad \text{for } E_c(\bar{k}) - E_v(\bar{k}) = \hbar\omega$$

$$\Rightarrow \frac{f_v(\bar{k}) - f_c(\bar{k})}{f_c(\bar{k}) [1 - f_v(\bar{k})]} = \frac{C V_p}{N_p} \quad \text{for } E_c(\bar{k}) - E_v(\bar{k}) = \hbar\omega$$

$$\Rightarrow e^{(E_c(\bar{k}) - E_v(\bar{k}))/KT} - 1 = C V_p (e^{\hbar\omega/KT} - 1) \quad \text{for } E_c(\bar{k}) - E_v(\bar{k}) = \hbar\omega$$

$$\Rightarrow C = \frac{1}{V_p}$$

The rate of spontaneous emission is therefore,

$$R_{sp}(\omega) = \left(\frac{q}{m}\right)^2 \left(\frac{\pi}{\omega n n_g^M \epsilon_0}\right) \left(\frac{1}{V_p}\right) \left\langle \left| \hat{p}_{cv} \cdot \hat{n} \right|^2 \right\rangle 2 \times \int_{\text{FBZ}} \frac{d^3 \bar{k}}{(2\pi)^3} f_c(\bar{k}) [1 - f_v(\bar{k})] \delta(E_c(\bar{k}) - E_v(\bar{k}) - \hbar\omega)$$

The above result is striking. It shows that the rate of spontaneous emission of a photon into a radiation mode is the same as the rate of stimulated emission into the same radiation mode provided one assumes that there is only one photon inside the radiation mode. Much more complicated techniques from the quantum theory of radiation gives exactly the same result that Einstein obtained relying on simple thermodynamic considerations.

3.5.8 Population Inversion and Optical Gain in Semiconductors:

In the presence of optical absorption due to interband absorption the intensity of an electromagnetic wave travelling inside a semiconductor decays as,

$$\frac{dI(x)}{dx} = -\alpha I(x)$$

$$\Rightarrow I(x) = I(x=0)e^{-\alpha x}$$

where the loss coefficient $\alpha(\omega)$ is given by the expression,

$$\begin{aligned} \alpha(\omega) &= \frac{R_{\uparrow}(\omega) - R_{\downarrow}(\omega)}{n_p \left(c/n_g^M \right)} \\ &= \left(\frac{q}{m} \right)^2 \left(\frac{\pi}{\epsilon_0 n \omega c} \right) \left\langle \left| \hat{p}_{cv} \cdot \hat{n} \right|^2 \right\rangle 2 \times \int_{\text{FBZ}} \frac{d^3 \bar{k}}{(2\pi)^3} \left[f_v(\bar{k}) - f_c(\bar{k}) \right] \delta(E_c(\bar{k}) - E_v(\bar{k}) - \hbar\omega) \end{aligned}$$

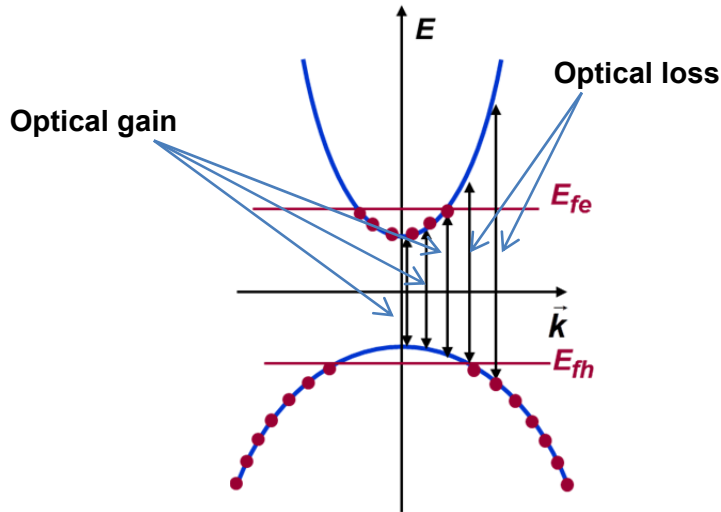
The question arises if $\alpha(\omega)$ can be made negative. If $\alpha(\omega)$ were negative then the radiation intensity would increase with distance instead of decreasing and the radiation would get amplified! Note that a negative $\alpha(\omega)$ implies that the rate of stimulated emission $R_{\downarrow}(\omega)$ is larger than the rate of stimulated absorption $R_{\uparrow}(\omega)$. $\alpha(\omega)$ can be negative provided,

$$\begin{aligned} &\left(\frac{q}{m} \right)^2 \left(\frac{\pi}{\epsilon_0 n \omega c} \right) \left\langle \left| \hat{p}_{cv} \cdot \hat{n} \right|^2 \right\rangle 2 \times \int_{\text{FBZ}} \frac{d^3 \bar{k}}{(2\pi)^3} \left[f_v(\bar{k}) - f_c(\bar{k}) \right] \delta(E_c(\bar{k}) - E_v(\bar{k}) - \hbar\omega) < 0 \\ &\Rightarrow f_v(\bar{k}) - f_c(\bar{k}) < 0 \quad \text{for} \quad E_c(\bar{k}) - E_v(\bar{k}) = \hbar\omega \\ &\Rightarrow \frac{1}{1 + e^{(E_v(\bar{k}) - E_f)/KT}} - \frac{1}{1 + e^{(E_c(\bar{k}) - E_f)/KT}} < 0 \quad \text{for} \quad E_c(\bar{k}) - E_v(\bar{k}) = \hbar\omega \\ &\Rightarrow e^{(E_c(\bar{k}) - E_f)/KT} - e^{(E_v(\bar{k}) - E_f)/KT} < 0 \quad \text{for} \quad E_c(\bar{k}) - E_v(\bar{k}) = \hbar\omega \\ &\Rightarrow E_c(\bar{k}) - E_v(\bar{k}) < 0 \quad \text{for} \quad E_c(\bar{k}) - E_v(\bar{k}) = \hbar\omega \end{aligned}$$

The above inequality can never be satisfied. The catch is that we implicitly assumed thermal equilibrium by assuming the same Fermi level for conduction band electrons and valence band electrons (or holes). In non-equilibrium situations this is not the case, as in biased pn diode. Allowing for the possibility of different Fermi levels for the conduction band electrons and the valence band electrons (or holes) one obtains the condition that $\alpha(\omega)$ can be negative provided,

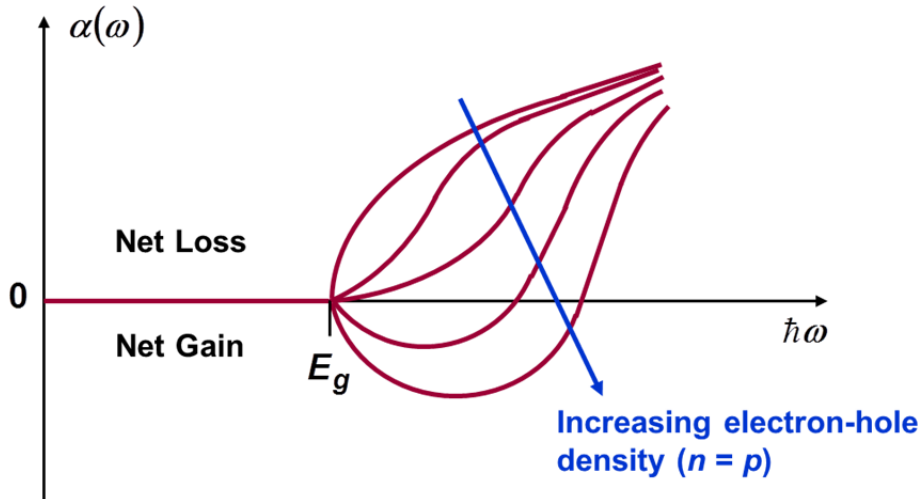
$$\begin{aligned} &\left(\frac{q}{m} \right)^2 \left(\frac{\pi}{\epsilon_0 n \omega c} \right) \left\langle \left| \hat{p}_{cv} \cdot \hat{n} \right|^2 \right\rangle 2 \times \int_{\text{FBZ}} \frac{d^3 \bar{k}}{(2\pi)^3} \left[f_v(\bar{k}) - f_c(\bar{k}) \right] \delta(E_c(\bar{k}) - E_v(\bar{k}) - \hbar\omega) < 0 \\ &\Rightarrow f_v(\bar{k}) - f_c(\bar{k}) < 0 \quad \text{for} \quad E_c(\bar{k}) - E_v(\bar{k}) = \hbar\omega \\ &\Rightarrow \frac{1}{1 + e^{(E_v(\bar{k}) - E_{fn})/KT}} - \frac{1}{1 + e^{(E_c(\bar{k}) - E_{fe})/KT}} < 0 \quad \text{for} \quad E_c(\bar{k}) - E_v(\bar{k}) = \hbar\omega \\ &\Rightarrow e^{(E_c(\bar{k}) - E_{fe})/KT} - e^{(E_v(\bar{k}) - E_{fn})/KT} < 0 \quad \text{for} \quad E_c(\bar{k}) - E_v(\bar{k}) = \hbar\omega \\ &\Rightarrow E_c(\bar{k}) - E_{fe} < E_v(\bar{k}) - E_{fn} \quad \text{for} \quad E_c(\bar{k}) - E_v(\bar{k}) = \hbar\omega \\ &\Rightarrow E_g < \hbar\omega < E_{fe} - E_{fn} \end{aligned}$$

The above results shows that $\alpha(\omega)$ can be negative for those optical frequencies for which the photon energy $\hbar\omega$ is smaller than the Fermi level splitting (but larger than the bandgap).



Given a value for the Fermi level splitting, optical frequencies for which $E_g < \hbar\omega < E_{fe} - E_{fh}$ experience optical gain and frequencies for which $\hbar\omega > E_g, E_{fe} - E_{fh}$ experience optical loss. The condition $E_g < \hbar\omega < E_{fe} - E_{fh}$ is the condition for population inversion and can be realized if, for example, electrons are removed from the valence band and placed in the conduction band, as shown in the Figure above. Note that for the situation shown in the Figure, optical gain ($\alpha(\omega) < 0$) will be experienced by radiation with frequency in the range, $E_g < \hbar\omega < E_{fe} - E_{fh}$ but radiation with frequency in the range $\hbar\omega > E_g, E_{fe} - E_{fh}$ will experience optical loss ($\alpha(\omega) > 0$).

In the Figure below, the loss coefficient is plotted as a function of the photon frequency for different values of the electron and hole densities assuming that electrons are taken from the valence band and placed in the conduction band thereby creating population inversion. Note that the bandwidth of the photon frequencies over which net gain is present increases as the level of population inversion increases.



Optical gain is used to realize semiconductor optical amplifiers and semiconductor lasers, topics that we will discuss in the Chapters to follow. When $\alpha(\omega)$ is negative, one usually defines the optical gain $g(\omega)$ as,

$$g(\omega) = -\alpha(\omega)$$

In terms of the optical gain, the net stimulated emission rate can be written as,

$$R_{\downarrow}(\omega) - R_{\uparrow}(\omega) = \frac{c}{n_g^M} g(\omega) n_p = v_g^M g(\omega) n_p$$

3.5.9 Optical Transitions Rates for Multiple Valence Bands:

In most semiconductors there are two valence bands, the heavy hole band and the light hole band, that are degenerate at the zone center. The transition rates between the conduction band and both these valence bands must be taken into account. For example, the optical loss coefficient and the optical gain can be written as,

$$\begin{aligned} \alpha(\omega) &= \alpha_{hh}(\omega) + \alpha_{lh}(\omega) \\ g(\omega) &= g_{hh}(\omega) + g_{lh}(\omega) \end{aligned}$$

where the contributions from the transitions between the conduction band and the heavy hole band and between the conduction band and the light hole band have been added.

3.6 Density of States for Photons

3.6.1 Definition of Density of States for Photons:

The density of states for photons refers to the number of radiation modes per unit frequency interval per unit volume of real space. This quantity plays an important role in many optoelectronic devices. Here we consider the density of states for photons in a material of refractive index $n(\omega)$ (which could be frequency dependent). We assume that in real space the mode volume of all these radiation modes is V_p .

The radiation modes are plane waves characterized by a wavevector \vec{q} and a polarization direction given by the unit vector \hat{n} which can take two possible values in the plane perpendicular to \vec{q} ,

$$\vec{A}(\vec{r}, t) = \hat{n} \left[\frac{A_0}{2} \frac{e^{i\vec{q}\cdot\vec{r}}}{\sqrt{V_p}} e^{-i\omega t} + \frac{A_0}{2} \frac{e^{-i\vec{q}\cdot\vec{r}}}{\sqrt{V_p}} e^{i\omega t} \right]$$

The frequency of the mode is related to the wavevector via the dispersion relation,

$$\omega = \frac{q c}{n(\omega)}$$

In q-space, in a volume of size $d^3\vec{q}$ there are $V_p d^3\vec{q}/(2\pi)^3$ different plane waves. Since for each wavevector, a radiation mode can have two different polarizations, there are $2 \times V_p d^3\vec{q}/(2\pi)^3$ different radiation modes in volume $d^3\vec{q}$ of q-space. The dispersion relation gives,

$$\begin{aligned} \left[n(\omega) + \omega \frac{dn}{d\omega} \right] d\omega &= dq c \\ \Rightarrow d\omega &= v_g^M dq \end{aligned}$$

Here, the group velocity v_g^M is defined as,

$$v_g^M = \frac{c}{\left[n(\omega) + \omega \frac{dn}{d\omega} \right]} = \frac{c}{n_g^M}$$

Since,

$$2 \times V_p \frac{d^3 \vec{q}}{(2\pi)^3} = V_p \frac{q^2 dq}{\pi^2} = V_p \left(\frac{\omega n}{\pi c} \right)^2 \frac{d\omega}{v_g^M} = V_p g_p(\omega) d\omega$$

this implies that there are $V_p g_p(\omega)$ different radiation modes per unit frequency interval. The function $g_p(\omega)$ is the density of states function for the photons. The density of states for photons can be drastically modified in optical cavities because of photon confinement.

3.6.2 Total Spontaneous Emission Rates in Semiconductors:

We again consider a semiconductor in which the conduction band and valence band energy dispersions are given by,

$$E_c(\vec{k}) = E_c + \frac{\hbar^2 k^2}{2m_e}$$

$$E_v(\vec{k}) = E_v - \frac{\hbar^2 k^2}{2m_h}$$

The spontaneous emission rate for photon emission into just one radiation mode of frequency ω and mode volume V_p was calculated earlier and is given as,

$$R_{sp}(\omega) = \left(\frac{q}{m} \right)^2 \left(\frac{\pi}{\omega n n_g^M \epsilon_0} \right) \left(\frac{1}{V_p} \right) \left\langle \left| \hat{p}_{cv} \cdot \hat{n} \right|^2 \right\rangle 2 \times \int_{\text{FBZ}} \frac{d^3 \vec{k}}{(2\pi)^3} f_c(\vec{k}) [1 - f_v(\vec{k})] \delta(E_c(\vec{k}) - E_v(\vec{k}) - \hbar\omega)$$

The spontaneous emission rate $R_{sp}(\omega)$ can also be written in terms of the absorption coefficient $\alpha(\omega)$ or the gain $g(\omega)$ as follows,

$$R_{sp}(\omega) = v_g^M \alpha(\omega) \left[\frac{1}{e^{(\hbar\omega - qV)/KT} - 1} \right] \frac{1}{V_p}$$

$$R_{sp}(\omega) = v_g^M g(\omega) \left[\frac{1}{1 - e^{(\hbar\omega - qV)/KT}} \right] \frac{1}{V_p} = v_g^M g(\omega) \frac{n_{sp}(\omega)}{V_p}$$

The spontaneous emission factor $n_{sp}(\omega)$ is defined as,

$$n_{sp}(\omega) = \frac{1}{1 - e^{(\hbar\omega - qV)/KT}}$$

and relates the gain $g(\omega)$ to the spontaneous emission rate. A semiconductor can emit photons into many radiation modes (provided the emission process satisfies the energy conservation rules). Therefore, in order to calculate the total spontaneous emission rate R_{Tsp} (per unit volume of the material) we need to sum the emission rates into all the individual radiation modes,

$$R_{Tsp} = \int_0^\infty R_{sp}(\omega) V_p g_p(\omega) d\omega$$

The above expression will play an important role in semiconductor light emitting diodes and semiconductor lasers, as we will see later in the course. It can also be written as,

$$R_{Tsp} = \int_0^\infty v_g^M \alpha(\omega) \frac{g_p(\omega)}{e^{(\hbar\omega - qV)/KT} - 1} d\omega$$