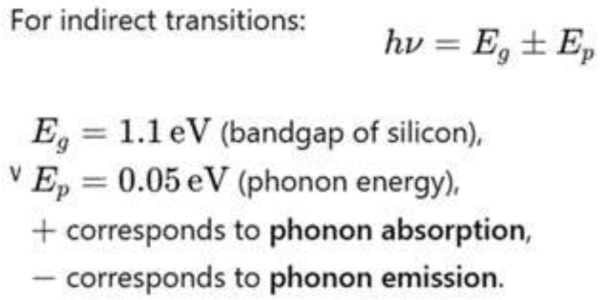
Tutorial 2 answers

Exercise 1: Fundamental Absorption & Indirect Transitions



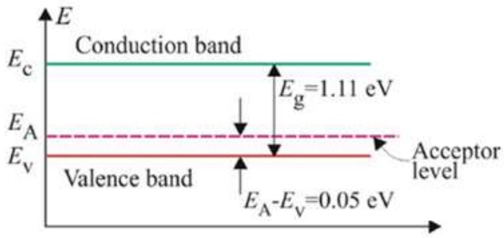
For indirect transitions: $$h\nu = E_g \pm E_p$$

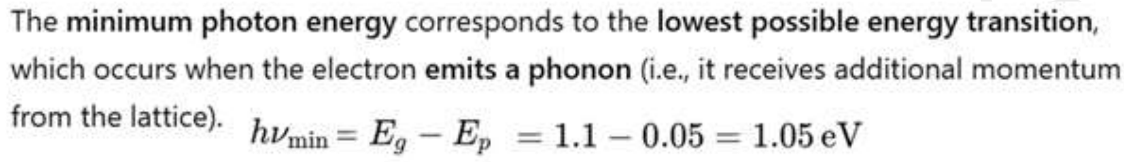
$E_g = 1.1\,\mathrm{eV}$ (bandgap of silicon),

$E_p = 0.05\,\mathrm{eV}$ (phonon energy),

$+$ corresponds to **phonon absorption**,

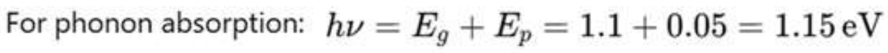
$-$ corresponds to **phonon emission**.



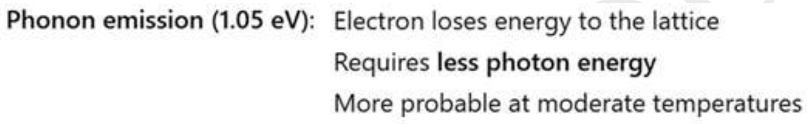


The **minimum photon energy** corresponds to the **lowest possible energy transition**, which occurs when the electron **emits a phonon** (i.e., it receives additional momentum from the lattice). $h\nu_{\min} = E_g - E_p \;= 1.1 - 0.05 = 1.05\,\mathrm{eV}$

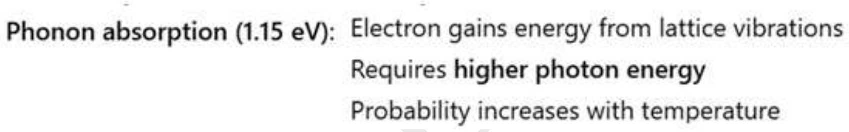
The maximum energy absorption



For phonon absorption: $h\nu = E_g + E_p = 1.1 + 0.05 = 1.15\,\mathrm{eV}$



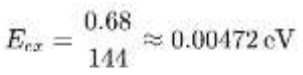
Phonon emission (1.05 eV): Electron loses energy to the lattice
Requires **less photon energy**
More probable at moderate temperatures



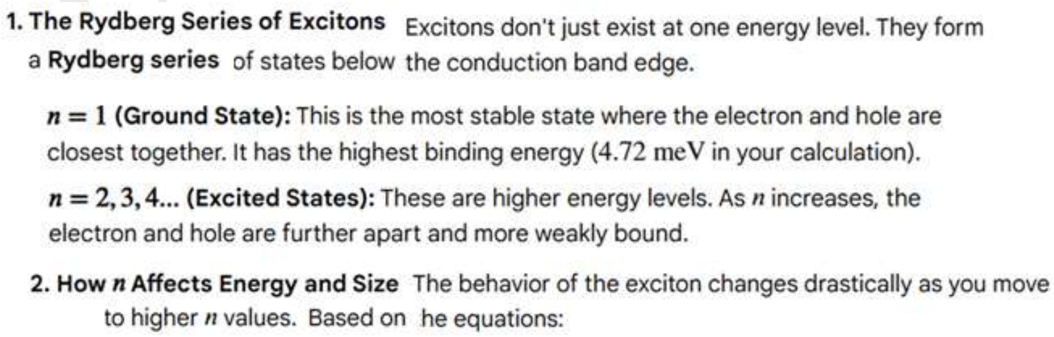
Phonon absorption (1.15 eV): Electron gains energy from lattice vibrations
Requires **higher photon energy**
Probability increases with temperature

Exercise 2: Exciton & Impurity Absorption

An **exciton** is a neutral, hydrogen-like bound state of an electron and a hole in a semiconductor, playing a central role in optical and electronic processes, particularly near the bandgap.



$$E_{ex} = \frac{0.68}{144} \approx 0.00472\,\mathrm{eV}$$

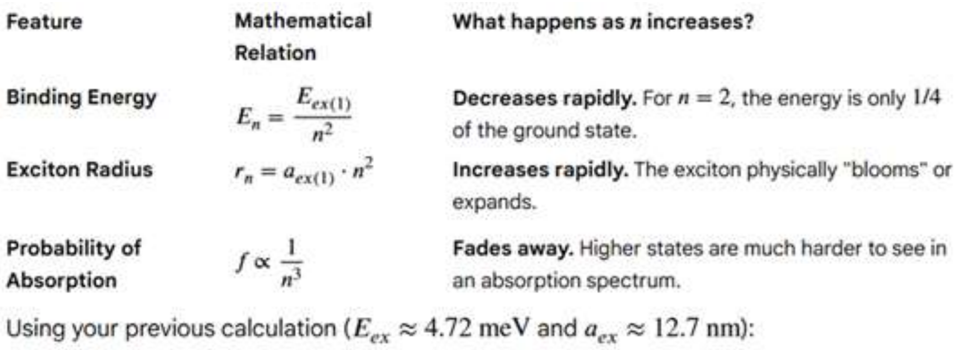


1. **The Rydberg Series of Excitons** Excitons don't just exist at one energy level. They form a **Rydberg series** of states below the conduction band edge.

   $n = 1$ (Ground State): This is the most stable state where the electron and hole are closest together. It has the highest binding energy (4.72 meV in your calculation).

   $n = 2, 3, 4...$ (Excited States): These are higher energy levels. As n increases, the electron and hole are further apart and more weakly bound.

2. **How n Affects Energy and Size** The behavior of the exciton changes drastically as you move to higher n values. Based on he equations:



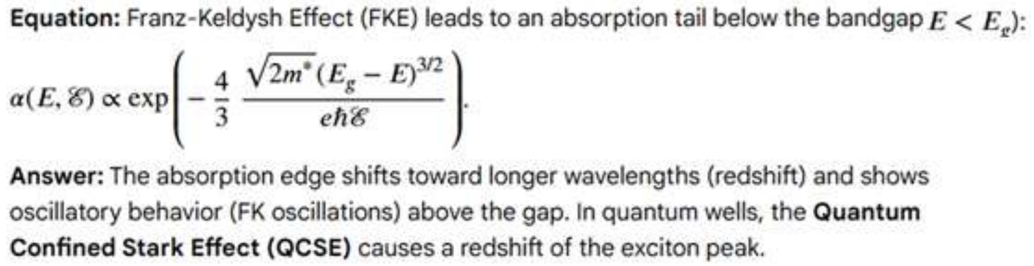
Feature	Mathematical Relation	What happens as n increases?
Binding Energy	$E_n = \frac{E_{ex(1)}}{n^2}$	**Decreases rapidly.** For $n = 2$, the energy is only 1/4 of the ground state.
Exciton Radius	$r_n = a_{ex(1)} \cdot n^2$	**Increases rapidly.** The exciton physically "blooms" or expands.
Probability of Absorption	$f \propto \frac{1}{n^3}$	**Fades away.** Higher states are much harder to see in an absorption spectrum.

Using your previous calculation ($E_{ex} \approx 4.72$ meV and $a_{ex} \approx 12.7$ nm):

Exercise 3: Electric Field Effects (Franz-Keldysh & Stark Effects)

The **effective mass** is a concept in solid-state physics that describes how a charge carrier (electron or hole) behaves inside a crystal as if it were a free particle, but with a modified mass that accounts for the influence of the periodic lattice.

The **effective mass** is a parameter that describes how charge carriers in a crystal respond to forces, incorporating the effects of the lattice by modifying the inertia of the particle through the curvature of the band structure.



Equation: Franz-Keldysh Effect (FKE) leads to an absorption tail below the bandgap $E < E_g$):

$$\alpha(E, \mathscr{E}) \propto \exp\left(-\frac{4}{3}\frac{\sqrt{2m^*}(E_g - E)^{3/2}}{e\hbar\mathscr{E}}\right).$$

Answer: The absorption edge shifts toward longer wavelengths (redshift) and shows oscillatory behavior (FK oscillations) above the gap. In quantum wells, the **Quantum Confined Stark Effect (QCSE)** causes a redshift of the exciton peak.

Key Physical Phenomena

Redshift: The absorption edge shifts toward longer wavelengths (lower energies) due to the presence of the electric field.

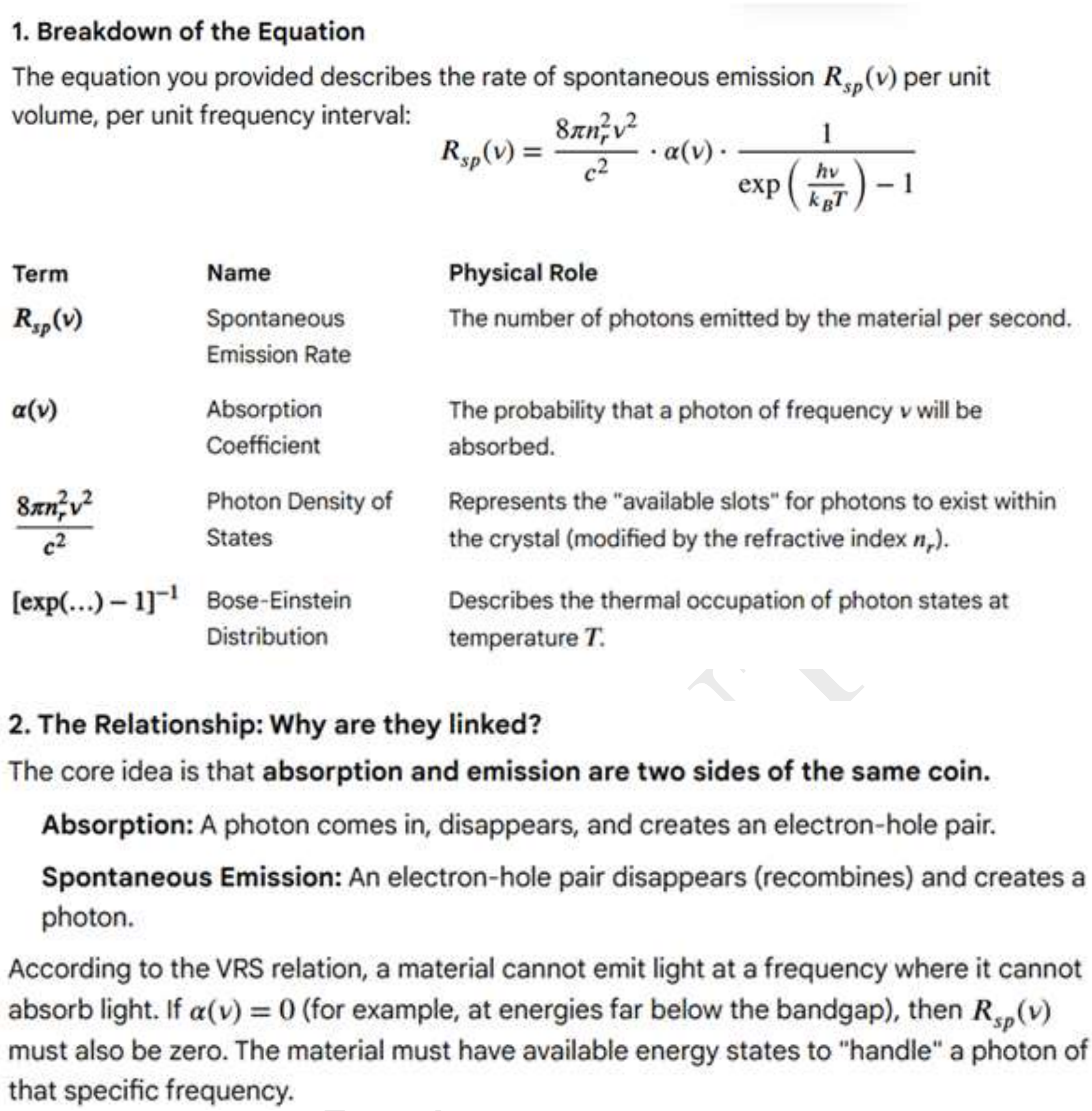
FK Oscillations: Above the bandgap energy, the absorption spectrum exhibits oscillatory behavior.

Quantum Confined Stark Effect (QCSE): While FKE occurs in bulk semiconductors, QCSE is the analogous effect in **quantum wells**, where the electric field causes a redshift specifically in the **exciton peak**.

Exercise 4. Radiation & Emission-Absorption Relation

The **Van Roosbroeck-Shockley (VRS) relation** is the fundamental link between how a semiconductor absorbs light and how it emits light. It is essentially an application of the **principle of detailed balance**, which states that in thermal equilibrium, every process (like absorption) must be exactly balanced by its inverse process (like emission).

Here is the detailed breakdown of the relation and the physics behind it.



1. Breakdown of the Equation

The equation you provided describes the rate of spontaneous emission $R_{sp}(\nu)$ per unit volume, per unit frequency interval:

$$R_{sp}(\nu) = \frac{8\pi n_r^2 \nu^2}{c^2} \cdot \alpha(\nu) \cdot \frac{1}{\exp\left(\frac{h\nu}{k_B T}\right) - 1}$$

Term	**Name**	**Physical Role**
$R_{sp}(\nu)$	Spontaneous Emission Rate	The number of photons emitted by the material per second.
$\alpha(\nu)$	Absorption Coefficient	The probability that a photon of frequency ν will be absorbed.
$\frac{8\pi n_r^2 \nu^2}{c^2}$	Photon Density of States	Represents the "available slots" for photons to exist within the crystal (modified by the refractive index n_r).
$[\exp(\ldots) - 1]^{-1}$	Bose-Einstein Distribution	Describes the thermal occupation of photon states at temperature T.

2. The Relationship: Why are they linked?

The core idea is that **absorption and emission are two sides of the same coin.**

Absorption: A photon comes in, disappears, and creates an electron-hole pair.

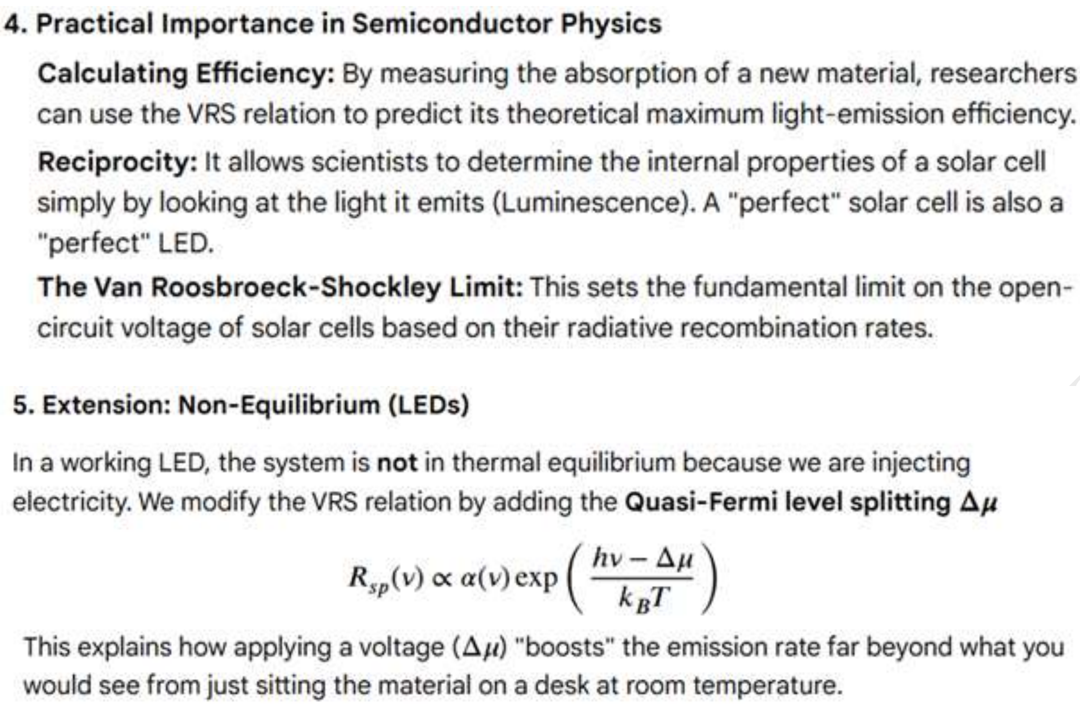
Spontaneous Emission: An electron-hole pair disappears (recombines) and creates a photon.

According to the VRS relation, a material cannot emit light at a frequency where it cannot absorb light. If $\alpha(\nu) = 0$ (for example, at energies far below the bandgap), then $R_{sp}(\nu)$ must also be zero. The material must have available energy states to "handle" a photon of that specific frequency.

3. Spectral shapes

Note that the spectral shape of emission in semiconductors results from the interplay between **density of states, carrier statistics, and broadening mechanisms**, producing a generally **asymmetric, broadened profile** with possible **sharp excitonic features** under suitable conditions.

Mechanism	**Spectral Shape**
Band-to-band	Asymmetric, broadened
Exciton	Sharp peak (narrow)
Thermal	Exponential tail
Lifetime	Lorentzian
Disorder	Gaussian



4. Practical Importance in Semiconductor Physics

Calculating Efficiency: By measuring the absorption of a new material, researchers can use the VRS relation to predict its theoretical maximum light-emission efficiency.

Reciprocity: It allows scientists to determine the internal properties of a solar cell simply by looking at the light it emits (Luminescence). A "perfect" solar cell is also a "perfect" LED.

The Van Roosbroeck-Shockley Limit: This sets the fundamental limit on the open-circuit voltage of solar cells based on their radiative recombination rates.

5. Extension: Non-Equilibrium (LEDs)

In a working LED, the system is **not** in thermal equilibrium because we are injecting electricity. We modify the VRS relation by adding the **Quasi-Fermi level splitting $\Delta\mu$**

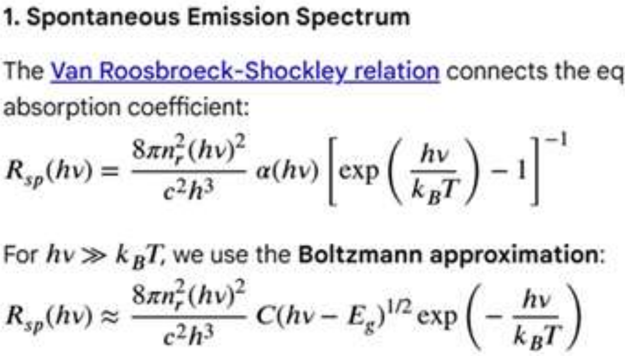
$$R_{sp}(\nu) \propto \alpha(\nu) \exp\left(\frac{h\nu - \Delta\mu}{k_B T}\right)$$

This explains how applying a voltage ($\Delta\mu$) "boosts" the emission rate far beyond what you would see from just sitting the material on a desk at room temperature.

Exercise 5:

Process	Governing Energy Condition	Key Feature
Direct Intrinsic	$h\nu \geq Eg$	Sharp absorption edge
Indirect Intrinsic	$h\nu \geq Eg \pm Ep$	Requires phonon for momentum
Exciton	$h\nu = Eg - Eex$	Sharp resonance peaks below Eg
Impurity	$h\nu = Eg - Ei$	Discrete lines or bands in the IR

Exercise 6:



1. Spontaneous Emission Spectrum

The Van Roosbroeck-Shockley relation connects the equilibrium emission rate to the absorption coefficient:

$$R_{sp}(h\nu) = \frac{8\pi n_r^2 (h\nu)^2}{c^2 h^3}\, \alpha(h\nu) \left[\exp\left(\frac{h\nu}{k_B T}\right) - 1\right]^{-1}$$

For $h\nu \gg k_B T$, we use the **Boltzmann approximation**:

$$R_{sp}(h\nu) \approx \frac{8\pi n_r^2 (h\nu)^2}{c^2 h^3}\, C(h\nu - E_g)^{1/2} \exp\left(-\frac{h\nu}{k_B T}\right)$$

2. Peak Emission Energy

To find the maximum, we simplify the expression. Near the bandgap ($h\nu \approx E_g$), the $(h\nu)^2$ term varies slowly compared to the exponential and square-root terms. Thus, the peak is dominated by:

$$f(h\nu) = (h\nu - E_g)^{1/2} \exp\left(-\frac{h\nu}{k_B T}\right)$$

Setting the derivative to zero:

$$\frac{d}{d(h\nu)}\left[(h\nu - E_g)^{1/2} \exp\left(-\frac{h\nu}{k_B T}\right)\right] = 0$$

$$\frac{1}{2}(h\nu - E_g)^{-1/2} - \frac{1}{k_B T}(h\nu - E_g)^{1/2} = 0$$

$$(h\nu)_{max} = E_g + \frac{1}{2}k_B T$$

At $T = 300\ \mathrm{K}$, $k_B T \approx 0.0259\ \mathrm{eV}$.

$$(h\nu)_{max} = 1.43\ \mathrm{eV} + \frac{0.0259}{2}\ \mathrm{eV} \approx \mathbf{1.443}\ \mathrm{eV}$$

3. Total Radiative Recombination Rate $\boldsymbol{R_0}$

The total rate R_0 is the integral of the spectral rate over all energies: $R_0 = \int_{E_g}^{\infty} R_{SP}(h\nu)\, d(h\nu)$

To calculate the **Total Radiative Recombination Rate $\boldsymbol{R_0}$** at equilibrium, we must integrate the spontaneous emission spectrum $R_{SP}(h\nu)$ over all possible photon energies ($E_g \rightarrow \infty$).

Substituting the expression derived from the **Van Roosbroeck-Shockley** relation using the Boltzmann approximation

$$R_0 = \int_{E_g}^{\infty} \frac{8\pi n^2 (h\nu)^2}{c^2 h^3} \cdot C(h\nu - E_g)^{1/2} \cdot \exp\left(-\frac{h\nu}{k_B T}\right) d(h\nu)$$

Since emission occurs primarily near the band edge, we treat $(h\nu)^2 \approx E_g^2$ as a constant and move it outside the integral:

$$R_0 \approx \frac{8\pi n^2 E_g^2 C}{c^2 h^3} \exp\left(-\frac{E_g}{k_B T}\right) \int_{E_g}^{\infty} (h\nu - E_g)^{1/2} \exp\left(-\frac{h\nu - E_g}{k_B T}\right) d(h\nu)$$

Let's use the substitution $x = \frac{h\nu - E_g}{k_B T}$. This implies $d(h\nu) = k_B T\, dx$. The integral part becomes:

$$I = \int_0^{\infty} (x \cdot k_B T)^{1/2} \cdot e^{-x} \cdot (k_B T\, dx) = (k_B T)^{3/2} \int_0^{\infty} x^{1/2} e^{-x}\, dx$$

The integral $\int_0^{\infty} x^{1/2} e^{-x}\, dx$ is the standard **Gamma Function** $\Gamma(3/2)$. Mathematically:

$$\Gamma(3/2) = \frac{1}{2}\Gamma(1/2) = \frac{\sqrt{\pi}}{2}$$

the integral result is: $\boldsymbol{I = \frac{\sqrt{\pi}}{2}(k_B T)^{3/2}}$.

Combining all terms, we get the final formula for the equilibrium recombination rate:

$$R_0 = \frac{4\pi^{3/2} n^2 E_g^2 C (k_B T)^{3/2}}{c^2 h^3} \exp\left(-\frac{E_g}{k_B T}\right)$$

$k_B T \approx 0.02585$ eV. $\exp(-1.43/0.02585) \approx 9.44 \times 10^{-25}$. This extremely small value shows that at equilibrium, very few photons are emitted because the bandgap is large compared to thermal energy. R_0 is approximately $\mathbf{3,600\ to\ 4,000\ cm^{-3}s^{-1}}$.

R_0 is used to determine the **Radiative Recombination Coefficient (B)**, which is a material-specific constant. It is defined by: $R_0 = B \cdot n_i^2$
Where n_i is the intrinsic carrier concentration. This coefficient B is crucial for designing efficient LEDs and Lasers, as it tells us how "good" a material is at converting electrical carriers into light.