# Chapter

# 2.3

**Page 1:**

Alright everyone, welcome to this segment of our Phys 608 Laser Spectroscopy course. Today, we delve into a truly foundational topic, Chapter 2.3, which covers "Absorption, Induced and Spontaneous Emission." These are the three fundamental ways light interacts with matter at the quantum level, and understanding them thoroughly is absolutely essential for everything that follows in laser physics and spectroscopy. This material was prepared by Distinguished Professor Doctor M. A. Gondal for the course here at KFUPM. Let’s begin.

**Page 2:**

So, we're starting with what we call the "Fundamental Light-Matter Interaction Processes." Our **Scope** here encompasses three distinct quantum processes. These are the mechanisms by which energy is exchanged between a radiation field – that is, light – and a molecule or an atom. And critically, this energy exchange happens in discrete packets, or quanta, where the energy $E$ of a single quantum is given by the famous Planck-Einstein relation, $E = h\nu$, where 'h' is Planck's constant and 'nu' (spelled n u) is the frequency of the radiation.

Now, what is the **Relevance** of understanding these three processes? It's twofold and profound. First, these processes collectively determine the intensity balance in black-body radiation. As you'll recall, a black-body is an idealized object that absorbs all incident electromagnetic radiation and emits radiation based purely on its temperature. The spectrum of this emitted radiation, described by Planck's law, can only be understood by considering these quantum interactions. Second, and central to this course, manipulating the *rates* of these processes is what enables laser action. By cleverly controlling whether absorption or one type of emission dominates, we can achieve light amplification.

So, what's our **Strategy for today's derivations**? We're going to build this understanding step-by-step:

First, we will precisely define each of these three processes – absorption, spontaneous emission, and stimulated emission. We need to be crystal clear on what each one entails at the microscopic level.

Second, we will introduce the Einstein coefficients, denoted as $A_{21}$ (A twenty-one), $B_{12}$ (B twelve), and $B_{21}$ (B twenty-one). These coefficients quantify the probability of each process occurring. We'll see how Albert Einstein, in a stroke of genius, postulated these coefficients and their relationships.

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Continuing with our strategy for today's derivations: Third, after defining the processes and their coefficients, we will enforce thermal-equilibrium conditions. What does this mean? We will consider a system of atoms or molecules interacting with a radiation field that is in thermal equilibrium, for example, like the radiation inside a heated cavity – a black-body. Under these equilibrium conditions, the rates of upward and downward transitions must balance, and this allows us to derive crucial algebraic relations between the Einstein coefficients. This is a classic physics approach: start with a well-defined equilibrium situation to find fundamental relationships.

Fourth, we will interpret photon statistics per single electromagnetic, or E M, mode. The radiation field isn't just a continuous wave; it's quantized into photons that occupy specific electromagnetic modes. We'll look at the average number of photons in a given mode at a certain temperature, which directly influences the rates of these interaction processes.

Our overall **Learning goal** for this lecture is to move from somewhat qualitative, pictorial descriptions of light-matter interaction to fully quantitative formulas. These formulas are not just abstract; they are directly usable and essential in practical spectroscopy for analyzing experimental data, and critically, in laser design for predicting and optimizing laser performance. So, we're bridging the gap between fundamental quantum concepts and real-world applications.

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Now, let’s look at a visual representation of these "Fundamental Light-Matter Interaction Processes." What we have here is a diagram depicting a two-level atom interacting with a radiation field, notionally inside a cavity, suggested by the grey vertical bars on either side representing cavity mirrors, which confine the radiation. The atom has two discrete energy levels, a lower energy level $E_1$ (E one) and a higher energy level $E_2$ (E two). Photons, the quanta of the radiation field, are stylized as wavy lines labeled $h\nu$, representing their energy. Remember, 'h' is Planck's constant, and 'nu' is the frequency. For an interaction to occur, the photon energy $h\nu$ must precisely match the energy difference between the two levels, that is, $E_2 - E_1$. This is the Bohr frequency condition.

Let's look at the three processes shown:

1. **Stimulated Absorption**: On the left. Here, the atom is initially in the lower energy state, $E_1$. An incident photon, with energy $h\nu$ (shown as a purple wavy arrow), comes along and interacts with the atom. If the photon energy matches the energy gap, the atom absorbs the photon and jumps to the higher energy state, $E_2$. The photon is annihilated in this process; its energy is now stored in the atom. This process is labeled with a 'B', hinting at the Einstein B coefficient associated with it, specifically $B_{12}$.

2. **Stimulated Emission**: In the middle. For this process, the atom must *already* be in the excited upper state, $E_2$. An incident photon, $h\nu$ (green wavy arrow), identical in properties (frequency, direction, polarization) to the photon that would be emitted if the atom decayed spontaneously, interacts

with this excited atom. This interaction *stimulates* or *induces* the atom to drop to the lower energy state, $E_1$, and in doing so, emit a *second* photon. Crucially, this newly emitted photon is a perfect clone of the incident photon – it has the same energy $h\nu$, the same direction, the same phase, and the same polarization. So, one photon comes in, and two identical photons go out. This is the process responsible for light amplification in lasers. This is also labeled with a 'B', hinting at $B_{21}$.

3. **Spontaneous Emission**: On the right. Here, the atom is again in the excited upper state, $E_2$. However, unlike stimulated emission, this process can occur *without* any external photons triggering it. The atom spontaneously decides to relax to the lower energy state, $E_1$, and emits a photon of energy $h\nu$ (orange wavy arrow with smaller divergent arrows). This emitted photon can go off in any random direction, and its phase is random relative to other spontaneously emitted photons. This process is labeled with an 'A', referring to the Einstein A coefficient, $A_{21}$.

These three processes – stimulated absorption, stimulated emission, and spontaneous emission – form the complete set of fundamental single-photon interactions for a two-level system. Their interplay governs how light and matter exchange energy.

**Page 5:**

Alright, let's do a quick review of the "Thermal Radiation Field." This is essential background for deriving the Einstein relations.

The first point is that a thermal electromagnetic, or E M, field at an absolute temperature, $T$, is characterized solely by its spectral energy density. This quantity is denoted by the Greek letter $\rho_\nu$ as a function of frequency $\nu$ and temperature $T$, so $\rho_\nu(\nu, T)$. What does this mean physically? It's the amount of electromagnetic energy per unit volume, per unit frequency interval.

So, imagine a box filled with thermal radiation at temperature $T$. $\rho_\nu$ tells us how much energy is contained in, say, one cubic meter of that space, within a narrow frequency band of, say, one Hertz, centered at frequency $\nu$. The units would therefore be Joules per meter cubed per Hertz, or equivalently, Joule-seconds per meter cubed.

The second point brings us to Planck's distribution. This is the famous formula, derived by Max Planck in 1900, which perfectly describes this spectral energy density. The slide correctly notes that this distribution arises from two key quantum ideas: first, the quantization of energy in the cavity modes – energy can only exist in discrete packets of $h\nu$ – and second, the application of Bose-Einstein statistics to these energy quanta, because photons are bosons. Remember, classical physics failed here, predicting the "ultraviolet catastrophe." Planck's quantum hypothesis resolved this.

The formula for Planck's distribution is:

$$\rho_\nu(\nu,T) = \frac{8\pi h\nu^3}{c^3\left(e^{\frac{h\nu}{kT}} - 1\right)}$$

Let's break down the terms: * $h$ is Planck's constant, given as $6.626 \times 10^{-34}$ Joule-seconds. It’s the fundamental constant scaling quantum effects. * $\nu$ is the frequency of the radiation in Hertz. * $c$ (which we'll see on the next slide) is the speed of light in vacuum. * $k$ (also on the next slide) is the Boltzmann constant, which relates temperature to energy. * $T$ is the absolute temperature in Kelvin.

The term $\frac{h\nu}{kT}$ is a crucial dimensionless ratio: the energy of a photon of frequency $\nu$ compared to the characteristic thermal energy $kT$. The factor $e^{\frac{h\nu}{kT}} - 1$ in the denominator is characteristic of Bose-Einstein statistics for particles like photons.

This Planck distribution is the bedrock of our understanding of thermal light.

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Continuing our review of the thermal radiation field, let's list the constants involved in Planck's law:

'c', the vacuum speed of light, is $2.998 \times 10^8$ meters per second (m $s^{-1}$).

'k', the Boltzmann constant, is $1.381 \times 10^{-23}$ Joules per Kelvin (J $K^{-1}$).

Now, a very important concept derived from Planck's distribution concerns the individual electromagnetic modes. The idea is that the thermal radiation field can be thought of as being composed of many discrete electromagnetic modes, each characterized by a specific frequency $\nu$.

The slide states: "Every discrete EM mode of frequency $\nu$ then contains on average..." and gives the formula for $\tilde{q}$, a variable often used to represent the mean photon occupancy per mode (though sometimes $\bar{n}$ is used). Let's use $\tilde{q}$ as on the slide, it's q with a tilde above it.

So, $\tilde{q}$, as a function of $\nu$ and $T$, equals 1 divided by the quantity ( $\exp\left(\frac{h\nu}{kT}\right) - 1$ ).

$$\tilde{q}(\nu, T) = \frac{1}{\exp\left(\frac{h\nu}{kT}\right) - 1}$$

This expression is precisely the Bose-Einstein distribution factor for photons. It tells us the average number of photons occupying a single electromagnetic mode of frequency $\nu$ when the radiation field is at thermal equilibrium at temperature $T$.

Notice this is exactly the part of Planck's law that depends on temperature and involves the Bose-Einstein statistics. In fact, Planck's law can be written as $\rho_\nu =$ (the number of modes per unit volume per unit frequency) times (the energy per photon, $h\nu$) times (this average number of photons per mode, $\tilde{q}$).

The slide correctly notes: "This mean occupancy, $\tilde{q}$, will later be compared with induced and spontaneous rates." This is a critical link. The strength of the radiation field, characterized by $\tilde{q}$, will directly determine the rate of stimulated absorption and stimulated emission. Understanding $\tilde{q}$ is key to understanding how thermal fields drive atomic transitions, and, by extension, how very non-thermal fields, like those in lasers where $\tilde{q}$ can be enormous, behave.

**Page 7:**

On this slide, we have a graph illustrating the "Spectral Energy Density of Thermal Radiation," which is, of course, Planck's Law.

Let's examine the graph carefully.

The vertical axis is labeled "$\rho_\nu$" (using P here but it is $\rho_\nu$) and its units are given as "times $10^{-15}$ Joule seconds per meter cubed" ($10^{-15}$ J s m$^{-3}$). Remember, $\rho_\nu$ itself has units of energy per unit volume per unit frequency, which is Joules per meter cubed per Hertz, or Joules seconds per meter cubed. So the scaling factor $10^{-15}$ is applied to the numerical values on the axis. The horizontal axis represents "Frequency $\nu$" in units of TeraHertz (THz), where 1 THz is $10^{12}$ Hertz. The axis runs from 0 to 1100 TeraHertz.

At the top, Planck's law is explicitly written:

$$\rho_\nu(\nu, T) = \frac{8\pi h\nu^3}{c^3}\frac{1}{e^{\frac{h\nu}{kT}} - 1}$$

This is the equation being plotted.

We see three distinct curves, each corresponding to a different absolute temperature: * The blue curve, the lowest one, is for $T = 1000$ K. * The green curve, in the middle, is for $T = 3000\,\text{K}$. This is typical of, say, a filament in an incandescent light bulb. * The red curve, the highest one, is for $T = 6000\,\text{K}$. This is approximately the surface temperature of the Sun.

Observe what happens as the temperature $T$ increases: First, the total energy density, which is the area under the curve, increases dramatically. The red curve ($6000\,\text{K}$) encompasses a much larger area than the blue curve ($1000\,\text{K}$). This is consistent with the Stefan-Boltzmann law, which states that the total power radiated by a black body is proportional to $T^4$.

Second, the peak of the distribution shifts to higher frequencies (shorter wavelengths) as the temperature increases. For $1000\,\text{K}$, the peak is well below $100\,\text{THz}$. For $3000\,\text{K}$, it's around, say, $180\,\text{THz}$. For $6000\,\text{K}$, the peak is around $350\,\text{THz}$. This is precisely what Wien's Displacement Law describes: $\lambda_{\text{max}} T =$ constant, meaning the wavelength of peak emission is inversely proportional to temperature.

There's an important annotation on the graph, with an arrow pointing to the high-frequency tail of the $6000\,\text{K}$ red curve. It says: "Low photon occupancy ($q_\nu, T \ll 1$) region (where $h\nu \gg kT$)."

Let's unpack this. In this region, the photon energy $h\nu$ is significantly larger than the characteristic thermal energy $kT$. When $h\nu$ is much larger than $kT$, the exponential term $\exp\left(\frac{h\nu}{kT}\right)$ becomes very large. Consequently, the minus 1 in the denominator of Planck's law (and in the expression for $\bar{q}$) becomes negligible. The distribution then approximates the Wien distribution, which has an exponential fall-off at high frequencies.

And $\bar{q}$, which is $\frac{1}{\exp\left(\frac{h\nu}{kT}\right)-1}$, becomes approximately $\exp\left(-\frac{h\nu}{kT}\right)$, which is indeed much less than 1 in this regime. So, at high frequencies, the average number of photons per mode is very small. The energy is just not high enough at that temperature to significantly populate these high-energy modes.

This graph beautifully visualizes how temperature shapes the spectrum of thermal radiation.

**Page 8:**

Now, we move to establish our theoretical framework with what we call the "Two-Level Atom/Molecule Model." While real atoms and molecules have many energy levels, this simplification to just two relevant levels is incredibly powerful for understanding the fundamental interaction processes, especially when the radiation frequency is tuned to resonate with a specific transition.

First, let's define the **Levels**: We consider a lower state, which we label using the Dirac ket notation as $|1\rangle$ (a vertical bar, the number 1, and an angle bracket). This state has an energy $E_1$ (E one). And we have an upper state, labeled as $|2\rangle$, with an energy $E_2$ (E two). A key condition is that $E_2 > E_1$; that is, $|2\rangle$ is the excited state and $|1\rangle$ is the ground state (or at least, the lower of the two considered states).

Next, the **Transition frequency**, which is governed by the Bohr frequency condition: The energy of a photon, $h\nu$, that can cause a transition between these two levels must precisely equal the energy difference between the levels. So,

$$h\nu = E_2 - E_1$$

Here, $h$ is Planck's constant, and $\nu$ is the frequency of the radiation. This equation establishes the resonant nature of light-matter interactions: only photons with the correct energy (and thus frequency) can be absorbed or emitted by this two-level system.

Finally, $\nu$ itself – this is the exact resonant frequency for the transition between state 1 and state 2. Its units are Hertz (Hz), or inverse seconds. For now, we consider this frequency to be perfectly sharp. In reality, atomic and molecular transitions have a finite linewidth due to various broadening mechanisms, which we will discuss later in the course, but the concept of an exact resonant frequency is the starting point.

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Continuing with our Two-Level Atom/Molecule Model, let's define some **Population symbols**:

We use capital $N_1$ (N one) to denote the number density of atoms or molecules in the lower state, ket $1$. "Number density" means the number of particles per unit volume, so its units are typically inverse meters cubed $(m^{-3})$.

Similarly, capital $N_2$ (N two) represents the number density of atoms or molecules in the upper state, ket $2$, also in units of inverse meters cubed $(m^{-3})$.

These populations, $N_1$ and $N_2$, will be crucial when we calculate the overall rates of absorption and emission in a macroscopic sample.

Now, a very important point: the **Assumptions for our derivations**. The model we are building relies on certain simplifying assumptions. It's vital to be aware of these:

1. We assume a **homogeneous, isotropic radiation field**. "Homogeneous" means the radiation field's energy density is the same at all points in space. "Isotropic" means the radiation field is the same in all directions. This greatly simplifies the mathematics, as we don't have to worry about spatial or directional variations in the field interacting with the atoms. This is a good approximation for, say, black-body radiation inside a cavity.

2. We assume **negligible collisions during the radiative event**. This implies that we are considering a situation of **complete radiative isolation for a single transition**. What this means is that an atom, while it's in the process of

absorbing or emitting a photon, is not significantly perturbed by collisions with other atoms or molecules. If collisions were frequent, they could interrupt the radiative process, or cause non-radiative transitions (i.e., energy exchange without photon emission/absorption), which would complicate our rate equations. So, we're focusing purely on the interaction with light. This assumption is often valid in low-pressure gases or for very fast radiative processes.

These assumptions allow us to develop the fundamental relationships for the Einstein coefficients in their purest form.

**Page 10:**

Here we have a simple yet very clear diagram illustrating the "Two-Level System Model" that we've just been discussing.

What you see are two horizontal dark grey lines, representing the two energy levels of our system. The lower line is labeled $E_1$ (E one) on the right, and on the left, it's labeled with the Dirac notation $|1\rangle$, representing the quantum state of the atom when it has energy $E_1$. The upper line, situated above the lower line to indicate higher energy, is labeled $E_2$ (E two) on the right, and $|2\rangle$ on the left, representing the quantum state with energy $E_2$.

Connecting these two levels is a prominent red vertical arrow, pointing downwards from the upper level $E_2$ to the lower level $E_1$. This arrow signifies a transition between the two states. In this particular depiction, a downward arrow would represent an emission process, where the atom loses energy. An upward arrow would represent an absorption process.

Crucially, next to this arrow, the fundamental Bohr frequency condition is written: $h\nu = E_2 - E_1$. This reminds us that the energy of the photon ($h\nu$) involved in any transition between these two specific states must precisely match the energy difference ($E_2 - E_1$) between them.

This diagram is the quintessential representation of a quantum system interacting with a photon of a specific energy, forming the basis for virtually all of spectroscopy and laser physics.

**Page 11:**

Now we're going to dive into the first of our three fundamental processes. This is "Process 1 – Induced, or Stimulated, Absorption." The number 1 in a circle highlights that it's the first process we're detailing.

Let's start with the **Microscopic description**: What happens at the level of a single atom and a single photon?

The first point states: "An incident photon in a specific EM mode is annihilated." This means a photon from the surrounding radiation field, which has the correct resonant frequency $\nu$, approaches the atom. The atom absorbs this photon, and the photon ceases to exist. Its energy is transferred entirely to the atom.

The second point describes the consequence for the atom: "Atom jumps from ket 1 to ket 2" (represented as ket 1 arrow ket 2). The atom, initially in the lower energy state (ket 1), uses the absorbed photon's energy to transition to the higher energy state (ket 2).

Now, how do we quantify the likelihood of this happening? We look at the **Probability per molecule, per second**: This is the rate at which a single molecule (or atom) in state 1 will undergo stimulated absorption when bathed in a radiation field. The slide gives this rate as:

$$\frac{dP_{12}}{dt} = B_{12}\, \rho_{\nu}(\nu)$$

Let's break this down:

- $\frac{dP_{12}}{dt}$ is the rate of change of probability, or the probability per unit time, for a transition from state 1 to state 2. So its units are per second ($s^{-1}$).

- $B_{12}$ is the Einstein coefficient for induced absorption. This is a proportionality constant that characterizes the intrinsic strength of this particular transition (1 to 2) in this specific atom or molecule. It depends on the nature of the states 1 and 2. We will discuss its units and origin shortly.

- $\rho_\nu(\nu)$ is the spectral energy density of the radiation field *at the resonant frequency* $\nu$. This is critical. Only photons with the correct frequency $\nu$ (matching $\frac{E_2 - E_1}{h}$) can efficiently cause this absorption. $\rho_\nu$, as we reviewed, has units of energy per unit volume per unit frequency (e.g., Joules seconds per meter cubed).

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Continuing with our discussion of Process 1, Induced Absorption, let's clarify the terms in our rate equation: $\frac{dP_{12}}{dt} = B_{12}\rho_\nu(\nu)$.

The slide specifies:

- Capital B subscript one two ($B_{12}$) is the Einstein coefficient for induced absorption. Its units are given here as meters cubed per Joule per second squared ($\text{m}^{3\,\text{J}^{-1}\,\text{s}^{-2}$). Let's quickly see if this makes sense. The left side, $\frac{dP_{12}}{dt}$, is a rate, so its units are $s^{-1}$. Rho sub nu ($\rho_\nu$), the spectral energy density, has units of Joules per meter cubed per Hertz ($\text{J m}^{-3}\text{ Hz}^{-1}$), which is $\text{J s m}^{-3}$. So, for the equation to balance dimensionally, $B_{12}$ must have units of $\frac{s^{-1}}{J\,s\,m^{-3}} = \text{m}^{3\,\text{J}^{-1}\,\text{s}^{-2}$. Yes, the units are consistent.

- rho sub nu of nu ($\rho_\nu(\nu)$) is the spectral energy density at the resonant frequency nu. We've already discussed this.

Now, what's the **Proportionality reason**? Why is the absorption rate proportional to rho sub nu? The slide puts it intuitively: "stronger field intensity implies more incident photons, which in turn implies a higher absorption rate." This makes perfect sense. If there are more photons of the correct frequency available to be absorbed, then the chances of an absorption event occurring in a given time interval will naturally be higher. Rho sub nu is precisely the measure of this availability of resonant photons.

Next, the **Quantum origin of** $B_{12}$. Where does this coefficient come from fundamentally? The $B_{12}$ coefficient is not just an empirical fitting parameter; it's determined by the quantum mechanical properties of the atom or molecule itself. Specifically, it is determined by the "squared transition dipole matrix element." The slide shows this proportionality: $B_{12} \propto |\langle 2|\, \hat{\mu} \cdot e\, |1\rangle|^2$.

Let's break this down further:

- ket 1 and ket 2 represent the wavefunctions of the initial (lower) and final (upper) states, respectively.
- mu-hat ($\hat{\mu}$) is the electric-dipole operator. For a simple system like a hydrogen atom, it's related to the charge of the electron times its position vector (e.g., $-e$ times r-vector). This operator describes how the charge distribution in the atom interacts with an electric field.
- 'e' is the unit vector representing the polarization of the incident electromagnetic field's electric component.
- The dot product $\hat{\mu} \cdot e$ means that only the component of the atom's dipole moment that aligns with the electric field of the light contributes to the interaction strength.
- The term $\langle 2|\, \hat{\mu} \cdot e\, |1\rangle$ is called the transition dipole moment. It involves an integral of the final state wavefunction, the operator, and the initial state wavefunction over all space. If this integral is zero, the transition is "dipole

forbidden." If it's non-zero, the transition is "dipole allowed," and its magnitude determines how strong the transition is.

- The modulus squared of this complex-valued transition dipole moment gives a real number that is proportional to the transition probability.

So, $B_{12}$ is fundamentally rooted in the wavefunctions of the states involved and the nature of the electric dipole interaction. It's an intrinsic property of the specific atomic or molecular transition.

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Let's delve deeper into this Einstein coefficient, $B_{12}$. The slide poses the question: "What Sets Its Numeric Value?"

The first key point is its **Dependence only on internal structure**:

* $B_{12}$ is determined by the **Wavefunctions** of the initial and final states, which we can denote as $\psi_1(r)$ and $\psi_2(r)$. These wavefunctions describe the spatial distribution of the electrons within the atom or molecule. As we saw, the transition dipole matrix element, which dictates $B_{12}$, involves integrals of these wavefunctions with the dipole operator. So, the shape and symmetry of these wavefunctions are paramount.

* This leads directly to **Selection rules** that arise from considerations of parity and angular momentum. For the transition dipole matrix element $\langle 2|\hat{\mu} \cdot e|1\rangle$ to be non-zero, there are strict rules about how the parity of the wavefunctions (whether they are symmetric or anti-symmetric under inversion) and their angular momentum quantum numbers must change. For example, in electric dipole transitions, parity must change, and the change in the angular momentum quantum number ($\Delta J$) is typically 0 or $\pm 1$ (with $J = 0$ to $J = 0$ forbidden). If these rules are not met, $B_{12}$ is zero (or very small, if higher-order multipole transitions are considered, but we're focused on electric dipole here).

The second crucial point is its **Independence from the external EM field**, with an important proviso: this independence holds "provided the field is weak enough not to perturb the level energies." This is often referred to as the **non-diabatic regime** or perturbative regime.

What does this mean? The $B_{12}$ coefficient is an intrinsic property of the atom/molecule. The external field provides the photons for absorption, and its strength ($\rho_{\nu}$) determines the *rate* of absorption, but it doesn't change $B_{12}$ itself.

However, if the external field becomes extremely intense (like with some very powerful lasers), it can start to significantly distort the atomic/molecular wavefunctions and shift the energy levels (e.g., through the AC Stark effect). In such strong-field, non-perturbative regimes, the simple picture of a constant $B_{12}$ breaks down. For most conventional spectroscopy and many laser applications we first encounter, the weak-field approximation holds well.

So, $B_{12}$ is a characteristic constant for a given transition in a given species, dictated by its quantum mechanical makeup, as long as we're not hitting it with overwhelmingly strong light.

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Let's continue our exploration of $B_{12}$.

First, let's re-examine its **Units**. We can think about the units from the fundamental definition of the absorption rate. The rate of absorption (probability per time) is $B_{12}$ times the spectral energy density $\rho_{\nu}$. So, $B_{12}$, or rather its dimensions, $[B_{12}]$, must be equal to (probability/time) divided by energy density. Probability is dimensionless. Time has units of $s$. Spectral energy density $\rho_{\nu}$ has units of energy per volume per frequency, which is Joules per meter cubed per Hertz ($J\, m^{-3}\, Hz^{-1}$), or $J\, s\, m^{-3}$.

$$[B_{12}] = \frac{1/s}{J\, s\, m^{-3}} = \frac{1}{J\, s^2\, m^{-3}} = m^3\, J^{-1}\, s^{-2}.$$

This is meters cubed per Joule per second squared, which perfectly matches what was stated earlier. It's always good practice to ensure dimensional consistency.

Next, how is $B_{12}$ determined **Experimentally**? One common method involves absorbance measurements. You shine light through a sample and measure how much of it is absorbed. This is quantified by the Beer-Lambert law, which states that absorbance is proportional to the concentration of the absorbing species and the path length of the light through the sample. The proportionality constant in the Beer-Lambert law (the molar absorptivity or absorption cross-section) is directly related to $N_1$ (the population density of the lower state) and $B_{12}$.

So, by performing an absorbance measurement and fitting the data to the Beer-Lambert law, one can extract $B_{12}$. This, of course, requires careful calibration of the incident light's spectral energy density, $\rho_\nu$, because the amount of absorption depends on it.

Finally, there's a crucial theoretical link: the slide notes that we "Will later link $B_{12}$ to the measurable spontaneous coefficient $A_{21}$." This refers to the Einstein relations, which we will derive. These relations connect $B_{12}$ (stimulated absorption), $B_{21}$ (stimulated emission), and $A_{21}$ (spontaneous emission). This is extremely powerful because sometimes $A_{21}$ (which is related to the radiative lifetime of the excited state) is easier to measure accurately or to calculate from first principles quantum mechanics. Once $A_{21}$ is known, $B_{12}$ and $B_{21}$ can be readily determined using these relations. This interconnectivity is a cornerstone of our understanding of these processes.

**Page 15:**

This slide presents a table of "Typical Values for the Einstein $B_{12}$ Coefficient" for a variety of atomic and molecular transitions. This gives us a feel for the magnitudes involved and how $B_{12}$ can vary.

The table has columns for: 1. **TRANSITION / SYSTEM**: The specific atom or molecule and the transition in question. 2. **WAVELENGTH (**$\Lambda$): The wavelength $\lambda$ of the light involved in the transition, typically given in nanometers (nm). 3. $B_{12}$: The value of the Einstein coefficient for stimulated absorption, in its standard units of M cubed J to the minus 1 S to the minus 2 (meters cubed per Joule per second squared). 4. **NOTES**: Additional relevant information, often including the ratio of degeneracies of the upper to lower states ($\frac{g_2}{g_1}$) and the corresponding $A_{21}$ coefficient.

Let's look at a few representative examples:

* **Sodium (Na) D$_2$-line**: This is the famous yellow line from sodium lamps. * Wavelength: 589 nanometers. * $B_{12}$: A very large value, $1.51 \times 10^{21}$. This indicates a very strong absorption. * Notes: $\frac{g_2}{g_1} = 2.00$. The $A_{21}$ coefficient is approximately $6.16 \times 10^7$ per second, meaning a very short excited state lifetime of about 16 nanoseconds.

* **Helium-Neon (HeNe) Laser**: The common red HeNe laser transition. * Wavelength: 632.8 nanometers. * $B_{12}$: $8.62 \times 10^{20}$. Also a large value. * Notes: $\frac{g_2}{g_1} = 1.67$. $A_{21}$ is approximately $3.4 \times 10^7$ per second.

* **Hydrogen Lyman-α**: The transition from $n = 2$ to $n = 1$ in hydrogen, in the ultraviolet. * Wavelength: 121.6 nanometers. * $B_{12}$: $2.03 \times 10^{20}$. * Notes: $\frac{g_2}{g_1} = 3.00$ (the $n = 2$ level is more degenerate than $n = 1$ if we consider orbital angular momentum; specifically the 2p to 1s part for Lyman-$\alpha$ if only counting orbital, but spin needs care). $A_{21}$ is very large, approximately $6.27 \times 10^8$ per second, indicating an extremely rapid spontaneous decay.

* **Ruby Laser ($Cr^{3+}$ in $Al_2O_3$)**: This is chromium ions (Cr three plus) doped into a sapphire crystal (Al two O three). * Wavelength: 694.3 nanometers (deep red). * $B_{12}$: Noticeably smaller, $5.02 \times 10^{15}$. This is orders of magnitude smaller than the atomic transitions above. Transitions in ions within a solid host often have different characteristics. * Notes: $\frac{g_2}{g_1} = 1.00$. The "Effective $A_{21}$" is much smaller, approximately 250 per second. This means the excited state is much longer-lived (metastable), which is crucial for achieving population inversion in this laser system.

* **$CO_2$ Laser (Vibrational-Rotational)**: A transition in the carbon dioxide molecule, in the far infrared. * Wavelength: 10600 nanometers, or 10.6 micrometers. * $B_{12}$: $3.58 \times 10^{17}$. * Notes: $\frac{g_2}{g_1} = 1.00$. $A_{21}$ is very small, approximately 5 per second. Vibrational transitions typically have much smaller dipole moments and thus smaller A and B coefficients compared to electronic transitions in atoms. This leads to very long radiative lifetimes.

The note at the bottom is very important: "These are approximate values and can vary based on specific conditions, fine/hyperfine structure, and averaging. $B_{12}$ is related to $A_{21}$ by the formula:

$$B_{12} = \frac{c^3}{8\pi h\nu^3} \frac{g_2}{g_1} A_{21}.$$

This is one of the key Einstein relations that we are building towards. It explicitly shows how $B_{12}$ depends on $A_{21}$, the degeneracies, and fundamental constants, inversely proportional to frequency cubed."

**Page 16:**

We now turn to the second fundamental light-matter interaction: "Process 2 – Induced, or more commonly, Stimulated Emission." The number 2 in a circle designates it as our second process.

First, the **Starting condition** is crucial: for stimulated emission to occur, the atom must *already be in the excited state*, which we've labeled ket 2. It has to have energy stored in it, ready to be released.

Next, what triggers the emission? An **Incident photon of the same mode triggers the downward transition** (indicated by a downward arrow). What does "of the same mode" mean? It means the incoming photon must have the same characteristics – specifically frequency, direction, and polarization – as a photon that *could* be spontaneously emitted by the atom when it transitions from state ket 2 to ket 1.

The most remarkable property of this process is that the **photon created is coherent with the trigger photon.** This is the absolute cornerstone of laser action. "Coherent" means the emitted photon is an exact replica of the incident photon: it has the same frequency, the same phase, the same direction of propagation, and the same polarization. So, if one photon comes in, it stimulates the atom to emit an identical photon, resulting in two identical photons leaving. This is amplification.

Now, let's quantify the **Probability per molecule, per second** for this process: Similar to stimulated absorption, the rate of stimulated emission is given by:

$$\frac{dP_{21}^{\text{ind}}}{dt} = B_{21}\,\rho_{\nu}(\nu)$$

Let's break this down:

- $\frac{dP_{21}^{\text{ind}}}{dt}$ is the probability per unit time for an atom in state 2 to be stimulated to emit a photon and transition to state 1. Units: $\mathrm{s}^{-1}$.

- $B_{21}$ is the Einstein coefficient for induced emission (or stimulated emission). Like $B_{12}$, it's a constant that characterizes the intrinsic strength of this particular 2 to 1 transition.

- $\rho_{\nu}(\nu)$ is, once again, the spectral energy density of the radiation field at the resonant frequency $\nu$. The presence of resonant photons in the environment is what drives this process.

So, the rate of stimulated emission, just like stimulated absorption, is proportional to the density of resonant photons and an intrinsic $B$ coefficient specific to the downward transition. The fact that the created photon is a clone of the incident one is what makes lasers possible.

**Page 17:**

Let's continue with stimulated emission. A key **Phase/Directionality property** is reiterated here: the emitted photon duplicates the phase, direction, polarization, and frequency of the incident (triggering) photon. This duplication is precisely why stimulated emission is the **key for optical amplification**. Imagine a wave of photons; each time it passes an excited atom, it can generate another identical photon, adding constructively to the wave, making it more intense.

Now, there's an important point about **Microscopic symmetry**: This symmetry suggests that the Einstein coefficients $B_{12}$ (for stimulated absorption from 1 to 2) and $B_{21}$ (for stimulated emission from 2 to 1) are **closely related**. The slide states this relationship "will be proven quantitatively later" when we derive the Einstein relations. This intuition comes from thinking about the fundamental time-reversal symmetry in quantum mechanics. The process of a photon stimulating an upward transition (1 to 2) should be, in some sense, the "reverse" of a photon stimulating a downward transition (2 to 1). This leads to an expectation that their intrinsic strengths (the B coefficients) are connected.

The slide also mentions an "[IMAGE REQUIRED: Animation concept: incoming wave stimulates second photon, wavefront doubles amplitude.]" Let's visualize this, as it's so important. Imagine an electromagnetic wave, representing the incident photon, approaching an excited atom. As this wave interacts with the atom, it causes the atom to release its stored energy by emitting a *new* wave. This new wave is perfectly in phase with the incident wave, travels in the same direction, and has the same frequency and polarization.

If you were to look at the combined electromagnetic field after the interaction, where there was one wave before, there are now two waves perfectly superimposed. If these are plane waves, the amplitude of the total electric field would effectively double at that point (assuming one photon interacting with one atom, and thinking about the field it generates). Since intensity is proportional to the square of the electric field amplitude, a doubling of amplitude would lead to a quadrupling of intensity *if they were filling the same mode*. More generally, one photon comes in, two photons come out, meaning the energy in that mode has increased by one quantum, $h\nu$. This amplification is the essence of how lasers work.

**Page 18**

We now arrive at the third and final fundamental interaction: "Process 3 – Spontaneous Emission." The circled 3 identifies it.

The first characteristic of spontaneous emission is that it **Occurs without any external field; vacuum fluctuations provide the trigger.** This is a remarkable and deeply quantum mechanical concept. An atom in an excited state ($\ket{2}$) can transition to a lower state ($\ket{1}$) and emit a photon, even if there are *no* external photons of the resonant frequency present. What causes this? According to Quantum Electrodynamics (QED), the vacuum is not truly empty. It's filled with "vacuum fluctuations" – fleeting electromagnetic fields that exist due to the zero-point energy of the quantum field. These vacuum fluctuations can be thought of as providing a tiny, ever-present "perturbation" that can "nudge" an excited atom into emitting a photon. So, spontaneous emission is, in a sense, *stimulated* by the vacuum field itself.

The **Probability per molecule, per second** for spontaneous emission is given as a field-independent constant:

$$\frac{dP_{21}^{\text{spon}}}{dt} = A_{21}$$

Let's dissect this: * $\frac{dP_{21}^{\text{spon}}}{dt}$ is the probability per unit time for an atom in state 2 to spontaneously emit a photon and transition to state 1. Its units are $s^{-1}$. * $A_{21}$ is the Einstein coefficient for spontaneous emission.

Crucially, $A_{21}$ is a **constant** that depends *only* on the properties of the atom and the specific transition (from state 2 to state 1). It does *not* depend on the external radiation field density $\rho_{\nu}$. This makes it fundamentally different from the B coefficients. The units of $A_{21}$ are simply per second ($s^{-1}$), as it represents a rate of decay.

Now, let's consider the **Photon characteristics** of the spontaneously emitted photon:

1. Its **Energy is fixed at $h\nu$**, where $h\nu = E_2 - E_1$. The photon carries away the exact energy difference between the upper and lower states. This is the same energy as in absorption or stimulated emission for this pair of levels.

**Page 19:**

Continuing with the characteristics of the photon in spontaneous emission: 2. The photon is **Emitted into *any* mode with equal probability**. This means that if there are no preferred directions or polarizations imposed by the environment (like a cavity or strong external fields), the spontaneously emitted photon can go off in any direction in space, and its polarization will be random (or an incoherent mixture if summed over many emission events). The slide notes this is "isotropic for non-preferred polarization/cavity."

This randomness in direction and phase of spontaneously emitted photons is why spontaneous emission from many atoms typically produces incoherent light, like that from an ordinary light bulb, in stark contrast to the highly directional and coherent light from stimulated emission in a laser.

From the $A_{21}$ coefficient, we can define a very important quantity: the **Radiative lifetime of level ket 2**: This is denoted by the Greek letter tau subscript 2 ($\tau_2$), and it's simply the reciprocal of $A_{21}$. $\tau_2 = \frac{1}{A_{21}}$. If $A_{21}$ is the probability per second that an atom in state 2 will spontaneously decay, then $\tau_2$ is the average time that an atom will spend in the excited state ket 2 before it spontaneously emits a photon and returns to a lower state (assuming this is the only decay path to state 1 or other states). So, if $A_{21}$ is large, the lifetime $\tau_2$ is short, and the decay is fast. If $A_{21}$ is small, $\tau_2$ is long, and the state is said to be metastable.

An important caveat is mentioned: this definition of radiative lifetime $\tau_2$ is "ignoring non-radiative decay channels." In many real systems, an excited atom can also lose its energy through processes other than photon emission. For example, it might collide with another atom and transfer its energy (collisional quenching), or in a solid, it might transfer energy to lattice vibrations (phonons). These are non-radiative decay paths. If such paths exist, they also contribute to depopulating the excited state, and the *total* lifetime of the state will be shorter than the purely radiative lifetime $\tau_2$. We will explore this more later, but for now, $A_{21}$ and $\tau_2$ refer specifically to the radiative process.

**Page 20:**

This slide provides a visual depiction of "Spontaneous Emission." In the center of the diagram, we see a blue circle labeled "(Excited Atom)". This represents our atom, initially in the upper energy state $E_2$. Radiating outwards from this central excited atom are numerous yellow arrows of varying lengths, all pointing in different directions. These arrows symbolize the photons being spontaneously emitted by the atom as it decays to a lower energy state. The fact that they are pointing in all directions illustrates the isotropic nature of spontaneous emission in free space – there's no preferred direction for the emitted photon. A dashed grey circle is drawn around the excited atom, encompassing the pattern of emitted photons, further emphasizing this idea of emission occurring into a wide range of angles.

Below the diagram, there's a crucial piece of text: "Rate governed by $A_{21}$". This reinforces that the fundamental rate at which this spontaneous emission process occurs for a single atom is determined by the Einstein A coefficient, $A_{21}$. This $A_{21}$ value is an intrinsic property of the atom and the specific transition involved.

So, this image captures the essence of spontaneous emission: an excited atom releasing a photon in a random direction, at a rate determined by $A_{21}$. This contrasts sharply with stimulated emission, where the emitted photon's direction and phase are dictated by the triggering photon.

**Page 21:**

Now, we need to discuss an important concept that affects these transition rates: "Statistical Weights and Degeneracy." This is denoted as Slide 8.

The first point states: "Angular momentum $J_{\mathrm{i}}$ of level i implies $g_{\mathrm{i}} = 2J_{\mathrm{i}} + 1$ degenerate Zeeman sub-levels (without an external field)." Let's break this down. Atomic and molecular energy levels are often characterized by a total angular momentum quantum number, $J$. For a given $J_{\mathrm{i}}$, there are $(2J_{\mathrm{i}} + 1)$ possible projections of this angular momentum onto an arbitrary axis. These projections are described by the magnetic quantum number, $m_\mathrm{J}$, which can take values from $-J_\mathrm{i}$ to $+J_\mathrm{i}$ in integer steps.

In the absence of any external fields (like a magnetic field that would cause Zeeman splitting, or an electric field that would cause Stark splitting), these $(2J_\mathrm{i}+1)$ sub-levels, corresponding to different $m_\mathrm{J}$ values, all have exactly the same energy. They are said to be "degenerate."

The quantity $g_\mathrm{i}=2J_\mathrm{i}+1$ is called the degeneracy or statistical weight of the level i. It counts how many distinct quantum states have the same energy $E_\mathrm{i}$. For example, if $J_\mathrm{i}=1$, then $m_\mathrm{J}$ can be $-1$, $0$, or $+1$, so $g_\mathrm{i}=3$.

Why is degeneracy important? "Degeneracy enters both population statistics and transition probabilities because dipole coupling may occur between multiple sublevel pairs."

* **Population statistics**: When we consider a collection of atoms in thermal equilibrium, more degenerate levels tend to hold a larger fraction of the total population, simply because there are more "slots" available at that energy. This will be reflected in the Boltzmann distribution.

* **Transition probabilities**: A transition we label as "i to j" is actually a collection of possible transitions between the sublevels of i and the sublevels of j. The electric dipole operator can couple different pairs of $\left(J_\mathrm{i},m_{J_\mathrm{i}}\right)$ and $\left(J_\mathrm{j},m_{J_\mathrm{j}}\right)$ sublevels. The overall observed strength of a transition (like the B coefficient) will be an average or sum over all these allowed sublevel-to-sublevel transitions, and the degeneracy factors $g_\mathrm{i}$ and $g_\mathrm{j}$ naturally come into play.

The final point on this slide is: "In the absence of external magnetic/electric fields, all sublevels [within a given degenerate level i] are equally populated in thermal equilibrium." This is a fundamental postulate of statistical mechanics. If multiple states (sublevels) have the same energy, each of those states has an equal probability of being occupied when the system is in thermal equilibrium.

So, degeneracy is not just a detail; it's a crucial factor in accurately describing both how atoms populate energy levels and the rates at which they transition between them.

**Page 22:**

This slide continues our discussion on Statistical Weights and Degeneracy.

There's a single, very important statement here, foreshadowing a key result: "Will explicitly see $g_1$ and $g_2$ in the relation $B_{12}$ equals $\frac{g_2}{g_1}$ times $B_{21}$." That is, $B_{12}$ (the Einstein coefficient for stimulated absorption from lower level 1 to upper level 2) is related to $B_{21}$ (the Einstein coefficient for stimulated emission from upper level 2 to lower level 1) by the ratio of the degeneracies of these levels. Specifically, $B_{12} = \frac{g_2}{g_1} B_{21}$, where $g_1$ is the degeneracy of the lower level $(2J_1 + 1)$ and $g_2$ is the degeneracy of the upper level $(2J_2 + 1)$.

This is one of the fundamental Einstein relations that we will derive shortly by considering the system in thermal equilibrium with a black-body radiation field.

What this relation implies is that if the upper level (level 2) is more degenerate than the lower level (level 1) – meaning $g_2 > g_1$ – then the coefficient $B_{12}$ for absorption will be larger than $B_{21}$ for stimulated emission. This makes intuitive sense: if there are more available states to transition *into* in the upper level, absorption is enhanced. Conversely, if the lower level is more degenerate ($g_1 > g_2$), then $B_{12}$ will be smaller than $B_{21}$.

If the levels happen to have the same degeneracy ($g_1 = g_2$), then $B_{12}$ simply equals $B_{21}$.

This relation highlights how the statistical weights of the energy levels directly influence the probabilities of stimulated absorption and emission between those levels.

**Page 23:**

Now we come to "Boltzmann Population Distribution in Equilibrium," labeled as Slide 9. This describes how atoms or molecules distribute themselves among their available energy levels when they are in thermal equilibrium at a given temperature.

First, the **Total molecular number density**: This is denoted by a capital $N$. It's simply the sum of the number densities in each individual level $i$. So, $N = \sum_\mathrm{i} N_\mathrm{i}$ (sum over all levels $i$ of $N_\mathrm{i}$), where $N_\mathrm{i}$ is the number of molecules per unit volume in energy level $i$.

Next, the crucial formula for the **Population of level i**: The number density of molecules in a specific energy level $i$, $N_\mathrm{i}$, is given by:

$$N_\mathrm{i} = N \cdot \frac{g_\mathrm{i} \exp\left(-\frac{E_\mathrm{i}}{kT}\right)}{Z}$$

Let's break this down: * $N$ is the total number density we just defined. * $g_\mathrm{i}$ is the degeneracy (or statistical weight) of level $i$, which we discussed on the previous slide ($g_\mathrm{i} = 2J_\mathrm{i} + 1$). * $\exp\left(-\frac{E_\mathrm{i}}{kT}\right)$ is the famous Boltzmann factor. * $E_\mathrm{i}$ is the energy of level $i$. * $k$ is the Boltzmann constant ($1.381 \times 10^{-23}$ J/K). * $T$ is the absolute temperature in Kelvin. This exponential factor tells us that levels with higher energy (larger $E_\mathrm{i}$) are exponentially less populated than levels with lower energy. The "$kT$" term represents the characteristic thermal energy available at temperature $T$. * $Z$ is the **partition function**. The slide notes "where partition function," implying $Z$ will be defined more fully, likely on the next page. The partition function is essentially a sum over all possible states that normalizes the distribution, ensuring that if you sum up all the $N_{\mathrm{i}}$, you get back the total $N$.

This Boltzmann distribution is a cornerstone of statistical mechanics and is fundamental to understanding how populations are distributed in systems at thermal equilibrium, which is the starting point for Einstein's derivation of the relations between his coefficients.

**Page 24:**

Continuing with the Boltzmann Population Distribution, this slide clarifies the partition function, $Z$, and then applies the distribution to our two-level system.

First, the **Partition function,** $Z$:

Z is defined as the sum over all possible energy levels $i$, of the term $\left(g_{\mathrm{i}} \times \exp\left(-\frac{E_{\mathrm{i}}}{kT}\right)\right)$. So,

$$Z = \sum_{\mathrm{i}} \left[g_{\mathrm{i}} \cdot \exp\left(-\frac{E_{\mathrm{i}}}{kT}\right)\right]$$

The role of the partition function is to **normalize probabilities**. When you divide $g_{\mathrm{i}} \times \exp\left(-\frac{E_{\mathrm{i}}}{kT}\right)$ by $Z$, you get the *fraction* of molecules that are in level $i$. Summing this fraction over all $i$ gives 1. The partition function effectively measures the total number of thermally accessible states in the system.

Now, let's apply this to a **For two-level subset**: We are interested in the ratio of populations in our upper state (ket 2, energy $E_2$) and lower state (ket 1, energy $E_1$). The population $N_2$ is

$$N_2 = N \times \frac{g_2 \cdot \exp\left(-\frac{E_2}{kT}\right)}{Z}$$

The population $N_1$ is

$$N_1 = N \times \frac{g_1 \cdot \exp\left(-\frac{E_1}{kT}\right)}{Z}$$

So, the ratio $\frac{N_2}{N_1}$ is:

$$\frac{N_2}{N_1} = \frac{N \times \frac{g_2 \cdot \exp\left(-\frac{E_2}{kT}\right)}{Z}}{N \times \frac{g_1 \cdot \exp\left(-\frac{E_1}{kT}\right)}{Z}}$$

The total population $N$ and the partition function $Z$ cancel out, leaving:

$$\frac{N_2}{N_1} = \frac{g_2}{g_1} \times \frac{\exp\left(-\frac{E_2}{kT}\right)}{\exp\left(-\frac{E_1}{kT}\right)}$$

$$\frac{N_2}{N_1} = \frac{g_2}{g_1} \times \exp\left(-\frac{E_2 - E_1}{kT}\right)$$

And since we know from the Bohr condition that $E_2 - E_1 = h\nu$ (where $\nu$ is the resonant frequency), we can write:

$$\frac{N_2}{N_1} = \frac{g_2}{g_1} \times \exp\left(-\frac{h\nu}{kT}\right)$$

This ratio is extremely important. The slide emphasizes that this is a "**crucial ratio used in Einstein-coefficient derivation**." To connect the microscopic $A$ and $B$ coefficients to the macroscopic properties of thermal radiation (Planck's Law), Einstein needed to know how the populations $N_1$ and $N_2$ are related at thermal equilibrium, and this Boltzmann ratio provides exactly that.

Note that since $E_2 > E_1$, the exponential term $\exp\left(-\frac{h\nu}{kT}\right)$ is always less than 1 (for $T > 0$). This means that in thermal equilibrium, $N_2$ is always less than $N_1$ (assuming $g_2 = g_1$, or more generally $\frac{N_2}{g_2} < \frac{N_1}{g_1}$). To achieve $N_2 > N_1$, as required for laser action, we need to move *away* from thermal equilibrium via a pumping mechanism.

Finally, the slide mentions: "**Bar charts showing relative Boltzmann populations for different T...**" which we expect to see on the next page, illustrating this temperature dependence.

**Page 25**

This slide presents four bar charts, each illustrating the "Boltzmann Population Distribution" for different temperatures, specifically for rotational energy levels of a molecule.

Let's look at the common features of these charts:

- The vertical axis of each chart is labeled "Fractional Population ($\frac{N_\mathrm{J}}{N}$)". This is the fraction of the total number of molecules ($N$) that are found in a specific rotational quantum state $J$ ($N_\mathrm{J}$).
- The horizontal axis is "Rotational Quantum Number ($J$)". Rotational levels are labeled by $J$, starting from $J = 0, J = 1, J = 2$, and so on. In these charts, $J$ goes up to $14$.
- Remember that rotational energy $E_\mathrm{J}$ is typically proportional to $J(J + 1)$, and the degeneracy $g_\mathrm{J}$ of a rotational level is $(2J + 1)$. The population $N_\mathrm{J}$ is proportional to $g_\mathrm{J} \times \exp\left(-\frac{E_\mathrm{J}}{kT}\right)$.

Now let's examine each chart:

1. **Top Left: Boltzmann Population Distribution at** $T = 99\,\mathrm{K}$. At this low temperature, only the lowest rotational levels are significantly populated. The distribution peaks around $J = 3$ or $J = 4$, and then falls off rapidly for higher $J$ values. The fractional population in any single $J$ state is relatively high for these low $J$ values compared to higher temperatures.

2. **Top Right: Boltzmann Population Distribution at** $T = 200\,\text{K}$. As the temperature increases to $T = 200\,\text{K}$, more thermal energy is available. We see that the peak of the distribution has shifted to higher $J$ values, now around $J = 5$ or $J = 6$. The distribution has also become broader, meaning a wider range of $J$ states are populated.

3. **Bottom Left: Boltzmann Population Distribution at** $T = 600\,\text{K}$. At $T = 600\,\text{K}$, the trend continues. The peak in the population distribution shifts significantly further to higher $J$ values, now around $J = 9$ or $J = 10$. The distribution is much broader, with a substantial fraction of molecules occupying higher rotational states.

4. **Bottom Right: Boltzmann Population Distribution at** $T = 1000\,\text{K}$. At this even higher temperature of $T = 1000\,\text{K}$, the population is spread over an even wider range of $J$ states, and the peak is shifted to $J$ values around $J = 12$ or $J = 13$. The maximum fractional population in any single state is lower than at cooler temperatures because the molecules are distributed over many more states.

**Overall Trend:**

- As temperature ($T$) increases, the population distribution shifts towards higher energy levels (higher $J$ in this case).
- The distribution also becomes broader, meaning more energy levels become significantly populated.

This is a direct consequence of the interplay between the $(2J + 1)$ degeneracy factor, which increases with $J$ (favoring higher $J$ states), and the $\exp\left(-\frac{E_J}{kT}\right)$ Boltzmann factor, which decreases with $J$ (disfavoring higher $J$ states). The peak of the distribution occurs at the $J$ value that optimally balances these two opposing trends for a given temperature. Understanding this behavior is crucial for interpreting molecular spectra at different temperatures.

**Page 26:**

Now we arrive at a pivotal point in our derivation:

**Slide 10: Imposing Detailed Balance: Photon Gain = Loss.**

This principle will allow us to find the relationships between the Einstein coefficients.

The fundamental premise is stated: **"At strict thermal equilibrium: energy density** $\rho_\nu(\nu)$ is time-independent."

This is the definition of thermal equilibrium. If the system is truly in equilibrium, its macroscopic properties, such as the spectral energy density of the radiation field, do not change over time.

**"Therefore, per unit volume: absorption rate = total emission rate *in the same mode*."**

This is an application of the principle of detailed balance. In equilibrium, for every process that occurs, its reverse process must occur at the same rate. Here, we're considering a specific electromagnetic mode (i.e., photons of a particular frequency $\nu$, direction, and polarization). The rate at which photons are removed from this mode by absorption must be exactly balanced by the rate at which photons are added to this mode by emission processes.

Let's look at the rates:

1. **Photon loss (due to absorption):**

The rate of absorption events per unit volume is given by $R_{\text{abs}}$.

$$R_{\text{abs}} = N_1 B_{12} \rho_\nu(\nu)$$

Here: * $N_1$ is the number density of atoms in the lower state (ket 1). * $B_{12}$ is the Einstein coefficient for stimulated absorption. * $\rho_\nu(\nu)$ is the spectral energy density of the radiation field at the resonant frequency $\nu$. Each absorption event removes one photon of frequency $\nu$ from the field.

2. **Photon gain (due to stimulated emission):**

The rate of stimulated emission events per unit volume is given by $R_{\text{ind.em}}$ (for induced emission).

$$R_{\text{ind.em}} = N_2 B_{21} \rho_\nu(\nu)$$

Here: * $N_2$ is the number density of atoms in the upper state (ket 2). * $B_{21}$ is the Einstein coefficient for stimulated emission. * $\rho_\nu(\nu)$ is again the spectral energy density. Each stimulated emission event adds one photon of frequency $\nu$ to the field, and this photon is coherent with the stimulating field (i.e., it goes into the same mode).

Now, we also need to consider spontaneous emission, which also contributes to transitions, and this will be on the next part of the slide. The key here is that in equilibrium, the flow of atoms upward must balance the flow of atoms downward.

**Page 27:**

Continuing with "Imposing Detailed Balance":

3. **Photon gain (spontaneous emission into all directions *including* the considered mode):**

The slide gives the rate of spontaneous emission events per unit volume as R_spon.em.

$$R_{\text{spon.em}} = N_2 A_{21}$$

Here: * $N_2$ is the number density of atoms in the upper state. * $A_{21}$ is the Einstein A coefficient for spontaneous emission.

Now, a subtlety: $A_{21}$ represents the total rate of spontaneous emission from state 2 to state 1, with photons being emitted isotropically into *all* available modes. The principle of detailed balance, as Einstein originally formulated it for deriving the coefficients, focused on the equilibrium of the *atomic populations* $N_1$ and $N_2$ under the influence of the radiation field $\rho_\nu(\nu)$ and spontaneous decay. The balance equation for the *populations* is that the rate of upward transitions (1 → 2) must equal the rate of downward transitions (2 → 1).

$$\text{Upward rate (per unit volume)} = N_1 B_{12} \rho_\nu(\nu)$$

$$\text{Downward rate (per unit volume)} = N_2 B_{21} \rho_\nu(\nu) + N_2 A_{21}$$

The $N_2 A_{21}$ term accounts for atoms leaving state 2 via spontaneous emission, irrespective of which mode the photon enters. These atoms then arrive in state 1.

The slide formulates the **Detailed balance condition** as:

$$R_{abs} = R_{ind.em} + R_{\text{spon.em}}$$

Substituting the expressions:

$$N_1 B_{12} \rho_\nu(\nu) = N_2 B_{21} \rho_\nu(\nu) + N_2 A_{21}$$

This is indeed the standard equation expressing that in thermal equilibrium, the rate at which atoms are excited from state 1 to state 2 by absorption is equal to the total rate at which atoms return from state 2 to state 1 by both stimulated and spontaneous emission.

The slide further states this condition is "**ensuring no net change in photon number for that mode.**"

This is true in the sense that if the atomic populations $N_1$ and $N_2$ are stable, and if $\rho_\nu(\nu)$ itself is the stable black-body distribution, then this equilibrium must hold. The absorption term removes photons from the mode defined by $\rho_\nu(\nu)$, while the stimulated emission term adds photons coherently back into that same mode. The spontaneous emission term $A_{21}$, while contributing to the population balance, emits photons into all modes. However, for the overall system (matter + radiation) to be in equilibrium, this population balance equation, which implicitly involves $\rho_\nu(\nu)$, must lead to the Planck distribution for $\rho_\nu(\nu)$ itself. This self-consistency is what Einstein exploited.

So, the core equation we will work with is:

$$N_1 B_{12} \rho_\nu(\nu) = N_2(B_{21} \rho_\nu(\nu) + A_{21})$$

**Page 28:**

**Slide 11: Algebraic Solution for $\rho_\nu(\nu)$**

Now we move to "Slide 11: Algebraic Solution for $\rho_\nu(\nu)$." We will use the detailed balance equation we just established and solve for the spectral energy density, $\rho_\nu(\nu)$.

First, we **Substitute explicit rates** into our detailed balance condition:

$$N_1 B_{12}\, \rho_\nu = N_2(B_{21}\, \rho_\nu + A_{21})$$

(Here, $\rho_\nu$ is understood to be $\rho_\nu(\nu)$). This equation states that the rate of atoms leaving state 1 for state 2 equals the rate of atoms leaving state 2 for state 1.

Next, we need to **Isolate** $\rho_\nu$:

Let's rearrange the equation to gather all terms containing $\rho_\nu$ on one side:

$$N_1 B_{12}\, \rho_\nu - N_2 B_{21}\, \rho_\nu = N_2 A_{21}$$

Now, factor out $\rho_\nu$ from the terms on the left-hand side:

$$\rho_\nu(N_1B_{12} - N_2B_{21}) = N_2A_{21}$$

Finally, divide by the term in the parenthesis to solve for $\rho_\nu$:

$$\rho_\nu = \frac{N_2A_{21}}{N_1B_{12} - N_2B_{21}}$$

To get this into the form shown on the slide, we can divide both the numerator and the denominator by $N_2B_{21}$:

$$\rho_\nu = \frac{\frac{N_2A_{21}}{N_2B_{21}}}{\frac{N_1B_{12}}{N_2B_{21}} - \frac{N_2B_{21}}{N_2B_{21}}}$$

This simplifies to:

$$\rho_\nu = \frac{\frac{A_{21}}{B_{21}}}{\frac{N_1}{N_2} \cdot \frac{B_{12}}{B_{21}} - 1}$$

This expression for $\rho_\nu$ is exactly what's presented on the slide. It gives the spectral energy density in terms of the Einstein coefficients and the ratio of the populations $\frac{N_1}{N_2}$.

The next step, as indicated, is to "**Replace population ratio using Boltzmann formula**." We know that in thermal equilibrium, the ratio $\frac{N_1}{N_2}$ (or $\frac{N_2}{N_1}$) is given by the Boltzmann distribution, which includes the temperature $T$ and the degeneracies $g_1$ and $g_2$.

**Page 29:**

Continuing with our algebraic solution for $\rho_\nu(\nu)$, we need to substitute the Boltzmann formula for the population ratio.

Recall from Page 24, for a two-level system in thermal equilibrium at temperature $T$:

$$\frac{N_2}{N_1} = \frac{g_2}{g_1} \exp\left(-\frac{h\nu}{kT}\right)$$

Therefore, the ratio $\frac{N_1}{N_2}$, which appears in our denominator, is the reciprocal of this:

$$\frac{N_1}{N_2} = \frac{g_1}{g_2} \exp\left(\frac{h\nu}{kT}\right)$$

The slide restates this relationship.

Now, we substitute this expression for $\frac{N_1}{N_2}$ into our formula for $\rho_\nu(\nu)$ from the previous page:

$$\rho_\nu(\nu) = \frac{A_{21}}{B_{21}} / \left[\frac{N_1}{N_2} \cdot \frac{B_{12}}{B_{21}} - 1\right]$$

becomes:

$$\rho_\nu(\nu) = \frac{A_{21}}{B_{21}} / \left[\frac{g_1}{g_2} \exp\left(\frac{h\nu}{kT}\right) \cdot \frac{B_{12}}{B_{21}} - 1\right]$$

This can be slightly rearranged in the denominator to group the coefficients:

$$\rho_\nu(\nu) = \frac{A_{21}}{B_{21}} / \left[\frac{g_1 B_{12}}{g_2 B_{21}} \exp\left(\frac{h\nu}{kT}\right) - 1\right]$$

This is the **Final expression** for the spectral energy density $\rho_\nu(\nu)$ as derived from the balance of absorption, stimulated emission, and spontaneous emission, assuming thermal equilibrium populations.

The slide makes an important **Note**: at this stage, there are "still unknown ratios $\frac{B_{12}}{B_{21}}$ and $\frac{A_{21}}{B_{21}}$ hiding inside."

Indeed, this formula for $\rho_\nu(\nu)$ contains these ratios of Einstein coefficients. Our next crucial step, pioneered by Einstein, is to compare this derived expression for $\rho_\nu(\nu)$ with the independently known formula for black-body radiation, namely Planck's Law. By forcing these two expressions for $\rho_\nu(\nu)$ to be identical (since they both must describe the same physical reality of thermal radiation in equilibrium), we will be able to determine these ratios of coefficients.

**Page 30:**

**Slide 12: Comparing with Planck Law to Extract Coefficient Relations**

This brings us to "Slide 12: Comparing with Planck Law to Extract Coefficient Relations." This is where Einstein's genius truly shines.

The strategy is straightforward: **"Set our derived** $\rho_\nu$ equal to Planck's $\rho_\nu^{\text{Planck}}$ for every $\nu$ and every $T$."

We have two expressions for the spectral energy density of thermal radiation:

1. Our derived expression (from the previous slide):

$$\rho_\nu(\nu) = \frac{A_{21}}{B_{21}} / \left[\frac{g_1 B_{12}}{g_2 B_{21}} \exp\left(\frac{h\nu}{kT}\right) - 1\right]$$

2. Planck's Law (from our review on Page 5):

$$\rho_\nu^{\text{Planck}}(\nu, T) = \frac{8\pi h\nu^3}{c^3} / \left[\exp\left(\frac{h\nu}{kT}\right) - 1\right]$$

The crucial insight is: **"Two functions are equal *only if* their denominators and numerators match identically."** Because this equality must hold for all frequencies $\nu$ and all temperatures $T$, the functional forms must be identical. This powerful requirement will yield two independent algebraic conditions, allowing us to solve for the ratios of the Einstein coefficients.

Let's start by comparing the denominators:

* Denominator of our derived $\rho_\nu$:

$$\left[\frac{g_1 B_{12}}{g_2 B_{21}} \exp\left(\frac{h\nu}{kT}\right) - 1\right]$$

* Denominator of Planck's $\rho_\nu$:

$$\left[\exp\left(\frac{h\nu}{kT}\right) - 1\right]$$

For these denominators to be identical, the factor multiplying the $\exp\left(\frac{h\nu}{kT}\right)$ term in our derived expression must be equal to 1.

Therefore, **Matching denominator exponential factors demands**:

$$\frac{g_1 B_{12}}{g_2 B_{21}} = 1$$

Rearranging this gives us our first Einstein relation:

$$B_{12} = \frac{g_2}{g_1} B_{21}$$

This is shown in the box on the slide. It states that the Einstein B coefficient for stimulated absorption ($B_{12}$) is equal to the Einstein B coefficient for stimulated emission ($B_{21}$) multiplied by the ratio of the degeneracies of the upper state ($g_2$) to the lower state ($g_1$). If the degeneracies are equal ($g_1 = g_2$), then $B_{12} = B_{21}$.

This is a profound result, obtained by requiring consistency between the microscopic processes and the macroscopic law of black-body radiation.

**Page 31:**

Continuing our comparison with Planck's Law to extract the coefficient relations:

We've just established from matching the denominators that $\frac{g_1 B_{12}}{g_2 B_{21}} = 1$.

Now, let's substitute this back into our derived expression for $\rho_\nu(\nu)$:

$$\rho_\nu(\nu) = \frac{\frac{A_{21}}{B_{21}}}{\left[\left(\frac{g_1 B_{12}}{g_2 B_{21}}\right)\exp\left(\frac{h\nu}{kT}\right) - 1\right]}$$

If $\frac{g_1 B_{12}}{g_2 B_{21}} = 1$, then the expression simplifies to:

$$\rho_\nu(\nu) = \frac{\frac{A_{21}}{B_{21}}}{\left[\exp\left(\frac{h\nu}{kT}\right) - 1\right]}$$

Now, we compare the **numerators** of this simplified derived $\rho_\nu(\nu)$ with the numerator of Planck's Law:

* Numerator of our (now simplified) derived $\rho_\nu$: $\frac{A_{21}}{B_{21}}$ * Numerator of Planck's $\rho_\nu$: $\frac{8\pi h\nu^3}{c^3}$

For our simplified $\rho_\nu(\nu)$ to be identical to Planck's $\rho_\nu^{\text{Planck}}(\nu, T)$, these numerators must be equal.

So, **Matching numerators gives**:

$$\frac{A_{21}}{B_{21}} = \frac{8\pi h\nu^3}{c^3}$$

This can be rewritten, as shown in the box on the slide, to express $A_{21}$ in terms of $B_{21}$:

$$A_{21} = \frac{8\pi h\nu^3}{c^3}\, B_{21}$$

This is our second fundamental Einstein relation. It connects the coefficient for spontaneous emission $A_{21}$ to the coefficient for stimulated emission $B_{21}$. Notice that this relation involves fundamental constants (Planck's constant $h$, speed of light $c$) and, very significantly, the cube of the transition frequency ($\nu^3$). This $\nu^3$ dependence means that spontaneous emission becomes dramatically more probable at higher frequencies (e.g., for X-ray transitions compared to radio frequency transitions).

The slide makes a critical concluding statement: "**These two boxed statements are Einstein relations; no approximation made besides thermal equilibrium.**"

The two relations are:

1. $B_{12} = \frac{g_2}{g_1} B_{21}$

2. $A_{21} = \frac{8\pi h \nu^3}{c^3} B_{21}$

Although we *derived* these relations by considering a system in thermal equilibrium, the relations themselves express fundamental properties of the atom or molecule and the way it interacts with electromagnetic radiation. Therefore, these relations between the coefficients $A_{21}$, $B_{12}$, and $B_{21}$ hold true *regardless* of whether the system is actually in thermal equilibrium or not, and irrespective of the actual form of the radiation field $\rho_\nu(\nu)$. The thermal equilibrium argument was a scaffold to uncover these intrinsic atomic properties. This universality is what makes them so powerful.

**Page 32:**

Now let's explore the "Slide 13: Physical Interpretation of $B_{12} = B_{21}\left(\frac{g_2}{g_1}\right)$." This is the first Einstein relation we derived.

The first point considers the simple case: **"If** $g_1 = g_2$: induced absorption and induced emission have identical probability coefficients." If the degeneracy of the lower state ($g_1$) is equal to the degeneracy of the upper state ($g_2$), then the ratio $\frac{g_2}{g_1}$ is 1. In this situation, $B_{12} = B_{21}$. This means that the intrinsic probability (per unit energy density) for a photon to stimulate an upward transition (absorption) is exactly the same as the intrinsic probability for it to stimulate a downward transition (emission), assuming the atom is in the appropriate initial state. This often holds for transitions between non-degenerate levels, or when we consider transitions between specific individual sublevels (where $g = 1$ for each sublevel).

What if there is **Unequal degeneracy**?

The slide states: **"higher** $g_2$ (more final states for absorption) naturally increases absorption probability." If the upper level (level 2) has a higher degeneracy than the lower level (level 1), so $g_2 > g_1$, then $B_{12} = \left(\frac{g_2}{g_1}\right) B_{21}$ will be *greater* than $B_{21}$. This means that absorption is inherently more probable (per $B$ coefficient definition) than stimulated emission from the upper level *when comparing* $B_{12}$ to $B_{21}$ for the overall levels.

Why? Imagine the transition from a single state in level 1 to one of $g_2$ states in level 2 for absorption. And for emission, from one of $g_2$ states in level 2 to a single state in level 1. The factor $\frac{g_2}{g_1}$ accounts for the number of available "pathways" or final states when we define $B_{12}$ and $B_{21}$ as coefficients for the overall levels 1 and 2, rather than for specific sublevel-to-sublevel transitions. If we were to consider transitions between *individual* non-degenerate sublevels $m_1$ of level 1 and $m_2$ of level 2, the corresponding $B(m_1 \rightarrow m_2)$ and $B(m_2 \rightarrow m_1)$ coefficients would be equal. The $g$ factors appear when we average over initial sublevels and sum over final sublevels to define the $B$ coefficients for the entire levels.

What is the deeper reason for this equality $\big(B(m_1 \rightarrow m_2) = B(m_2 \rightarrow m_1)\big)$?

The slide points to the **"Reciprocity principle backend: time reversal symmetry of QED matrix elements underlies equality."** This is a profound statement rooted in Quantum Electrodynamics (QED). The fundamental Hamiltonian describing the interaction between light and matter is Hermitian. This property, related to time-reversal symmetry, implies that the squared magnitude of the matrix element for a transition from an initial state to a final state (e.g., $|\langle\text{final}|H_{\text{interaction}}|\text{initial}\rangle|^2$) is the same as that for the time-reversed process (from final to initial, mediated by the same interaction). This underlying symmetry at the level of individual quantum states is what ultimately leads to the relationship between $B_{12}$ and $B_{21}$ involving the degeneracies when we consider transitions between entire degenerate levels.

**Page 33:**

Continuing with the physical interpretation and consequences of the Einstein relations, particularly $B_{12} = \frac{g_2}{g_1} B_{21}$.

A very **Useful consequence** of this relationship is that: "**measuring either absorption cross-section or gain cross-section suffices to know the other.**"

Let's understand why. The Einstein B coefficients are directly related to the concepts of absorption and gain cross-sections, often denoted by the Greek letter sigma ($\sigma$).

* The absorption cross-section, $\sigma_{\text{abs}}$ (or $\sigma_{12}$), quantifies how effectively an atom in the lower state absorbs a photon. It's proportional to $B_{12}$ (and also to a lineshape function, $g(\nu)$, that describes the frequency profile of the transition).

* Similarly, the stimulated emission (or gain) cross-section, $\sigma_{\text{gain}}$ (or $\sigma_{21}$), quantifies how effectively an excited atom is stimulated to emit a photon. It's proportional to $B_{21}$ (and the same lineshape function $g(\nu)$).

Since $B_{12} = \frac{g_2}{g_1} B_{21}$, it follows directly that the cross-sections are related by:

$$\sigma_{\text{abs}}(\nu) = \frac{g_2}{g_1} \sigma_{\text{gain}}(\nu)$$

(assuming the same lineshape).

This is incredibly practical in laser physics and spectroscopy. If you can measure, for example, the absorption spectrum of a material (which gives you $\sigma_{\text{abs}}(\nu)$), and you know the degeneracies $g_1$ and $g_2$ of the levels involved, you can then immediately calculate the gain cross-section $\sigma_{\text{gain}}(\nu)$ for that same transition. The gain cross-section is a critical parameter for predicting whether a material can act as a laser medium and how much amplification it can provide.

So, this theoretical link between $B_{12}$ and $B_{21}$ translates into a direct, experimentally verifiable, and highly useful relationship between measurable spectroscopic quantities.

**Page 34:**

**Slide 14: Spontaneous vs. Induced Emission into a Single Mode**

Now we turn to "Slide 14: Spontaneous vs. Induced Emission into a Single Mode." This will give us a very deep insight into the relative importance of these two emission processes.

First, let's recall the concept of the **Density of EM modes per unit volume, per unit frequency interval**. This is often denoted by $n(\nu)$ (or sometimes $\rho_{\text{modes}}(\nu)$ or $D(\nu)$ to avoid confusion with photon number).

The slide gives:

$$n(\nu) = \frac{8\pi\nu^2}{c^3}$$

This expression tells us how many distinct electromagnetic modes (essentially, available "slots" for photons) exist per unit volume of space, within a unit frequency interval centered at frequency $\nu$. It arises from counting the possible standing wave solutions for electromagnetic waves in a cavity and then extending to free space. The factor includes contributions from two independent polarizations for each spatial mode. The units are number of modes per (meter cubed times Hertz), which is seconds per $\mathrm{m}^{-3}$.

Next, we take our second Einstein relation:

$$A_{21} = \frac{8\pi h\nu^3}{c^3} B_{21}$$

And we **Divide this equation by** $n(\nu)$:

$$\frac{A_{21}}{n(\nu)} = \frac{\frac{8\pi h\nu^3}{c^3} B_{21}}{\frac{8\pi\nu^2}{c^3}}$$

Let's see what cancels: * The $8\pi$ in the numerator and denominator cancels. * The $c^3$ in the numerator and denominator cancels. * $\nu^3$ in the numerator divided by $\nu^2$ in the denominator leaves $\nu$.

So, the expression simplifies beautifully to:

$$\frac{A_{21}}{n(\nu)} = B_{21} h\nu$$

This equation, $\frac{A_{21}}{n(\nu)} = B_{21} h\nu$, is profoundly important. It relates the total spontaneous emission rate $A_{21}$, the density of modes $n(\nu)$, the stimulated emission coefficient $B_{21}$, and the energy of a single photon $h\nu$. Let's interpret this on the next page.

**Page 35:**

Let's delve into the **Interpretations** of the remarkable equation we just derived: $\frac{A_{21}}{n(\nu)} = B_{21} h\nu$.

***Left side = spontaneous per-mode probability, denoted \(A_{21}^\)*** (A twenty-one star).

$A_{21}$ is the *total* spontaneous emission rate from an atom in state 2, emitting into *all* possible modes.

$n(\nu)$ is the number of modes per unit volume per unit frequency interval.

So, $\frac{A_{21}}{n(\nu)}$ can be interpreted as the spontaneous emission rate *per mode* (strictly, per unit volume per unit frequency, which needs careful handling if we want rate into one specific discrete mode, but this ratio is proportional to it). Let's call $A_{21}^{*}$ the spontaneous emission probability (or rate) into a single, specific mode.

Then, $A_{21}^{*} = B_{21}h\nu$.

***Right side = induced probability when exactly* one* photon is already present.**

The term $B_{21}h\nu$ is indeed the stimulated emission probability (per atom, per second) if the energy density $\rho_{\mathrm{v}}(\nu)$ happens to be exactly that corresponding to one photon of energy $h\nu$ within the "volume and bandwidth of that mode." More simply, we know the stimulated emission rate per atom is $B_{21}\rho_{\mathrm{v}}(\nu)$. If we say that one photon in the mode contributes an energy density equivalent to "$h\nu$" (this is a slight conceptual simplification from $\rho_{\mathrm{v}}$, but leads to the right idea for q), then the rate due to one photon is $B_{21}$ times "hv-equivalent-energy-density". The relation $A_{21}^{*} = B_{21}h\nu$ is more direct.

Therefore, the profound conclusion is: **"Therefore, one photon in a mode causes stimulated emission at the same rate as vacuum causes spontaneous emission *into that same single mode*."**

This is a cornerstone statement in quantum optics. Think about it:

The vacuum itself, through its fluctuations, causes spontaneous emission into a given mode at a rate $A_{21}^{*}$.

If, instead of just vacuum, there is *one real photon* already occupying that mode, it will cause stimulated emission into that same mode at a rate $B_{21}$ * "hv-equivalent-density". Our equation shows these two rates are equal.

So, spontaneous emission into a mode can be thought of as the "zeroth order" of stimulated emission – it's like being stimulated by the zero-point energy of the vacuum field, which is equivalent in effect to one photon being present for stimulation.

This explains why spontaneous emission into the lasing mode is often called the "seed" for laser action. Once that first photon is spontaneously emitted into the mode, it can then stimulate further emission, and the process can build up if there's gain. This also highlights that spontaneous emission is the fundamental source of quantum noise in lasers, as it's an unavoidable random process that initiates amplification.

**Page 36:**

This brings us to "Slide 15: General Relation — Induced/Spontaneous Ratio = Photon Number $q$." We're now going to generalize the insight from the previous slide to understand how the ratio of stimulated to spontaneous emission rates depends on the number of photons, $q$, present in a specific mode.

First, let's consider the **Energy density in a single mode**:

The slide states:

$$\rho_{\nu}(\nu) = q\, h\nu$$

This is a crucial conceptual link. It's saying that the *effective* spectral energy density $\rho_{\nu}(\nu)$ that drives transitions *within a particular mode* is proportional to ' $q$ ', the number of photons in that mode, times the energy per photon, ' $h\nu$ '. More precisely, if a single mode has a certain effective volume $V_{\text{mode}}$ and frequency bandwidth $\Delta\nu_{\text{mode}}$, and it contains $q$ photons, then the total energy in that mode is

$$U_{\text{mode}} = q\,h\nu.$$

The spectral energy density would then be

$$\frac{U_{\text{mode}}}{V_{\text{mode}}\,\Delta\nu_{\text{mode}}}.$$

Here, for simplicity, $\rho_\nu(\nu)$ is being directly associated with $q\,h\nu$. This interpretation assumes that the B coefficient correctly links this $q\,h\nu$ to the transition rate. It captures the essential idea that the "strength" of the field in the mode, for the purpose of driving stimulated emission, scales with the number of photons $q$.

**where** $q =$ instantaneous photon count in that mode.

Now, let's look at the **Induced emission rate per excited molecule**:

This is the probability per second that a single molecule in the excited state (ket 2) will undergo stimulated emission. We'll call this $R_{\text{ind}}$.

$$R_{\text{ind}} = B_{21}\,\rho_\nu(\nu)$$

Substituting our expression for $\rho_\nu(\nu)$ in terms of $q$:

$$R_{\text{ind}} = B_{21}\,q\,h\nu$$

So, the stimulated emission rate per molecule is directly proportional to $B_{21}$, the photon energy $h\nu$, and, most importantly, the number of photons $q$ already present in that mode. This linear dependence on $q$ is key to amplification.

**Page 37:**

Continuing with "Slide 15: General Relation — Induced/Spontaneous Ratio."

We have the induced emission rate per excited molecule as $R_{\text{ind}} = B_{21}\, q\, h\nu$.

Now, let's consider the **Ratio to the spontaneous rate**:

Specifically, we want the ratio of the stimulated emission rate *into a particular mode* to the spontaneous emission rate *into that same mode*.

Let \(R_{\text{spon}}^\) *be the spontaneous emission rate per excited molecule into that single mode. From Slide 35, we identified \(A_{21}^* = B_{21}\, h\nu\) as this per-mode spontaneous rate (where $A_{21}^*$ was the notation on that slide for $A_{21}/n(\nu)$).

The slide writes the denominator as $A_{21}^*$, implying this single-mode spontaneous rate.

So, the ratio is:

\[\frac{R_{\text{ind}}}{R_{\text{spon}}^*} = \frac{B_{21}\, q\, h\nu}{A_{21}^*}\]

Since $A_{21}^* = B_{21}\, h\nu$, we substitute this into the denominator:

$$\frac{R_{\text{ind}}}{R_{\text{spon}}^*} = \frac{B_{21}\, q\, h\nu}{B_{21}\, h\nu}$$

The terms $B_{21}$ and $h\nu$ cancel out, leaving:

$$\frac{R_{\text{ind}}}{R_{\text{spon}}^*} = q$$

This is an extremely elegant and powerful result!

**The ratio of the stimulated emission rate (into a specific mode) to the spontaneous emission rate (into that same specific mode) is simply equal to** $q$, the number of photons already present in that mode.

The **Key takeaway** is clearly stated: **"each additional photon multiplies the induced rate linearly; the spontaneous rate (into that mode) is constant."**

So, if there's 1 photon in the mode ($q = 1$), stimulated emission occurs at the same rate as spontaneous emission into that mode.

If there are 10 photons ($q = 10$), stimulated emission is 10 times stronger.

If there are a million photons ($q = 10^6$), stimulated emission is a million times stronger!

This is why lasers work. By confining photons in a resonant cavity, $q$ can become very large for specific lasing modes. Consequently, stimulated emission in these modes overwhelmingly dominates spontaneous emission, leading to coherent amplification and the highly monochromatic, directional, and intense beams characteristic of lasers. In contrast, for thermal light sources where $q$ is typically much less than 1 for any given mode, spontaneous emission dominates.

**Page 38:**

### Slide 16: Practical Numbers — Thermal Field vs. Laser Cavity

Now let's look at "Slide 16: Practical Numbers — Thermal Field vs. Laser Cavity." This slide will really drive home the difference in photon occupancy $q$ between these types of light sources.

First, consider **Visible light at** $T = 3000$ Kelvin (approx. tungsten bulb): This is like the filament of an ordinary incandescent light bulb.

The slide states that for visible light photons, the ratio of photon energy to thermal energy, $\frac{h\nu}{kT}$, is approximately $5$. (For example, if $\nu$ is for green light $\sim 5.5 \times 10^{14}$ Hz, $h\nu \sim 2.28$ eV. At $T = 3000$ K, $kT \sim 0.258$ eV. So $\frac{h\nu}{kT} \sim 8.8$. If $\frac{h\nu}{kT} = 5$, then $h\nu \sim 1.29$ eV, which is in the near infrared, about $960$ nm. So "visible" is used a bit broadly here, or it's an average value. Let's proceed with $\frac{h\nu}{kT} \approx 5$ as given).

With $\frac{h\nu}{kT} \approx 5$, the average photon number per mode, $\bar{q}$ (which we previously defined as $\frac{1}{\exp\left(\frac{h\nu}{kT}\right)-1}$), becomes:

$$\bar{q} \approx \frac{1}{\exp(5) - 1} = \frac{1}{148.4 - 1} \approx \frac{1}{147.4} \approx 0.0067.$$

The slide approximates this as $\bar{q} \approx 10^{-2}$ (one one-hundredth).

So, for a thermal source like a light bulb, the average number of photons in any given mode in the visible/near-IR range is very small, much less than one photon per mode.

Consequently, **Induced emission is much, much less than spontaneous emission per mode.** Since the stimulated rate is $q$ times the spontaneous rate (into the same mode), if $q$ is $10^{-2}$, then stimulated emission is only $1\%$ of spontaneous emission. Thermal sources are overwhelmingly dominated by spontaneous emission.

Now, consider the **Same bulb but observed 10 centimeters away**: The actual photon number per mode $q$ that would be "seen" by an atom at this distance is even smaller, around $q \sim 10^{-8}$.

Why this drastic reduction? Because the intensity of light from the bulb (and thus the energy density) decreases as $\frac{1}{r^2}$ due to geometric dilution (as per the $4\pi r^2$ factor for spherical spreading). While $\bar{q} \approx 10^{-2}$ characterizes the photon occupancy *at the temperature of the filament*, the radiation field experienced by a target 10 cm away is much weaker. The effective $q$ driving transitions in a molecule at that distance is significantly diminished. This huge drop from $10^{-2}$ to $10^{-8}$ (a factor of a million) reflects this dilution over 10 cm for a small filament.

This illustrates just how "photon-starved" individual modes are in typical thermal radiation fields, especially at a distance from the source.

**Page 39:**

Continuing with "Practical Numbers — Thermal Field vs. Laser Cavity":

Next, consider a **High-pressure Mercury (Hg) lamp center, at a wavelength** $\lambda = 253.6$ nm: This wavelength is in the ultraviolet. The slide states that for this source, the average photon number per mode, **q-bar, is approximately** $10^{-2}$. This value, similar to the tungsten bulb *at its source*, suggests that even for this intense discharge lamp, which can appear very bright (though this line is UV), the photon occupancy per mode is still very low. (If we assumed a blackbody at, say, $7000$ K, for $\lambda = 253.6$ nm, $\frac{h\nu}{kT} \approx 8.1$, giving q-bar $\approx 3 \times 10^{-4}$. The $10^{-2}$ value might reflect non-blackbody characteristics or conditions right at the arc kernel where brightness is extremely high for that specific line). The key point remains: $\bar{q} \ll 1$. Thus, such lamps are also dominated by spontaneous emission.

Now, for a stark contrast, let's look at a **Helium-Neon (He-Ne) laser single-mode cavity**. Typical parameters given are an output power of $1$ mW and a mirror transmission of $1\%$ for the output coupler. Under these conditions, the slide states:

- **Stored photon number** $q \sim 10^7$ (ten million photons in the lasing mode within the cavity!). This is an astronomically larger number than the q-values for thermal sources ($10^{-2}$ or $10^{-8}$). (As a side note: from our previous calculation on page 48/49, $1$ mW output with $1\%$ transmission and $L = 0.3$ m led to $P_{\text{cav}} = 0.1$ W, $U = 1 \times 10^{-10}$ J, and my calculated $q$ was $\sim 3.18 \times 10^8$. So, $10^7$ is a conservative estimate here, but the order of magnitude is the key).
- What's the consequence of such a high $q$? **Stimulated emission is** $\sim 10^7$ times spontaneous emission per same mode. This follows directly from our relation:

$$\frac{\text{Rate (stimulated)}}{\text{Rate (spontaneous per mode)}} = q$$

If $q$ is $10^7$, then stimulated emission in the lasing mode is ten million times more probable than spontaneous emission into that same mode. This is why laser light is so different: it's an avalanche of coherent photons generated by stimulated emission, completely overwhelming the random spontaneous emissions within that lasing mode.

The comparison is dramatic: q values of $10^{-2}$ for bright thermal sources versus $10^7$ or more for a modest laser. This difference of many orders of magnitude is fundamental to what makes a laser a laser.

**Page 40:**

This slide presents a bar chart providing a "Comparison of Photon Number (q) per Mode" for the different light sources we've just discussed. This visual makes the differences strikingly clear.

The vertical axis of the chart displays "Photon Number (q) per mode" on a logarithmic scale, ranging from $10^{-8}$ (one hundred-millionth) at the bottom up to $10^8$ (one hundred million) at the top. Each major tick mark represents a factor of 100 increase ($10^{-8}$, $10^{-6}$, $10^{-4}$, $10^{-2}$, $1$, $10^2$, $10^4$, $10^6$, $10^8$).

The horizontal axis simply labels the "Light Source."

There are three bars:

1. **Tungsten Bulb (10cm)**: This is the first bar, colored blue. Its height corresponds to $q \approx 10^{-8}$ on the logarithmic scale. It's a very, very short bar, emphasizing the extremely low photon occupancy per mode from a typical thermal source at a modest distance.

2. **Hg Lamp (center)**: This is the middle bar, colored green. Its height corresponds to $q \approx 10^{-2}$ on the scale. While significantly higher than the

distant tungsten bulb (by a factor of a million), it's still far below $q = 1$. This means that even at the core of a bright discharge lamp, photon occupancy per mode is low.

3. **He-Ne Laser (cavity)**: This is the rightmost bar, colored red. Its height dramatically shoots up to $q \approx 10^7$ (ten million) on the scale. This bar is vastly taller than the other two.

**The Visual Impact**:

The chart powerfully illustrates the enormous disparity in photon occupancy per mode.

* Thermal sources (tungsten bulb, Hg lamp) have $q \ll 1$. * The laser cavity has $q \gg 1$, by many orders of magnitude (in this case, about 9 orders of magnitude, or a billion times more photons per mode than the tungsten bulb at 10cm, and about 9 orders of magnitude, or a billion times more, than the Hg lamp... no, wait, $10^7$ vs $10^{-2}$, that's 9 orders of magnitude higher for the laser vs Hg lamp).

This incredibly high photon number 'q' concentrated in a single (or few) modes within the laser cavity is precisely what enables stimulated emission to dominate and produce coherent, intense laser light. The chart serves as an excellent summary of the practical numbers discussed.

**Page 41:**

We now revisit a crucial conceptual point on "Slide 17: Independence of Einstein Coefficients from Radiation Field."

The slide emphasizes that the Einstein coefficients – $A_{21}$, $B_{12}$, and $B_{21}$ – depend **only** on intrinsic properties of the atom or molecule itself, not on the external radiation field it might be immersed in. Specifically, they depend on:

- **Transition frequency** $\nu$: As we saw, $A_{21}$ is proportional to $\nu^3$ through the $\frac{8\pi h\nu^3}{c^3}$ factor. Since $B_{12}$ and $B_{21}$ are related to $A_{21}$, they also inherently depend on the frequency that characterizes the energy difference $E_2 - E_1$.

- **Dipole matrix elements (intrinsic to molecule/atom)**: This is the fundamental quantum mechanical quantity $\langle 2|\hat{\mu} \cdot e|1\rangle$ that determines the strength of the coupling between the light and the matter for a specific transition. This matrix element depends on the wavefunctions of the initial and final states ($\psi_1$ and $\psi_2$) and the electric dipole operator.

The slide then clarifies what *is* affected by the external field:

**"External field strength (i.e.,** $\rho_\nu$), direction, spectrum influence populations $N_1$ and $N_2$ but *not* the coefficients, provided the field does not Stark-shift levels."

This is a critical distinction. The radiation field (its intensity $\rho_\nu$, its spectral distribution, its polarization) determines the *rates* of stimulated absorption and stimulated emission, and thereby it drives changes in the populations $N_1$ and $N_2$. However, the proportionality constants in those rate equations – the $A$ and $B$ coefficients – remain fixed values for that specific atomic/molecular transition.

The important caveat "provided field does not Stark-shift levels" means we are operating in the weak-field, perturbative regime. If the external field is extremely strong, it can significantly alter the energy levels $E_1$ and $E_2$ (this is the Stark effect for electric fields), which would then change $\nu$ and potentially the wavefunctions themselves, thereby modifying the $A$ and $B$ coefficients. But for the conditions under which these coefficients are typically defined and used, they are considered constants of the material.

So, think of $A_{21}$, $B_{12}$, and $B_{21}$ as fingerprints of the specific transition within an atom or molecule. The light field determines how often these transitions happen, but not the intrinsic capacity for them to happen.

**Page 42:**

Continuing from the previous point about the independence of Einstein coefficients from the radiation field:

The profound consequence is stated here: **"Hence Einstein relations (slides 12-14 referenced) remain valid for *any*** $\rho_\nu(\nu)$: thermal, laser, incoherent lamp, or even vacuum."

The Einstein relations we derived are:

1. $B_{12} = \left(\frac{g_2}{g_1}\right) B_{21}$

2. $A_{21} = \left(\frac{8\pi h\nu^3}{c^3}\right) B_{21}$ (And by implication, $A_{21} = \left(\frac{8\pi h\nu^3}{c^3}\right)\left(\frac{g_1}{g_2}\right) B_{12}$)

These relationships, which connect the three coefficients, were derived by considering a specific scenario: matter in thermal equilibrium with a black-body (thermal) radiation field. However, because the A and B coefficients themselves are intrinsic properties of the atom/molecule and do not depend on the nature of the external field (in the weak-field limit), the relationships *between* these coefficients must also be universally valid.

So, whether the radiation field $\rho_\nu(\nu)$ is:

- **Thermal** (like black-body radiation),
- **Laser** light (highly monochromatic, directional, and intense, very non-thermal),
- From an **incoherent lamp** (like a discharge lamp, also non-thermal in its detailed spectrum),

- Or even in **vacuum** (where $\rho_\nu(\nu) = 0$ for external fields, though vacuum fluctuations still exist to drive spontaneous emission via $A_{21}$),

these Einstein relations hold true. They are fundamental constants that describe how that particular two-level system interacts with photons of frequency $\nu$.

This universality is what makes the Einstein A and B coefficients, and the relations between them, so incredibly powerful and fundamental in all areas of spectroscopy, quantum electronics, and laser physics. They provide a universal language for describing light-matter interactions at the single-photon level.

**Page 43:**

**Slide 18: Reformulating with Angular Frequency** $\omega$ (omega)

Sometimes, particularly in theoretical treatments, it's more convenient to work with angular frequency $\omega$ instead of cyclic frequency $\nu$.

The **Definition** is straightforward:

$$\omega = 2\pi\nu \quad \text{(omega equals two pi nu)}$$

Angular frequency $\omega$ has units of radians per second, while $\nu$ has units of Hertz (cycles per second).

Let's look at how some quantities change form:

* **Mode density per unit** $\omega$: This is the number of electromagnetic modes per unit volume, per unit *angular* frequency interval. Let's call this $n(\omega)$. The slide gives:

$$n(\omega) = \frac{\omega^2}{\pi^2 c^3}$$

(omega squared, divided by pi squared times cee cubed). We previously had

$$n(\nu) = \frac{8\pi\nu^2}{c^3}.$$

Since the number of modes in an interval must be the same,

$$n(\omega)\, d\omega = n(\nu)\, d\nu.$$

As

$$d\omega = 2\pi\, d\nu,$$

we get

$$n(\omega) = \frac{n(\nu)}{2\pi}.$$

Substituting

$$\nu = \frac{\omega}{2\pi}$$

into $\frac{n(\nu)}{2\pi}$ gives

$$\frac{8\pi\left(\frac{\omega}{2\pi}\right)^2/c^3}{2\pi} = \frac{8\pi\omega^2/(4\pi^2c^3)}{2\pi} = \frac{2\omega^2/(\pi c^3)}{2\pi} = \frac{\omega^2}{\pi^2c^3}.$$

This matches the slide.

* **Spectral energy density per** $\omega$: This is denoted $\rho_\omega(\omega)$ (rho sub omega of omega) and represents energy per unit volume per unit *angular* frequency interval. The slide states:

$$\rho_\omega(\omega) = n(\omega)\, \hbar\omega\, \left[\frac{1}{\exp\left(\frac{\hbar\omega}{kT}\right) - 1}\right]$$

Which can be written as:

$$\rho_\omega(\omega) = \frac{\omega^2}{\pi^2 c^3}\ \hbar\omega \left[\frac{1}{\exp\left(\frac{\hbar\omega}{kT}\right) - 1}\right]$$

So,

$$\rho_\omega(\omega) = \frac{\hbar\omega^3}{\pi^2 c^3 \left(\exp\left(\frac{\hbar\omega}{kT}\right) - 1\right)}.$$

Here, $\hbar$ (h-bar) is the reduced Planck constant, $\hbar = \frac{h}{2\pi}$. So $h\nu = \hbar\omega$.

These reformulations are primarily for mathematical convenience, often simplifying expressions by absorbing factors of $2\pi$ into $\hbar$ and $\omega$. The underlying physics, of course, remains the same.

**Page 44:**

Continuing with the reformulation in terms of angular frequency $\omega$:

The slide now considers how the **Coefficient ratio $A_{21}/B_{21}$ becomes**:

$$\frac{A_{21}}{B_{21}} = \frac{\hbar\omega^3}{\pi c^3}$$

(A twenty-one divided by B twenty-one equals h-bar omega cubed, all divided by pi cee cubed).

And it reminds us that $\hbar = \frac{h}{2\pi}$.

Let's quickly verify this transformation. We had

$$\frac{A_{21}}{B_{21}(\nu)} = \frac{8\pi h\nu^3}{c^3}$$

When we switch from $\nu$ to $\omega$, the definition of the B coefficient itself can change depending on whether it's defined with respect to $\rho_\nu(\nu)$ (energy density per unit cyclic frequency) or $\rho_\omega(\omega)$ (energy density per unit angular frequency). If the rate of transition is $B_{21}(\nu)\rho_\nu(\nu)$ and also $B_{21}(\omega)\rho_\omega(\omega)$, and since

$$\rho_\omega(\omega) = \frac{\rho_\nu(\nu)}{\frac{d\omega}{d\nu}} = \frac{\rho_\nu(\nu)}{2\pi},$$

it implies that $B_{21}(\omega) = 2\pi B_{21}(\nu)$ for the rate to be the same.

So,

$$\frac{A_{21}}{B_{21}(\omega)} = \frac{A_{21}}{2\pi B_{21}(\nu)} = \frac{1}{2\pi} \cdot \frac{8\pi h\nu^3}{c^3} = \frac{4\,h\nu^3}{c^3}.$$

Now, substitute $h = 2\pi\hbar$ and $\nu = \frac{\omega}{2\pi}$:

$$\frac{A_{21}}{B_{21}(\omega)} = \frac{4(2\pi\hbar)\left(\frac{\omega}{2\pi}\right)^3}{c^3} = \frac{8\pi\hbar\left(\frac{\omega^3}{8\pi^3}\right)}{c^3} = \frac{\hbar\omega^3}{\pi^2 c^3}.$$

My derivation consistently yields $\frac{\hbar\omega^3}{\pi^2 c^3}$. The slide has $\frac{\hbar\omega^3}{\pi c^3}$, which differs by a factor of $\pi$ in the denominator. Such discrepancies often arise from different conventions in defining $B(\omega)$ or the spectral energy density used (e.g., some definitions of $\rho_\omega$ might already include a factor of $2\pi$ relative to $\rho_\nu$). For the purpose of this lecture, we will adhere to the formula given on the slide:

$$\frac{A_{21}}{B_{21}} = \frac{\hbar\omega^3}{\pi c^3}.$$

It's important to be aware that when consulting different textbooks, one might encounter variations in these factors of $\pi$ depending on the precise definitions employed for the B coefficients in the angular frequency domain.

The slide then makes an important clarifying point:

"Factor $2\pi$ distinction arises solely from change of variable $\nu \leftrightarrow \omega$; physical predictions unchanged."

This is a key reassurance. While the mathematical forms of coefficients or densities might pick up or lose factors of $2\pi$ when switching between $\nu$ and $\omega$, any physically measurable quantity (like a transition rate in atoms per second, or an emitted power in Watts) must remain the same regardless of which frequency variable ($\nu$ or $\omega$) was used in the intermediate calculations. The choice is one of mathematical convenience.

**Page 45:**

**Slide 19: Example 1 — 100 W Tungsten Light Bulb.**

This will help us apply the concepts and see the magnitudes involved for a common thermal source.

First, the **Parameters** given for this example:

* Filament Temperature: $T \approx 2800$ Kelvin. This is a typical operating temperature for a tungsten filament in an incandescent bulb. * Observation point distance: $r = 0.10$ meters (which is 10 centimeters). We are interested in the radiation field at this distance from the bulb. * Wavelength of interest: $\lambda = 500$ nanometers. This is green light, near the peak of human eye sensitivity.

The goal is to perform a **Step-by-step photon number per mode (q) calculation**:

The slide outlines the general steps:

1. **Energy density at bulb surface from Stefan-Boltzmann law and geometric dilution.** First, we'd estimate the total power radiated by the filament using the Stefan-Boltzmann law (Power = emissivity × Stefan-Boltzmann constant × Area × $T^4$). Then, from this power, we'd find the intensity at the filament's surface. The energy density at the surface is roughly this intensity divided by $c$.

Crucially, this energy density then gets geometrically diluted as it spreads out. At a distance '$r$' from a small source, the intensity (and thus energy density) falls off as $1/r^2$ (or more precisely, related to the filament area and the $4\pi r^2$ area at distance $r$). So the energy density at the $0.10$ m observation point will be much lower than at the filament surface.

2. **Convert to** $\rho_\nu$ at $\lambda$ (or corresponding $\nu$) using Planck formula. Once we have the (diluted) total energy density at the observation point corresponding to the filament temperature $T$, we need the *spectral* energy density $\rho_\nu(\nu)$ at our target frequency $\nu = c/\lambda$. This means using Planck's law,

$$\rho_\nu(\nu, T) = \frac{8\pi h\nu^3}{c^3\left(\exp\left(\frac{h\nu}{kT}\right) - 1\right)}$$

and then applying the geometric dilution factor to this spectral quantity. Effectively, we're calculating $\rho_\nu(\nu, T)$ at the source and then scaling it down for the observation point.

3. **Divide by** $h\nu$. If we have $\rho_\nu(\nu)$ (the spectral energy density at the observation point in J s $m^{-3}$), dividing it by the energy of a single photon, $h\nu$ (in J), gives us the number of photons per unit volume per unit frequency interval (units: s $m^{-3}$ or photons $m^{-3}$ $Hz^{-1}$).

The fourth step will be on the next slide, which involves dividing by the mode density to get $q$.

**Page 46:**

Continuing with Example 1, the 100 W Tungsten Light Bulb, and our step-by-step calculation of the photon number per mode, $q$. We had just calculated (conceptually) the number of photons per unit volume per unit frequency at the observation point.

The fourth and final step is:

4. **Divide by mode density** $n(\nu)$. Recall that $n(\nu) = \frac{8\pi\nu^2}{c^3}$ is the number of electromagnetic modes per unit volume per unit frequency. The photon number per mode, $q$, is then:

$$q = \frac{\rho_\nu(\nu)/(h\nu)}{n(\nu)}$$

Substituting the Planck formula for $\rho_\nu(\nu, T)$ at the source and then applying the dilution factor, or recognizing that this whole expression for $q$ (if $\rho_\nu(\nu)$ is taken at the source temperature without dilution yet) simplifies to $q_{\text{source}} = \frac{1}{\exp(h\nu/kT)-1}$. The crucial part is that the $\rho_\nu(\nu)$ used here must be the *diluted* spectral energy density at the observation point ($r = 0.10\,\text{m}$). If $q_{\text{source}}$ is the photon occupancy per mode *at the filament temperature*, then the effective $q$ at the observation distance $r$ will be $q_{\text{source}}$ multiplied by the same geometric dilution factor that reduced the energy density.

Now, for the **Numerical outcome**:

The slide states that after performing these calculations, the result is $q \approx 10^{-8}$. Let's quickly check the source $q$ value: For $T = 2800\,\text{K}$ and $\lambda = 500\,\text{nm}$ ($\nu = 6 \times 10^{14}\,\text{Hz}$), $\frac{h\nu}{kT} \approx 10.28$. So, $q_{\text{source}} = \frac{1}{\exp(10.28)-1} \approx \frac{1}{29215-1} \approx 3.4 \times 10^{-5}$. To get from $q_{\text{source}} \approx 3.4 \times 10^{-5}$ down to $q_{\text{observed}} \approx 10^{-8}$ requires a dilution factor of about $\frac{3.4\times10^{-5}}{10^{-8}} = 3400$. This factor reflects the geometric spread of light from the filament to the $10\,\text{cm}$ observation point. This $q \approx 10^{-8}$ is an extremely small number.

What is the **Consequence** of such a low $q$? "Stimulated processes in a molecular probe [placed at the observation point] are essentially zero; fluorescence remains spontaneous." If an incident photon from the bulb happens to excite a molecule at the observation point, that molecule will almost certainly de-excite via spontaneous emission (fluorescence). The probability of stimulated emission, which is proportional to $q$, is negligible when $q$ is $10^{-8}$ compared to the $1$ associated with spontaneous emission into a mode. This example underscores how weak thermal light fields are in terms of photon occupancy per mode, especially at everyday distances from the source.

**Page 47:**

**Slide 20: Example 2 — High-Pressure Hg (Mercury) Lamp.**

This is another common type of thermal (or quasi-thermal) light source, often used in spectroscopy for its strong emission lines.

The parameters given:

* **Mercury arc kernel** $T \sim 7000$ Kelvin. This is the very hot central part of the arc discharge. * **Strongest line (relevant here)** $\lambda = 253.6$ nanometers. This is a well-known, intense UV emission line of mercury. * **Similar four-step evaluation (as for the tungsten bulb, presumably evaluating** $q$ at or very near the arc kernel) gives $q \sim 10^{-2}$.

Let's compare with a blackbody calculation: $T = 7000$ K, $\lambda = 253.6$ nm ($\nu = 1.183 \times 10^{15}$ Hz).

$$\frac{h\nu}{kT} \approx 8.11$$

$$q_{\text{blackbody}} = \frac{1}{\exp(8.11) - 1} \approx \frac{1}{3327 - 1} \approx 3.0 \times 10^{-4}$$

The slide's value of $q \sim 10^{-2}$ is about 33 times higher than this blackbody estimate. This difference likely arises because an arc discharge is not a perfect blackbody; it can have very high brightness concentrated in its emission lines, leading to a higher effective photon occupancy per mode for those specific lines than what a pure thermal equilibrium blackbody at that temperature would suggest across all modes. For our purposes, we accept the slide's value of $q \sim 10^{-2}$ for this source at this line.

The key consequence, even with this relatively "high" $q$ for a non-laser source:

**"Although the lamp appears extremely bright to the human eye (or would, if 253.6nm were visible; other visible Hg lines contribute to perceived brightness), induced emission is much, much less than spontaneous emission per mode."**

Since $q \sim 10^{-2}$, which is still much less than 1, the rate of stimulated emission (proportional to $q$) is only about 1% of the rate of spontaneous emission into a given mode (proportional to 1). So, even for very bright, high-temperature discharge lamps, the light emission mechanism at the level of individual modes is overwhelmingly dominated by spontaneous emission. They are not like lasers.

**Page 48:**

Now we turn to "Slide 21: Example 3 — Single-Mode HeNe Laser Cavity." This will provide a stark contrast to the thermal sources.

The parameters for a typical small Helium-Neon laser:

- **Output power:** $P_{\text{out}} = 1\,\text{mW}$, which is $10^{-3}\,\text{W}$. This is the power of the laser beam that actually comes out of the laser.
- **Mirror transmission:** $T = 0.01$ (or 1%). This is the transmittance of the output coupler mirror, the partially transparent mirror from which the beam emerges.

From these, we can calculate the **Intracavity power,** $P_{\text{cav}}$:

The power circulating *inside* the laser cavity is much higher than the output power. If the output coupler transmits only 1% of the light incident upon it from inside, then to get 1 mW out, the power inside hitting that mirror must be $\frac{P_{\text{out}}}{T}$.

$$P_{\text{cav}} = \frac{P_{\text{out}}}{T} = \frac{1\,\text{mW}}{0.01} = 100\,\text{mW} = 0.1\,\text{W}.$$

So, there's $0.1\,\text{W}$ of power continuously bouncing back and forth inside the laser cavity.

Next, the **Energy stored in the lasing mode** within the cavity:

The total energy $U$ stored in the resonant mode of length $L$ is related to the intracavity power $P_{\text{cav}}$ and the speed of light $c$ by the formula:

$$U = \frac{P_{\text{cav}} \cdot L}{c}.$$

This formula arises because $P_{\text{cav}}$ is the energy flowing per unit time, and $L/c$ is the time it takes for light to traverse the cavity length $L$ once. So, $U$ is roughly the energy "in flight" within the cavity.

Taking a typical cavity length for a small HeNe laser as $L = 0.3\,\text{m}$:

$$U \approx \frac{(0.1\,\text{W}) \cdot (0.3\,\text{m})}{3 \times 10^8\,\text{m/s}}.$$

$$U \approx \frac{(0.03\,\text{J/s} \cdot \text{m})}{3 \times 10^8\,\text{m/s}}.$$

$$U \approx 1.0 \times 10^{-10}\,\text{J}.$$

This is a very small amount of energy in absolute terms, but as we'll see, it corresponds to a very large number of photons.

The slide will continue with the **Photon count** on the next page.

**Page 49:**

Continuing with Example 3, the Single-Mode HeNe Laser Cavity. We just found the energy stored in the mode, $U \approx 1.0 \times 10^{-10}$ Joules.

Now, let's calculate the **Photon count,** $q$: The number of photons, $q$, in the mode is simply the total energy stored in the mode, $U$, divided by the energy of a single photon, $h\nu$.

$$q = \frac{U}{h\nu}$$

For a HeNe laser, the wavelength $\lambda$ is 632.8 nanometers (632.8 $\times 10^{-9}$ meters).

The frequency $\nu = \frac{c}{\lambda} = \frac{3\times10^{8}\text{ m/s}}{632.8\times10^{-9}\text{ m}} \approx 4.74 \times 10^{14}$ Hz.

The energy per photon $h\nu = (6.626 \times 10^{-34}\text{ J s}) \times (4.74 \times 10^{14}\text{ s}^{-1}) \approx 3.139 \times 10^{-19}$ J.

So,

$$q = \frac{1.0 \times 10^{-10}\text{ J}}{3.139 \times 10^{-19}\text{ J/photon}} \approx 3.185 \times 10^{8}\text{ photons.}$$

That's approximately 318 million photons!

The slide states that $q$ is approximately $10^{7}$ (ten million) photons. Our calculation based on the $U$ value from the previous slide gave a higher number, around $3.2 \times 10^{8}$. The exact number can depend on precise parameters like mode volume and exact definition of $P_{\text{cav}}$, but the crucial point is the order of magnitude. Both $10^{7}$ and $3 \times 10^{8}$ are vastly larger than the $q$ values for thermal sources. Let's use the slide's $q \approx 10^{7}$ for consistency with its typical representation.

Now, the critical implication:

"Stimulated emission overwhelms spontaneous emission (since $q \gg 1$)."

With $q \approx 10^7$ (or even higher), meaning millions of photons are already in the lasing mode, the rate of stimulated emission (which is $q$ times the spontaneous rate into that mode) is enormous compared to the spontaneous emission into that same mode. This is the hallmark of laser action.

"Nevertheless, spontaneous emission into *all other* modes still supplies the primary noise seed."

Even though stimulated emission dominates in the lasing mode, atoms in the gain medium are still spontaneously emitting photons in all directions and into all other non-lasing modes. A tiny fraction of this spontaneous emission happens to go into the lasing mode itself. These spontaneously emitted photons that get "caught" by the lasing mode are then amplified by stimulated emission. They are, in essence, the "seeds" from which the laser light grows. They are also the fundamental source of quantum noise in the laser output, for instance, determining the ultimate linewidth of the laser.

This example beautifully illustrates the conditions inside an operating laser.

**Page 50**

This slide presents a "Sketch: Fabry-Pérot Cavity (HeNe Laser)," which visually summarizes the HeNe laser example we've just discussed.

Let's describe the components shown in this diagram:

• We see two mirrors facing each other, forming the optical resonator, also known as a Fabry-Pérot cavity. • The mirror on the left is labeled "HR Mirror," which stands for High Reflector. This mirror would typically have a reflectivity very close to 100% at the laser wavelength. • The mirror on the right is labeled "Output Coupler (OC)." This mirror is partially transparent, and the diagram indicates its transmission $T = 0.01$, meaning 1% of the light incident on it from inside the cavity is transmitted out to form the laser beam.

- The space between the mirrors is filled with the "HeNe Gain Medium," depicted as a pink shaded region. This is where the helium-neon gas mixture is located, and where the electrical discharge creates the population inversion necessary for lasing.

- Inside the cavity, a red sinusoidal wave pattern is drawn, representing the standing electromagnetic wave of the resonant lasing mode. The light bounces back and forth between the mirrors, being amplified by the gain medium on each pass.

- The length of the cavity is labeled as $L = 0.3$ m.

- Associated with the light inside, it's noted that the intracavity power, $P_{\text{cav}} = 0.1$ W.

- A red arrow is shown emerging from the Output Coupler, representing the output laser beam, labeled $P_{\text{out}} = 1$ mW.

Below the cavity, key numbers summarizing the state of the light mode are given:

- $q \approx 10^7$ photons – the number of photons in the lasing mode.

- $U \approx 1.0 \times 10^{-10}$ J – the total energy stored in that mode.

- And in parentheses, $(q \gg 1)$ – emphasizing that the photon number is much greater than one, the condition for stimulated emission to dominate.

(As we noted, there's a slight inconsistency between $U = 1.0 \times 10^{-10}$ J and $q \approx 10^7$ photons for HeNe photons where $h\nu \approx 3.14 \times 10^{-19}$ J. $U = 1.0 \times 10^{-10}$ J actually corresponds to $q \approx 3.18 \times 10^8$ photons. Conversely, $q = 10^7$ photons would correspond to $U \approx 3.14 \times 10^{-12}$ J. However, the diagram presents these values together, so we acknowledge them as given in this illustrative sketch, representing typical orders of magnitude involved).

This diagram provides a clear, concise visual summary of the physical setup and key parameters inside a common HeNe laser.

**Page 51:**

**Slide 22: Conceptual Bridge to Lasers**

Now we're at "Slide 22: Conceptual Bridge to Lasers." This slide synthesizes what we've learned about the Einstein coefficients and photon occupancy to explain the fundamental principles of laser operation.

The first crucial point is: **"Laser gain medium engineered to invert populations ($N_2 > N_1$)**." This is the absolute prerequisite for laser action. In thermal equilibrium, the lower state $N_1$ is always more populated than the upper state $N_2$ (or $\frac{N_1}{g_1} > \frac{N_2}{g_2}$ more generally). A laser requires a "population inversion," where there are more atoms or molecules in the upper energy state of the lasing transition than in the lower state (or more precisely $\frac{N_2}{g_2} > \frac{N_1}{g_1}$ for net gain). This non-equilibrium condition must be actively created by an external energy source, a process called "pumping." When $\frac{N_2}{g_2} > \frac{N_1}{g_1}$, then stimulated emission ($N_2 B_{21}$) can overcome absorption ($N_1 B_{12}$), leading to net amplification, because $\frac{g_1}{g_2} B_{12} = B_{21}$.

Second: **"Large** $q$ accumulated in resonator → induced emission dominates → exponential amplification."

* The "resonator" (the optical cavity formed by mirrors) plays a vital role by trapping photons of specific resonant frequencies. This allows the number of photons $q$ in these preferred modes to build up to very large values.

* As we know, when $q$ is large, stimulated emission (whose rate is proportional to $q$) vastly outweighs spontaneous emission (whose rate into that mode is like $q = 1$ stimulation).

* This dominance of stimulated emission leads to **exponential amplification** of light within the cavity. If light makes a round trip through the gain medium and experiences a net gain greater than 1, its intensity will grow exponentially with each pass, until other limiting factors (like saturation of the gain) come into play.

Third: **"Selective feedback (mirrors) confines energy to very few modes → increases** $q$ further without raising spontaneous emission."

* The mirrors provide "selective feedback" because they are only highly reflective for light that is traveling along the axis of the cavity and has a wavelength that satisfies the standing wave condition (an integer number of half-wavelengths must fit between the mirrors). This means energy is channeled primarily into a very small number of specific spatial and frequency modes.

* By confining the stimulated emission to these few modes, $q$ (the photon number per mode) for these modes becomes extremely high.

*Importantly, this buildup of* $q$ in specific modes does not* increase the fundamental spontaneous emission rate $A_{21}$ of the atoms themselves. Spontaneous emission still occurs isotropically into all $4\pi$ steradians, and most of it is lost from the cavity and does not contribute to the lasing mode.

Finally: **"Einstein-coefficient framework remains valid; only** $N_1$, $N_2$ deviate from Boltzmann distribution."

The A and B coefficients are intrinsic properties of the atoms/molecules. They are the same whether the system is in thermal equilibrium or in a highly non-equilibrium state like a population inversion. What changes in a laser is that the populations $N_1$ and $N_2$ are driven far from the Boltzmann distribution that would characterize them at thermal equilibrium. It's this engineered, non-thermal population distribution that allows for light amplification via stimulated emission.

**Page 52:**

We've reached "Slide 23: Key Take-Home Messages." This slide summarizes the core concepts from this entire lecture segment on absorption and emission processes.

First: **"Three elementary processes fully characterize linear light-matter interaction for a single transition."**

These are, of course: 1. Stimulated Absorption (rate proportional to $N_1\, B_{12}\, \rho_\nu$) 2. Stimulated Emission (rate proportional to $N_2\, B_{21}\, \rho_\nu$) 3. Spontaneous Emission (rate proportional to $N_2\, A_{21}$)

The term "linear" here refers to the fact that the stimulated rates are linearly proportional to the radiation energy density $\rho_\nu$ (or photon number $q$). This holds when the field is not so strong as to cause non-linear optical effects. "Single transition" reminds us we've primarily used a two-level atom model.

Second: **"Einstein relations enforce self-consistency with black-body radiation; no additional adjustable parameters."**

The relationships $B_{12} = \left(\frac{g_2}{g_1}\right) B_{21}$ and $A_{21} = \frac{8\pi h\nu^3}{c^3} B_{21}$ are fundamental. They were derived by requiring that the microscopic quantum processes, when in thermal equilibrium, must reproduce the empirically and theoretically known Planck distribution for black-body radiation. This means the A and B coefficients are not independent adjustable parameters; once one is known (along with degeneracies and frequency), the others are determined. This interconnectivity ensures a self-consistent framework.

Third: **"Spontaneous emission sets fundamental noise floor; stimulated term scales with photon occupancy** $q$."

Spontaneous emission is an inherent quantum process, occurring even in vacuum. The portion of spontaneous emission that goes into a particular mode (e.g., a lasing mode) acts as the ultimate irreducible "seed" or "noise floor" for that mode. From this seed, amplification can occur.

The stimulated emission rate, on the other hand, scales directly with $q$, the number of photons already present in the mode. This is what allows for massive amplification when $q$ becomes large, as in a laser. The ratio of stimulated to spontaneous emission (into the same mode) is simply $q$.

**Page 53:**

Continuing with our "Key Take-Home Messages":

Fourth: **"Real-world bright thermal sources rarely reach** $q \sim 1$; laser cavities routinely reach $q \gg 1$, enabling coherent amplification." This is a crucial practical distinction. As we saw in our examples, for thermal sources like incandescent bulbs or even bright discharge lamps, the average photon occupancy per mode ($q$) is typically much less than $1$ (e.g., $10^{-2}$ to $10^{-8}$). This means spontaneous emission dominates.

In contrast, laser cavities are designed to build up an extremely high photon occupancy ($q$ can be $10^7$, $10^8$, or even much higher) in one or a few modes. When $q \gg 1$, stimulated emission overwhelmingly dominates spontaneous emission within those modes, leading to the highly coherent and amplified light characteristic of lasers. The threshold $q \sim 1$ is where stimulated emission becomes comparable to spontaneous emission (into the same mode).

Fifth, and critically important for your future studies: **"Mastery of** $A_{21}, B_{12}, B_{21}$ is prerequisite for quantitative laser-rate modeling, saturation spectroscopy, and fluorescence lifetime analysis." Understanding these Einstein coefficients and their interrelations is not just an academic exercise. It's absolutely fundamental for:

* **Quantitative laser-rate modeling**: The equations that describe how laser light builds up and how populations in the gain medium evolve over time (the laser rate equations) are built directly upon the A and B coefficients.

* **Saturation spectroscopy**: This is a powerful high-resolution spectroscopic technique that involves using a strong laser beam to significantly alter the populations $N_1$ and $N_2$ (e.g., depleting $N_1$). Understanding how the absorption or gain "saturates" depends directly on the B coefficients and the intensity of the laser field.

* **Fluorescence lifetime analysis**: The radiative lifetime of an excited state ($\tau_{rad} = 1/A_{21}$) is a fundamental spectroscopic parameter that can provide rich information about molecular structure and dynamics. Measuring fluorescence decay curves allows experimental determination of $A_{21}$.

So, the concepts we've covered today form the essential toolkit for analyzing and understanding a vast range of phenomena in laser spectroscopy and quantum electronics.

This concludes our detailed exploration of Chapter 2.3: Absorption, Induced, and Spontaneous Emission. I trust this has provided you with a solid foundation for these vital concepts. Thank you.