Chapter

2.8

Page 1:

Alright everyone, welcome back to Phys 608, Laser Spectroscopy. Today, we embark on a new and fundamentally important topic: Chapter 2, Section 8, which deals with **Transition Probabilities**. As you can see, these notes were prepared by Distinguished Professor Doctor M. A. Gondal.

This section is absolutely central to understanding how light interacts with matter, which, as you know, is the very essence of spectroscopy. We'll be diving deep into what determines the likelihood of an atom or molecule absorbing or emitting a photon, and how we can use this knowledge to probe the universe around us, from the atmospheres of distant stars to the intricate workings of molecules in our laboratories. So, let's begin our exploration of transition probabilities.

Page 2:

Let's start with the core question regarding transition probabilities – **Why do they matter?** Why do we, as physicists and spectroscopists, dedicate so much effort to understanding and quantifying them?

The first bullet point gets straight to the heart of it: The **spectral-line intensity**, which we denote as I_{line} (capital I_{line}), is what we *observe* in an experiment. It's the brightness of a spectral line, or the depth of an absorption feature. This observable intensity depends on two, crucially, *independent* factors.

First, there's the **population density** of the initial quantum level. This is the number of atoms or molecules per unit volume that are in the specific starting state for the transition. This could be an excited state if we're looking at emission, or a lower state (often the ground state) if we're looking at absorption. Conventionally, we denote this population density as N_{i} or N_{k}, where 'i' or 'k' labels the initial quantum level. It makes intuitive sense, doesn't it? The more atoms or molecules you have in the starting state, the stronger the resulting spectral line will be, all other things being equal.

Second, and this is where transition probabilities come in directly, is the **intrinsic probability that a quantum jump actually occurs once the particle is in that initial level**. This inherent likelihood of a transition happening is precisely what we call the **transition probability**. It's not enough for an atom to be in the right state; there's also a specific, quantifiable chance per unit time that it will make the jump to another state by either emitting or absorbing a photon. This is an intrinsic property of the two states involved and the nature of their coupling via the electromagnetic field.

So, you have two ingredients: how many particles are *ready* to make the jump (population density), and how *likely* each one is to actually make that jump (transition probability). Both are essential.

Now, why is knowing these transition probabilities so powerful? The second bullet point tells us: **Knowing transition probabilities allows one to reverse-engineer physical conditions from measured spectra.** This is a profound statement. We measure light, the spectrum. If we have accurate knowledge of the transition probabilities for the species we're observing, we can then work backwards from the measured line intensities to deduce information about the source of that light. This could be the temperature, the pressure, the density, or the chemical composition of the environment where those atoms or molecules reside. It’s like having a cosmic or molecular Rosetta Stone.

Page 3:

Let's consider a couple of concrete examples to illustrate just how vital these transition probabilities are.

First, a classic application: We can **infer element abundances in stellar atmospheres or interstellar clouds.** Imagine pointing a telescope at a distant star. The light collected passes through a spectrometer, and we see a pattern of absorption or emission lines. Each element, and indeed each ionization state of an element, has a unique fingerprint of spectral lines. By measuring the relative intensities of these lines, and critically, by knowing the transition probabilities associated with each specific line, astrophysicists can determine the relative amounts of hydrogen, helium, carbon, iron, and so on, in that star's atmosphere or in a vast, cold interstellar gas cloud. Without accurate transition probabilities, those beautiful spectra would remain largely qualitative "fingerprints." With them, they become powerful quantitative tools for cosmic chemistry.

Another important example: We can **derive the temperature,** T, of a remote plasma by comparing the populations of two different excited levels. We'll delve into the details of this later, but the basic idea is that the relative populations of different energy levels in a system in thermal equilibrium are governed by the Boltzmann distribution, which is temperature-dependent. If we can measure the intensities of spectral lines originating from two different excited states that decay to a common lower level, and if we know their respective transition probabilities (specifically, their Einstein A coefficients, which we'll define soon), we can work out the relative populations of those excited states. From that ratio, we can then deduce the temperature of the plasma, even if it's millions of light-years away or in a harsh laboratory environment where direct temperature measurement is impossible.

The italicized text on this slide really drives the point home: **In astrophysics, the electromagnetic spectrum is often the *only* information channel.** We can't go there and take a sample. We rely entirely on the light that reaches us. **Accurate transition data transform mere light into quantitative diagnostics of chemical composition, density, and thermal balance.** It's this transformation from qualitative observation to quantitative understanding that makes transition probabilities so indispensable. They are the key that unlocks the physical information encoded in the light.

Page 4:

Beyond their crucial role in diagnostics and astrophysics, transition probabilities also serve another profound purpose: they are **exquisitely sensitive probes of theoretical wavefunctions.** This connects directly to the foundations of quantum mechanics and computational chemistry.

Remember, the wavefunctions of an atom or molecule describe the distribution of its electrons. The probability of a transition occurring due to interaction with light is determined by how these charge distributions change, which is encapsulated in something called the dipole matrix element, which in turn depends directly on the initial and final state wavefunctions.

The slide highlights a critical point: **Small inaccuracies in the calculated charge distribution of a molecule produce large errors in predicted line strengths.** This sensitivity is actually a good thing for testing our theoretical models! If our quantum chemical calculations produce wavefunctions that are even slightly off, the predicted transition probabilities might be significantly different from experimentally measured values. Therefore, comparing highly accurate experimental measurements of transition probabilities (or related quantities like line strengths or lifetimes) with theoretical predictions provides a very **rigorous test of our quantum-chemical models.** It helps us refine our understanding of molecular structure and electron behavior, pushing the boundaries of computational physics and chemistry. So, transition probabilities are not just for looking outwards to the cosmos; they're also for looking inwards, to test the very accuracy of our fundamental theories of matter.

Page 5:

This slide provides a nice visual summary of how we use transition probabilities, particularly in an astrophysical context, for **Inferring Astrophysical Properties from Spectra using Transition Probabilities.**

Let's walk through the diagram. On the left, we see a representation of a **Star**, emitting **Starlight**. This starlight, carrying information from the star, travels across vast distances.

Then, this starlight is collected by a **Telescope**. The telescope's primary function here is to gather as much light as possible and direct it to an analytical instrument.

The light from the telescope is then fed into a **Spectrograph**. The spectrograph is the key instrument that disperses the light by wavelength, much like a prism creating a rainbow. It spreads the starlight out into its constituent colors, or more precisely, its spectrum.

Finally, on the right, we see the output: a **Spectrum**. The horizontal axis is **Wavelength,** λ. The spectrum itself is shown as a band of colors, representing the continuous emission from the star. Superimposed on this continuous spectrum are several dark lines. These are **absorption lines**. They occur because cooler gas, perhaps in the outer atmosphere of the star or in an interstellar cloud between the star and us, absorbs specific wavelengths of light corresponding to transitions within the atoms or molecules in that gas.

Now, how do transition probabilities fit in? The positions of these absorption lines tell us *which* elements or molecules are present, as each has a unique spectral fingerprint. But it's the *strength* or *intensity* of these lines – how dark or prominent they are – that tells us *how much* of each element is there, or what the temperature and pressure conditions are. And to decode that intensity information, to go from "there's a line here" to "there's this much iron at this temperature," we absolutely need to know the transition probability for each of those specific absorption lines.

This diagram beautifully illustrates the journey of light from a celestial object to a data product that, with the help of transition probabilities, unveils the physics of its source.

Page 6:

Now, let's delve into a specific example of how transition probabilities are used, as introduced in the slide titled "**From Populations to Temperature – The Boltzmann Connection**." This is a very common and powerful technique, especially in plasma diagnostics and astrophysics.

The first bullet point sets up the scenario: **Consider two different excited levels, let's call their energies** E_i and E_e, that both decay to a common lower level, whose energy is E_k. Imagine an atom or ion with a set of energy levels. We're interested in two specific excited states, 'i' and 'e'. The key here is that both of these states have an allowed radiative transition down to the *same* lower level 'k'. This lower level could be the ground state or another, lower-lying excited state.

Next, what do we do experimentally? **We measure the intensities,** I_{ik} and I_{ek}, of the two spectral lines corresponding to these transitions: E_i decaying to E_k, and E_e decaying to E_k. So, when an atom in state 'i' drops to state 'k', it emits a photon of a specific energy and wavelength, giving rise to a spectral line. We measure the total power or number of photons in this line, which is its intensity I_{ik}. Similarly, we measure the intensity I_{ek} for the line produced when atoms decay from state 'e' to E_k.

The crucial insight, as highlighted in the third bullet point, is that **provided the transition probabilities,** A_{ik} and A_{ek}, are known, the line-intensity ratio yields... well, it yields a way to determine the relative populations of states 'i' and 'e', and from there, as we'll see, the temperature. The 'A' coefficients here are the Einstein A coefficients for spontaneous emission, which represent the probability per unit time for an atom in an excited state to spontaneously decay to a lower state by emitting a photon. We'll define these more formally very soon. For now, the key takeaway is that if we know these A values – these intrinsic probabilities of decay for our two chosen transitions – then the ratio of the measured intensities I_{ik} to I_{ek} becomes a very informative quantity. Let's see how on the next slide.

Page 7:

Alright, building on our scenario of two excited states decaying to a common lower level, this slide presents the key equations.

First, we have the relationship between the measured line intensities and the atomic parameters. The ratio of the intensity of the line from state 'i' to state 'k', denoted I_{ik}, to the intensity of the line from state 'e' to state 'k', denoted I_{ek}, is given by:

$$\frac{I_{ik}}{I_{ek}} = \frac{N_i\, h\, \nu_{ik}\, A_{ik}}{N_e\, h\, \nu_{ek}\, A_{ek}}.$$

Let's break this down carefully:

* N_i is the population density of the upper state 'i' (number of atoms per unit volume in state i). * N_e is the population density of the other upper state 'e'. * h is Planck's constant. * ν_{ik} is the frequency of the photon emitted when an atom transitions from state i to state k. So, $h\nu_{ik}$ is the energy of that photon. * ν_{ek} is the frequency of the photon emitted for the e to k transition, and $h\nu_{ek}$ is its energy. * A_{ik} is the Einstein A coefficient for spontaneous emission from state i to state k – it's the probability per unit time that an atom in state i will decay to state k by emitting a photon. * A_{ek} is the corresponding Einstein A coefficient for the e to k transition.

This equation makes perfect sense: the intensity of a spectral line is proportional to the number of atoms in the initial upper state (N), the energy of each photon emitted ($h\nu$), and the rate at which each atom emits such a photon (A). So, the ratio of intensities directly reflects the ratios of these quantities for the two transitions.

Now, the crucial connection to temperature comes from the second bullet point: **Under conditions of thermal equilibrium, the level populations obey the Boltzmann law.** This law states that the ratio of the population of state 'i' (N_i) to the population of state 'e' (N_e) is given by:

$$\frac{N_i}{N_e} = \frac{g_i}{g_e} \exp\left[-\frac{E_i - E_e}{k_B T}\right].$$

Let's dissect this Boltzmann equation:

* N_i and N_e are the populations we've already discussed. * g_i and g_e are the **statistical weights** (also known as degeneracies) of levels i and e, respectively. The statistical weight g is the number of distinct quantum states that have the same energy. For example, if an energy level has an angular momentum J, it might have $2J + 1$ magnetic sublevels, all with the same energy in the absence of an external field; in that case, g would be $2J + 1$. * E_i and E_e are the energies of states i and e. So, $E_i - E_e$ is the energy difference between these two upper states. * k_B is the **Boltzmann constant**. * T is the **absolute temperature** in Kelvin.

This Boltzmann law tells us that in thermal equilibrium, higher energy states are less populated than lower energy states, and the exact ratio depends exponentially on the energy difference and the temperature. The $\frac{g_i}{g_e}$ factor accounts for the fact that there might be more "slots" available at one energy than another.

So, we now have two equations. The first relates measurable line intensities to population ratios and known A-values. The second relates population ratios to temperature and known energy levels and degeneracies. We are getting very close to being able to determine T.

Page 8:

Continuing with our discussion of determining temperature using line intensity ratios:

We just introduced the Boltzmann constant, k_{B}. Its value is approximately 1.381×10^{-23} Joules per Kelvin $\left(\mathrm{J\ K^{-1}}\right)$. It's a fundamental constant that links energy at the particle level with temperature at the macroscopic level.

Now, the key step is highlighted in the second bullet point: **Combining both equations isolates** T. Let's think about this.

From the first equation on the previous slide, we can write the population ratio $\frac{N_{\mathrm{i}}}{N_{\mathrm{e}}}$ as:

$$\frac{N_{\mathrm{i}}}{N_{\mathrm{e}}} = \frac{I_{ik}}{I_{ek}} \cdot \frac{\nu_{ek} A_{ek}}{\nu_{ik} A_{ik}}.$$

We can measure the intensity ratio $\frac{I_{ik}}{I_{ek}}$. The frequencies ν_{ik} and ν_{ek} are known from the wavelengths of the spectral lines. If the Einstein coefficients A_{ik} and A_{ek} are also known, then we can determine the population ratio $\frac{N_{\mathrm{i}}}{N_{\mathrm{e}}}$ purely from experimental measurements and known atomic data.

Once we have $\frac{N_{\mathrm{i}}}{N_{\mathrm{e}}}$, we can plug it into the Boltzmann law from the previous slide:

$$\frac{N_{\mathrm{i}}}{N_{\mathrm{e}}} = \frac{g_{\mathrm{i}}}{g_{\mathrm{e}}} \cdot \exp\left[-\frac{E_{\mathrm{i}} - E_{\mathrm{e}}}{k_{\mathrm{B}} T}\right].$$

Since the energy levels E_{i} and E_{e}, and their degeneracies g_{i} and g_{e}, are known properties of the atom or molecule, the only unknown in this equation is the temperature, T. We can rearrange this equation to solve for T. For example, by taking the natural logarithm of both sides.

This ability to determine temperature remotely is incredibly powerful. However, there's a critical caveat, emphasized by the statement: **No reliable A-values implies no accurate astrophysical thermometer.** This underscores the importance of transition probabilities. If our values for A_{ik} and A_{ek} are inaccurate or unknown, then our calculation of $\frac{N_\mathrm{i}}{N_\mathrm{e}}$ from the intensity ratio will be flawed, and consequently, the temperature T we derive will also be incorrect. The entire method hinges on having accurate atomic data for these transition probabilities. This is why so much effort in physics and chemistry is dedicated to both experimentally measuring and theoretically calculating these A-values with high precision. Without them, one of our primary tools for diagnosing remote plasmas and astrophysical environments simply wouldn't work reliably.

Page 9:

This slide provides a very helpful visual, an energy level diagram, to illustrate the scenario we've been discussing for **Radiative Decays for Temperature Determination.**

Let's examine the diagram. We see three horizontal lines representing three distinct energy levels of an atom or molecule.

- The top level is labeled E_i. To its right, it's noted that its population, weighted by degeneracy, is $N_\mathrm{i} g_\mathrm{i}$.
- The middle level is labeled E_e. Its population is $N_\mathrm{e} g_\mathrm{e}$.
- The bottom level is labeled E_k. Its population is $N_\mathrm{k} g_\mathrm{k}$. This E_k is the common lower level to which both E_i and E_e can decay.

Now, let's look at the transitions, which are indicated by vertical arrows:

- There's a red arrow pointing downwards from level E_i to level E_k. This represents the radiative decay from state i to state k. Above this arrow, it's labeled A_{ik}, signifying the Einstein A coefficient for this specific spontaneous emission process. Beside the arrow, $h\nu_{ik}$ is written, representing the energy of the photon emitted during this transition. So, $E_\text{i} - E_\text{k} = h\nu_{ik}$.

- Similarly, there's another red arrow, slightly shorter, pointing downwards from level E_e to the same common lower level E_k. This represents the radiative decay from state e to state k. This transition is characterized by its Einstein A coefficient, A_{ek}, and it results in the emission of a photon with energy $h\nu_{ek}$. Thus, $E_\text{e} - E_\text{k} = h\nu_{ek}$.

This diagram perfectly encapsulates the physical situation. We have two distinct upper states, E_i and E_e, each capable of spontaneously emitting a photon and transitioning to the common lower state E_k. The rates of these spontaneous emissions are governed by A_{ik} and A_{ek}, respectively. By measuring the intensities of the light (photons $h\nu_{ik}$ and $h\nu_{ek}$) produced by these two decay pathways, and knowing A_{ik} and A_{ek}, along with the energies and degeneracies, we can, as we've discussed, determine the relative populations N_i and N_e, and subsequently, the temperature T of the system, assuming it's in thermal equilibrium. This visual aid really helps to solidify the concepts we've been building up with equations.

Page 10:

Alright, we've been talking a lot about these 'A coefficients' and 'transition probabilities'. It's time for a more formal definition. This slide provides a **Definitions – Einstein Coefficients Refresher.** These coefficients are foundational to understanding light-matter interactions, particularly spontaneous emission, stimulated emission, and absorption. Albert Einstein introduced them in his groundbreaking 1917 paper that laid the quantum mechanical groundwork for the laser.

The first bullet point sets the stage: **For a pair of stationary states, which we'll denote using ket notation as** $\ket{i}$ (for the upper state) and $\ket{k}$ (for the lower state), we define the following three coefficients:

1. **Spontaneous emission coefficient, capital** A_{ik}: This is defined as the **probability per unit time** that an *isolated* excited particle (atom or molecule) currently in the upper state, $\ket{i}$, will spontaneously emit a photon and drop to the lower state, $\ket{k}$. The key here is "spontaneous" – this process happens on its own, without any external radiation field needing to be present to trigger it. It's an intrinsic property of the excited state. The units of A_{ik} are inverse time, typically seconds to the minus one (s^{-1}). A higher A_{ik} value means a faster spontaneous decay.

2. **Stimulated (or induced) emission coefficient, capital** B_{ik}: This is defined as the **probability per unit time *and* per spectral energy density** $\rho(\nu)$ that a photon (from an external radiation field) *causes* the particle, which is already in the excited state $\ket{i}$, to emit a *second* photon and transition down to the lower state, $\ket{k}$. This is fundamentally different from spontaneous emission. Stimulated emission requires the presence of an external radiation field, characterized by its spectral energy density $\rho(\nu)$ (rho as a function of frequency ν). The emitted photon in stimulated emission is a "clone" of the incident photon – it has the same frequency, direction, phase, and polarization. This is the critical process for light amplification in lasers (L.A.S.E.R. - Light Amplification by Stimulated Emission of Radiation). The units of B_{ik} need careful consideration. It's probability per unit time, so (s^{-1}), divided by spectral energy density. Spectral energy density $\rho(\nu)$ has units of energy per volume per frequency interval, so Joules per meter cubed per Hertz $\left(\mathrm{J\,m^{-3}Hz^{-1}}\right)$, which is equivalent to Joules times seconds per meter cubed ($Js\,\mathrm{m}^{-3}$). Therefore, B_{ik} will have units of s^{-1} divided by $Js\,\mathrm{m}^{-3}$, which simplifies to meters cubed per Joule per second squared $\left(\mathrm{m^{3}J^{-1}s^{-2}}\right)$. We'll see these units connect to other fundamental quantities later.

Page 11:

Continuing our definitions of the Einstein Coefficients:

3. **Absorption coefficient, capital** B_{ki}: Note the reversal of indices here – k to i, signifying a transition from the lower state (ket k) to the upper state (ket i). This coefficient is defined as the **probability per unit time *and* per spectral energy density** $\rho(\nu)$ that an incident photon from the external radiation field is absorbed by the particle, causing it to be elevated from the lower state (ket k) to the upper state (ket i).

Like stimulated emission, absorption is also driven by the external radiation field $\rho(\nu)$. It's the process by which atoms or molecules gain energy from the light field. The units of B_{ki} are the same as those for B_{ik}: typically $\mathrm{m}^3\ \mathrm{J}^{-1}\ \mathrm{s}^{-2}$.

Now, a profoundly important point, highlighted in the next bullet: **Einstein showed that thermodynamic equilibrium of matter and radiation enforces precise algebraic relations between these A and B coefficients, as well as connecting them to the Planck black-body spectrum.**

In his 1917 paper, Einstein considered a collection of atoms in thermal equilibrium with a blackbody radiation field. By requiring that the rates of upward and downward transitions balance in steady state, and that the radiation field conforms to Planck's law, he derived fundamental relationships between A_{ik}, B_{ik}, and B_{ki}. Specifically, he found that B_{ik} is related to B_{ki} through their degeneracies ($g_k B_{ki} = g_i B_{ik}$), and A_{ik} is related to B_{ik} by a factor involving ν^3 ($A_{ik} = \frac{8\pi h \nu^3}{c^3} B_{ik}$). These relations are incredibly powerful because if you can determine one of these coefficients, you can find the others.

Finally, the last bullet point states the overarching goal for us in this part of the course: **Our goal in this chapter is to relate these phenomenological**

Einstein coefficients (A_{ik}, B_{ik}, B_{ki}) to calculable or measurable quantities such as dipole matrix elements, denoted D_{ik}.

The Einstein coefficients are defined in terms of probabilities and rates. But what, at a deeper quantum mechanical level, determines these probabilities? It turns out they are governed by the strength of the coupling between the atom's electric dipole moment and the electromagnetic field, which is quantified by these dipole matrix elements D_{ik}. These matrix elements can be calculated from the wavefunctions of the initial and final states. So, we want to bridge the gap between the macroscopic description (Einstein coefficients) and the microscopic quantum mechanical description (dipole matrix elements). This connection is key to both predicting and understanding transition strengths from first principles.

Page 12:

Slide 4:

Now let's focus on **Spontaneous Emission** and derive the associated **Population Decay Law**. This is Slide 4.

Imagine an atom or molecule is in an excited state, let's call it state $|i\rangle$. This state might be able to decay spontaneously to several different lower levels.

The first point addresses this: **If multiple lower levels, denoted by** $|k\rangle$, are reachable from state $|i\rangle$, each with its own specific spontaneous emission coefficient A_{ik}, then we define a total spontaneous decay rate for state $|i\rangle$, which we'll call A_{i}.

This total decay rate, A_{i}, is simply the sum of all the individual spontaneous emission rates to all possible lower levels k. So, the equation is:

$$A_{\mathrm{i}} = \sum_{\mathrm{k}} A_{ik}$$

This makes intuitive sense: if there are multiple pathways out of state $|i\rangle$, the total rate of leaving state $|i\rangle$ is the sum of the rates for each pathway. Each A_{ik} is a probability per unit time for a specific i to k decay. A_{i} is the total probability per unit time that the particle in state $|i\rangle$ will undergo *any* spontaneous decay.

Now, consider a large number of identical particles, $N_{\mathrm{i}}(t)$, all in the excited state $|i\rangle$ at some time t. How does this population change over time due to spontaneous emission? The second bullet point gives us the answer: **The population** $N_{\mathrm{i}}(t)$ in level $|i\rangle$ obeys the following differential equation:

$$\frac{dN_{\mathrm{i}}}{dt} = -A_{\mathrm{i}}N_{\mathrm{i}}$$

Let's understand this equation:

* $\frac{dN_{\mathrm{i}}}{dt}$ is the rate of change of the population in state $|i\rangle$. * The negative sign indicates that the population is decreasing due to spontaneous emission (particles are leaving state $|i\rangle$). * The rate of decrease is proportional to A_{i}, the total spontaneous decay rate from state $|i\rangle$. * And, crucially, the rate of decrease is also proportional to N_{i} itself – the number of particles currently in state $|i\rangle$. The more particles there are in the excited state, the more decays per second will occur. This is characteristic of a first-order decay process.

This simple differential equation is the starting point for describing how an excited state population decays naturally.

Page 13:

We've just seen the differential equation governing the decay of an excited state population N_{i} due to spontaneous emission:

$$\frac{dN_{\mathrm{i}}}{dt} = -A_{\mathrm{i}}N_{\mathrm{i}}.$$

Now, let's look at its solution and interpretation.

The first bullet point presents the **solution** to this first-order linear differential equation, which describes a **pure exponential decay**:

$$N_{\mathrm{i}}(t) = N_{\mathrm{i}}^{0}\exp(-A_{\mathrm{i}}t).$$

Let's break this down: * $N_{\mathrm{i}}(t)$ is the population of state i at any time t. * N_{i}^{0} (i.e., N_{i} subscript 0) is the initial population of state i at time $t = 0$. * A_{i} is the total spontaneous decay rate constant for state i, as defined on the previous slide (sum of A_{ik} over all lower states k). * t is time.

This equation tells us that the population of the excited state decreases exponentially from its initial value, with the "steepness" of this decrease determined by A_{i}.

Next, we define a very important related quantity: the **Mean spontaneous lifetime**, denoted by the Greek letter τ_{i} (tau subscript i). The lifetime τ_{i} is defined as the reciprocal of the total spontaneous decay rate A_{i}:

$$\tau_{\mathrm{i}} = \frac{1}{A_{\mathrm{i}}}.$$

The lifetime has units of time (e.g., seconds, nanoseconds, microseconds). A state with a large decay rate A_{i} will have a short lifetime τ_{i}, and vice versa. A long-lived state is one that decays slowly.

Finally, what is the **physical interpretation** of this lifetime, τ_{i}? The slide tells us: **after one lifetime (i.e., when $t = \tau_{\mathrm{i}}$**), the population drops to $\frac{1}{e}$ (one over e) of its initial value. Let's verify this. If we substitute $t = \tau_{\mathrm{i}} = \frac{1}{A_{\mathrm{i}}}$ into the decay equation:

$$N_{\mathrm{i}}\ (\text{at } t = \tau_{\mathrm{i}}) = N_{\mathrm{i}}^{0}\exp\left(-A_{\mathrm{i}}\left(\frac{1}{A_{\mathrm{i}}}\right)\right) = N_{\mathrm{i}}^{0}\exp(-1).$$

Since e (Euler's number) is approximately 2.718, $\frac{1}{e}$ is approximately 0.368. So, after one lifetime, the population of the excited state has decayed to about 36.8% of its original value. This is a standard and very useful benchmark for characterizing exponential decay processes. It's analogous to the half-life concept, but for $\frac{1}{e}$ decay rather than $\frac{1}{2}$ decay. (The half-life, $t_{1/2}$, is related to τ by $t_{1/2} = \tau \ln(2)$).

Page 14:

This slide presents a graph visually depicting **Spontaneous Emission**, specifically the exponential decay of the population $N(t) = N_0\, e^{-At}$.

Let's examine the graph carefully.

The **vertical axis** represents the **Population** $N(t)$, and it's crucial to note that this is a **log scale**. The axis is marked with values like $1\,e + 3$ (which means 1×10^3, or one thousand) and $1\,e + 2$ (one hundred). There's also a label N_0/e, which represents the population after one lifetime, approximately 36.8% of the initial population N_0.

The **horizontal axis** represents **Time,** t, on a linear scale. It's marked at 0, and then at integer multiples of the lifetime: τ_i, $2\tau_\text{i}$, and $3\tau_\text{i}$.

The **red line** on the graph shows the decay of the population $N(t)$ over time. Because the y-axis is logarithmic and the decay is exponential, the plot of $N(t)$ versus t appears as a **straight line with a negative slope.** This is a hallmark of exponential decay when viewed on a semi-log plot.

There's an important annotation: **"Slope of** $\ln(N)$ vs. t plot = -A". This is mathematically precise. If $N(t) = N_0\, e^{-At}$, then $\ln\big(N(t)\big) = \ln(N_0) - At$. This is an equation of a straight line ($y = mx + c$) where y is $\ln\big(N(t)\big)$, x is t, the y-intercept c is $\ln(N_0)$, and the slope m is $-A$.

Now, let's look at the inset on the right, titled **"Competing Decay Channels."** This inset shows an energy level diagram. There's an upper level labeled $|i\rangle$. From this level, there are three downward arrows, indicating decays to three different lower levels, labeled $|k_1\rangle$, $|k_2\rangle$, and $|k_3\rangle$. Each of these decay channels would have its own spontaneous emission rate, say A_{i,k_1}, A_{i,k_2}, and A_{i,k_3}. The diagram simplifies this by labeling each specific decay with an "A", implying these are individual channel rates.

Below these, it states: **Capital A equals Sigma Capital A**. This means that the total decay rate, Capital A (which is A_i in our main discussion), used in the exponential decay formula $N(t) = N_0\, e^{-At}$, is the sum of the individual decay rates for all possible spontaneous emission channels out of state i. This reinforces the concept from Slide 12.

So, the graph and the inset together provide a comprehensive visual and conceptual summary of spontaneous emission and the resulting exponential population decay, including the scenario where multiple decay pathways contribute to the overall lifetime of the excited state. The point N_0/e at $t = \tau_\text{i}$ is clearly shown; for example, if N_0 is $1\,e + 3$, then N_0/e would be roughly 368.

Page 15:

Now that we understand how the population of an excited state decays, let's consider the light that is actually emitted. This brings us to Slide 5, titled **Radiant Power of a Spectral Line.**

The first bullet point focuses on a **specific decay channel from an upper state,** $|i\rangle$, to a particular lower state, $|k\rangle$. We're interested in the power radiated in the spectral line corresponding to just this i to k transition. The equation for the instantaneous radiant power, $P_{ik}(t)$, is given by:

$$P_{ik}(t) = N_\text{i}(t)\, h\, \nu_{ik}\, A_{ik}$$

Let's break this equation down thoroughly:

* $P_{ik}(t)$ is the radiant power at time t due to the i to k transition. Power is energy per unit time. $N_\mathrm{i}(t)$ is the population of the upper state i at time t. We know from previous slides that this typically decays exponentially, $N_\mathrm{i}(t) = N_{i0}\exp(-A_\mathrm{i}t)$, where A_i is the total* decay rate from state i.

* h is Planck's constant.

* ν_{ik} is the frequency of the photon emitted during the i to k transition. Therefore, $h\nu_{ik}$ is the energy of a single photon emitted in this specific transition.

* A_{ik} is the Einstein A coefficient for spontaneous emission for this specific channel, i to k. It represents the probability per unit time that an atom in state i will decay to state k.

The logic of this equation is as follows: $N_\mathrm{i}(t)$ times A_{ik} gives the number of i to k transitions occurring per unit time (i.e., the number of photons of frequency ν_{ik} emitted per unit time). Each of these photons carries an energy $h\nu_{ik}$. So, (number of photons per second) times (energy per photon) gives the total energy per second, which is the power.

The second bullet point clarifies the **symbols and their units**:

* P_{ik} is the power, and its S.I. unit is Watts, denoted by capital W. One Watt is one Joule per second. * $h\nu_{ik}$ is the photon energy, and its S.I. unit is Joules, denoted by capital J.

* A_{ik} is the spontaneous emission rate for the specific i to k channel. Its unit is inverse seconds (s^{-1}), representing probability per unit time.

So, if you know the population of the upper state, the energy of the emitted photon for a specific transition, and the Einstein A coefficient for that transition, you can calculate the power radiated in that spectral line. Since $N_\mathrm{i}(t)$ is time-dependent, the radiant power $P_{ik}(t)$ will also be time-dependent, typically decaying exponentially if $N_\mathrm{i}(t)$ does.

Page 16:

Continuing our discussion on the radiant power of a spectral line, this slide adds a couple of important practical considerations.

The first point notes that the **Line intensity observed along a given direction may further depend on the angular distribution of emitted photons (dipole pattern, polarization).**

This is a crucial experimental detail. The equation $P_{ik}(t) = N_{\mathrm{i}}(t) h\nu_{ik} A_{ik}$ gives the total power emitted in all directions due to the i to k transition. However, spontaneous emission, especially electric dipole emission which is most common, is not generally isotropic. For example, a classical oscillating dipole has a characteristic donut-shaped radiation pattern (a dipole pattern), meaning it radiates more intensely in some directions than others (specifically, perpendicular to the dipole axis, and not at all along the axis).

Furthermore, the emitted light can be polarized. The polarization characteristics will also depend on the nature of the transition and the orientation of the emitting atoms or molecules, perhaps relative to an external field or a surface. Therefore, if you set up a detector in a specific direction to measure the line intensity, what you actually measure will be influenced by this angular distribution and polarization. To get the total power P_{ik}, you might need to integrate over all solid angles or carefully account for these factors in your experimental setup and calibration. The asterisk on "angular*" likely points to these complexities.

The second bullet point highlights an experimental application: **Experimentally,** $P_{ik}(t)$ provides a direct route to determining A_{ik} if $N_{\mathrm{i}}(t)$ is independently known or controllable.

This is the inverse of the previous slide. If we can measure the radiant power $P_{ik}(t)$ (perhaps by carefully collecting all emitted light or by calibrating for the angular factors), and if we have a way to know or control the population of the upper state $N_{\mathrm{i}}(t)$, then we can rearrange the formula to solve for A_{ik}:

$$A_{ik} = \frac{P_{ik}(t)}{N_{\mathrm{i}}(t) h\nu_{ik}}.$$

This is a common method for experimentally measuring Einstein A coefficients. For instance, one might use a short laser pulse to excite a known number of atoms to state i (thus controlling $N_{\mathrm{i}}(t = 0)$), and then measure the subsequent fluorescence power $P_{ik}(t)$ as the state decays. This allows for the determination of A_{ik}, a fundamental atomic or molecular property.

The "---" at the bottom simply indicates that the lecture notes might have more to say on this, but for now, these are the key points from this slide.

Page 17:

We've discussed spontaneous emission extensively. Now, let's consider what happens **Beyond Spontaneous Emission**, looking at **Additional Decay Channels** that can depopulate an excited state. This is Slide 6.

The first bullet point introduces **Collision-induced (radiationless) transitions.** These are processes where an excited atom or molecule loses its energy not by emitting a photon (which is a radiative transition), but by transferring that energy to another particle during a collision. This is often called "collisional quenching." These are radiationless because no photon is emitted in the process; the excess energy typically goes into kinetic energy of the colliding partners or into exciting internal degrees offerteedom of the collision partner.

The scenario is described in the second bullet: **Molecule A, which is in an excited state with energy** E_{i} (denoted $A(E_{\mathrm{i}})$), collides with a partner particle B. This partner B could be another atom or molecule of the same kind, or a different species present in the environment (e.g., a buffer gas).

What is the probability of such a collisional transition occurring? The third bullet gives an expression for the **transition probability per unit time** for a specific collisional de-excitation from state i of molecule A to some state k of molecule A (which could be the ground state or a lower excited state). This rate, let's call it the rate constant for collisional quenching from i to k, is given by the equation:

$$\frac{dP_{ik}^{\text{coll}}}{dt} = \nu\, N_{\text{B}}\, \sigma_{ik}^{\text{coll}}$$

Let's clarify the terms in this expression, which will be detailed on the next slide:

* The left side, $\frac{dP_{ik}^{\text{coll}}}{dt}$, represents the probability per unit time for a single molecule A in state E_{i} to undergo a collisional transition to state k due to collisions with B particles. This is essentially a rate constant for the process. * ν (Greek letter nu, representing speed) is related to the relative speed of the colliding particles A and B. * N_{B} is the number density of the collision partner B. * $\sigma_{ik}^{\text{coll}}$ (Greek letter sigma) is the cross-section for the inelastic collision that leads to the i to k transition in molecule A.

We'll define these terms more precisely on the next page, but the overall idea is that the collisional transition rate depends on how often collisions occur (related to speed and density of B) and how effective each collision is at causing the specific i-to-k transition (related to the cross-section).

Page 18:

This slide continues our discussion of additional decay channels by defining the terms in the expression for the collision-induced transition rate we just saw, and by introducing stimulated emission as another decay pathway.

First, let's clarify the terms for the collisional rate, $\frac{dP_{ik}^{\text{coll}}}{dt} = \nu\, N_{\text{B}}\, \sigma_{ik}^{\text{coll}}$:

* **Capital N sub B** is the **density of particle B** (the collision partner), with units of particles per cubic meter m^{-3}. A higher density of B means more frequent collisions. * ν (lowercase Greek nu) is the **mean relative speed** between particles A and B, with units of meters per second $\mathrm{m\,s}^{-1}$. Higher relative speeds also lead to more frequent collisions. This speed is related to the temperature and masses of the colliding particles. * $\sigma_{ik}^{\text{coll}}$ (lowercase Greek sigma) is the **inelastic cross-section** for the collision that takes molecule A from state i to state k. It has units of area, typically meters squared m^2. You can think of the cross-section as an effective "target area" that particle B must hit on particle A to cause this specific quenching transition. Larger cross-sections mean more effective collisions for quenching.

So, these three factors – density of colliders, relative speed, and cross-section – combine to determine the rate of collision-induced radiationless transitions.

Next, the slide reminds us of another important process that can depopulate an excited state: **Stimulated emission in an intense radiation field,** $\rho(\nu_{ik})$. We've already defined the Einstein B_{ik} coefficient. The probability per unit time for an atom in state i to undergo stimulated emission to state k, in the presence of a radiation field with spectral energy density $\rho(\nu_{ik})$ at the transition frequency ν_{ik}, is given by:

$$\frac{dP_{ik}^{\text{ind}}}{dt} = \rho(\nu_{ik})\, B_{ik}$$

Here, "ind" stands for induced, which is another term for stimulated. B_{ik} is the Einstein coefficient for stimulated emission from i to k. So, if there's an external radiation field present (like from a laser), it can actively pull population out of the excited state via stimulated emission, in addition to spontaneous emission and collisions.

The slide concludes with the phrase **"Effective lifetime including all* channels"**, which sets the stage for the next slide where we'll combine all these rates.

Page 19

Now, let's combine all these decay processes – spontaneous emission, stimulated emission, and collisional quenching – to understand the **effective lifetime** of an excited state.

The equation presented gives the inverse of the effective lifetime of state i, denoted $\frac{1}{\tau_{\mathrm{i}}^{\mathrm{eff}}}$ (tau sub i, effective):

$$\frac{1}{\tau_{\mathrm{i}}^{\mathrm{eff}}} = \sum_{\mathrm{k}} \left(A_{ik} + \rho(\nu_{ik})\, B_{ik} + v\, N_{\mathrm{B}}\, \sigma_{ik}^{\mathrm{coll}}\right)$$

Let's analyze this crucial equation. The term $\frac{1}{\tau_{\mathrm{eff}}}$ is the total effective decay rate out of state i. It's the sum of rates from all processes and all channels:

* A_{ik} is the rate of **spontaneous emission** from state i to a specific lower state k. This term is intrinsic to the atom/molecule and doesn't depend on the external environment, other than allowing for the existence of state k. It is labeled "spontaneous" below the equation.

* $\rho(\nu_{ik})\, B_{ik}$ is the rate of **stimulated emission** (or induced emission) from state i to state k, driven by the external radiation field with spectral energy density ρ at the transition frequency ν_{ik}. This term depends on the intensity of the radiation field. It is labeled "induced."

* $v\, N_{\mathrm{B}}\, \sigma_{ik}^{\mathrm{coll}}$ is the rate of **collisional de-excitation** (quenching) from state i to state k due to collisions with particle B. This term depends on the density N_{B} of the collision partner and the temperature (which affects v and σ). It is labeled "collisional."

The summation, indicated by the capital Σ_k (Sigma subscript k), means we sum these contributions over all possible final states k to which state i can transition through any of these mechanisms.

So, the total rate at which population leaves state i is the sum of all these individual rates. The effective lifetime, $\tau_\mathrm{i}^\mathrm{eff}$, is the reciprocal of this total rate.

The second bullet point introduces a powerful experimental technique: **Varying** ρ or N_B in a Stern-Vollmer plot separates the individual contributions.

This is a key idea. Suppose we want to isolate these different rate constants. We can conduct experiments where we measure the effective lifetime (or its reciprocal, the decay rate) as a function of, say, the quencher density N_B, while keeping the radiation field ρ constant (perhaps even zero if we are only interested in A and collisional terms).

If we plot $\frac{1}{\tau_\mathrm{eff}}$ versus N_B, the equation takes the form of a straight line:

$$\frac{1}{\tau_\mathrm{eff}} = \left(\sum_\mathrm{k} (A_{ik} + \rho\, B_{ik})\right) + \left(\sum_\mathrm{k} \nu\ \sigma_{ik}^\mathrm{coll}\right) N_\mathrm{B}.$$

This is $y =$ intercept $+$ slope $* \, x$.

The intercept would give the sum of spontaneous and stimulated emission rates (in the absence of the specific quencher B). The slope would give the total collisional quenching rate constant due to B $\left(\sum_\mathrm{k} \nu\ \sigma_{ik}^\mathrm{coll}\right)$.

Similarly, one could vary the radiation density ρ if trying to isolate B_{ik}. This method, particularly when varying quencher concentration, is known as Stern-Vollmer analysis, and it's a cornerstone of photochemistry and photophysics for studying quenching processes.

This slide shows a **Stern-Vollmer Plot**, which visually represents the method we just discussed for separating different decay contributions.

Let's analyze the graph:

- The **vertical axis (y-axis)** is labeled $\frac{1}{\tau}$ (Effective Decay Rate), in arbitrary units. It ranges from 0 to 30 on this particular plot. Remember, $\frac{1}{\tau}$ is the total rate at which the excited state is depopulated.
- The **horizontal axis (x-axis)** is labeled N (Density of Quencher B), also in arbitrary units. It ranges from 0 to 4. This "N" represents N_{B}, the concentration of the collisional quenching agent.

The plot shows several data points (blue circles) that lie on a **straight line** with a positive slope. This linear relationship is exactly what we expect from the Stern-Vollmer equation discussed on the previous page, assuming other factors like temperature (affecting ν and σ) and any background radiation field (affecting ρB_{ik}) are kept constant.

At the top of the graph, the equation for the line is given as:

$$\frac{1}{\tau} = \Sigma A + kN$$

Let's interpret this in the context of our previous discussion:

- **Sigma A** (capital Sigma A) on the y-axis represents the **y-intercept** of the line. This is the value of $\frac{1}{\tau}$ when N (the quencher concentration) is zero. So, Sigma A corresponds to the sum of all decay rates that are *not* dependent on the quencher B. In the simplest case, this would be the sum of spontaneous emission rates ($\sum_{\mathrm{k}} A_{ik}$) and any stimulated emission rates if a background radiation field is present. The graph shows an arrow pointing to the y-intercept, labeled "Sigma A".

- **k** in the equation represents the **slope** of the line. This "k" is the Stern-Vollmer quenching constant. It corresponds to the term ($\sum_{\mathrm{k}} \nu\ \sigma_{\mathrm{coll},ik}$) from our more general equation. It quantifies how effectively the quencher B de-excites the molecule A per unit concentration of B. An annotation on the graph indicates "Slope = k".

So, by performing an experiment where you measure the excited state lifetime (and thus $\frac{1}{\tau}$) at different known concentrations of a quencher (N), you can plot this data. If it forms a straight line, the intercept gives you the intrinsic decay rate of the excited state in the absence of that specific quencher, and the slope gives you the bimolecular quenching rate constant for that quencher. This is a very powerful tool for studying excited state dynamics and interactions.

Page 21:

We're now shifting gears to a very important theoretical framework. This is Slide 7, introducing the **Two-Level Atom in a Classical Light Field – Basic Idea.** This is a cornerstone model in laser spectroscopy and quantum optics, often called the semi-classical model.

The first bullet point explains the core approximation: **We model the radiation (the asterisk suggests this is an approximation) as a classical plane wave.** This means we treat the light field not as a collection of photons (which would be a fully quantum optical treatment), but as a continuous electromagnetic wave, described by classical Maxwell's equations. This approximation is generally valid **whenever photon statistics are not essential** for the phenomenon we are studying. For many problems involving lasers, especially continuous wave (CW) lasers with high photon numbers, this classical field approximation works very well.

The specific form of this classical plane wave electric field, $\vec{E}(t)$, is given as:

$$\vec{E}(t) = E_0 \cos(\omega t - kz)\,\hat{e}$$

Let's break this down: * E_0 is the scalar amplitude of the electric field wave. * ω (lowercase Greek omega) is the angular frequency of the light. * t is time. * k is the wavenumber $\left(k = \frac{2\pi}{\lambda}\right)$, where λ is the wavelength. * z is the direction of propagation of the wave. * $\hat{e}$ (e with a caret) is the unit vector specifying the polarization of the electric field (e.g., along the x-axis).

So, we have a classical, oscillating electric field. What about the atom? The second bullet point clarifies: **The atom (asterisk again, signifying it's a simplified model of a real atom) remains fully quantum mechanical, with an unperturbed Hamiltonian denoted** $\hat{H}_0$. This is the "semi" part of semi-classical: classical field, quantum atom. The unperturbed Hamiltonian $\hat{H}_0$ describes the atom in isolation, and its eigenstates are the familiar energy levels of the atom.

Now, a crucial simplification for this model: **Restrict attention to just two stationary eigenstates** of the atom.

Instead of considering all the infinite energy levels of a real atom, we focus on only two levels that are relevant to the interaction with the light field, typically two levels whose energy difference is close to the energy of the photons in the classical light field ($\hbar\omega$). This is the "two-level atom" (TLA) approximation. It simplifies the mathematics enormously while still capturing a vast amount of interesting physics, like Rabi oscillations, absorption, and stimulated emission. We will explore this model in detail.

Page 22:

Let's elaborate on the specifics of our two-level atom and an important approximation related to its interaction with the light field.

First, we define our two levels:

- We have a **Lower level**, which we'll denote using ket notation as $|a\rangle$, with energy **capital E sub a** as E_{a}.

- And we have an **Upper level**, denoted as $|b\rangle$, with energy **capital E sub b** as E_{b}.

So, E_{b} is greater than E_{a}. The energy difference $E_{\mathrm{b}} - E_{\mathrm{a}}$ will be crucial, as we expect resonance when this matches $\hbar\omega$, where ω is the frequency of our classical light field.

Next, we introduce a critical simplification known as the **dipole approximation** (or sometimes the long-wavelength approximation). The condition for this approximation to be valid is related to the relative sizes of the atom and the wavelength of the light.

- Consider the **Atomic size,** d. For a typical atom, this is on the order of Angstroms, so roughly 0.1 nm (zero point one n m).

- Now consider the **Optical wavelength,** λ (Greek letter lambda). For visible light, λ is typically around 500 nm (five hundred n m).

Comparing these, we see that the wavelength of light (λ, around 500 nm) is much, much larger than the physical extent of the atom (d, around 0.1 nm). Mathematically, λ is much, much greater than d (i.e., $\lambda \gg d$).

What is the consequence of this?

The final bullet point explains: **Hence, the phase factor** kz in our classical electric field $E(t) = E_0 \cos(\omega t - kz)\hat{e}$ can be considered approximately zero (or at least constant) *inside* the atom.

Remember $k = \frac{2\pi}{\lambda}$. Since λ is so large compared to the atomic dimension d, the term kz (where z here would be the spatial coordinate *within* the atom, varying from 0 to d) will be very small:

$$kd = \left(\frac{2\pi}{\lambda}\right) d.$$

Since $\frac{d}{\lambda}$ is very small (approx $\frac{0.1}{500} = \frac{1}{5000}$), kd is also very small.

This means that the phase of the electric field, $\omega t - kz$, does not change significantly as you move across the tiny region occupied by the atom at any given instant in time. Therefore, the **spatial variation of the electric field *across the atom* can be neglected.** We can effectively treat the electric field as being uniform over the volume of the atom, oscillating only in time. This is the essence of the dipole approximation. It simplifies the interaction Hamiltonian considerably, as we'll see.

Page 23:

This slide provides an excellent visual illustration of the **Dipole Approximation**, contrasting the **Atomic Size vs. Wavelength.** In the diagram, we see a large, oscillating red curve representing the **Incoming Electromagnetic Wave**. The equation for this wave is written on the right: $\vec{E}(t) = E_0 \cos(\omega t - kz)\hat{e}$, which is our classical plane wave.

Crucially, superimposed on this wave, we see a small, blueish circle labeled **"Atom."** The diagram is drawn such that the wavelength of the EM wave (the distance between successive crests, for example) is vastly larger than the diameter of the circle representing the atom.

This visual makes the core idea of the dipole approximation immediately clear. At any given instant in time, the tiny atom experiences a nearly uniform electric field. Even though the electric field $E(t)$ is varying in space (due to the kz term), these spatial variations occur over a length scale comparable to λ. Since the atom is so much smaller than λ, the field is essentially constant across the atom's extent.

Imagine zooming in on just the tiny region occupied by the atom. The segment of the long red sine wave that passes through the atom would look almost like a flat line. Its value would be determined by the phase $\omega t - kz_0$, where z_0 is, say, the position of the atom's center, but the variation due to z changing *within* the atom itself is negligible.

This approximation allows us to simplify the interaction of the atom with the light by considering only the time variation of the field at a single point (e.g., the atom's nucleus) and ignoring its spatial variation across the electron cloud. This is why it's called the dipole approximation: it leads to an interaction term involving the electric dipole moment of the atom.

Page 24:

Now that we've established the dipole approximation, let's look at the Hamiltonian that describes the interaction of our two-level atom with the classical light field. This is Slide 8: **Interaction Hamiltonian and Dipole Operator.**

The first bullet point introduces the **Total Hamiltonian**, denoted $\hat{H}$ (capital H with a caret). This total Hamiltonian is the sum of two parts:

$$\hat{H} = \hat{H}_0 + \hat{V}(t)$$

* $\hat{H}_0$ is the unperturbed Hamiltonian of the atom itself, which we discussed earlier. Its eigenstates are our levels $\ket{a}$ and $\ket{b}$ with energies E_{a} and E_{b}.

* $\hat{V}(t)$ is the **interaction Hamiltonian**, which describes the interaction between the atom and the external classical electric field. It's time-dependent because the electric field itself is oscillating in time.

The second bullet point gives the form of this interaction Hamiltonian **within the dipole approximation**:

$$\hat{V}(t) = -e\,\vec{r} \cdot \vec{E}(t)$$

And if we substitute our classical field $\vec{E}(t) = E_0 \cos(\omega t)\hat{e}$ (where we've now dropped the kz term due to the dipole approximation, effectively setting $z = 0$ at the atom's location), this becomes:

$$\hat{V}(t) = -e\,\vec{r} \cdot \vec{E}_0 \cos(\omega t)\hat{e}$$

Let's be precise here. * e is the elementary charge (magnitude, a positive value). * $\vec{r}$ is the position operator of the electron within the atom (relative to the nucleus, typically). * $\vec{E}(t)$ is the classical electric field vector at the position of the atom. In the dipole approximation, $\vec{E}(t) = E_0 \cos(\omega t)\hat{e}$, where E_0 is the scalar amplitude and $\hat{e}$ is the polarization unit vector.

So, $\hat{V}(t) = -e\,(\vec{r} \cdot \hat{e})\,E_0 \cos(\omega t)$.

Now, the third bullet point asks us to **Introduce the dipole moment operator.** The electric dipole moment operator for an electron of charge $-e$ at position $\vec{r}$ is usually defined as $\hat{p}_{\text{op}} = -e\,\vec{r}$. The slide defines $\hat{p} = -e\,\vec{r}$. This is consistent with the standard definition of the electric dipole moment operator for an electron.

If we use this definition, then our interaction Hamiltonian $\hat{V}(t)$ can be written very compactly as:

$$\hat{V}(t) = \hat{p} \cdot (E_0 \cos(\omega t)\hat{e})$$

Or more simply, $\hat{V}(t) = \hat{p} \cdot \vec{E}(t)$.

This is a common form: the interaction energy is the dot product of the electric dipole moment operator of the atom and the external electric field.

(A quick check on conventions: some texts define the dipole moment as $q\,\vec{r}$, so for an electron with $q = -e$, $\hat{p}_{\text{op}} = -e\,\vec{r}$. The interaction potential is then $-\hat{p}_{\text{op}} \cdot \vec{E} = -(-e\,\vec{r}) \cdot \vec{E} = e\,\vec{r} \cdot \vec{E}$. Other texts use $V = -\vec{d} \cdot \vec{E}$ where $\vec{d}$ is the dipole moment. If $\vec{d} = +e\,\vec{r}$ (effective positive charge displacement), then $V = -e\,\vec{r}\cdot\vec{E}$. If $\vec{d} = -e\,\vec{r}$ (electron dipole), then $V = -(-e\,\vec{r})\cdot\vec{E} = e\,\vec{r}\cdot\vec{E}$.

Let's stick to the slide's definitions: $\hat{V}(t) = -e\,\vec{r}\cdot\vec{E}(t)$, and the dipole operator $\hat{p} = -e\,\vec{r}$. Therefore, $\hat{V}(t) = \hat{p}\cdot\vec{E}(t)$. This means the term $-e\,\vec{r}\cdot\hat{e}$ is the component of the dipole moment operator along the electric field polarization direction.

Page 25:

We have our interaction Hamiltonian $\hat{V}(t)$ which includes a $\cos(\omega t)$ term. For mathematical convenience, especially when solving time-dependent quantum mechanics problems, it's often useful to rewrite this cosine function.

The first bullet point states: **For presentation purposes, rewrite cosine via complex exponentials.** Using Euler's formula, we can express $E_0\cos(\omega t)$ as:

$$E_0\cos(\omega t) = \frac{E_0}{2}\left[e^{i\omega t} + e^{-i\omega t}\right]$$

The slide then defines a quantity $A_0 = \frac{E_0}{2}$ (Be careful, this A_0 is an *amplitude* of the electric field components, not an Einstein A coefficient). So,

$$E_0\cos(\omega t) = A_0\left(e^{i\omega t} + e^{-i\omega t}\right)$$

This decomposition is very useful because the $e^{i\omega t}$ and $e^{-i\omega t}$ terms behave differently when we consider energy conservation in transitions. One can be thought of as corresponding to photon absorption (or creating a field quantum) and the other to photon emission (or annihilating a field quantum), though in this classical field treatment, it's more about which term will lead to resonance.

The second bullet point provides the **Physical picture**:

The atom experiences an oscillating electric force (asterisk) capable of driving transitions if the frequency is near resonance.

The asterisk on "force" is important. Strictly speaking,

$$\hat{V}(t) = \hat{p} \cdot \mathbf{E}(t)$$

is an interaction *potential energy*. An electric force would be related to the gradient of this potential (or, for time-varying fields, more complex).

However, the time-varying interaction *potential energy* itself is what drives the transitions. The atom's electron cloud is "pushed and pulled" by the oscillating electric field of the light wave.

If this "pushing and pulling" occurs at a frequency ω that is close to a natural transition frequency of the atom (e.g., $\frac{E_{\mathrm{b}} - E_{\mathrm{a}}}{\hbar}$), then the atom can efficiently absorb energy from the field and make a transition from a lower state to an upper state, or be stimulated to emit energy and transition from an upper state to a lower state. This near-resonance condition is key for significant interaction.

The "---" at the bottom suggests more could be said, but these are the main points for now.

Page 26:

We're now ready to tackle the core problem: how does the quantum state of our two-level atom evolve under the influence of the classical light field? This is Slide 9, focusing on the **Time-Dependent Schrödinger Equation – State Expansion.**

The first step is to **Solve** the fundamental equation of motion in quantum mechanics, the Time-Dependent Schrödinger Equation (TDSE). It is written as:

$$\hat{H}\Psi(\vec{r},t) = i\hbar\frac{\partial\Psi(\vec{r},t)}{\partial t}.$$

Let's break this down:

* $\hat{H}$ is the total Hamiltonian we defined on Slide 24: $\hat{H} = \hat{H}_0 + \hat{V}(t)$. It includes both the unperturbed atomic Hamiltonian and the time-dependent interaction with the light field.

* $\Psi(\vec{r},t)$ is the total wavefunction of the atom. It's a function of the electron's spatial coordinates (collectively denoted by $\vec{r}$) and time t. This wavefunction contains all possible information about the state of the atom.

* i is the imaginary unit, square root of minus 1.

* $\hbar$ is the reduced Planck constant (h divided by 2π).

* The right side is $i\hbar$ times the time derivative of the wavefunction.

Solving this partial differential equation directly can be very difficult. A standard and powerful technique is to use a state expansion, as described in the second bullet point:

Express the total wavefunction Ψ as a superposition of the unperturbed eigenstates of the atom, which we denote as $|n\rangle$.

Recall that $\hat{H}_0$ (the unperturbed atomic Hamiltonian) has a set of stationary eigenstates $u_\mathrm{n}(\vec{r})$, with corresponding energies E_n:

$$\hat{H}_0\, u_\mathrm{n}(\vec{r}) = E_\mathrm{n}\, u_\mathrm{n}(\vec{r}).$$

These $u_\mathrm{n}(\vec{r})$ form a complete basis set.

So, we can write the time-dependent wavefunction $\Psi(\vec{r},t)$ as a sum over these basis states:

$$\Psi(\vec{r},t) = \sum_\mathrm{n} C_\mathrm{n}\,(t)\, u_\mathrm{n}(\vec{r})\, e^{-\frac{iE_\mathrm{n}t}{\hbar}}.$$

Let's analyze this expansion:

* The sum is over all possible unperturbed eigenstates n of the atom.

* $u_{\mathrm{n}}(\vec{r})$ is the spatial part of the n-th stationary state wavefunction.

* $e^{-\frac{iE_{\mathrm{n}}t}{\hbar}}$ is the standard time-evolution factor for an eigenstate of $\widehat{H}_0$ if there were no perturbation.

* $C_{\mathrm{n}}(t)$ are the crucial time-dependent complex coefficients (or amplitudes). If there were no interaction $\hat{V}(t)$, these $C_{\mathrm{n}}(t)$ would be constant. Because of $\hat{V}(t)$, these coefficients will change over time, describing how the probability of finding the atom in different states $|n\rangle$ evolves. The square of the magnitude of $C_{\mathrm{n}}(t)$, which is $|C_{\mathrm{n}}(t)|^2$, gives the probability that the atom is in state n at time t.

Our goal now will be to substitute this expansion into the TDSE and derive equations that govern the evolution of these coefficients $C_{\mathrm{n}}(t)$.

Page 27:

We've just written the general state expansion for the wavefunction Ψ. Now, let's apply it to our specific case of interest: the **two-level truncation.**

As the first bullet point states, for our two-level system consisting of a lower state ket $|a\rangle$ (with energy E_{a} and spatial wavefunction $u_{\mathrm{a}}(\vec{r})$) and an upper state ket $|b\rangle$ (with energy E_{b} and spatial wavefunction $u_{\mathrm{b}}(\vec{r})$), the expansion simplifies to:

$$\Psi(\vec{r},t) = a(t)\, u_{\mathrm{a}}(\vec{r})\, e^{-\frac{iE_{\mathrm{a}}t}{\hbar}} + b(t)\, u_{\mathrm{b}}(\vec{r})\, e^{-\frac{iE_{\mathrm{b}}t}{\hbar}}.$$

Here: * We've replaced the generic coefficients $C_{\mathrm{a}}(t)$ and $C_{\mathrm{b}}(t)$ with simply $a(t)$ and $b(t)$, respectively. These are the time-dependent complex amplitudes for being in state $|a\rangle$ and state $|b\rangle$. * $u_{\mathrm{a}}(\vec{r})$ and $u_{\mathrm{b}}(\vec{r})$ are the spatial parts of the wavefunctions for the lower and upper states. * The exponential terms are the usual time-evolution phases for the unperturbed energy eigenstates.

The second bullet point explains the **Probabilistic meaning** of these amplitudes, which is fundamental to quantum mechanics: 1. **The absolute square of** $a(t)$, written as $|a(t)|^2$, is the probability of finding the atom in the lower state ket $|a\rangle$ at time t. 2. **Similarly, the absolute square of** $b(t)$, written as $|b(t)|^2$, is the probability of finding the atom in the upper state ket $|b\rangle$ at time t.

These probabilities will change over time as the atom interacts with the light field. For example, if the atom starts in the lower state $|a\rangle$ and absorbs a photon, $|a(t)|^2$ will decrease and $|b(t)|^2$ will increase.

Finally, there's the **Normalization condition**: 3. **Normalization:** $|a(t)|^2 + |b(t)|^2 = 1$.

This equation states that the sum of the probabilities of being in state $|a\rangle$ or state $|b\rangle$ must always be 1. This is true **if there is no decay to other states** or if we are considering only the population within this two-level manifold. It means the atom is *somewhere* within these two levels. In more advanced treatments where spontaneous emission to other levels or ionization is included, this sum might be less than 1, indicating "loss" from the two-level system. But for a closed, ideal two-level system, this normalization holds.

Our task now is to find equations that tell us how $a(t)$ and $b(t)$ change over time.

Page 28:

This slide, titled **"Deriving Coupled Amplitude Equations – Full Algebra,"** outlines the mathematical steps to find out how our state amplitudes $a(t)$ and $b(t)$ evolve.

The first instruction is to **Insert the two-level expansion (for $\Psi(r,t)$** from the previous slide) into the full Time-Dependent Schrödinger Equation ($\hat{H}\Psi = i\hbar\frac{d\Psi}{dt}$), and then project onto each state ($\ket{a}$ and $\ket{b}$).

This is a standard procedure. "Projecting onto a state" means, for example, to get the equation for $a(t)$, we would multiply the entire Schrödinger equation from the left by the complex conjugate of the spatial wavefunction of state a ($u_{\mathrm{a}}^{*(r))}$ and then integrate over all spatial coordinates $(d\tau)$. We use the orthogonality of the eigenfunctions ($\langle u_{\mathrm{a}}|u_{\mathrm{b}}\rangle = 0$ if a is not equal to b, and $\langle u_{\mathrm{a}}|u_{\mathrm{a}}\rangle = 1$). This process will isolate a differential equation for $\dot{a}(t)$ (the time derivative of $a(t)$) and similarly another one for $\dot{b}(t)$. These will typically be coupled, meaning $\dot{a}$ will depend on b, and $\dot{b}$ will depend on a.

Next, we need to **Define the energy splitting between the two levels in angular frequency units.** This is often called the Bohr frequency for the transition. The slide defines:

$$\omega_{ab} = \frac{E_{\mathrm{a}} - E_{\mathrm{b}}}{\hbar}$$

It also notes that

$$\omega_{ab} = -\omega_{ba}.$$

Let's be very careful with this definition. We defined $\ket{a}$ as the lower level (energy E_{a}) and $\ket{b}$ as the upper level (energy E_{b}), so $E_{\mathrm{b}} > E_{\mathrm{a}}$. Therefore, $E_{\mathrm{a}} - E_{\mathrm{b}}$ is a *negative* quantity. This means ω_{ab}, as defined here, will be a *negative* angular frequency. The more conventional positive transition frequency would be

$$\omega_0 = \frac{E_{\mathrm{b}} - E_{\mathrm{a}}}{\hbar},$$

so, $\omega_{ab} = -\omega_0$. This sign convention is important and we must keep it in mind as we proceed.

Finally, the slide says **Introduce dipole matrix element***. The asterisk indicates that the definition or more details will follow, presumably on the next slide. This dipole matrix element will be the key quantity that couples the two states via the interaction Hamiltonian $V(t)$. It will appear in our coupled equations for $a(t)$ and $b(t)$.

Page 29:

Here we see the definition of the dipole matrix element and the resulting coupled amplitude equations.

First, the **dipole matrix element, capital** D_{ab}, is defined as:

$$D_{ab} = -e \int u_\text{a}^{*(\mathbf}{r}) \, (\mathbf{r} \cdot \hat{e}) \, u_\text{b}(\mathbf{r}) \, d\tau.$$

It's also stated that $D_{ab} = D_{ba}^{*}$ (D subscript ba with an asterisk for complex conjugate).

Let's break down D_{ab}:

* $-e$ is the charge of the electron (e being the positive elementary charge). \(u_\text{a}^{(\mathbf}{r})\) is the complex conjugate of the spatial wavefunction for the lower state $|a\rangle$. * $\mathbf{r}$ is the electron position operator. * $\hat{e}$ is the unit vector defining the polarization of the classical electric field. So, $(\mathbf{r} \cdot \hat{e})$ is the component of the electron's position vector along the direction of the electric field. * $u_\text{b}(\mathbf{r})$ is the spatial wavefunction for the upper state $|b\rangle$. * The integral is over all spatial coordinates $(d\tau)$.

This D_{ab} represents the matrix element of the operator $-e(\mathbf{r} \cdot \hat{e})$ between states $|a\rangle$ and $|b\rangle$. Recall that our interaction Hamiltonian $V(t)$ was $-e(\mathbf{r} \cdot \hat{e})$ times $E_0 \cos(\omega t)$. So D_{ab} is essentially $\langle a|V(t)|b\rangle$ divided by $E_0 \cos(\omega t)$. It quantifies the strength of the coupling between states $|a\rangle$ and $|b\rangle$ by the electric field component along $\hat{e}$.

The relation $D_{ab} = D_{ba}^*$ is standard for Hermitian operators like $-e(\mathbf{r} \cdot \hat{e})$, as long as

$$D_{ba} = \langle b|-e(\mathbf{r} \cdot \hat{e})|a\rangle.$$

The next bullet point states an important property: D_{ab} vanishes for $a = b$ (i.e., D_{aa} or D_{bb}) by parity -> no diagonal Stark term. For systems with inversion symmetry, like atoms, the diagonal matrix elements

$$D_{aa} = \langle a|-e(\mathbf{r} \cdot \hat{e})|a\rangle$$

are zero. This means that the interaction Hamiltonian $V(t)$ we are using does not cause a first-order energy shift (a linear Stark shift) to the levels $|a\rangle$ and $|b\rangle$ themselves; it only couples them off-diagonally. (Quadratic Stark shifts can occur from second-order perturbation theory).

Finally, we arrive at the **Resulting amplitude equations (exact, before approximation):**

The time derivative of $a(t)$, denoted $\dot{a}(t)$, is:

$$\dot{a}(t) = -\frac{i}{\hbar}\, b(t)\, D_{ab}\, E_0 \cos(\omega t)\, e^{i\omega_{ab}t}.$$

And the time derivative of $b(t)$, denoted $\dot{b}(t)$, is:

$$\dot{b}(t) = -\frac{i}{\hbar}\, a(t)\, D_{ba}\, E_0 \cos(\omega t)\, e^{-i\omega_{ab}t}.$$

Let's analyze these important equations:

* They are a pair of coupled, first-order linear differential equations for the amplitudes $a(t)$ and $b(t)$. * The rate of change of $a(t)$ ($\dot{a}(t)$) depends on the current amplitude of $b(t)$, and vice-versa. This is the coupling. * The coupling strength involves the dipole matrix element (D_{ab} or D_{ba}), the electric field amplitude (E_0), and is inversely proportional to $\hbar$. * The term $\cos(\omega t)$ comes

directly from our oscillating electric field. * The exponential terms, $\exp(i\omega_{ab}t)$ and $\exp(-i\omega_{ab}t)$, involve our previously defined atomic transition frequency

$$\omega_{ab} = \frac{E_\mathrm{a} - E_\mathrm{b}}{\hbar}.$$

Since $E_\mathrm{a} < E_\mathrm{b}$, ω_{ab} is negative. Let $\omega_{ab} = -\omega_0$, where

$$\omega_0 = \frac{E_\mathrm{b} - E_\mathrm{a}}{\hbar}$$

is the positive Bohr frequency. Then

$$\exp(i\omega_{ab}t) = \exp(-i\omega_0\, t),$$

and

$$\exp(-i\omega_{ab}t) = \exp(i\omega_0\, t).$$

These equations are the exact result of substituting the two-level expansion into the TDSE and projecting, assuming $D_{aa} = D_{bb} = 0$. They form the starting point for further approximations, like the Rotating Wave Approximation.

Page 30:

This slide offers a physical interpretation of the coupled amplitude equations we just derived.

It states: **Mathematics encodes physically intelligible statement: amplitude of one level changes proportional to amplitude of the other, field strength, and phase mismatch.**

Let's unpack this concise summary by looking back at the equations from the previous page, for instance, the one for $\dot{a}(t)$:

$$\dot{a}(t) = -\frac{i}{\hbar}\, b(t)\, D_{ab}\, E_0 \cos(\omega t) \exp(i\omega_{ab}t)$$

1. **"amplitude of one level changes proportional to amplitude of the other"**: The rate of change of $a(t)$ (i.e., $\dot{a}(t)$) is directly proportional to $b(t)$, the current amplitude of the other state. Similarly, $\dot{b}(t)$ is proportional to $a(t)$. This signifies that for a transition to occur from state $|b\rangle$ to state $|a\rangle$ (thus changing $a(t)$), there must be some population amplitude in state $|b\rangle$ to begin with. The system is driven between the two states.

2. **"field strength"**: The rate of change is also proportional to E_0, the amplitude of the external electric field. A stronger field will drive transitions more effectively, leading to faster changes in the amplitudes $a(t)$ and $b(t)$. The dipole matrix element D_{ab} also contributes to this "strength" of interaction.

3. **"phase mismatch"**: This is captured by the time-dependent terms: $\cos(\omega t)$ and $\exp(i\omega_{ab}t)$. Recall that

$$\cos(\omega t) = \frac{1}{2}[\exp(i\,\omega t) + \exp(-i\,\omega t)].$$

So the product $\cos(\omega t)\exp(i\omega_{ab}t)$ will produce terms like $\exp(i(\omega + \omega_{ab})t)$ and $\exp(i(-\omega + \omega_{ab})t)$. Let's use

$$\omega_0 = \frac{E_\mathrm{b} - E_\mathrm{a}}{\hbar}$$

(positive atomic frequency), so $\omega_{ab} = -\omega_0$. Then the terms become $\exp(i(\omega - \omega_0)t)$ and $\exp(-i(\omega + \omega_0)t)$. The term $\exp(i(\omega - \omega_0)t)$ contains the difference between the applied field frequency (ω) and the atomic transition frequency (ω_0). This difference, $\omega - \omega_0$, is the detuning. If this detuning is small (i.e., ω is close to ω_0, or "near resonance"), this exponential term oscillates slowly. If the detuning is large, it oscillates rapidly. The term $\exp(-i(\omega + \omega_0)t)$ involves the sum of frequencies and always oscillates rapidly. The efficiency of driving the transition (how quickly $a(t)$ and $b(t)$ change) will be critically sensitive to this "phase mismatch" or detuning. We expect the strongest interaction when ω is very close to ω_0. These phase factors govern the coherent accumulation of probability amplitude in the target state.

The "---" at the bottom indicates that this is a summary point. These exact equations, while physically intelligible, are still a bit complex to solve directly due to the rapidly oscillating terms. This will lead us to the Rotating Wave Approximation.

Page 31:

The exact coupled amplitude equations we derived contain terms that oscillate at high frequencies. To simplify them and gain more insight, we introduce a very common and powerful approximation. This is Slide 11: **Rotating-Wave Approximation (RWA) and Rabi Frequency.**

The first step is to **Write cosine as sum of co-rotating and counter-rotating* exponentials.** As we've seen, the term $E_0\cos(\omega t)$ from the electric field can be written as $\frac{E_0}{2}[\exp(i\omega t) + \exp(-i\omega t)]$. When this is multiplied by the atomic phase factors like $\exp(i\omega_{ab}t)$ or $\exp(-i\omega_{ab}t)$ from the previous equations, we get terms involving sums and differences of frequencies.

Let's be very clear about frequencies. Let $\omega_0 = \frac{E_\mathrm{b} - E_\mathrm{a}}{\hbar}$ be the *positive* natural transition frequency of the atom (assuming $E_\mathrm{b} > E_\mathrm{a}$). Our previous ω_{ab} was $\frac{E_\mathrm{a} - E_\mathrm{b}}{\hbar} = -\omega_0$.

The equations for $\dot{a}(t)$ and $\dot{b}(t)$ involved terms like:

For $\dot{a}(t)$:

$$\cos(\omega t)\exp(i\omega_{ab}t) = \cos(\omega t)\exp(-i\omega_0 t)$$

$$= \frac{1}{2}[\exp(i\omega t) + \exp(-i\omega t)]\exp(-i\omega_0 t)$$

$$= \frac{1}{2}[\exp(i(\omega - \omega_0)t) + \exp(-i(\omega + \omega_0)t)]$$

For $\dot{b}(t)$:

$$\cos(\omega t)\exp(-i\omega_{ab}t) = \cos(\omega t)\exp(i\omega_0 t)$$

$$= \frac{1}{2}[\exp(i\omega t) + \exp(-i\omega t)]\exp(i\omega_0 t)$$

$$= \frac{1}{2}[\exp(i(\omega + \omega_0)t) + \exp(-i(\omega - \omega_0)t)]$$

Now, let's look at the slide's statements about which terms vary slowly or fast, keeping in mind their definition $\omega_{ab} = \frac{E_{\mathrm{a}} - E_{\mathrm{b}}}{\hbar}$. If state 'a' is lower and 'b' is upper (as per page 22), then ω_{ab} is negative. The slide states: * **Terms like** $e^{i(\omega - \omega_{ab})t}$ vary slowly near resonance. If $\omega_{ab} = -\omega_0$, then $(\omega - \omega_{ab}) = (\omega + \omega_0)$. This term $\exp(i(\omega + \omega_0)t)$ is a *fast* oscillating term, as ω and ω_0 are both large optical frequencies. * **Terms like** $e^{i(\omega + \omega_{ab})t}$ oscillate very fast -> average to zero over relevant timescales. If $\omega_{ab} = -\omega_0$, then $(\omega + \omega_{ab}) = (\omega - \omega_0)$. This term $\exp(i(\omega - \omega_0)t)$ contains the detuning $(\omega - \omega_0)$. If ω is near ω_0 (resonance), this term varies *slowly*.

It appears the slide's labeling of "slow" and "fast" here is reversed if we strictly follow their definition of $\omega_{ab} = \frac{E_{\mathrm{a}} - E_{\mathrm{b}}}{\hbar}$ with $E_{\mathrm{a}} < E_{\mathrm{b}}$. The RWA *always* keeps the terms that vary as $\exp(\pm i(\omega - \omega_0)t)$, where ω_0 is the positive atomic transition frequency. These are the "near-resonant" or "co-rotating" terms. The terms that vary as $\exp(\pm i(\omega + \omega_0)t)$ are the "far off-resonant" or "counter-rotating" terms.

So, the principle of the RWA is: **Neglect fast counter-rotating terms (formally equivalent to secular approximation).** These fast terms (involving $\omega + \omega_0$) oscillate very rapidly, typically at twice the optical frequency. Over the timescale of significant evolution of the amplitudes $a(t)$ and $b(t)$ (which is governed by the strength of interaction, related to the Rabi frequency), these fast terms average out to nearly zero and do not contribute significantly to the long-term evolution. By neglecting them, we simplify the equations considerably. This approximation is extremely good for most cases in laser spectroscopy involving optical frequencies.

Page 32

Having introduced the Rotating-Wave Approximation (RWA), we can now write down the simplified coupled amplitude equations. But first, we need to define a key parameter that emerges naturally.

The first bullet point is to **Define Rabi frequency (strength of coherent coupling)**.

The Rabi frequency, often denoted by a capital Omega (Ω), quantifies the strength of the coherent interaction between the two-level atom and the light field. The slide defines it as:

$$\Omega_{ab} = \frac{D_{ab} E_0}{\hbar}$$

Let's analyze this:

- Capital D_{ab} is the dipole matrix element $\langle a|(-e\, r\, \hat{e})|b\rangle$ we defined earlier. It represents the strength of the electric dipole coupling between states $|a\rangle$ and $|b\rangle$ along the field polarization $\hat{e}$.
- E_0 is the amplitude of the classical electric field.
- $\hbar$ is the reduced Planck constant.

The units of $D_{ab}E_0$ are (charge × length × electric field), which is energy. Energy divided by $\hbar$ is angular frequency. So, Ω_{ab} indeed has units of angular frequency (radians per second). A larger D_{ab} or a stronger field E_0 leads to a larger Rabi frequency, meaning the atom is driven more strongly between the two levels.

Now, for the **Simplified amplitude equations under RWA**:

The slide presents them as:

$$\dot{a}(t) = -\frac{i}{2}\Omega_{ab}\exp(i\,\Delta\omega\,t)\,b(t)$$

$$\dot{b}(t) = -\frac{i}{2}\Omega_{ba}\exp(-i\,\Delta\omega\,t)\,a(t)$$

(Note: $\Omega_{ba} = \frac{D_{ba}E_0}{\hbar}$. Since \(D_{ba} = D_{ab}^\ *), then \(\Omega_{ba} = \Omega_{ab}*^\).)

Let's carefully consider the **detuning, Capital** $\Delta\omega$, which appears in the exponent.

The slide defines it as:

$$\Delta\omega = \omega - \omega_{ab}$$

If we use our convention: ω is the field's angular frequency. $\omega_{ab} = \frac{E_\mathrm{a} - E_\mathrm{b}}{\hbar}$. Since E_a is the lower level and E_b is the upper, $E_\mathrm{a} - E_\mathrm{b}$ is negative. Let

$$\omega_0 = \frac{E_\mathrm{b} - E_\mathrm{a}}{\hbar}$$

be the positive atomic transition frequency. So, $\omega_{ab} = -\omega_0$.

Then, the slide's $\Delta\omega = \omega - (-\omega_0) = \omega + \omega_0$.

If this $\Delta\omega = \omega + \omega_0$ is used in the exponents, then the terms $\exp(i(\omega + \omega_0)t)$ are the *fast oscillating (counter-rotating) terms* that the RWA is supposed to discard!

This indicates a persistent notational inconsistency on the slides. For the RWA equations to be correct, the exponential terms must involve the *true detuning* from resonance, which is $\Delta = \omega - \omega_0$.

So, if we assume the RWA equations written here *are* the intended correct forms after applying RWA, then the $\Delta\omega$ in *these specific equations* must represent the true detuning.

Let's proceed by assuming the RWA correctly selected the slowly varying terms: The term for $\dot{a}(t)$ (which drives population from b to a) should involve $\exp(i(\omega_{\text{field}} - \omega_{\text{atomic transition}})t)$. The term for $\dot{b}(t)$ (which drives population from a to b) should involve $\exp(-i(\omega_{\text{field}} - \omega_{\text{atomic transition}})t)$.

Let's assume $\Delta\omega$ in these equations is actually $\delta = \omega - \omega_0$.

Then:

$$\dot{a}(t) = -\frac{i}{2}\Omega_{ab}\exp(i\,\delta t)\,b(t)$$

$$\dot{b}(t) = -\frac{i}{2}\Omega_{ba}\exp(-i\,\delta t)\,a(t)$$

These equations describe the coherent evolution of the amplitudes $a(t)$ and $b(t)$ under the RWA. They are much simpler than the exact equations because the rapidly oscillating terms have been removed. These are the fundamental equations for phenomena like Rabi oscillations.

I will state the equations as on the slide, and define Rabi frequency Ω_{ab} as $\frac{D_{ab}E_0}{\hbar}$. For the detuning, I will use the symbol $\Delta\omega$ as on the slide, but clarify that it should represent the difference between the applied field frequency ω and the actual atomic resonance frequency $\omega_0 = \frac{E_{\text{b}} - E_{\text{a}}}{\hbar}$ for the equations to correctly describe the physics of the RWA.

Page 33:

This slide addresses the **accuracy of the Rotating-Wave Approximation (RWA).**

It states: **RWA is exceptionally accurate when the absolute value of** $\mathit{\Delta}\omega$, denoted $|\mathit{\Delta}\omega|$, and the Rabi frequency, $\mathit{\Omega}_{ab}$, are both much, much less than ω_{ab} (in the optical domain).

Let's clarify the terms here to be consistent with standard understanding:

* $|\mathit{\Delta}\omega|$ should be interpreted as the magnitude of the **detuning**, i.e., $|\omega_{\text{field}} - \omega_{\text{atomic resonance}}|$. Let's call this $|\delta|$. * $\mathit{\Omega}_{ab}$ here refers to the **Rabi frequency**, which quantifies the coupling strength. Let's call this $\mathit{\Omega}_{\mathrm{R}}$. * The ω_{ab} on the right side of the inequality must refer to the **atomic transition frequency** itself, $\omega_0 = \frac{E_{\mathrm{b}} - E_{\mathrm{a}}}{\hbar}$, which is typically an optical frequency (e.g., $\sim 10^{15}$ rad/s).

So, the condition for the RWA's high accuracy is:

$$|\delta| \ll \omega_0 \quad \text{and} \quad \mathit{\Omega}_{\mathrm{R}} \ll \omega_0.$$

This makes physical sense:

1. The detuning $|\delta|$ being small compared to ω_0 ensures that the "slowly" varying terms $\exp(i\delta t)$ are indeed much slower than the optical frequency itself.

2. The Rabi frequency $\mathit{\Omega}_{\mathrm{R}}$ being small compared to ω_0 ensures that the timescale for significant population transfer (which is inversely proportional to $\mathit{\Omega}_{\mathrm{R}}$) is much longer than the period of the optical field ($2\pi/\omega_0$). This gives the "fast" counter-rotating terms (oscillating at frequencies around $2\omega_0$) enough time to average out effectively before the atomic state changes much.

In the **optical domain**, ω_0 is very large. Rabi frequencies $\mathit{\Omega}_{\mathrm{R}}$ (even for intense lasers) and achievable detunings $|\delta|$ (while still getting appreciable interaction) are typically many orders of magnitude smaller than ω_0. For example, ω_0 might be 10^{15} rad/s, while Ω_R might be 10^9 rad/s (for a strong field) or less, and $|\delta|$ might also be in a similar range for resonant spectroscopy. Since $10^9 \ll 10^{15}$, the RWA holds extremely well.

The RWA can break down for very high field intensities (where Ω_R becomes comparable to ω_0) or in different frequency regimes (e.g., microwave transitions where ω_0 is much smaller, and Ω_R might not be negligible in comparison). But for most laser spectroscopy in the optical regime, it's a remarkably robust and accurate approximation.

Page 34:

This slide presents a **Phasor Diagram** to help visualize the **Rotating Wave Approximation.**

Imagine the complex plane, with a real axis (Re) and an imaginary axis. The terms like $\exp(i\phi)$ can be represented as vectors (phasors) of unit length, making an angle ϕ with the real axis. As time t evolves, these phasors rotate in the complex plane.

The diagram shows a circle, representing the path of a unit phasor. There are two key phasors depicted:

1. A **red vector** is labeled as the **"Counter-rotating term: $e^{i(\omega+\omega_{ab})t}$"** and is also marked **"(fast)"**. The caption above it says: "This term rotates very rapidly (at approximately $2\omega_{ab}t$, assuming ω is close to ω_{ab}) and averages to zero." Here, to be consistent with the idea of a fast term, ω_{ab} should be interpreted as the positive atomic frequency, ω_0. So this is $e^{i(\omega+\omega_0)t}$. This phasor spins around the origin very quickly. Over any significant timescale for atomic evolution, its average value will be close to zero. This is the term discarded by the RWA.

2. A **blue vector** is labeled as the **"Co-rotating term: $e^{i(\omega-\omega_{ab})t}$"**, which is then equated to **"$e^{i\Delta\omega t}$"** and marked **"(slow)"**. The caption below it says: "Near

resonance ($\Delta\omega$ small), this term rotates slowly." Again, interpreting ω_{ab} as ω_0 (positive atomic frequency), this term is $e^{i(\omega-\omega_0)t} = e^{i\delta t}$, where $\delta = (\omega - \omega_0)$ is the detuning. If ω is close to ω_0, then δ is small, and this phasor rotates slowly in the complex plane. This is the term that the RWA *keeps*, as its slow evolution allows it to coherently drive the atomic system.

This phasor diagram provides a very intuitive picture. The interaction Hamiltonian effectively has two driving components in this semi-classical picture when we expand $\cos(\omega t)$. One component (the counter-rotating one) rotates so fast in the interaction frame that its effect averages out. The other component (the co-rotating one) rotates slowly (or is nearly stationary if on resonance) and can thus effectively and coherently "push" the atomic state vector, leading to transitions.

The RWA essentially says we can ignore the dizzyingly fast red vector and only pay attention to the more leisurely blue vector when we are near resonance. This greatly simplifies the description of the system's dynamics.

Page 35:

Now we consider a further simplification beyond the RWA, applicable in certain limits. This is Slide 12: **Weak-Field (Perturbative) Approximation.** This approach is essentially equivalent to first-order time-dependent perturbation theory.

First, we **Assume an initial condition: all atoms are in the ground state.** For our two-level system $|a\rangle$ (lower) and $|b\rangle$ (upper), if $|a\rangle$ is the ground state, this means:

- The amplitude $a(0)$ equals 1. (Probability of being in state $|a\rangle$ at $t = 0$ is $|a(0)|^2 = 1$.)
- The amplitude $b(0)$ equals 0. (Probability of being in state $|b\rangle$ at $t = 0$ is $|b(0)|^2 = 0$.)

The system starts entirely in the lower state.

Next, we make a crucial assumption about the interaction:

Further assume the field is so weak and/or the interaction time is so short that the absolute square of $b(t)$, $|b(t)|^2$, remains much, much less than 1 throughout the evolution.

This means that the probability of the atom transitioning to the upper state $|b\rangle$ remains very small. Only a tiny fraction of the population (if any) is transferred to the excited state.

What's the consequence of this assumption?

Under these conditions, we can set the amplitude of the ground state $a(t)$ approximately equal to 1 in the right-hand side of the coupled RWA equations, and then integrate the equation for $b(t)$.

Recall the RWA equation for $\dot{b}(t)$ (from slide 32, assuming $\Delta\omega$ is the true detuning $\delta = \omega - \omega_0$):

$$\dot{b}(t) = -\frac{i}{2}\Omega_{ba}e^{-i\delta t}a(t).$$

If $|b(t)|^2 \ll 1$, and since $|a(t)|^2 + |b(t)|^2 = 1$ (for a closed system), then $|a(t)|^2$ must be approximately 1. We can thus approximate $a(t)$ by its initial value, $a(0) = 1$.

So, the equation for $\dot{b}(t)$ becomes:

$$\dot{b}(t) \approx -\frac{i}{2}\Omega_{ba}e^{-i\delta t}.$$

This is now a much simpler differential equation for $b(t)$ because $a(t)$ is no longer a time-varying unknown on the right-hand side. We can directly integrate this equation with respect to time (from 0 to t) with the initial condition $b(0) = 0$ to find $b(t)$. This is the essence of first-order perturbation theory for this system.

Page 36:

Having made the weak-field (perturbative) approximation, we can now solve for the amplitude $b(t)$ of the upper state.

The slide states: **Obtain** $b(t)$ (keeping both rotating and counter-rotating parts before the RWA step).

This is an interesting instruction. It implies that for this particular derivation of $b(t)$ in the perturbative limit, we might go back to the equations *before* applying the RWA (from Slide 29), set $a(t) = 1$, and integrate.

The exact equation for $\dot{b}(t)$ was:

$$\dot{b}(t) = -\frac{i}{\hbar}\, a(t)\, D_{ba}\, E_0 \cos(\omega t) \exp(-i\,\omega_{ab}\, t).$$

Let $a(t) = 1$. Recall $\omega_{ab} = \frac{E_\mathrm{a} - E_\mathrm{b}}{\hbar} = -\omega_0$ (where ω_0 is the positive atomic frequency $\frac{E_\mathrm{b} - E_\mathrm{a}}{\hbar}$).

And

$$\cos(\omega t) = \frac{1}{2}[\exp(i\,\omega t) + \exp(-i\,\omega t)].$$

And

$$\Omega_{ba} = \frac{D_{ba}\, E_0}{\hbar}.$$

So,

$$\dot{b}(t) = -\frac{i}{2}\, \Omega_{ba}\, [\exp(i\,\omega t) + \exp(-i\,\omega t)]\exp(i\,\omega_0 t)$$

which can be written as

$$\dot{b}(t) = -\frac{i}{2}\,\Omega_{ba}\,[\exp(i(\omega+\omega_0)t) + \exp(-i(\omega-\omega_0)t)].$$

Integrating this from 0 to t with $b(0) = 0$ gives:

$$b(t) = -\frac{i}{2}\,\Omega_{ba}\left[\frac{\exp(i(\omega+\omega_0)t) - 1}{i(\omega+\omega_0)} + \frac{\exp(-i(\omega-\omega_0)t) - 1}{-i(\omega-\omega_0)}\right].$$

This can be simplified to

$$b(t) = -\frac{1}{2}\,\Omega_{ba}\left[\frac{\exp(i(\omega+\omega_0)t) - 1}{\omega+\omega_0} - \frac{\exp(-i(\omega-\omega_0)t) - 1}{\omega-\omega_0}\right].$$

The equation on the slide for $b(t)$ is:

$$b(t) = \frac{\Omega_{ab}}{2}\left[\frac{\exp(i\,\Delta\omega\,t) - 1}{\Delta\omega} - \frac{\exp(i(\omega+\omega_{ab})t) - 1}{\omega+\omega_{ab}}\right].$$

Here, $\Omega_{ab} = \frac{D_{ab}\,E_0}{\hbar}$. And $\Delta\omega$ was defined on Slide 32 as

$$\Delta\omega = \omega - \omega_{ab} = \omega - (-\omega_0) = \omega + \omega_0.$$

And

$$\omega + \omega_{ab} = \omega - \omega_0.$$

So the slide's equation is:

$$b(t) = \frac{\Omega_{ab}}{2}\left[\frac{\exp(i(\omega+\omega_0)t) - 1}{\omega+\omega_0} - \frac{\exp(i(\omega-\omega_0)t) - 1}{\omega-\omega_0}\right].$$

This form is similar to my derived one if Ω_{ab} is related to $-\Omega_{ba}$. ($D_{ab} = D_{ba}^*$).

The key is that it contains two terms: one involving the sum frequency $\omega + \omega_0$, which is the counter-rotating term, and one involving the difference frequency $\omega - \omega_0$, which is the co-rotating (resonant) term. This expression for $b(t)$ has indeed kept both.

Now, the second bullet point: **Near resonance, where the magnitude of the detuning** $|\Delta\omega|$ (which should be $|\omega - \omega_0|$) is much less than ω_{ab} (which should be ω_0, the atomic frequency), we drop the second, rapidly oscillating fraction -> this leads to the standard first-order perturbation result.

If we are near resonance ($\omega \approx \omega_0$), then the term with denominator $\omega + \omega_0$ (approx $2\omega_0$) is much smaller than the term with denominator $\omega - \omega_0$ (which is small). So, the first term in the square brackets of the slide's equation (related to $\omega + \omega_0$, the counter-rotating part) is often neglected. The remaining term (related to $\omega - \omega_0$, the resonant part) is the standard RWA result for $b(t)$ in first-order perturbation theory.

If the slide's "$\Delta\omega$" is $\omega + \omega_0$ and $\omega + \omega_{ab}$ is $\omega - \omega_0$, then we would drop the first term and keep the second. The slide's labeling here for which term is dropped might need careful reading. The term that is "rapidly oscillating" refers to its contribution to $b(t)$; near resonance, the term with $\omega - \omega_0$ in the denominator is dominant.

Essentially, applying the RWA at this stage simplifies $b(t)$.

Page 37:

We're now ready to calculate the probability of finding the atom in the excited state $|b\rangle$ after some interaction time t, based on our perturbative calculation of $b(t)$. This is Slide 13: **Transition Probability vs. Detuning – Sinc-Squared Profile.**

The first bullet point states: **The probability to find the atom in state ket b after time** t, which we denote $P_{a\to b}(t)$ (P from a to b at time t), is simply the absolute square of the amplitude $b(t)$: $|b(t)|^2$. If we take the expression for $b(t)$ obtained under the RWA and in the perturbative limit (keeping only the resonant term), and then calculate its squared magnitude, we arrive at a famous result:

$$P_{a\to b}(t) = \left(\frac{\Omega_{ab}}{2}\right)^2 \left[\frac{\sin\left(\frac{\Delta\omega\, t}{2}\right)}{\frac{\Delta\omega}{2}}\right]^2.$$

Let's analyze this equation:

- Ω_{ab} is the Rabi frequency $\left(\frac{D_{ab}E_0}{\hbar}\right)$. It represents the strength of the atom-field coupling.
- $\Delta\omega$ is the detuning from resonance $(\omega_{\text{field}} - \omega_{\text{atomic resonance}})$.
- t is the interaction time.

The term $\frac{\sin(x)}{x}$ is known as the (unnormalized) sinc function, $\operatorname{sinc}(x)$. So the expression is proportional to $\left[\operatorname{sinc}\left(\frac{\Delta\omega\, t}{2}\right)\right]^2$.

Next, let's look at the **Key features** of this sinc-squared profile:

1. **Maximum at exact resonance, i.e., when** $\Delta\omega = 0$. When the laser frequency ω is exactly equal to the atomic transition frequency ω_0, the detuning $\Delta\omega$ is zero. In this case, we need to take the limit of $\frac{\sin(x)}{x}$ as x approaches 0. This limit is 1. So, at resonance,

$$P_{a\to b}(t) = \left(\frac{\Omega_{ab}}{2}\right)^2 t^2 = \left(\frac{\Omega_{ab}\, t}{2}\right)^2.$$

This shows that on resonance, the transition probability (in this perturbative regime) grows quadratically with the interaction time t and quadratically with the Rabi frequency Ω_{ab}.

This sinc-squared lineshape is fundamental in many areas of physics, including diffraction and Fourier analysis, and it appears here as the natural lineshape for transitions induced by a coherent field for a finite interaction time.

Page 38:

Continuing with the key features of the sinc-squared profile for the transition probability:

2. **Width of the central lobe is inversely proportional to the interaction time** t (this is a manifestation of the Fourier limit).

The sinc-squared function, $\left[\frac{\sin\left(\frac{\Delta\omega t}{2}\right)}{\frac{\Delta\omega}{2}}\right]^2$, has its first zeros when the argument of the sine function, $\left(\frac{\Delta\omega t}{2}\right)$, is equal to $\pm\pi$ (plus or minus pi), $\pm 2\pi$, and so on (but not zero).

So, $\sin\left(\frac{\Delta\omega t}{2}\right) = 0$ when $\frac{\Delta\omega t}{2} = n\pi$, for $n = \pm 1, \pm 2, \ldots$

This means the first zeros occur at $\Delta\omega = \pm\left(\frac{2\pi}{t}\right)$.

The width of the central maximum (e.g., the full width between the first two zeros) is therefore $\left(\frac{4\pi}{t}\right)$.

More commonly, the full width at half maximum (FWHM) of this central peak is approximately $0.886 \times \left(\frac{2\pi}{t}\right)$, or roughly proportional to $\frac{1}{t}$.

This inverse relationship between the spectral width (in terms of $\Delta\omega$) and the interaction time t is a direct consequence of the time-frequency uncertainty principle, often referred to as the Fourier limit.

To get a very sharply defined transition in terms of frequency (small $\Delta\omega$ width), you need a long interaction time t.

Conversely, a short interaction time t inherently leads to a broader range of frequencies that can cause the transition.

3. **The envelope is a classic sinc squared (**sinc^2) pattern (compare this to single-slit diffraction analogy).

The overall shape of $P(\Delta\omega)$ vs $\Delta\omega$ shows a prominent central peak, followed by successively smaller side-lobes on either side.

This mathematical form is identical to the intensity pattern observed in Fraunhofer diffraction from a single slit, where the sinc function arises from the Fourier transform of the rectangular slit aperture.

The analogy is quite deep: the finite interaction time t in our spectroscopy problem plays a role similar to the finite width of the slit in diffraction.

Finally, the slide reiterates the on-resonance case:

* **At resonance (when $\Delta\omega = 0$)**:

The transition probability, $P_{a\to b}^{\text{res}}(t)$ (P resonant from a to b at time t), is given by:

$$\left(\frac{\Omega_{ab}t}{2}\right)^2$$

As we noted, this shows a quadratic dependence on both the Rabi frequency (field strength) and the interaction time, under the condition that this probability remains small (the perturbative regime).

Page 39:

Now, a crucial point about the validity of the weak-field perturbation theory we've been using.

The slide states the **Validity constraint for weak-field perturbation:**

The quantity $\frac{\Omega_{ab}t}{2}$ must be much, much less than 1 ($\frac{\Omega_{ab}t}{2} \ll 1$).

Let's understand why. Our perturbative calculation assumed that the population of the upper state, $|b(t)|^2$, remains small, and consequently, the population of the lower state, $a(t)$, remains approximately 1. The expression for the transition probability on resonance ($\Delta\omega = 0$) is $P_{\text{res}} = \left(\frac{\Omega_{ab}t}{2}\right)^2$. So, the condition $|b(t)|^2 \ll 1$ directly translates to $\left(\frac{\Omega_{ab}t}{2}\right)^2 \ll 1$, which is equivalent to $\frac{\Omega_{ab}t}{2} \ll 1$. If this condition is met, our approximation holds. The transition probability grows, but doesn't become so large as to significantly deplete the ground state or violate the smallness assumption for $|b(t)|^2$.

What happens if this condition is **violated**? This occurs **for long pulses (large** t) or strong fields (large Ω_{ab}). If $\frac{\Omega_{ab}t}{2}$ is NOT much less than 1, then the probability $|b(t)|^2$ can become significant. This means $a(t)$ can no longer be approximated as 1. The system can undergo substantial population transfer, and even population inversion, with the population cycling back and forth between states $|a\rangle$ and $|b\rangle$. This phenomenon is known as Rabi oscillation or Rabi flopping. In such cases, the simple perturbative solution is no longer accurate. We **need the full (non-perturbative) Rabi solution**, which involves solving the coupled RWA equations for $a(t)$ and $b(t)$ without approximating $a(t) = 1$. This leads to sinusoidal oscillations in the populations $|a(t)|^2$ and $|b(t)|^2$ as a function of time and field strength.

So, the weak-field approximation is very useful for understanding the initial growth of transition probability and the lineshape, but it breaks down when the interaction becomes too strong or too long, at which point the more complete Rabi model is required.

Page 40:

This slide presents a graph of the **Transition Probability** P versus Detuning $\Delta\omega$, visually showing the sinc-squared profile we've been discussing.

Let's examine the graph:

- The **vertical axis** is labeled $P(\Delta\omega, t)$, representing the transition probability from state $|a\rangle$ to state $|b\rangle$ as a function of detuning $\Delta\omega$ and for a fixed interaction time t. The scale shown goes from 0.00 up to around 0.19, but the peak seems to be higher, near an indicated value.

- The **horizontal axis** is labeled **Detuning** $(\Delta\omega = \omega_{\text{field}} - \omega_{\text{atomic}})$. The center is at $\Delta\omega = 0$ (exact resonance). The axis is marked in units of $\frac{2\pi}{t}$ (i.e. $\frac{2\pi}{t}$). So we see points like $-3\left(\frac{2\pi}{t}\right)$, $-2\left(\frac{2\pi}{t}\right)$, $-1\left(\frac{2\pi}{t}\right)$, 0, $+1\left(\frac{2\pi}{t}\right)$, $+2\left(\frac{2\pi}{t}\right)$, $+3\left(\frac{2\pi}{t}\right)$.

The plotted curve, shown in orange, has the characteristic **sinc-squared shape**:

- A **tall central maximum** occurs at $\Delta\omega = 0$ (exact resonance). The peak value of this probability is labeled on the graph as $P = \left(\frac{\Omega t}{2}\right)^2$. This matches our formula for the on-resonance probability in the perturbative regime. The y-axis also has a tick mark labeled $\left(\frac{\Omega t}{2}\right)^2$ at the peak.

- The probability drops to **zero** at detunings where $\frac{\Delta\omega\, t}{2} = \pm\pi, \pm 2\pi, \ldots$ This means the first zeros occur when $\Delta\omega = \pm\frac{2\pi}{t}$. These points are clearly visible on the x-axis labels.

- Between these zeros, there are **sidelobes** of diminishing intensity. For example, there are smaller peaks centered roughly around $\Delta\omega = \pm\frac{3\pi}{t}$, $\Delta\omega = \pm\frac{5\pi}{t}$, and so on.

This graph beautifully illustrates several key concepts:

1. The resonant nature of the interaction: the transition is most probable when the laser is tuned exactly to the atomic frequency.

2. The spectral width of the transition is inversely proportional to the interaction time t. A shorter t would make this central peak wider (and the zeros further apart). A longer t would make it narrower.

3. The possibility of exciting the atom even when off-resonance, albeit with lower probability, especially within the central lobe.

This profile is fundamental to understanding how coherent light interacts with a two-level system for a finite duration.

Page 41:

This slide, titled **"Interaction Time, Fourier Limit, and Spectral Resolution,"** delves deeper into the relationship between the duration of the light-matter interaction and the resulting spectral features.

First, it suggests we **Define a characteristic time scale**, denoted by a capital T. The slide gives: Capital T equals $\frac{2}{\Omega_{ab}}$, which is also written as $\frac{\hbar}{\frac{D_{ab}E_0}{2}}$. Let's check the consistency here. On page 32, the Rabi frequency Ω_{ab} was defined as $\frac{D_{ab}E_0}{\hbar}$. So, $\frac{2}{\Omega_{ab}}$ would be $\frac{2\hbar}{D_{ab}E_0}$. The slide has $T = \frac{\hbar}{\frac{D_{ab}E_0}{2}}$ which is also $\frac{2\hbar}{D_{ab}E_0}$. So these are consistent.

This characteristic time $T = \frac{2}{\Omega_{ab}}$ is related to the Rabi cycle. For example, on resonance, the probability of transition $P_{\text{res}} = \left(\frac{\Omega_{ab}t}{2}\right)^2$. If we set $P_{\text{res}} = 1$ (a full transition, though this violates perturbation theory), then $\frac{\Omega_{ab}t}{2} = 1$, so $t = \frac{2}{\Omega_{ab}}$. This 't' is our capital T. So, T is the time it would take to achieve unit probability (a pi-pulse condition, where population is fully inverted) if the perturbative formula were extrapolated. This T marks the boundary where perturbation theory definitely breaks down.

The second bullet point then states: **For interaction times** t much, much less than this characteristic time T (i.e., $t \ll T$), the perturbative regime holds, and the spectral profile (the sinc-squared function) derived earlier is valid. This is consistent with our earlier condition $\frac{\Omega_{ab}t}{2} \ll 1$. Since $T = \frac{2}{\Omega_{ab}}$, the condition $t \ll T$ implies $t \ll \frac{2}{\Omega_{ab}}$, or $\frac{\Omega_{ab}t}{2} \ll 1$. So, as long as the actual interaction time t is short compared to this characteristic time T, our weak-field approximation and the resulting sinc-squared lineshape are good descriptions.

Finally, a fundamental point: **Finite interaction time implies inherent spectral uncertainty.** This is a direct consequence of the Fourier transform relationship between time and frequency. If an interaction occurs only for a finite duration t, then the energy (and thus frequency) of the transition cannot be defined with perfect precision. There will be an inherent spread or uncertainty in the frequency response, as we saw with the width of the sinc-squared profile. This is not just a limitation of our instruments; it's a fundamental aspect of quantum mechanics and wave phenomena.

Page 42:

Continuing with the theme of interaction time and spectral uncertainty:

The slide first gives the approximate relationship for this spectral uncertainty: **Capital** $\Delta\omega$ is on the order of $\frac{1}{t}$ ($\Delta\omega \sim \frac{1}{t}$). This means the characteristic width of the spectral feature (e.g., the central lobe of our sinc-squared profile) in terms of angular frequency ($\Delta\omega$) is inversely proportional to the interaction time (t). For a more precise measure, the full width between the first zeros of the sinc-squared profile was $\frac{4\pi}{t}$, and the FWHM is also proportional to $\frac{1}{t}$. So,

$\Delta\omega \sim \frac{1}{t}$ is a good rule of thumb for the minimum achievable spectral width given an interaction time t.

An example is provided: **Laser pulses with a duration** $t = 10\,\text{ns}$ possess a transform-limited linewidth of approximately $100\,\text{MHz}$. Let's check this. If $t = 10\,\text{ns} = 10 \times 10^{-9}\,\text{s} = 10^{-8}\,\text{s}$. Then $\frac{1}{t} = \frac{1}{10^{-8}\,\text{s}} = 10^{8}\,\text{s}^{-1} = 10^{8}\,\text{Hz} = 100\,\text{MHz}$. This is the spectral width in terms of ordinary frequency ν ($\Delta\nu$). Since $\Delta\omega = 2\pi\Delta\nu$, if $\Delta\nu \sim \frac{1}{t}$, then $\Delta\omega \sim \frac{2\pi}{t}$. This is consistent. A $10\,\text{ns}$ pulse inherently cannot define an energy or frequency with a precision better than about $100\,\text{MHz}$. This is the Fourier limit or transform limit.

The final bullet point emphasizes the practical importance of this concept: **Understanding this time-frequency reciprocity is essential for designing selective excitation schemes and for high-resolution spectroscopy.** If you want to excite only a very specific, narrow energy level without affecting nearby levels (selective excitation), you need a spectrally narrow excitation source. This implies, from time-frequency reciprocity, that you need a long interaction time. This could mean using a continuous wave (CW) laser or very long pulses. For high-resolution spectroscopy, where the goal is to distinguish very closely spaced spectral lines, you also need to achieve very narrow effective linewidths. This again points to the need for maximizing the coherent interaction time between the light and the atoms/molecules. Techniques like Ramsey interferometry are specifically designed to achieve long effective interaction times to overcome this limit.

The "---" at the end suggests this topic has more depth, but these are the key takeaways for now.

Page 43:

So far, we've mostly considered interaction with a monochromatic (single-frequency) light field. Now, let's broaden our perspective.

Slide 15: Broadband Radiation – Introducing Spectral Energy Density.

The first point acknowledges a reality of many light sources:

Realistic sources often possess a bandwidth, let's call it lowercase $\delta\omega$ (to distinguish from detuning Capital $\Delta\omega$), which is much larger than the Fourier limit of $\frac{1}{t}$ (where t is the interaction time or coherence time of the atom).

Think of thermal light sources (like a lamp), which are inherently broadband. Even some lasers, like mode-locked lasers producing ultrashort pulses, have very large bandwidths. If this source bandwidth $\delta\omega$ is much larger than the natural width of the atomic transition (or the Fourier width $\frac{1}{t}$ if t is short), then our previous single-frequency treatment needs modification.

The crucial step is: **Replace the single-frequency field amplitude (like** E_0) with a spectral energy density*, denoted $\rho(\omega)$ (rho as a function of omega).

$\rho(\omega)$ is the **spectral energy density**. Its units are given as J m^{-3} rad^{-1} s.

Let's break this down:

* Joules per meter cubed (J m^{-3}) is energy density (energy per unit volume).

* So, $\rho(\omega)$ is the energy density per unit angular frequency interval. If you integrate $\rho(\omega)\,d\omega$ over a small range of angular frequencies $d\omega$, you get the energy density of the radiation field within that frequency range. The rad^{-1} s is equivalent to $(\mathrm{rad/s})^{-1}$, which is $(\text{angular frequency})^{-1}$.

The definition of $\rho(\omega)$ is further clarified by how it **relates to the total field energy**, which will be shown on the next slide. The idea is that instead of a single E_0 at a single ω, we now have a distribution of energy across a range of frequencies, described by $\rho(\omega)$. This is essential for dealing with non-monochromatic light.

Page 44:

Continuing with broadband radiation, this slide provides the connection between the spectral energy density $\rho(\omega)$ and the total field energy, and then shows how to calculate the transition probability with a broadband source.

First, the relationship of $\rho(\omega)$ to total field energy density:

The integral from 0 to ∞ of $\rho(\omega)\, d\omega$ equals $\frac{\epsilon_0 E_0^2}{2}$.

Let's interpret this carefully:

- The left side, integral of $\rho(\omega)\, d\omega$ over all positive angular frequencies, represents the **total energy density (U)** of the radiation field, in Joules per meter cubed.

- The right side, $\frac{\epsilon_0 E_0^2}{2}$, is the familiar expression for the energy density of a *monochromatic* plane wave with amplitude E_0 (ϵ_0 is the permittivity of free space).

So, this equation is essentially saying that if you sum up all the energy contributions from all frequencies in your broadband field (as given by $\rho(\omega)$), the total energy density is U. The E_0^2 on the right might be interpreted as $2\, U/\epsilon_0$, defining an "effective" total field amplitude squared, or it's a way to normalize $\rho(\omega)$ if the total energy density is known.

Next, how does the interaction strength change with a broadband source?

The Dipole interaction strength at each frequency component ω of the field now becomes $\Omega_{ab}(\omega) = \frac{D_{ab} E(\omega)}{\hbar}$.

Here, $E(\omega)$ is not the total field amplitude, but rather represents the electric field amplitude *per unit angular frequency interval* associated with $\rho(\omega)$. (Specifically,

$$\rho(\omega)\, d\omega = \frac{1}{2} \epsilon_0\, |E(\omega)\, d\omega|^2$$

if $E(\omega)$ is a spectral field amplitude, or related through a proportionality). This means the coupling strength itself can be frequency-dependent if the source spectrum $E(\omega)$ is not flat.

Now, the crucial part: **The transition probability integrated over the broadband source.**

The total probability of transition from state a to b after time t, $P_{ab}(t)$, is given by an integral:

$$P_{ab}(t) = \frac{D_{ab}^2}{2\epsilon_0\hbar^2}\int_{-\infty}^{+\infty} \rho\,(\omega)\left[\frac{\sin\left(\frac{(\omega_{ba}-\omega)t}{2}\right)}{\frac{(\omega_{ba}-\omega)}{2}}\right]^2 d\omega.$$

The sinc-squared function is: $\left[\frac{\sin\left(\frac{(\omega_{ba}-\omega)t}{2}\right)}{\frac{(\omega_{ba}-\omega)}{2}}\right]^2$.

Let's break this down:

- The prefactor $\frac{D_{ab}^2}{2\epsilon_0\hbar^2}$ involves the squared dipole matrix element $|D_{ab}|^2$ (with D_{ab} here given by $\langle a|(-er\cdot\hat{e})|b\rangle$), permittivity of free space, and $\hbar$ squared.
- $\rho(\omega)$ is the spectral energy density of the incident broadband radiation.
- The sinc-squared term is the transition probability profile we found for a *monochromatic* field of frequency ω, where ω_{ba} is the atomic transition frequency $\frac{E_\mathrm{b}-E_\mathrm{a}}{\hbar}$, and $(\omega_{ba}-\omega)$ is the detuning.
- We are integrating this product over all frequencies ω of the incident light (from $-\infty$ to $+\infty$, though $\rho(\omega)$ is usually defined for positive ω; often the sinc^2 is symmetric so the integral can be taken from 0 to ∞ and doubled, or $\rho(\omega)$ is defined for negative frequencies too via Fourier transforms).

This equation makes intuitive sense: the broadband source is like a collection of many monochromatic components. Each component ω contributes to the transition probability according to the sinc-squared profile centered at that ω (or rather, centered at ω_{ba} for the atomic response). We sum up all these contributions, weighted by how much energy density $\rho(\omega)$ there is at each frequency ω. This is a standard way to handle transitions induced by a non-monochromatic field.

The "---" at the bottom implies more to come.

Page 45:

Now we evaluate the integral for the transition probability $P_{ab}(t)$ under a specific condition. This is **Slide 16: Result for Slowly Varying** $\rho(\omega)$ – Linear Growth in Time.

The first key assumption is: **If** $\rho(\omega)$ (the spectral energy density of the source) varies slowly across the spectral region where the sinc-squared kernel is appreciable, we can approximate $\rho(\omega)$ as being constant and equal to its value at resonance, $\rho(\omega_{ba})$.

Let's visualize this. The sinc-squared function,

$$\left[\frac{\sin\left(\frac{(\omega_{ba}-\omega)t}{2}\right)}{\frac{\omega_{ba}-\omega}{2}}\right]^2,$$

is sharply peaked around $\omega = \omega_{ba}$ (the atomic resonance frequency). Its width is approximately $\frac{1}{t}$. If the source spectrum $\rho(\omega)$ is much broader than this width $\frac{1}{t}$, and doesn't change much across this narrow region, then we can effectively pull $\rho(\omega)$ out of the integral from the previous slide, evaluating it at $\omega = \omega_{ba}$.

The second step is to **Evaluate the remaining integral using a standard identity.**

The integral we need to evaluate is:

$$\int_{-\infty}^{\infty} \left[\frac{\sin\left(\frac{(\omega_{ba} - \omega)t}{2}\right)}{\frac{\omega_{ba} - \omega}{2}} \right]^2 d\omega.$$

Let $Y = \omega_{ba} - \omega$. Then $dY = -d\omega$. As ω goes from $-\infty$ to ∞, Y goes from ∞ to $-\infty$.

The integral becomes:

$$\int_{\infty}^{-\infty} \left[\frac{\sin\left(\frac{Yt}{2}\right)}{\frac{Y}{2}} \right]^2 (-dY) = \int_{-\infty}^{\infty} \left[\frac{\sin\left(\frac{Yt}{2}\right)}{\frac{Y}{2}} \right]^2 dY.$$

This is of the form

$$\int_{-\infty}^{\infty} \left[\frac{\sin(ax)}{x} \right]^2 dx$$

where $a = \frac{t}{2}$. The full integral

$$\int_{-\infty}^{\infty} \left[\frac{\sin(ax)}{x} \right]^2 dx$$

is equal to $|a|\pi$.

Here, the form is

$$\int \left[\frac{\sin\left(\frac{Yt}{2}\right)}{\frac{Y}{2}} \right]^2 dY.$$

Let $u = \frac{Y}{2}$. Then $dY = 2\,du$.

The integral becomes

$$\int \left[\frac{\sin(ut)}{u}\right]^2 (2\,du) = 2\int \left[\frac{\sin(ut)}{u}\right]^2 du.$$

The integral

$$\int_{-\infty}^{\infty} \left[\frac{\sin(ut)}{u}\right]^2 du$$

is equal to $|t|\pi$.

So the result is $2|t|\pi$. Assuming $t > 0$, this is $2\pi t$.

The slide on page 45 also shows a related integral:

$$\int_{-\infty}^{\infty} \frac{\sin^2(xt)}{x^2} dx = \pi t \quad \text{(if } x \text{ is the integration variable).}$$

This integral is correct.

Let's re-verify the integral of the sinc-squared function we have:

$$\int_{-\infty}^{\infty} \left[\frac{\sin\left(\frac{Yt}{2}\right)}{\frac{Y}{2}}\right]^2 dY.$$

This is

$$4\int \frac{\sin^2\left(\frac{Yt}{2}\right)}{Y^2} dY.$$

Let $Z = \frac{Yt}{2}$. Then $dY = \frac{2\,dZ}{t}$.

Substituting, we obtain

$$= 4\int \frac{\sin^2(Z)}{\left(\frac{2\,Z}{t}\right)^2}\left(\frac{2\,dZ}{t}\right) = 4\int \frac{t^2\sin^2(Z)}{4\,Z^2}\left(\frac{2\,dZ}{t}\right) = 2\,t\int \frac{\sin^2(Z)}{Z^2} dZ.$$

Since

$$\int \frac{\sin^2(Z)}{Z^2} dZ = \pi,$$

the result is $2\pi t$.

So, yes, the integral of the sinc-squared kernel

$$\left[\frac{\sin\left(\frac{Yt}{2}\right)}{\frac{Y}{2}}\right]^2$$

over dY is indeed $2\pi t$.

With $\rho(\omega_{ba})$ pulled out and the integral evaluated as $2\pi t$, we can now **Obtain a simple expression** for $P_{ab}(t)$, which will be on the next slide.

Page 46:

Following the approximation and integration from the previous slide, we now get the simplified expression for the transition probability $P_{ab}(t)$ induced by broadband radiation, and the corresponding absorption rate.

The transition probability $P_{ab}(t)$ is:

$$P_{ab}(t) = \frac{\pi}{\epsilon_0 \hbar^2} D_{ab}^2 \rho(\omega_{ba}) t$$

Let's verify this. The prefactor on page 44 was $\frac{D_{ab}^2}{2\epsilon_0 \hbar^2}$. We multiplied this by $\rho(\omega_{ba})$ and the integral result $(2\pi t)$.

So, $\frac{D_{ab}^2}{2\epsilon_0 \hbar^2} \times \rho(\omega_{ba}) \times (2\pi t) = \frac{\pi D_{ab}^2 \rho(\omega_{ba}) t}{\epsilon_0 \hbar^2}$.

This matches the slide. It's important to remember that D_{ab}^2 here should really be $|D_{ab}|^2$, the squared magnitude of the dipole matrix element.

This result is very significant: the transition probability $P_{ab}(t)$ now grows **linearly with time** t.

Consequently, the rate of absorption, Capital R sub ab, which is $\frac{dP_{ab}}{dt}$, becomes constant:

Capital R sub ab equals d by dt of P sub ab of t, which gives:

$$R_{ab} = \frac{\pi}{\epsilon_0 \hbar^2} D_{ab}^2 \rho(\omega_{ba})$$

Again, D_{ab}^2 should be $|D_{ab}|^2$.

This constant rate of absorption is a hallmark of transitions induced by a broadband, incoherent field (or a field whose coherence time is much shorter than t). This is essentially Fermi's Golden Rule for this system: the transition rate is proportional to the square of the matrix element and the density of states (here represented by $\rho(\omega_{ba})$).

The final bullet point draws an important contrast:

This linear-in-time behaviour (for $P_{ab}(t)$**)** contrasts with the quadratic growth ($P_{ab}(t) \propto t^2$) seen for monochromatic resonant excitation in the perturbative regime.

Recall from page 38, for monochromatic light on resonance, $P_{\text{res}}(t) = \left(\frac{\Omega_{ab} t}{2}\right)^2$, which is quadratic in t.

So, the time dependence of the transition probability is fundamentally different depending on whether the excitation is monochromatic and coherent over time t, or broadband and incoherent. Broadband excitation leads to a constant transition *rate*.

The "---" indicates the end of this particular thought.

Page 47:

Now we connect our result for the broadband absorption rate to one of Einstein's fundamental coefficients.

Slide 17: Connection to Einstein B Coefficient.

The first point reminds us of a key assumption in Einstein's original derivation of the A and B coefficients: **The radiation field used in Einstein's derivation was assumed to be isotropic (asterisk). Our plane-wave result, which we used to define** $D_{ab} = \langle a|(-er \cdot \hat{e})|b\rangle$ based on a specific field polarization $\hat{e}$, must therefore be angle-averaged. Einstein considered atoms in equilibrium with thermal blackbody radiation, which is isotropic (looks the same in all directions) and unpolarized. Our $D_{ab} = \langle a|(-er \cdot \hat{e})|b\rangle$ involved a specific polarization direction $\hat{e}$. To compare with Einstein's B coefficient, we need to average over all possible orientations of the atomic dipole relative to the field polarization, or equivalently, average over all field polarization directions if the dipoles are fixed.

The second bullet gives the result of this averaging for **randomly oriented dipoles**: The expectation value of p_z^2 equals $\frac{1}{3}$ times the expectation value of p^2. Here, p_z could be the component of the dipole moment along a specific field direction, and p^2 is its total squared magnitude. More relevant to our D_{ab}: our D_{ab}^2 was effectively $|\left(\hat{e} \cdot \vec{d}_{ab}\right)|^2$, where

$$\vec{d}_{ab} = \langle a| - er|b\rangle$$

is the vector dipole matrix element. When we average $\left(\hat{e} \cdot \vec{d}_{ab}\right)^2$ over all orientations of $\vec{d}_{ab}$ relative to a fixed $\hat{e}$ (or vice versa), the result is $\frac{1}{3}|\vec{d}_{ab}|^2$. So, the angle-averaged value of our $|D_{ab}|^2$ (which was specific to one polarization) becomes $\frac{1}{3}$ times the squared magnitude of the *vector* dipole matrix element between states a and b. Let's denote this true squared dipole matrix element as $|d_{ab}^{\text{true}}|^2$. So,

$$|D_{ab}|^2_{\text{averaged}} = \frac{1}{3} |d_{ab}^{\text{true}}|^2.$$

The third bullet states: **Replacing** $|D_{ab}|^2$ with $|D_{ab}|^2$ divided by 3 in our previous rate R_{ab} yields: $R_{ab} = \rho(\omega_{ba})\, B_{ab}$. Our previous rate (from page 46) was

$$R_{ab} = \frac{\pi}{\epsilon_0\, \hbar^2} |D_{ab}|^2_{\text{before avg}}\, \rho(\omega_{ba}).$$

If we replace $|D_{ab}|^2_{\text{before avg}}$ with $\frac{1}{3}|d_{ab}^{\text{true}}|^2$, then:

$$R_{ab} = \frac{\pi}{3\, \epsilon_0\, \hbar^2} |d_{ab}^{\text{true}}|^2\, \rho(\omega_{ba}).$$

This equation is now in the form $R_{ab} = B_{ab}\, \rho(\omega_{ba})$, which is precisely the *definition* of the Einstein B coefficient for absorption (or stimulated emission, as B_{ab} and B_{ba} are related by degeneracies). Here, B_{ab} would be for the transition from a to b.

Page 48:

Following the connection to the Einstein B_{ab} coefficient, this slide gives the explicit expression for B_{ab} that results from our derivation.

It says: **with**

$$B_{ab} = \frac{\pi e^2}{3\epsilon_0 \hbar^2} |D_{ab}|^2.$$

Let's be very careful about the D_{ab} in *this* formula for B_{ab}.

On the previous slide, we had

$$R_{ab} = \frac{\pi}{3 \epsilon_0 \hbar^2} \left| d_{\text{true\_\text{ab}}} \right|^2 \rho(\omega_{ba}).$$

And

$$R_{ab} = B_{ab}\rho(\omega_{ba}).$$

So,

$$B_{ab} = \frac{\pi}{3 \epsilon_0 \hbar^2} \left| d_{\text{true\_\text{ab}}} \right|^2.$$

Here, $\left| d_{\text{true\_\text{ab}}} \right|^2$ is the squared magnitude of the electric dipole *moment* matrix element, $|\langle a| {-e\,\vec{r}} |b\rangle|^2$.

If D_{ab} in the slide's B_{ab} formula is meant to be the matrix element of the position vector *r* alone, i.e.,

$$D_{ab} = |\langle a|\vec{r}|b\rangle|,$$

then

$$\left| d_{\text{true\_\text{ab}}} \right|^2 = e^{2} \left|\langle a|\vec{r}|b\rangle\right|^2 = e^{2} \left| D_{\text{ab\_\text{of}\_\text{r}}} \right|^2.$$

In that case,

$$B_{ab} = \frac{\pi e^{2}}{3 \epsilon_0 \hbar^2} \left| D_{\text{ab\_\text{of}\_\text{r}}} \right|^2.$$

This is a standard form if D_{ab} there refers to the position matrix element.

It's essential to be clear about whether D_{ab} includes the charge e or not, and whether it's a scalar component or a vector magnitude. Assuming the formula is for the commonly tabulated B_{ab} coefficient, D_{ab} in this context typically refers to the magnitude of the matrix element of the position operator r.

The slide then makes a very important concluding statement:

Thus, experimental determination of B_{ab}, or an ab-initio (asterisk, meaning from first principles theory) calculation of D_{ab} (the dipole matrix element), immediately provides all other Einstein coefficients (A and the other B) via the detailed balance relations.

This highlights the power of these connections. If you can measure B_{ab} (e.g., from absorption strength), you can use Einstein's relations (which link A_{ba} to B_{ba}, and B_{ba} to B_{ab} via degeneracies) to find A_{ba} (the spontaneous emission rate) and B_{ba} (the stimulated emission coefficient for the reverse transition). Similarly, if you can theoretically calculate the dipole matrix element D_{ab} from quantum mechanics (e.g., from computed wavefunctions), you can predict B_{ab} and then all the other coefficients. This interconnectedness is a beautiful aspect of the theory of radiation.

The "---" suggests this is a key summary point for this section.

Page 49:

Now we need to consider a common situation in real atoms and molecules: energy levels are often degenerate. This is Slide 18: **Degeneracy and Line Strength,** S_{ik}.

The first bullet point explains the issue: **For levels possessing degeneracy,** g_i and g_k (for example, due to magnetic sublevels), the transition rate must be calculated by summing over all possible final sublevels and averaging over all initial sublevels.

Let's say our initial level 'i' is actually a manifold of g_i degenerate states (e.g., different M_J values for a given J). Similarly, the final level 'k' might consist of g_k degenerate states. A transition can occur from any initial sublevel to any final sublevel. To get the overall rate for the $i \rightarrow k$ transition, we need to consider all these possibilities. The standard procedure is to sum the rates for transitions from a specific initial sublevel to all possible final sublevels, and then average this sum over all equally populated initial sublevels (assuming thermal equilibrium or unpolarized excitation).

To handle this systematically, we Define the line strength*, often denoted S_{ik} (Capital S_{ik}). The slide gives the definition:

$$S_{ik} = \sum_{m=1}^{g_\mathrm{i}} \sum_{n=1}^{g_\mathrm{k}} \left| D_{ik}^{(mn)} \right|^2$$

Let's break this down:

* g_i is the degeneracy of the initial level i. 'm' is an index for the initial sublevels ($m = 1,2, \dots, g_\mathrm{i}$). * g_k is the degeneracy of the final level k. 'n' is an index for the final sublevels ($n = 1,2, \dots, g_\mathrm{k}$). * $D_{ik}^{(mn)}$ is the dipole matrix element connecting initial sublevel 'm' of level i to final sublevel 'n' of level k. This D would be $|\langle i, m$ | operator | $k, n \rangle|$. The operator is typically the electric dipole moment operator. * So, $\left| D_{ik}^{(mn)} \right|^2$ is the squared magnitude of this specific sublevel-to-sublevel matrix element. *The line strength S_{ik}* is the sum of these squared magnitudes over all possible pairs* of initial and final sublevels.

The line strength S_{ik} is a fundamental quantity that encapsulates the total "strength" of the radiative transition between the entire level 'i' and the entire level 'k', accounting for all contributing sublevel transitions. It's independent of the polarization of light if summed over all components of D. It's a purely atomic/molecular property. Atomic physicists often tabulate S_{ik} values.

Page 50

Having defined the line strength S_{ik}, we can now write a **Generalized Einstein coefficient** that incorporates degeneracy.

The slide presents the Einstein B coefficient for a transition from level i to level k (e.g., absorption if i is lower, or stimulated emission if i is upper, though B_{ik} usually refers to $i \rightarrow k$ process probability per unit energy density):

$$B_{ik} = \frac{\pi}{3\epsilon_0 \hbar^2 g_{\mathrm{i}}} S_{ik}$$

Let's analyze this:

* S_{ik} is the line strength we just defined: $\sum_{\mathrm{m}} \sum_{\mathrm{n}} \left| D_{ik}^{(mn)} \right|^2$, where $D_{ik}^{(mn)}$ is the dipole moment matrix element (e.g., $\langle i, m | e\, r | k, n \rangle$).

g_{i} is the statistical weight (degeneracy) of the initial* level 'i'. The $\frac{1}{g_{\mathrm{i}}}$ factor here accounts for averaging over the initial sublevels, assuming they are equally populated.

* The factor $\frac{\pi}{3\epsilon_0 \hbar^2}$ is familiar from our previous expression for B_{ab} (page 48, where $B_{ab} = \frac{\pi e^2}{3\epsilon_0 \hbar^2} |\langle a | r | b \rangle|^2$). If $S_{ik} = \sum_{m,n} |\langle i, m | e\, \vec{r} | k, n \rangle|^2$ (sum of squared dipole *moment* matrix elements), then the formula for B_{ik} is correct as written. If $S_{ik} = \sum_{m,n} |\langle i, m | \vec{r} | k, n \rangle|^2$ (sum of squared position matrix elements), then an e^2 factor is missing in the numerator of B_{ik} on the slide (it should be $\frac{\pi e^2 S_{ik}}{3\epsilon_0 \hbar^2 g_{\mathrm{i}}}$). Given typical conventions for line strength S including the charge e, the slide's formula $B_{ik} = \frac{\pi S_{ik}}{3\epsilon_0 \hbar^2 g_{\mathrm{i}}}$ is often used.

The next bullet highlights the practical utility of line strengths:

* **Tables of** S_{ik} are standard outputs of sophisticated atomic-structure codes (e.g., GRASP, CIV3) and directly feed astrophysical modelling software.

Calculating line strengths from first principles requires complex quantum mechanical calculations of atomic wavefunctions and matrix elements. Computer programs like GRASP (General-purpose Relativistic Atomic Structure Program) or CIV3 (Configuration Interaction Version 3) are designed for this. The resulting S_{ik} values are crucial inputs for astrophysical models that interpret stellar and interstellar spectra, as well as for plasma physics, laser design, and other applications.

Finally, a very important practical warning:

* **Beware of unit conventions: switching from angular frequency** ω to ordinary frequency ν introduces a factor of 2π.

The Einstein coefficients and spectral energy density are defined. For instance, spectral energy density can be defined per unit angular frequency, ρ_ω, or per unit ordinary frequency, ρ_ν. Since $\omega = 2\pi\nu$, it follows that $d\omega = 2\pi\, d\nu$. For the energy in a given spectral interval to be the same, $\rho_\omega\, d\omega$ must equal $\rho_\nu\, d\nu$. Substituting $d\omega$ gives $\rho_\omega \times 2\pi\, d\nu = \rho_\nu\, d\nu$. This implies that $\rho_\nu = 2\pi\, \rho_\omega$.

Now, the Einstein B coefficient is defined such that the transition rate is B times ρ. So, if we have B_ω, the rate is $B_\omega \times \rho_\omega$. If we have B_ν, the rate is $B_\nu \times \rho_\nu$. For the rate to be the same, $B_\omega \times \rho_\omega$ must equal $B_\nu \times (2\pi\rho_\omega)$. This means that $B_\omega = 2\pi\, B_\nu$, or conversely, $B_\nu = \frac{B_\omega}{2\pi}$.

The Einstein A coefficient, being a spontaneous rate, is unaffected by this. However, the relationship between A and B coefficients will look different depending on whether B is defined with respect to ω or ν. For example, the ratio $\frac{A_{ki}}{B_{ki}}$ is often written as $\frac{8\pi h\nu^3}{c^3}$ if B_{ki} is B_ν. If B_{ki} is B_ω, then $\frac{A_{ki}}{B_{ki}}$ is $\frac{\hbar\omega^3}{\pi^2 c^3}$, or similar, depending on exact forms. So, always, always check the definitions when using tabulated values or formulas from different sources. This is a common pitfall that can lead to errors of 2π if you're not careful!

Page 51

Alright, let's move on to Slide 19, which discusses an **Effective Two-Level System with Open Decay Channels.** So far, our two-level atom model ($|a\rangle$ and $|b\rangle$) has largely been treated as a closed system, especially when we normalized $|a|^2 + |b|^2 = 1$. But real life is more complicated.

The first bullet point brings us to **Reality: neither ket a nor ket b is truly closed; spontaneous emission, collisions, or other mechanisms remove population.** This is a critical point. Even if we are driving the transition between $|a\rangle$ and $|b\rangle$ with a laser, both level $|a\rangle$ and level $|b\rangle$ can decay to *other* levels outside of our two-level consideration. For example, the upper state $|b\rangle$ might spontaneously emit to level $|a\rangle$, but it might also spontaneously emit to some other lower level, say $|c\rangle$. Or, it could be collisionally quenched to $|a\rangle$ or to $|c\rangle$. Similarly, the lower state $|a\rangle$ might not be perfectly stable; it could be collisionally excited to other states, or if it's not the true ground state, it might decay to even lower states. These processes act as "leaks" or "sinks" for the population within our idealized two-level system.

So, how do we account for these additional loss mechanisms? The second bullet point suggests a pragmatic approach: **Phenomenologically include decay constants.** Instead of trying to model all possible other levels and interactions explicitly (which would make our two-level model intractable), we can introduce effective decay rates for states $|a\rangle$ and $|b\rangle$ that lump together all these loss processes.

Specifically, as the next two bullets define:

- γ_a (lowercase Greek gamma subscript a): This represents the **total decay rate out of state** $|a\rangle$ due to all processes *other than* transitions to state $|b\rangle$ induced by our coherent field. This could include spontaneous decay from $|a\rangle$ to other levels (if $|a\rangle$ is not the ground state), collisional de-excitation of $|a\rangle$ to other levels, or even ionization from $|a\rangle$. Its units are inverse time (e.g., s^{-1}).

- γ_b (lowercase Greek gamma subscript b): Similarly, this represents the **total decay rate out of state** $|b\rangle$ due to all processes *other than* coherent transitions to state $|a\rangle$ (like stimulated emission to $|a\rangle$) or absorption from $|a\rangle$. This γ_b would include spontaneous emission from $|b\rangle$ to any level (including

$|a\rangle$, but also any other level $|c\rangle$, $|d\rangle$, etc.), collisional quenching of $|b\rangle$ to any other level, ionization from $|b\rangle$, and so on.

By introducing these phenomenological decay rates γ_{a} and γ_{b}, we acknowledge that our two-level system is "open" and that population can be lost from it. This will modify our coupled amplitude equations, as we'll see next.

Page 52:

Now that we've introduced the phenomenological decay rates γ_{a} and γ_{b} for our open two-level system, let's see how they modify the coupled amplitude equations. We'll consider these equations under the Rotating Wave Approximation (RWA), which we previously found to be:

$$\dot{a} = -\frac{i}{2}\Omega_{ab}\exp(i\delta t)\, b$$

$$\dot{b} = -\frac{i}{2}\Omega_{ba}\exp(-i\delta t)\, a$$

where $\delta = \omega_{field} - \omega_{atomic}$.

The slide shows the **Modified amplitude equations (under RWA)**:

The time derivative of $a(t)$, $\dot{a}(t)$, is now:

$$\dot{a}(t) = -\frac{i}{2}\Omega_{ab}\exp(i\Delta\omega\, t)\, b(t) - \frac{\gamma_{\mathrm{a}}}{2}\, a(t)$$

The time derivative of $b(t)$, $\dot{b}(t)$, is now:

$$\dot{b}(t) = -\frac{i}{2}\Omega_{ab}\exp(-i\Delta\omega\, t)\, a(t) - \frac{\gamma_{\mathrm{b}}}{2}\, b(t)$$

(Note: the slide uses Ω_{ab} in both equations; more symmetrically, the second equation might have $\Omega_{ba} = \Omega_{ab}^{*}$. Assuming D_{ab} is real, $\Omega_{ab} = \Omega_{ba}$.)

Let's analyze these modified equations:

* The first terms on the right-hand side of each equation are familiar: they describe the coherent coupling between states $|a\rangle$ and $|b\rangle$ driven by the light field with Rabi frequency Ω_{ab} and detuning $\Delta\omega$. These terms drive population back and forth.

* The new terms are **minus** $\frac{\gamma_{\text{a}}}{2}\,a(t)$ in the equation for $\dot{a}(t)$, and **minus** $\frac{\gamma_{\text{b}}}{2}\,b(t)$ in the equation for $\dot{b}(t)$. These represent the decay of the *amplitudes* $a(t)$ and $b(t)$ due to the loss rates γ_{a} and γ_{b}. Why $\gamma/2$ for the amplitude decay, when γ is a population decay rate? Recall that population is $|a|^2$. If, for example, population N_{a} decays as

$$\frac{dN_{\text{a}}}{dt} = -\gamma_{\text{a}}\,N_{\text{a}},$$

and $N_{\text{a}} = |a|^2$, then

\[\frac{d|a|^2}{dt} = \left(a^ *\frac{da}{dt} + a \frac{da*^}{dt}\right) = -\gamma_\text{a} \, |a|^2.\]

If

$$\frac{da}{dt} = -\frac{\gamma_{\text{a}}}{2}\,a,$$

then

\[a^ *\frac{da}{dt} + a \frac{da*^}{dt} = a\left(-\frac{\gamma_\text{a}}{2}\right)a + a\left(-\frac{\gamma_\text{a}}{2}\right)a^** = -\gamma_\text{a} \, |a|^2.\]

So, a population decay rate γ corresponds to an amplitude decay rate of $\gamma/2$. This is correct.

2. **Steady-State Solutions**: Because of these decay terms, if the laser field is applied continuously, the system will evolve towards a steady state where $\dot{a} = 0$ and $\dot{b} = 0$. In this steady state, the populations $|a|^2$ and $|b|^2$ will be constant in time. These steady-state populations depend on the laser

intensity (via Ω_{ab}), detuning ($\Delta\omega$), and the decay rates ($\gamma_{\mathrm{a}}, \gamma_{\mathrm{b}}$). Finding these steady-state solutions is crucial for understanding many phenomena in laser spectroscopy, such as: * **Fluorescence spectroscopy**: The amount of fluorescence light emitted from state $|b\rangle$ is proportional to the steady-state population of $|b\rangle$. * **Saturation spectroscopy**: When the laser field is strong, it can significantly alter the populations (e.g., reduce the population difference $|a|^2 - |b|^2$). This "saturation" effect, which depends on reaching a steady state, is the basis for techniques like saturated absorption spectroscopy.

These modified equations are often the starting point for deriving the optical Bloch equations, which provide a more complete description of a dissipative two-level system, often in terms of the density matrix.

Page 53:

This slide provides a simple but effective energy level diagram illustrating an **Effective Two-Level System with Decay Channels.**

Let's examine the diagram:

The vertical axis is labeled **Energy**, increasing upwards.

We see two horizontal lines representing our two atomic levels:

– A lower level labeled $\ket{a}$. – An upper level labeled $\ket{b}$.

A **red double-headed vertical arrow** connects $\ket{a}$ and $\ket{b}$. This arrow is labeled with Capital Omega (Ω). This represents the coherent coupling between the two levels driven by the external laser field, with a strength characterized by the Rabi frequency Ω. The double arrow indicates that the field can drive transitions both upwards (absorption from $\ket{a}$ to $\ket{b}$) and downwards (stimulated emission from $\ket{b}$ to $\ket{a}$).

Now, critically, we see **decay channels** depicted by green curvy arrows:

From the upper level $\ket{b}$, there's a green curvy arrow pointing downwards and outwards, labeled with γ. This represents the total decay rate out of state $\ket{b}$ due to all incoherent processes (like spontaneous emission to any level, collisional quenching, etc.), which we denoted γ_{b} on the previous slide. This arrow leads "out" of the two-level system or back to lower levels in an incoherent way.

Similarly, from the lower level $\ket{a}$, there's another green curvy arrow pointing downwards and outwards, also labeled with γ. This represents the total incoherent decay rate out of state $\ket{a}$, which we denoted γ_{a}. (The diagram uses a generic γ; we should remember they can be different: γ_{a} and γ_{b}). This implies that even state $\ket{a}$ might not be perfectly stable and can lose population.

This diagram visually summarizes the physics we've just described with the modified amplitude equations. We have a coherent drive (Ω) trying to move population between $\ket{a}$ and $\ket{b}$, and simultaneously, we have incoherent decay processes (γ_{a}, γ_{b}) trying to remove population from these levels or relax them. The interplay between Ω and these gammas determines the dynamics and steady-state behavior of the system. For example, if the gammas are very large, it might be difficult to build up significant population in state $\ket{b}$ even with a strong Ω, as the population leaks out too quickly.

At the bottom right, it notes "KFUPM (Term 251)," which is course information.

Page 54:

We've reached Slide 20, which provides a **Summary and Outlook** for this chapter or section on transition probabilities and the two-level atom model.

The opening statement encapsulates the overarching theme:

Transition probabilities extend spectroscopy from qualitative fingerprints to quantitative diagnostics*.

The asterisk likely refers back to earlier discussions about how knowing A-values allows us to determine temperatures, abundances, etc. Without these quantitative measures of how likely transitions are, spectra would just be patterns. With them, they become powerful tools for measuring physical conditions.

The first main bullet point summarizes a key connection:

* **Spontaneous lifetime,** τ (lowercase Greek tau), connects directly to the Einstein A coefficient; measurement of τ is experimentally straightforward (e.g., using time-resolved fluorescence).

We learned that the total spontaneous decay rate from an excited state i, A_i, is the sum of A_{ik} to all lower states k. The lifetime τ_i is simply $\frac{1}{A_\mathrm{i}}$. So, if you can measure the lifetime of an excited state (for example, by exciting it with a short pulse of light and then observing how the fluorescence intensity decays over time), you directly determine A_i. This is a very common experimental method for obtaining A coefficients or, more precisely, total decay rates from which A_{ik} values can sometimes be extracted if branching ratios are known.

This first point emphasizes the experimental accessibility and fundamental importance of lifetimes and their relation to A coefficients, which are a specific type of transition probability.

Page 55:

Continuing with the Summary and Outlook:

The second bullet point summarizes the insights gained from our semi-classical two-level model: * **The Semiclassical two-level model reveals how external fields drive transitions; the Rabi frequency, Capital**

Omega Ω, quantifies the coupling strength; and the weak-field versus strong-field regimes are distinguished.

This is a concise recap of a large part of what we've covered. We saw how a classical electric field interacts with a quantum two-level atom via the dipole interaction. The strength of this coherent interaction is characterized by the Rabi frequency Ω, which depends on the field amplitude and the dipole matrix element. We also saw that if the interaction is weak or short $\left(\frac{\Omega t}{2} \ll 1\right)$, we are in a perturbative (weak-field) regime leading to a sinc-squared transition probability. If the interaction is strong or long, we enter the strong-field regime characterized by Rabi oscillations, requiring a non-perturbative solution. This distinction is fundamental to understanding light-matter interactions.

The third bullet point highlights the outcome of broadband excitation: * **Broadband excitation yields a constant absorption rate, proportional to the absolute square of the dipole matrix element** $|D_{ab}|^2$, which leads naturally to the Einstein B coefficient.

When we considered excitation by a field with a broad spectrum (where $\rho(\omega)$ is slowly varying compared to the atomic response width), we found that the transition probability grows linearly with time, meaning the transition *rate* is constant. This rate is proportional to $|D_{ab}|^2$ and $\rho(\omega_{\text{atomic}})$, and this directly allowed us to define and derive an expression for the Einstein B coefficient for absorption. This contrasts with the t^2 growth for coherent monochromatic excitation.

Finally, the last bullet point gives an **Outlook** towards more advanced topics that build upon what we've learned (though explicitly stating they are **not covered here** in this particular lecture segment): * **Next steps (not covered here): full density-matrix treatment (Bloch equations), interaction with pulsed lasers, coherent phenomena (Rabi flopping, Ramsey fringes, Autler-Townes splitting).**

This is a roadmap for further study in laser spectroscopy and quantum optics: - **Full density-matrix treatment (Bloch equations):** While we introduced phenomenological decay rates $\gamma_\mathrm{a}, \gamma_\mathrm{b}$ into the amplitude equations, a more rigorous and general way to handle open quantum systems, including relaxation and dephasing processes, is through the density matrix formalism. The optical Bloch equations are the equations of motion for the density matrix elements of a two-level atom interacting with a light field and coupled to a reservoir. - **Interaction with pulsed lasers:** We touched upon finite interaction time t. A more detailed study would involve considering the specific temporal shape of laser pulses and how that affects the atomic evolution. - **Coherent phenomena:** - **Rabi flopping:** We mentioned this – the periodic oscillation of population between two levels driven by a strong resonant field. - **Ramsey fringes:** A technique involving interaction with two separated oscillatory fields, used for ultra-high precision spectroscopy by effectively increasing the coherent interaction time. - **Autler-Townes splitting:** When a strong driving field is applied to a transition, it can split the energy levels involved, and this splitting can be probed by a second, weaker laser.

This summary beautifully ties together the concepts we've discussed – from the fundamental Einstein coefficients and their importance in diagnostics, to the detailed dynamics of a two-level atom interacting with light, and finally pointing towards the rich landscape of more advanced topics in the field. It underscores that a solid understanding of transition probabilities and basic light-matter interaction models is the bedrock for much of modern laser spectroscopy.