9. RADIATIVE PROCESSES I -- ATOMS AND LIGHT

We have discussed the field as a system and described it in terms of excitations of its normal modes. We now want to describe the coupling of the field to an atom.

The early approach, pioneered by Einstein, is to regard the atom as being a tiny structure within a field that is a very large reservoir of energy described in an essentially classical manner . In this approach, the atom's transitions are described but the field's gains and losses of energy are disregarded, and the physics of spontaneous emission is not included. The Einstein approach is worth studying because it is relatively simple, because it does provide useful insights on the relationship between spontaneous and stimularted processes, and because much of its terminology is still used to describe actual situations.

The more modern approach of quantum electrodynamics (QED) is to discuss both the atom and the field as quantum systems. The field is described in terms of the occupation numbers of its normal modes; the atom in terms of its quantum number. Energy is conserved in the atom-field system as described in QED, so that the emission of a photon from an atom is recognized as increasing the energy in a mode of the cavity. The results from QED enable us to describe not only radiative processes but also energy level displacements (e.g. the Lamb shift). Moreover, the methods of QED have shown the way for later theories (e.g. Quantum Chromodynamics) that find application over a much broader range of energies than we are discussing here. t

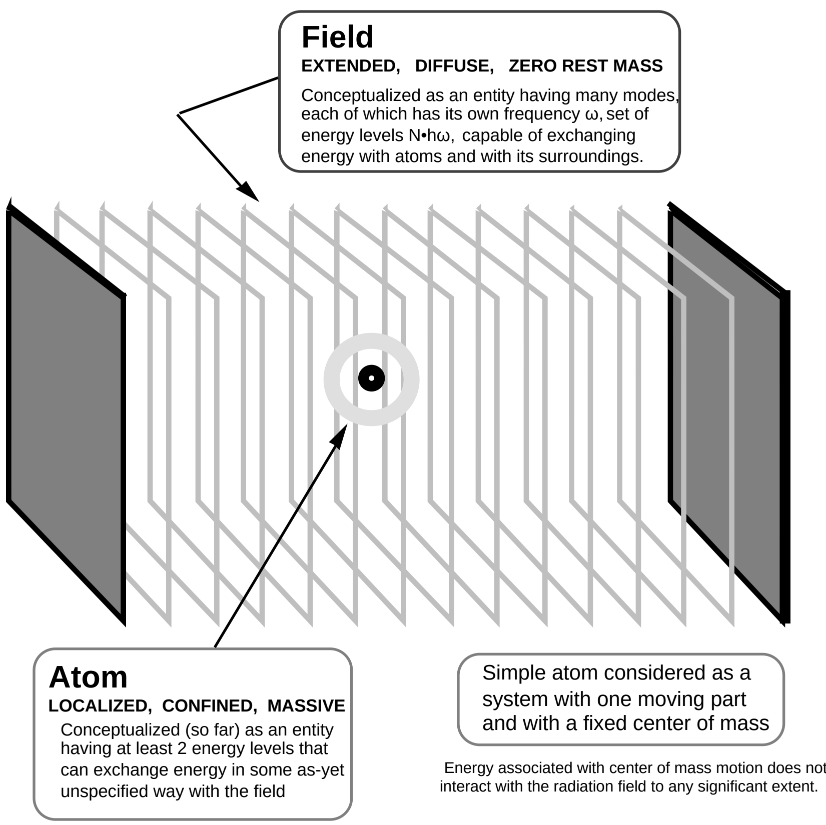


Fig. 9.1 Conceptual representation of an atom in a radiation field

What happens to resonant light as it passes through a dilute gas?

In the diagram below we depict the possible fate of photons as they go through a dilute gas. By "dilute" we mean that the density of atoms is low enough so that they may be considered for the most part as isolated entities, colliding only occasionally. The adjective "resonant" reminds us that the coupling of the radiation field to the isolated om is extremely small unless the energy of the photons is a match to the energy level separation between the ground state and the first excited state of the atom.

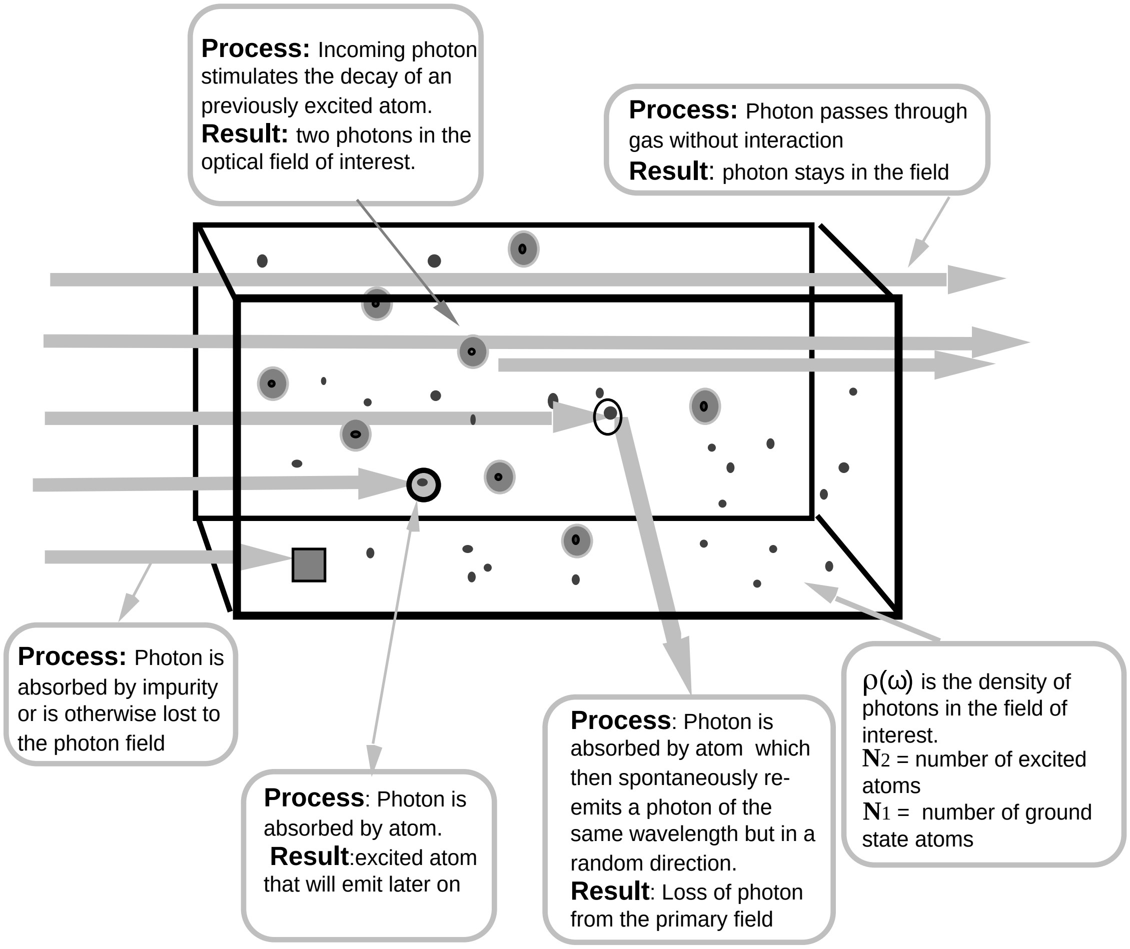


Fig. 9.2 Possible Interactions between radiation and atoms

9.1 The Einstein Description of Radiative Processes

Einstein described the exchange of energy between an atom and an electromagnetic field in terms of the quantized emission and absorption by the atom when it interacts with an essentialy classical field.

Suppose we have a sample of N atoms subjected to a time-varying electromagnetic field that has an energy density $\rho(\nu)$. [The function $\rho(\nu)d\nu$ gives the radiative energy per unit volume that exists in the frequency range $\nu \leftrightarrow \nu+d\nu$. It is proportional to the number of photons per unit volume that have energies in the range $h\nu \leftrightarrow h(\nu+d\nu)$.]

Suppose also that the atoms of this gas are in either of two energy states, with N_1 atoms in the state $|1\rangle$ with energy E_1, and N_2 in state $|2\rangle$ with a higher energy E_2. We take as given that the number of atoms $N=N_1+N_2$ is conserved. The atoms respond most strongly to radiation at their resonance frequency $\nu_{21} = (E_2 - E_1)/h$, and following Einstein, we can write rate equations that describe how the populations N_1 and N_2 change with time.

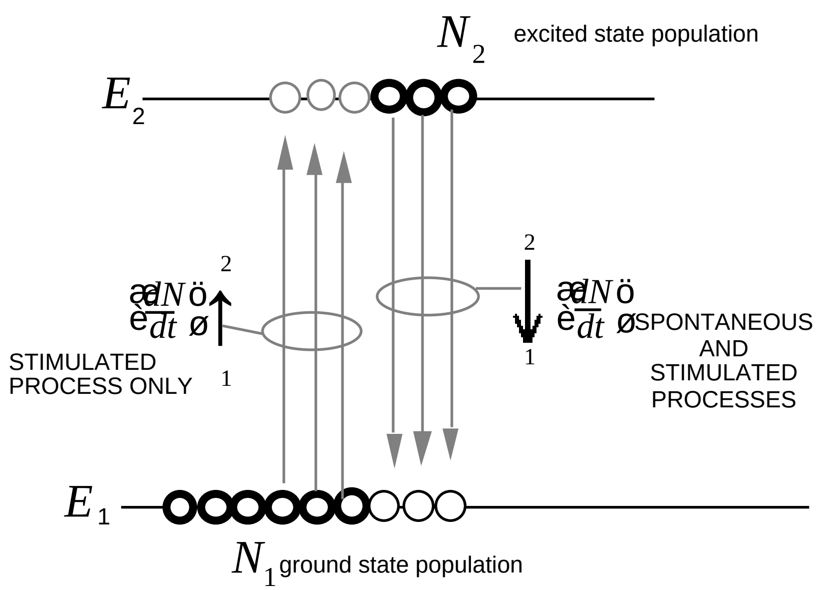


FIG 9.3 Radiative transitions in a Two-level system.

ABSORPTION: We can describe the process whereby atoms absorb photons and are stimulated to make the $1 \rightarrow 2$ transition by the radiation. For a sample of N_1 atoms in state $|1\rangle$ at time t, the rate of absorption is::

$$\left(\frac{dN}{dt}\right)_{\uparrow} = N_1(t)\; B_\nu \;\rho(\nu) \tag{9.1}$$

where B_ν, denoted the *Einstein B coefficient* , is a phenomenological quantity used to express the propensity of the atom to make the upward transition when subjected to radiation at frequency ν.

EMISSION: We now need to describe the rate for downward $(2 \rightarrow 1)$ transitions . If those transitions only occurred when stimulated by the applied radiation, then the rate at which a population $N_2(t)$ changes would be given by $N_2(t) \times B_\nu \times \rho(\nu)$. [This assumes microscopic reversibility in using the same rate coefficient for stimulated emission and stimulated absorption.]

However we know from observation that excited atoms tend to decay to lower energy levels even without apparent stimulation [i.e. in the limit $\rho(\nu) \rightarrow 0$], so the total rate from state 2 to state 1 must include the possibility that the $2 \rightarrow 1$ transition goes spontaneously. To allow for this, Einstein introduced *ad hoc* an additional term [the *Einstein A coefficient*] in the expression for downward transitions:

$$\underbrace{\left(\frac{dN}{dt}\right)\downarrow}_{\text{photons emitted per sec}} = \underbrace{N_2(t)}_{\text{atoms in excited state}} \left[\underbrace{A_{21}}_{\text{spontaneous}} + \underbrace{B_\nu \overbrace{\rho(\nu)}^{\text{photons}}}_{\text{stimulated}} \right] \tag{9.2}$$

[Cf. also Eq. (9.7) below]

The relative magnitudes of Einstein's phenomenological coefficients (A and B) can be found from thermodynamic arguments, as follows: In *any* equilibrium situation, the number of atoms undergoing transition $1 \rightarrow 2$ in absorption equals the number of those undergoing the $2 \rightarrow 1$ transition in emission:

$$\underbrace{\left(\frac{dN}{dt}\right)\uparrow = \left(\frac{dN}{dt}\right)\downarrow}_{\text{ANY equilibrium}} \longrightarrow \underbrace{N_2\left[A_{21} + B_\nu\rho\right] = N_1(t)\;B_\nu\;\rho}_{\text{ANY equilibrium}} \rightarrow \underbrace{\frac{N_2}{N_1} = \frac{B_\nu\;\rho}{A_{21} + B_\nu\rho}}_{\text{ANY equilibrium}} \tag{9.3}$$

Now a system in *thermal* equilibrium is a special (albeit common) condition where the disribution of energy in the system is given by a distribution function that depends only on the temperature.

For the atoms, we know (from Boltzmann) how the ratio of populations of the atomic levels (N_2/N_1 depends on temperature T_{ATOM}

For the radiation field, we know (from Planck) the form of $\rho(\nu)$ which specifies how the radiant energy is distributed over frequencies (ν) within a cavity when it is at temperature T_C.

$$\underbrace{\frac{N_2}{N_1} = e^{-\frac{\Delta E_{21}}{kT}}}_{\substack{\text{THERMAL equilibrium}\\ (\text{Boltzmann})}} \qquad \underbrace{\rho(\nu) = \frac{8\pi h}{c^3}\,\frac{\nu^3}{\left(e^{\frac{h\nu}{kT}} - 1\right)}}_{\text{THERMAL equilibrium (Planck)}} \tag{9.4a,b}$$

It is very common to have a composite system in which the atoms are in thermal equilibrium with the cavity ($T_{ATOM}=T_C = T$). With a common temperature T, we can then combine Eq. (9.3) and Eq. (9.4) to express the relative magnitudes of the A and B coefficients:

$$A_{21} = \left(\frac{8\pi h}{c^3}\right) B_{\nu} \, \nu^3 \tag{9.5}$$

Einstein reasoned that even though Eq. (9.5) had been derived from a thermal equilibrium situation, the derived relationship of A to B (the propensities for spontaneous/stimulated decay) should also be valid in non-equilibrium situations. From this he obtained an important result that applies when the cavity dimensions are large compared to the transition wavelength:

The tendency toward spontaneous decay increases with the *cube* of the transition frequency .

With this reasoning, Einstein felt justified in putting (9.5) into the expression (9.2) for spontaneous emission rate. The result is a prediction for the total rate at which atoms will make the $2 \rightarrow 1$ transition: It can be written in the form

$$\underbrace{\left(\frac{dN}{dt}\right)_{\downarrow}}_{\substack{\textit{emission}\\ \textit{rate}}} = \underbrace{N_2(t)}_{\substack{\textit{number}\\ \textit{of atoms}\\ \textit{in state 2}}} \overbrace{B_{21}}^{\substack{\textit{property}\\ \textit{of the}\\ \textit{atom}}} \left[\overbrace{\underbrace{\left(\frac{8\pi h}{c^3}\right) \nu^3}_{\substack{\textit{always}\\ \textit{present}}} + \underbrace{\rho(\nu)}_{\substack{\textit{applied}\\ \textit{by}\\ \textit{experimenter}}}}^{\substack{\textit{Properties of the}\\ \textit{radiation field}}} \right] \tag{9.6}$$

As it stands, the Einstein B coefficient is the only factor of (9.6) that is not yet specified in terms of known constants and experimental parameters. We will see later that B is a measure of how easily an applied field can induce an electric dipole moment in the atom. This dipole susceptibility (and therefore the value of B) depends on which states of the atom are actually involved in the transition.

Because the transitions, whether stimulated or spontaneous, are ascribable to an electric dipole coupling between the atom and its surroundings, one might think it more reasonable to write Eq.(9.2) in the form that distinguishes between the field we can control and the zero-point field that is always there:

$$\left(\frac{dN}{dt}\right)_{\downarrow} = N_2(t) \; B_{21} \left(\rho_{\substack{zero\\ point}} + \rho_{applied}\right) \tag{9.7}$$

But tradition dies hard, so the Einstein notation of Eqs.(9.2) and (9.6) is still the convention

Comments: The coefficients A and B both arise from the electric dipole interaction between the atom and the field, but A differs from B because it includes the density of zero-point field energy near the transition frequency ν, a density that increases dramatically with increasing energy.

Extrapolation from the thermal equilibrium case: Einstein's approach begins with an analysis of the situation at thermal equilibrium and then, by assumption of what would now be called time reversal invariance, extends to the more general case for the relationship between spontaneous and stimulated transition rates This is an example of how careful reasoning from a special case produces a far more general theoretical result.

[Can you think of other examples where reasoning from the partiicular case to the general has been important in physics?]

A-Coefficient: We will show, after heuristic justification, that the *spontaneous* transitions are a result of electric dipole interactions between the atom and the zero-point fluctuations of the electromagnetic field, i.e. fluctuations that are unavoidably present even if we make every effort to create a "zero E-field" condition.

B-Coefficient: We will show that *stimulated* transitions are a result of the electric dipole interactions between the atom and the applied electromagnetic field, a coupling that is particularly effective when the field photons have an energy to match E_2 -E_1 of the atom..

9.2 Natural Lifetime

The rate at which atoms are observed to make transitions from state 2 to state 1 is proportional to N_2, and as seen from Eq. (9.6) the transition will occur even if the experimenter applies no radiation at all [i.e. r(n) = 0]. Under those circumstance, the absorption $1 \rightarrow 2$ does not occur at all, so the excited state population that decays exponentially: :

$$N_2(t) = N_2(0)\ e^{-\gamma_{21} t} \qquad \text{where} \qquad \gamma_{21} = B_\nu \left(\frac{8\pi h}{c^3}\right) \nu^3 = A_{21} \tag{9.8}$$

The constant γ_{21} describes the decay rate of state 1;
$1/\gamma_{21} = T_{21}$ is the *natural lifetime* of the excited state |2

The dependence of the decay rate on the cube of the frequency has interesting implications. We know from direct measurements that the lifetime of the upper state in an allowed optical transition ($\Delta E \approx 2$eV; $\lambda \approx 600$ nm) is on the order of 10^{-8} sec. From this datum and the proportionality between lifetime and λ^3 we obtain the following table:

Wavelength	**Lifetime**
60 nm (soft x-rays)	10^{-11} sec
300 nm (near uv)	10^{-9} sec
600 nm (visible)	10^{-8} sec
1200 nm (near IR)	10^{-7} sec
106 nm (microwave)	10^{+2} sec

These values, estimated from our proportionality, are relatively close to what is found in nature.

The lifetimes constrain what can be done with excited atoms. For example, when constructing a laser one ordinarily needs to sustain an inverted population (N2>N1) long enough to get stimulated processes to take over. It gets progressively harder to create an maintain inverted populations as one moves form the visible to the x-ray regime; this accounts for the difficulties encountered when trying to build lasers for shorter wavelengths. Also it becomes harder to measure excited state lifetimes by direct timing as one goes from the infrared through the visible and into the ultraviolet; one usually relies on the spectral linewidth $\delta\nu$ to yield the lifetime via $\delta t = 1/\delta\nu$

[We note that by adding another active level it is possible under some circumstances to get lasing without actual population inversion]

At the other end of the scale, we find that the lifetimes become so long that much else can happen (e.g. wall collisions) before spontaneous decay occurs. In fact it is very difficult to measure lifetimes longer than 1 millisecond with conventional laboratory techniques. Not only do collisions interfere, but also the energy of the photons is so low that photon counting is no longer practical.

Lifetime and Linewidth

As discussed in Sec. 6, a sinusoidal oscillation at frequency ω_0 that dies away exponentially with decay constant γ, has a spectral distribution of radiation that follows from the Fourier transform of that decaying oscillation: The distribution, with its peak at frequency ω_0 and a width γ, is in the form of a *Lorentzian* distribution:

$$I(\omega) = \frac{\left(\frac{\gamma}{2}\right)^2}{\left[(\omega-\omega_0)^2 + \left(\frac{\gamma}{2}\right)^2\right]} \tag{9.9}$$

Exercise: show that (9.) is the transform of a decaying exponential.

Any excited atomic state has a finite decay rate because it is inevitably coupled to the ambient electromagnetic field, and usually the coupling increases with the cube of the excited state's energy (a consequence of the increased density of field states at higher freuqencies). Transitions that arise from coupling of the atom with the very weak fluctuations in what we conventionally call "zero field" give rise to spontaneous emission and the quantity $(1/\gamma)$ is called the *natural lifetime* of the state. And if this is the only inducement to decay, the observed line is said to have its *natural width*.

9.3 Gain and Loss of Energy in a Beam of Light

For the following discussion, it is important to note that in *spontaneous* emission, the emitted photon's phase and propagation direction are *random.* In *stimulated* emission, on the other hand, the emitted photon's phase and direction are strongly correlated with the phase and direction of the stimulating radiation.

Consider an ensemble of atoms in a long tube. The atoms have ground state |1 , excited state |2 .Radiation at frequency $\nu_{21} = (E_2 - E_1)/h$ enters the tube and causes transitions to occur at a rate (dN/dt)≡**R**. What can happen to a photon as it traverses the cell? What will come out?

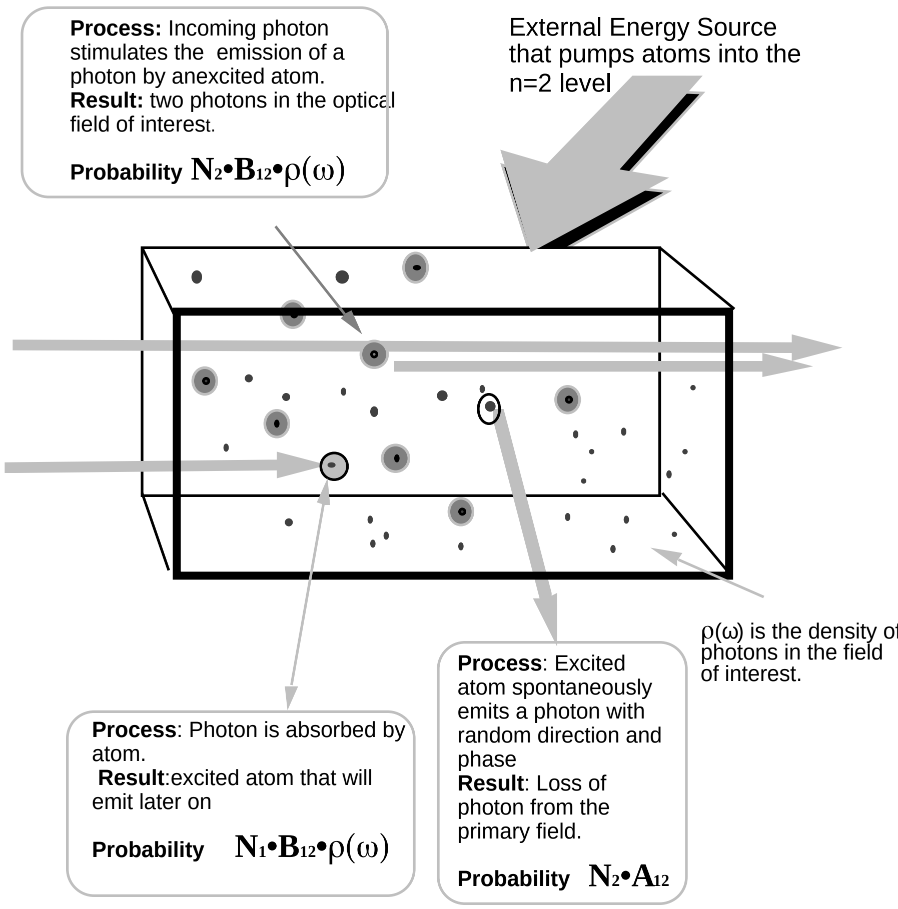


Fig. 9.4.

1. No interaction at all...just passes through. RESULT: one photon
2. May be absorbed by an atom that was in n=1 state RESULT: no photon
3. May stimulate emission of a photon from an atom. RESULT: two photons
4. May be absorbed or scattered by foreign atom. RESULT: no photon

Process #2 may not result in a permanent loss of the photon's energy since the newly-excited atom may be stimulated to emit by a later photon.

Process #4, on the other hand, symbolizes a permanent loss of the photon's energy from the useful reservoir in the system.

The incoming light induces 1 → 2 transitions in the atoms; the power absorbed from the light beam in this process is:

$$h\nu \; R\uparrow = h\nu \; N_1 \; B \; \rho \tag{9.10}$$

For convenience we abbreviate $\mathbf{B}_{21}$, the coefficient for stimulated transitions just as **B**, and $\rho(\nu_{21})$, the energy density at frequency ν_{21}, just as ρ,.

If we are in a regime where the spontaneous decay rate is negligible compared to the stimulated rate, the power put back into the beam is:

$$h\nu \; R\downarrow = h\nu \; N_2 \; B \; \rho \tag{9.11}$$

The net power gain is the rate of stimulated emission in the sample diminished by the rate of absorption:

$$G = \left(R\uparrow - R\downarrow\right) \; h\nu = \left[\left(N_2 - N_1\right) \; B \; \rho\right] h\nu \tag{9.12}$$

(Note that we have not yet included any power loss from dirt effects or from extracting optical power from the device.),

To get a positive gain we need the population of the excited state to exceed that of the ground state: $N_2 / N_1 > 1$. This condition is called a *population inversion* because it is the inverse of the population ratio expected in thermodynamic equilibrium at positive temperatures where excited states have lower populations: With $\Delta E_{21} > 0$, we expect $N_2/N_1 = \exp[-\Delta E_{21}/kT] < 1$.

Also to get positive gain an energy density $\rho(\nu_{21})$ large enough to assure that the stimulated transitions occur at a rate $\mathbf{B}\cdot\rho$ that completely dominates the spontaneous 2 → 1 transitions that occur at rate A. The relative importance of stimulated and /spontaneous) transitions (cf. Sec. 9.1) is given by

$$\frac{B}{A}\rho = \left(\frac{c^3}{8\pi h\nu^3}\right)\rho = \left(\frac{c^3}{8\pi\nu^2}\right)\frac{\rho}{h\nu} = \left(\frac{c^3}{8\pi\nu^2}\right)\langle n_\nu \rangle \tag{9.13}$$

The last equality follows since ρ is the energy density of the field at frequency ν, so the quantity $[\rho/(h\nu)] \equiv n_\nu$ is the number density of photons of frequency ν. We see from Eq.(9.13) that the relative importance of stimulated processes goes directly with the photon density and inversely with the square of the frequency. We need $\mathbf{B}\rho/\mathbf{A} >> 1$ in order that the device provide gain for radiation of frequency ν.

Suppose we want to construct a device (as in the above figure) from which we can extract some useful amount of light. Our principal way of putting raw energy *into* the system is by pumping atoms (by optical excitation, collisional excitation, or chemical reactions) to the n=2 state. Our energy output is a beam of light that derives its energy from the stimulated emission of radiation from the n=2 atoms.

Imagine now that this device is working and that we want to understand the criterion for its operation. In our mind's eye we stop everything at an arbitrary time t=0 and consider the gas of atoms and the ensemble of photons that interact with the atoms at that moment.

The ensemble of n_ν photons per unit volume in a cavity at time t=0 represents an energy density of $\rho = n_\nu \times h\nu$. A photon may bounce back and forth in the cavity for a few times if we have arranged appropriate mirrors, but eventually the photon leaves, either as part of the useful output or in some other way.

The probability (per unit time) for a photon's loss is fixed, by the experimental conditions, at a constant value; as a result, we anticipate that the photons will decay exponentially:

$$\langle n_\nu(t)\rangle = \langle n_\nu(0)\rangle \; e^{-t/\tau} \qquad \longrightarrow \qquad \frac{d\langle n_\nu\rangle}{dt} = \frac{-1}{\tau}\langle n_\nu(t)\rangle \tag{9.14}$$

Thus the energy density in this set of photons being lost at a rate,

$$\frac{d\rho}{dt} = \frac{-1}{\tau} \tag{9.15}$$

This energy loss must be overcome by the energy gain [Eq.(3.3.9)] from tapping the excited atoms that can add photons to the ensemble.

$$\underbrace{\left[(N_2 - N_1)\; B \;\; \rho\right] h\nu}_{Gain} \;\; \geq \underbrace{\frac{1}{\tau}\;\rho\;\; h\nu}_{Loss} \tag{9.16}$$

So the required population inversion is:,

$$(N_2 - N_1) \geq \frac{1}{\tau\;\; B} \tag{9.17}$$

where B is a measure of how easily the applied field induces the $2 \rightarrow 1$ transition and where τ is the lifetime of a photon within the cavity, taking all loss mechanisms into account.

Comments

Note that photons leave in direct proportion to their number, i.e. $d\rho/dt = B\rho$. Thus the length of time that a typical photon exists within the volume, the *photon lifetime* τ, is given by $\tau = 1/B$. In the simplest case the photon makes a single traverse of the cavity and the lifetime is on the order of $\tau \sim 1L/c$, where L is the geometric length of the cavity. If there are mirrors at the cavity ends, however, the photon may bounce back and forth many times and thus have a longer lifetime.

---> note that $d\rho/dt = \rho/\tau$ as τ is defined here.

These quantities have obvious interpretations:,

$N_2 \times B\rho$ rate at which atoms contribute photons to the field in the cavity.,

$N_1 \times B\rho$ = rate at which atoms absorb photons from the field in the cavity.,

$\delta N_2 /dt$ = rate at which pump mechanism provides atoms in the n=2 state.,

The rate at which cavity-mode photons are created is $N_2 \times B\rho$; the cavity mode photons are lost either by being absorbed by the N=1 atoms at a rate $N_1 \times B\rho$ or by leaving the cavity at a rate ρ/τ. If this is to be a steady state situation, we require:,

$$N_2 \; B\rho \geq N_1 \; B\rho + \frac{\rho}{\tau} \quad \to \quad \left(N_2 - N_1\right) \; B \geq \frac{1}{\tau} \tag{9.18}$$

So the population inversion required to sustain oscillations is as in Eq. (9.17) above, and we note that this does *not* depend on the number of photons within the cavity.,

The energy within the optical cavity is being lost at a rate ρ/τ. The only energy input to the cavity is that from the source that excites the atoms at a rate $\delta N_2/dt$ Evidently the required pumping rate is ,

$$\frac{\delta N_2}{dt} \geq \frac{\rho}{\tau} \tag{9.19}$$

9.4 Controlling Output Frequency: Gas Lasers and Dye Lasers:

In the previous discussion we emphasized the situation where a dilute gas of atoms serves as the active medium within an optical resonator. The atoms have a simple energy level structure with well-defined spectral line frequencies (although some tuning of the lines may be done with the Zeeman or Stark effects). The length of the cavity is adjusted so that one of its modes overlaps the desired spectral line of the atom.

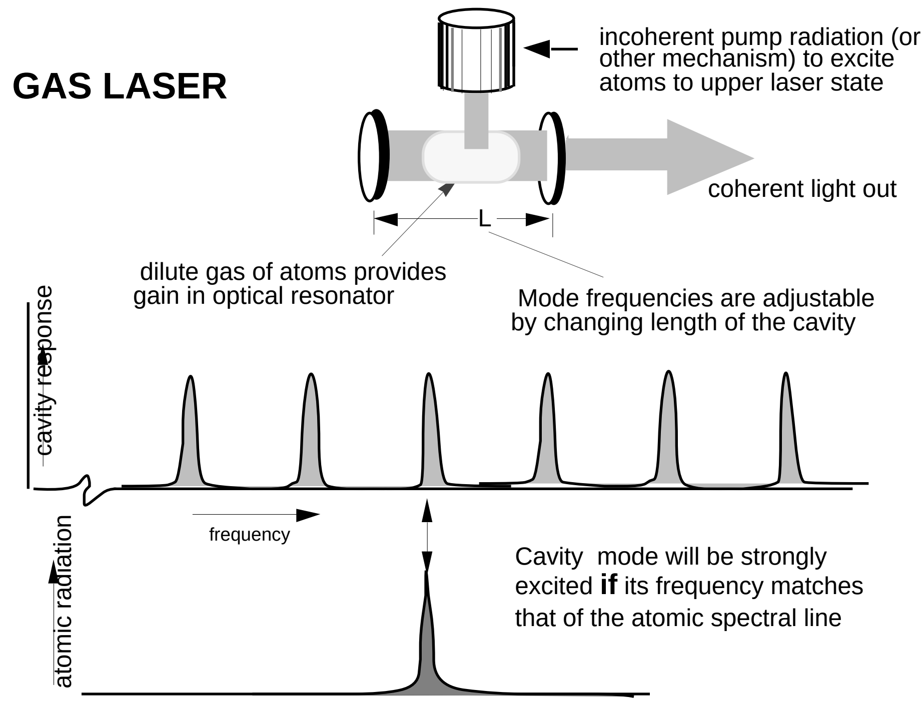


Fig. 9.5 Atomic resonance sets output frequency of gas laser

In this situation, *the natural transition frequency of the atom is the dominant influence on the frequency of the output radiation.*

The acoustic analogy is when one has a primary oscillator with set frequency (for example a standard tuning fork or one bar of a marimba) and then adjusts the length of a long tube to resonate with that frequency:

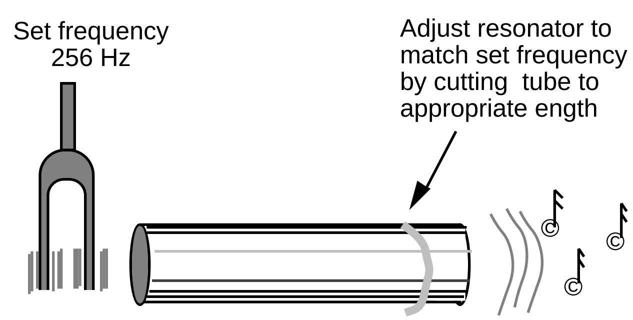


Fig 9.6 Adjusting acoustic resonator to match pre-set frequency

The n-th mode of a simple resonator of length L has a wavelength that is an integer fraction of the longest wavelength ($\lambda_{MAX} = 2L$). at which it will resonate. For most optical resonators, n is quite large, so we can express the mode spacing in a simple way:.

$$\underbrace{\lambda_n = \frac{2L}{n}}_{\text{n-th mode wavelength}} \rightarrow \quad \Delta\lambda \equiv \lambda_n - \lambda_{n-1} \xrightarrow{\text{large } n} \underbrace{\Delta\lambda \approx -\frac{\lambda_n}{n}}_{\text{wavelength difference between adjacent modes}} \qquad (9.20)$$

The cleanest laser operation is when the atomic transition aligns with a single cavity resonance, and when the intrinsic linewidth of the atomic transition is much less than the separation between adjacent cavity modes.

Dye Lasers

We now want to consider the situation in which the frequency of the cavity is the dominant influence on the frequency of the output radiation. To do this we use complicated molecules (e.g. a dye molecule such as Rhodamine 6G) for the active medium. The reason for this choice is that molecules, with their many rotational and vibration sublevels of each electronic level, can absorb and emit radiation over a wide range of wavelengths.

The absorption and emission spectrum of a typical dye molecule is as shown in the figure below. Absorption is usually out of one of the lower sublevels of N=1 since those will be most populated under ordinary thermal conditions. Absorption to a high level of N=2 may be followed by a fast, non-radiative relaxation to a lower state within the N=2 manifold, but that state will finally de-excite by emission of a photon in going to N=1.

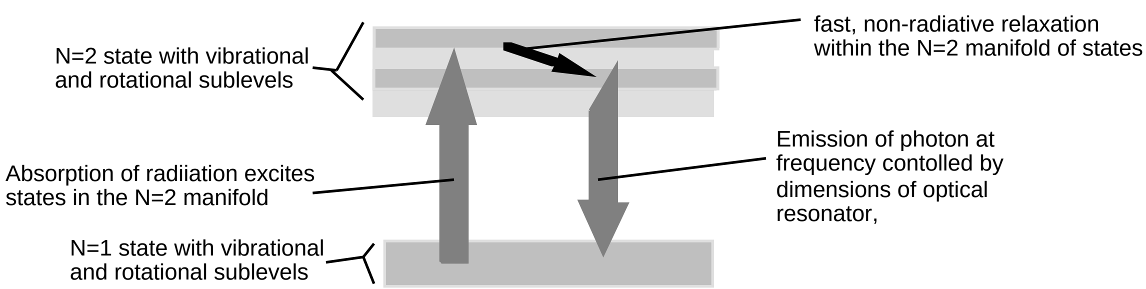


Fig. 9.7 Schematic diagram of dye molecule energy levels in laser operation.

If left to itself, an excited dye molecule in an N=2 state will undergo spontaneous emission, but that de-excitation, termed *fluorescence*, may be to any of the numerous N=1 sublevels, so the resultant light appears over a very broad range (often extending 50 nanometers or more)of the visible spectrum.

If, however, the excited dye molecule is subjected to the radiation field of well-defined frequency, as within an optical resonator, then the stimulation from this field will encourage the molecule to emit its energy in the form of a photon that is the same frequency and direction as the stimulating radiation. This contributes to the coherent radiation that is the output of the laser.

In a tunable laser of this sort, we arrange that dye molecules within the optical resonator are excited by a radiation or other means (the so-called "pump") and then are encouraged to de-excite by emission of a particular frequency that is determined by the resonator.

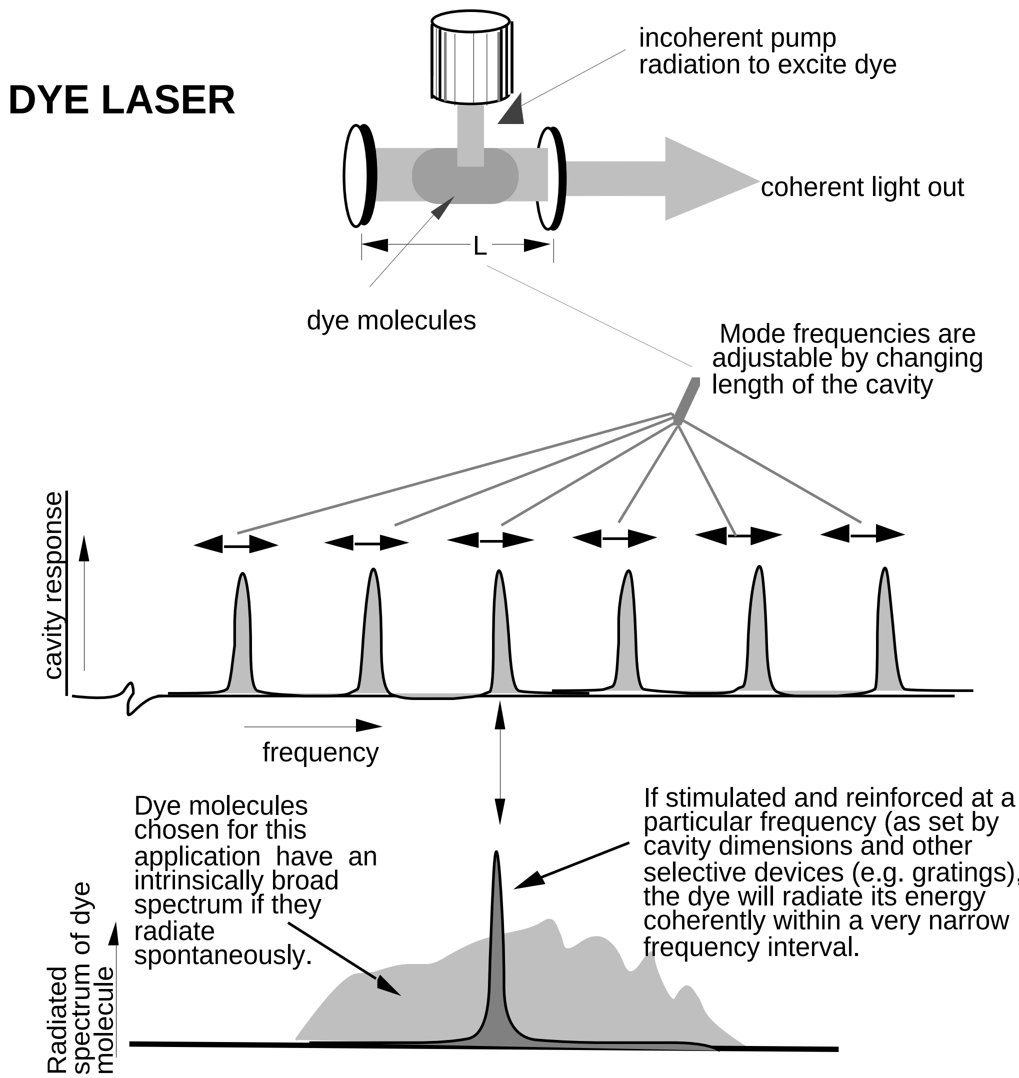


Fig 9.8 Cavity resonance sets output frequency of dye laser

Diffraction gratings and prisms can be used to enhance one particular mode at the expense of others that might also resonate in a simple cavity

Acoustic analogy to dye laser: The lip of a horn player (or the reed of a clarinet) is a source of oscillating energy that can operate over a wide range of frequencies. When the lip is coupled to the horn, however, the player finds that the lip vibrates only at those frequencies determined by the effective length of the air column within the horn. If the horn is quite simple (e.g. a bugle) then the player has only a limited scope (G, C, E, G'…) from a fixed fundamental and integer overtones. If the horn length is adjustable (either by valves as in a trumpet or by slide as in a trombone) then there is a wider choice of frequencies. A French horn provides extra flexibility because the player may choose from a set of very high overtones of the fundamental and may, in addition, use valves to change that fundamental.

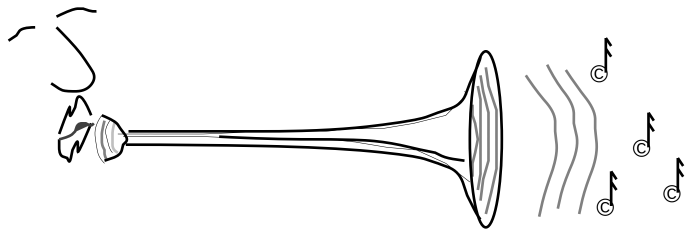


Fig 9.9 Lip as broad-band energy source; horn resonance governs lip frequency

But it is the geometry of the acoustic resonator, not the frequency of the energy source (lip), that determines the frequency of the sound produced by the horn. This parallels the situation in a dye laser where the geometry of the optical resonator, not the properties of the energy source (dye molecule) that determines the frequency of the output light.

9.5 Ways To Create A Population Inversion

Population Inversion and Negative Temperature

We know, from statistical thermodynamics, that states *a,b* of a system in thermal equilibrium at temperature T are populated in the ratio:

$$\frac{N_b}{N_a} = \frac{g_b}{g_a}\; e^{-\frac{E_b - E_a}{kT}} \qquad (9.21)$$

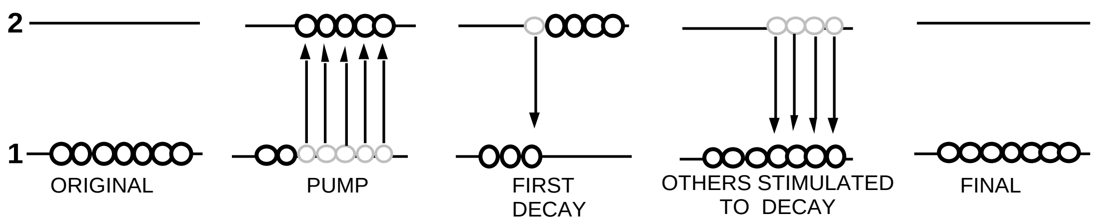
where g_a and g_b are the degeneracies of states *a* and *b*.

If $E_b > E_a$ then, for positive T, we have $N_b < N_a$: under normal conditions the population of the lower state exceeds that of the upper state.
However we know from our earlier discussions that a system (e.g. a gas within an optically-resonant cavity) with a *population inversion*, $N_b > N_a$ is essential if the system is to act as a laser and produce coherent radiation .

If one regards the temperature as that parameter which, when used in Eq. (9.22) describes the ratio of two populations, then the condition of population inversion can be described in terms of a *negative temperature*. This has some convenient aspects (for example one can do some thermodynamic calculations using negative temperatures), but it is also counter-intuitive in many respects... for example a system at a high negative temperature can deliver considerable energy to anyone who touches it.

Two Level System:

The conceptually simplest system involves only two levels:



Fi
g 9.10 Stages in operation of 2 level system with pulsed output

We begin with almost all atoms in state 1, as will be the case for optical transitions where ΔE is much greater than kT for the sample. Then the application of the pump mechanism (whether by radiation, collision, or …) causes most of the atoms to make the transition to state 2, and the consequence is an inverted populations of states 1 and 2. The first atom to undergo the decay $2 \rightarrow 1$ then begins to produce the radiation field that will stimulate the rest of the atoms to radiate in the same direction, frequency, and phase. Finally the atoms are again all in state 1, ready to be pumped again.

> Of course energy is conserved in all our systems, so one might ask whether there is any advantage to a two level system. Why not use the pumping energy directly for whatever final purpose we have in mind? The answer is that we can get monochromatic and highly coherent radiation in emission even if the pumping process has no frequency or phase selectivity. ,

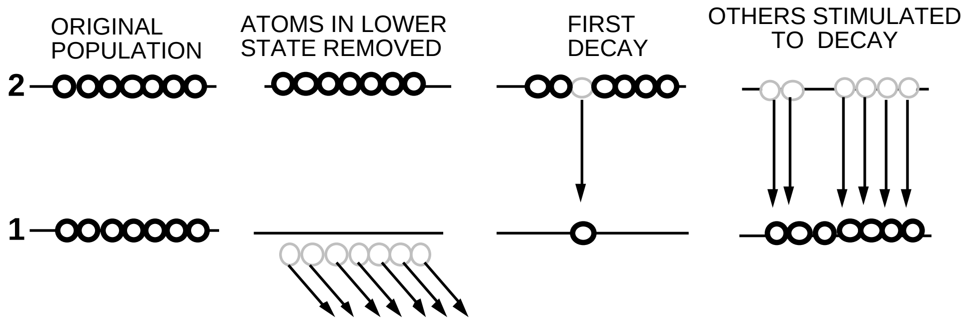
The pumping process may occur *in situ*, as is usual when optical radiation is used to excite atoms (molecules) to the upper laser level,

Or the pumping may occur in a location away from where the coherent radiation is generated. In the NH_3 maser and in the Hydrogen maser, for example, the N=2 population is physically segregated from the N=1 by having atoms (molecules) undergo different trajectories in state selecting magnetic fields; those in the N=2 state are directed into a resonant microwave cavity.

Or one can have the lasing species (molecule AB, say) be the product of a chemical reaction **AC**+**B**$\rightarrow$ **AB*** + **C** that takes place just before the molecules enter the resonator.

Two-Level Population Inversion by Removal of Atoms in Lower State

In some situations the original thermal distribution is such that the upper and the lower level have no significant population difference. This occurs in situations where ΔE associated with the $2 \rightarrow 1$ transition is much less than kT, for example in transitions at microwave frequencies between sublevels of the ground electronic state in an atom or a molecule.



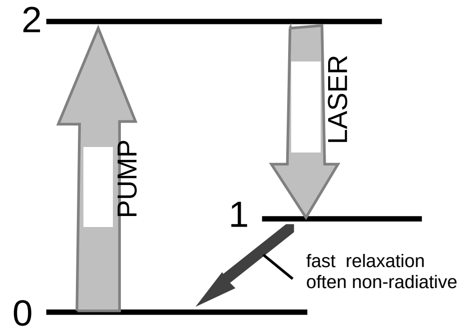
g 9.11 Stages in operation of 2 level system based on removal of lower state atoms

In this situation, the atoms in the lower state are physically removed from the sample in order to create the inverted population necessary for the operation of the stimulated radiation generator. In practice his is done by passing a beam of the atoms (or molecules) through an inhomogeneous static field that focuses atoms in state 2 and defocuses atoms in state 1. The state-selected beam passes into a resonant cavity and there stimulates the production of microwave radiation.... this is the method used for the atomic hydrogen maser and the NH_3 maser.

The NH_3 experiment that generated 23 GHz radiation by exploiting the large electric dipole moment associated with the inversion transition was the first to employ these general principles, hence the name Microwave Amplification by Stimulation of Emitted Radiation [MASER]. Later these methods were extended to optical transitions, and that led to the name Light Amplification by Stimulation of Emitted Radiation [LASER]

Three Level System:

It is usually difficult to create a population inversion when the lower of the two states is the ground state [population N_0 , energy E_0] of the atom or molecule because that state is ordinarily highly populated. It is simpler to work between two excited states that are basically unpopulated under normal conditions; the pumping process then involves populating the upper laser level in a preferential manner.

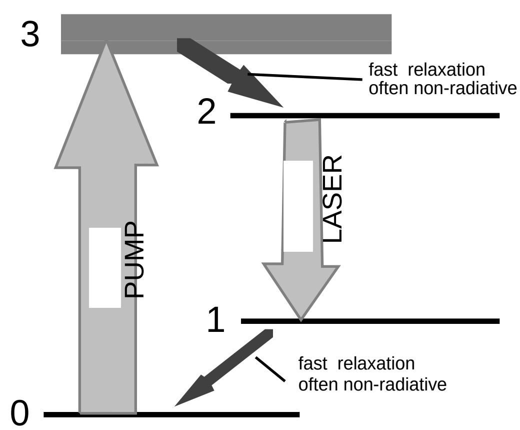


g 9.12 Energy level diagram showing pump and laser transitions in a 3-level system

The atoms, having completed the laser transition $2 \rightarrow 1$ then undergo a second, relaxation transition and return to the ground state.

Four Level System:

Given the realities of thermal populations, selection rules, and other constraints, it is sometimes easier to manage level populations working between four levels,



g 9.13 Energy level diagram showing pump and laser transitions in a 4-level system

Note that the pumping is not necessarily with radiation. Excitation is often done with collisions (with excited atoms or with electrons), with dissociative excitation, or with chemical reactions. In the helium-neon laser, for example, the pumping of the neon atom occurs when it collides with an excited helium atom, and the relaxation from state 1 to state 0 often occurs when the neon atom in state 1 hits the wall of the tube that encloses the laser gas.