

Lec1

Light: Generation

Fluorescence

- Luminescence
 - Comprised of fluorescence and phosphorescence
 - The phenomenon that a given substance emits light
- Light in the visible spectrum is due to *electronic transitions*
 - *Vibrationally excited states* can give rise to lower energy photons, i.e. infrared radiation
 - *Rotational modes* produce even lower energy radiation, in the microwave region.
- Application
 - Fluorescence-based measurements
 - Microscopy, flow cytometry, medical diagnosis, DNA sequencing, and many other areas.
 - Biophysics and biomedicine
 - Fluorescence microscopy, image at cellular and molecular scale, even single molecule scale.
 - Fluorescent probes, specifically bind to molecules of interest, revealing localization information and activity (i.e., function).
 - Challenge in microscopy: Merge information from the molecular and cellular scales.

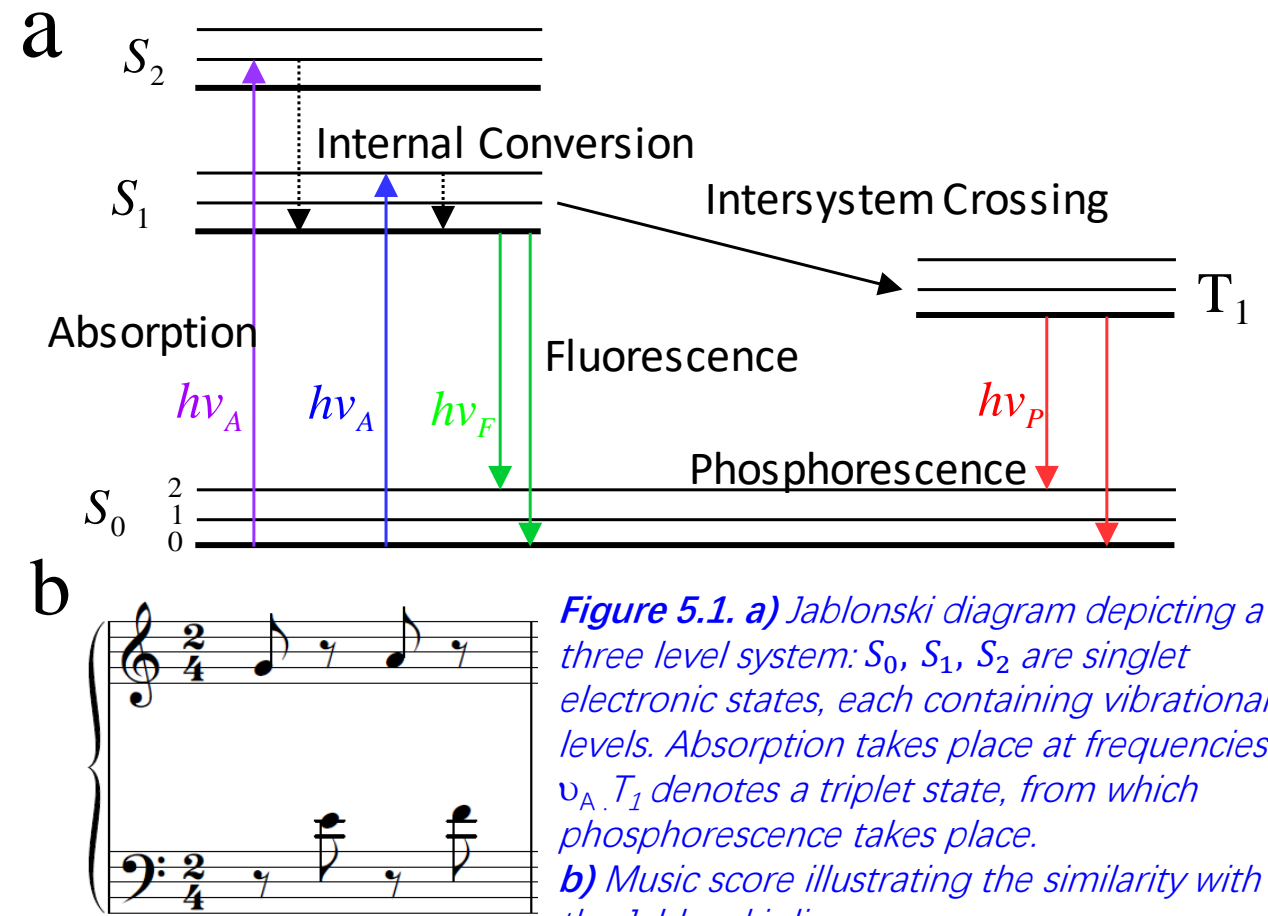
Jablonski Diagram

- Fluorescence
 - The radiative transition between two electronic states of the same spin multiplicity.
 - Spin multiplicity: $M_s=2s+1$, with s the spin of the state.
- The spin s
 - s is the sum of the spins from all the electrons on that electronic state.
 - $s=0$, two paired (antiparallel spins) electrons on the electronic state.
 - $s=1/2$, a single, unpaired electron in the state.
 - $s=1$, two electrons of parallel spins.
- Electronic states
 - Singlets ($M_s=2s+1=1, s=0$)
 - Doublets ($M_s=2, s=1/2$)
 - Triplets ($M_s=3, s=1$)
 - The singlet-singlet transition is the most common in fluorescence.

Jablonski Diagram

- Jablonski diagram

- The energy levels of a molecule.
- S_0 , S_1 , S_2 denote the ground, first, and second electronic state.
- A typical scenario:
 - Absorb a photon of energy $h\nu_A$, $S_0 \rightarrow S_2$, at the $1fs=10^{-15}s$ scale
 - Internal conversion: $S_2 \rightarrow S_1$, within $1ps=10^{-12}s$ or less.
 - Emit a photon of energy $h\nu_F$, $S_2 \rightarrow S_1$, in an average time of $10^{-9}—10^{-8}s$.
 - Assume:** The internal conversion is complete prior to emission.



Jablonski Diagram

- Born-Oppenheimer approximation
 - A molecule's wave function can be factorized into an electronic and nuclear (vibrational and rotational) components.

$$\psi_{total} = \psi_{\bar{e}} \times \psi_N$$

- Phosphorescence
 - *Intersystem crossing*: The conversion from the S_1 state to the first triplet state T_1
 - *Phosphorescence*: Triplet emission (emission from T_1), which is generally shifted to lower energy (longer wavelengths)
 - Phosphorescence has lower rate constants than fluorescence.
 - Phosphorescence with decay times of seconds or even minutes.
 - Molecules of heavy atoms tend to be phosphorescent.

Emission Spectra

- Symmetry property between the power spectrum of absorption (or excitation) and emission (or radiative decay) — mirror symmetry
 - Excitation: Absorption, $S_0 \rightarrow S_1$ (higher vibrational levels) \rightarrow nonradiative decay, S_1 (lowest vibrational level).
 - Emission: Radiatively decays, $S_1 \rightarrow S_0$ (high vibrational level) \rightarrow thermal equilibration, S_0 (ground vibrational state).
 - The peaks in both absorption and emission correspond to vibrational levels, which results in perfect symmetry.

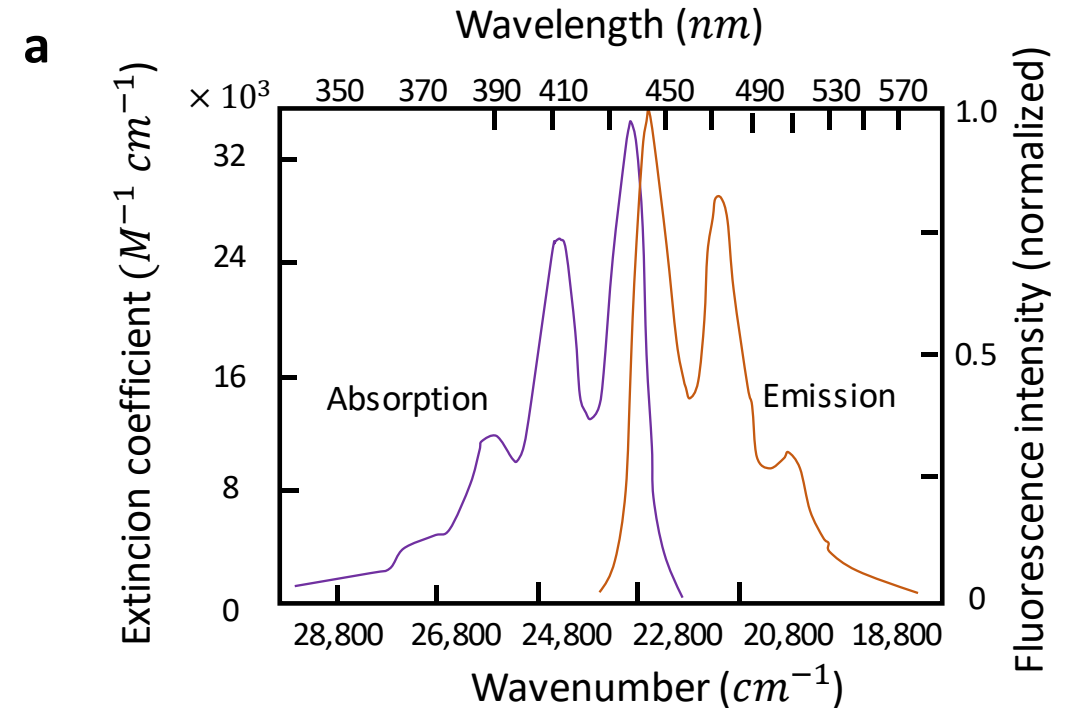


Figure 5.2. a) Mirror-image rule (perylene in benzene).

Emission Spectra

- **Note:** The local maxima are due to the individual vibration levels.
- The emission spectrum remains constant irrespective of the excitation wavelength (exceptions exist).
- Exception to the mirror rule
 - Absorption spectrum: The first peak is due to $S_0 \rightarrow S_2$, the larger wavenumber peak is from $S_0 \rightarrow S_1$.
 - Emission: Occurs predominantly from S_1 , the second peak is absent.

b

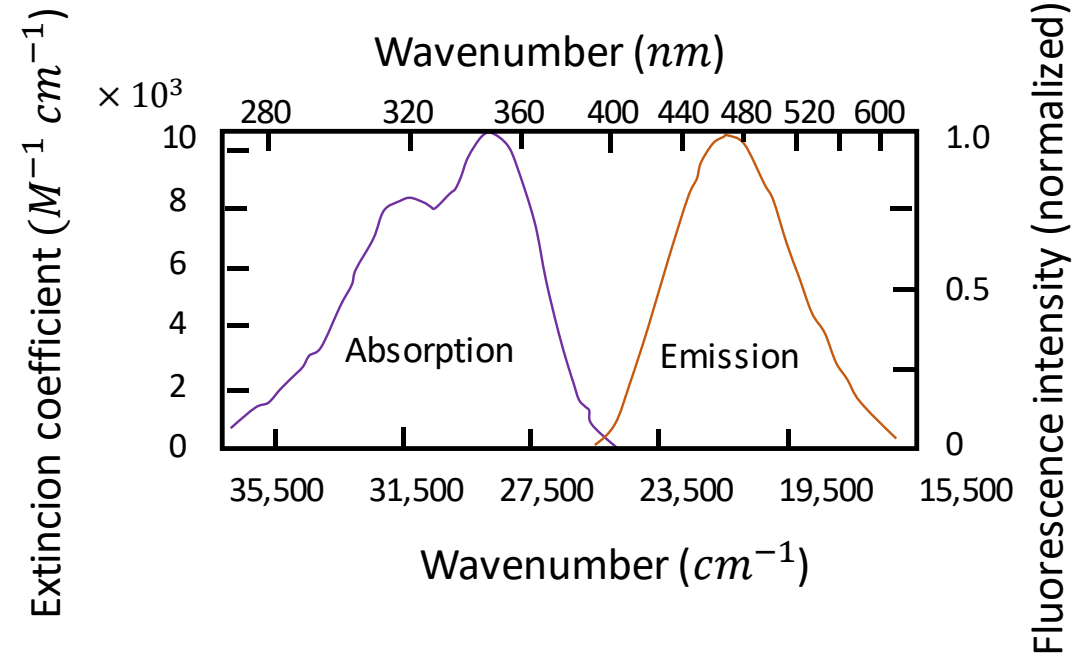


Figure 5.2. b) Exception to the mirror rule (quinine sulfate in H₂SO₄). Adapted from Lakowicz, J. R. (2013). Principles of fluorescence spectroscopy, Springer Science & Business Media.

Rate Equations

- The population of each level is determined by the rate of absorption, nonradiative decay, spontaneous emission, and stimulated emission.

- Stimulated emission

- The radiative transition from an excited state to the ground state triggered (stimulated) by the excitation field.
- By stimulated emission, one excitation photon results in two identical emitted photons (development of lasers).

- Rate equations for levels S_0 and S_1

$$\frac{dN_1}{dt} = B_{01}N_0 - B_{10}N_1 - A_{10}N_1 - \gamma_{nr}N_1$$

$$\frac{dN_0}{dt} = -B_{01}N_0 + B_{10}N_1 + A_{10}N_1 + \gamma_{nr}N_1 = -\frac{dN_1}{dt}$$

Assume: $N_0 + N_1 = \text{const}$, or $d(N_0 + N_1)/dt = 0$

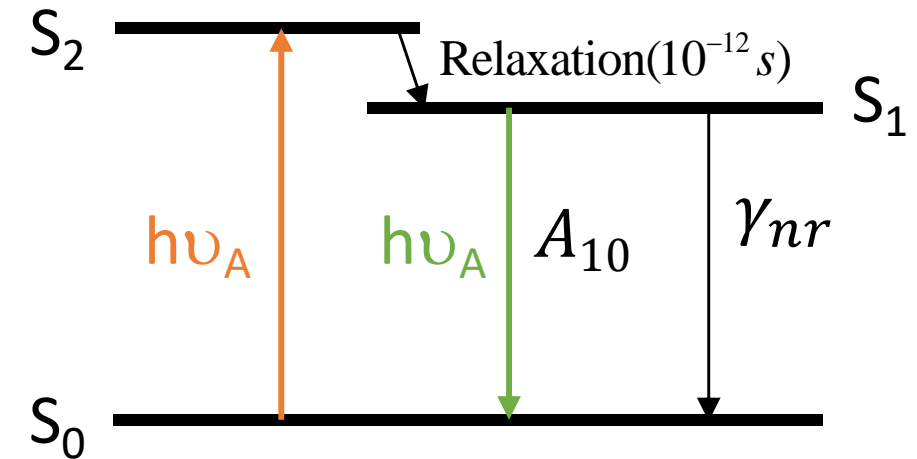


Figure 5.3. Jablonski diagram for a three-level system.

$N_{0,1}$ — concentrations, m^{-3}

B_{01} — absorption rate, s^{-1}

B_{10} — stimulated emission rate

($B_{01} = B_{10}$ for nondegenerate levels)

A_{10} — spontaneous emission rate

γ_{nr} — rate of nonradiative decay

Rate Equations

- **Note:** The energy lost from nonradiative decay, γ_{nr} , eventually converts into heat.
- For thermal equilibrium
 - $N_I \ll N_0$, the stimulated emission term can be neglected ($B_{I0}N_I \approx 0$)
 - **Note:** The rate of decay is much higher than that of absorption, $A_{0I} + \gamma_{nr} \gg B_{I0}$.
- For active medium
 - $N_I > N_0$, when there is population inversion.
- The solutions for the populations of the two levels

$$\begin{array}{lcl} N_0 + N_1 = N & \Longrightarrow & N_0 = N \frac{A_{10} + \gamma_{nr}}{B_{01} + A_{10} + \gamma_{nr}} \\ B_{01}N_0 - A_{10}N_1 - \gamma_{nr}N_1 = 0 & & N_1 = N \frac{B_{01}}{B_{01} + A_{10} + \gamma_{nr}} \end{array}$$

Quantum Yield

- The fluorescence quantum yield
 - The ratio of the number of photons emitted to that of photons absorbed

$$Q = \frac{N_1 A_{10}}{N_0 B_{01}} = \frac{A_{10}}{A_{10} + \gamma_{nr}}$$

- For thermal equilibrium

$$N_1 / N_0 = B_{01} / (A_{10} + \gamma_{nr})$$

- The quantum yield can approach unity if the nonradiative decay, γ_{nr} , is much smaller than the rate of radiative decay, A_{10} .
- **Note:** Even for 100% quantum yield, the energy conversion is always less than unity because the wavelength of the fluorescent light is longer (the frequency is higher, i.e. $h\omega_A > h\omega_F$).

Fluorescence Lifetime

- The lifetime of the excited state
 - The average time the molecule spends in the excited state before returning to the ground state.
 - For a simplified Jablonski diagram, the lifetime is the inverse of the decay rate.

$$\tau = \frac{1}{A_{10} + \gamma_{nr}}$$

- Natural lifetime τ_0
 - The lifetime of a fluorophore in the absence of nonradiative processes, $\gamma_{nr} \rightarrow 0$.
 - Depends on the absorption spectrum, extinction coefficient, and emission spectrum of the fluorophore.
- Natural lifetime τ_0 and measured lifetime τ ($\tau > \tau_0$, nonradiative processes)

$$\tau_0 = \frac{1}{A_{10}}$$

$$\tau = \tau_0 \frac{A_{10}}{A_{10} + \gamma_{nr}} = Q \tau_0$$

$$\tau_0 = \frac{\tau}{Q}$$

Quenching

- Fluorescence quenching
 - The nonradiative decay to the ground state.
- Collisional quenching
 - Due to the contact between the fluorophore and quencher, in thermal diffusion.
 - Quenchers include: halogens, oxygen, amines, etc.
- Other quenching
 - Static quenching: The fluorophore can form a nonfluorescent complex with the quencher
 - The attenuation of the incident light by the fluorophore itself or other absorbing species.
- Photon absorption takes place at femtosecond scale, $10^{-15} s$, while emission occurs over a larger period of time.

Quenching

- During its lifetime, a fluorophore can interact with quenchers from within a radius of 7 nm.

The diffusion coefficient of oxygen in water $D = 2.5 \cdot 10^{-5} \text{ m}^2/\text{s}$, the lifetime of a fluorophore $t = 10 \text{ ns}$

The root mean squared distance that the oxygen molecule can travel during this time $\langle \Delta x^2 \rangle = 2Dt$.

The significant distance $\sqrt{\langle \Delta x^2 \rangle} = 7 \text{ nm}$, the thickness of a cell membrane bilayer is 4-5 nm .

- It is possible for a molecule to absorb light outside the cell and fluoresce from the inside (and vice versa), one lifetime later.

Black Body Radiation

Black Body Radiation

- Black body
 - An idealized model of a physical object that absorbs all incident electromagnetic radiation, and an ideal emitter of thermal radiation.
 - Spectral distribution of radiation by bodies at thermal equilibrium led into the development of quantum mechanics.
- Thermal radiation
 - Reverse process to absorption: Internal energy \rightarrow Thermal radiation.
 - Cavity mode: The spatial frequency content of the electromagnetic field within the cavity, which satisfies the condition of vanishing electric field at the wall.

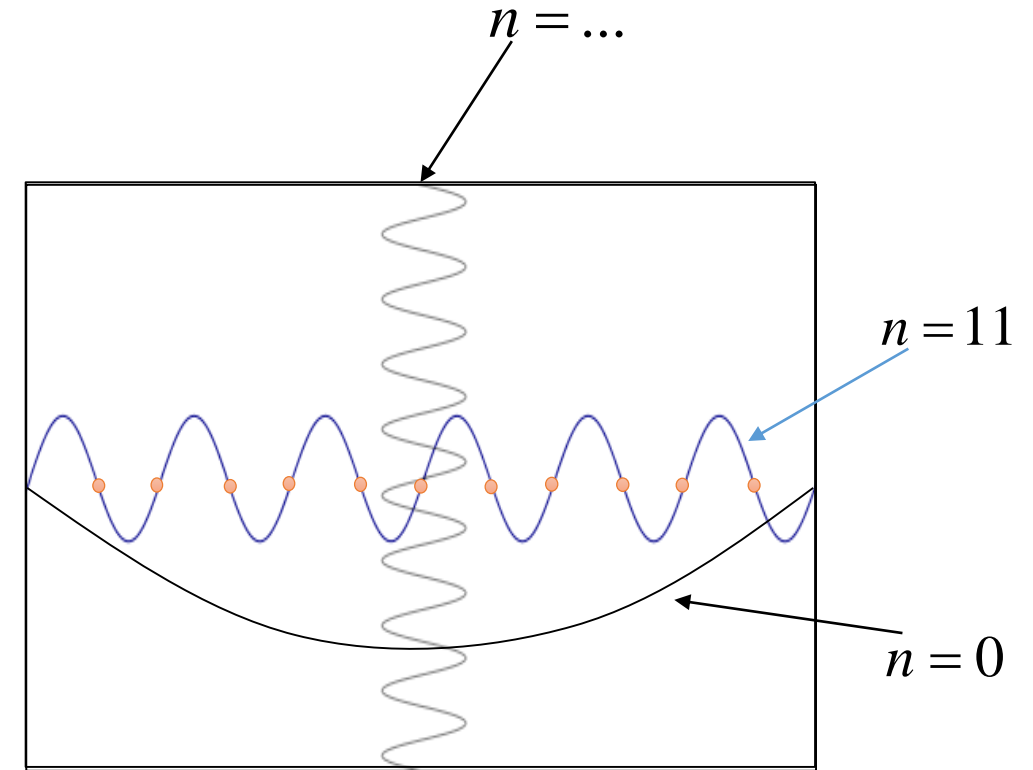


Figure 6.1. Cavity modes: the sinusoids represent the real part of the electric field. All surviving field modes have zero values at the boundary. The modes are indexed by n , the number of zeros along an axis (orange dots).

Planck's Radiation Formula

- Planck's Radiation Formula

- Planck's formula predicts the spectral density of the radiation emitted by a black body, at thermal equilibrium, as a function of temperature.
- The radiated energy per mode, per unit volume is:

$$du(\nu) = 2f \frac{h\nu}{V} dN$$

V — Volume dN — The number of modes
 ν — Frequency

- f is the probability of occupancy associated with a given mode, obtained from the Bose-Einstein statistics.

$$f = \frac{1}{e^{\frac{h\nu}{k_B T}} - 1}$$
$$k_B = 1.38 \cdot 10^{-23} \text{ J/K} \quad (\text{Boltzmann's constant})$$

- The average energy per mode:

$$\langle E \rangle = fh\nu = \frac{h\nu}{e^{\frac{h\nu}{k_B T}} - 1}$$

Planck's Radiation Formula

- Calculate the number of modes per frequency interval dN

- The spherical shell in the first octant of the k-space is:

$$dV_k = \frac{1}{8} 4\pi k^2 dk = \frac{\pi}{2} k^2 dk$$

- Volume in k-space formed by the smallest spatial frequencies

$$V_k^{\min} = \frac{\pi^3}{L_x L_y L_z}$$

- The volume of the cavity

$$L_x L_y L_z = V$$

- Dispersion relation

$$k = 2\pi \frac{\nu}{c}$$

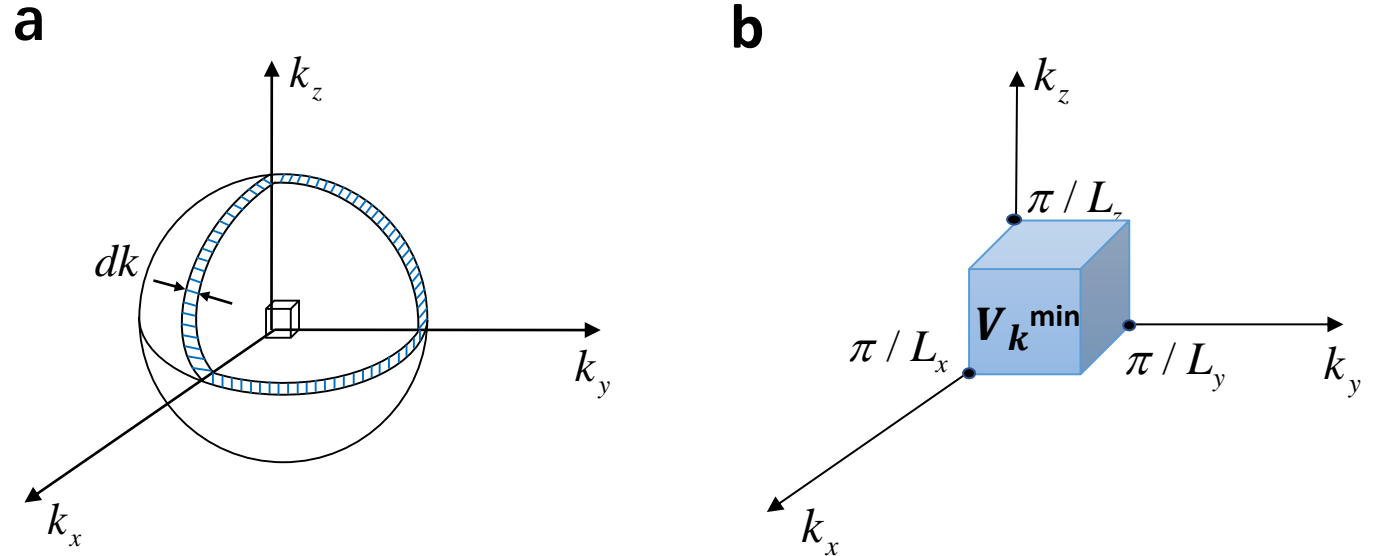


Figure 6.2. a) Mode distribution in a cavity. b) The cube at the origin in a) is the smallest volume in k-space, defined by the inverse dimensions of the cavity.

- The number of modes per frequency interval

$$dN = \frac{dV_k}{V_k^{\min}} = \frac{\pi}{2} \frac{V}{\pi^3} k^2 dk = \frac{\pi}{2} \frac{V}{\pi^3} \frac{4\pi^2 \nu^2}{c^2} \frac{2\pi}{c} d\nu = \frac{4\pi V}{c^3} \nu^2 d\nu$$

Planck's Radiation Formula

- The radiated energy per unit frequency range and unit volume, $p(\nu)$
 - It is fundamental to calculating any quantity related to blackbody radiation.

$$p(\nu) = \frac{du(\nu)}{d\nu} = \frac{8\pi h}{c^3} \frac{\nu^3}{e^{\frac{h\nu}{k_B T}} - 1} \quad k_B = 1.38 \cdot 10^{-23} \text{ J/K}$$

- Calculate the power flowing from the cavity
 - Through a surface A and element of solid angle $d\Omega$, per unit of frequency ν .

$$d^2 P(\nu) = \frac{c}{2} du(\nu) \frac{A \cos \theta d\Omega}{2\pi} = \frac{c}{2} p(\nu) d\nu \frac{A \cos \theta d\Omega}{2\pi}$$

$$d\Omega = 2\pi \sin \theta d\theta$$

$$dP(\nu) = \frac{c}{2} du(\nu) A \int_0^\pi \cos \theta \sin \theta d\theta$$

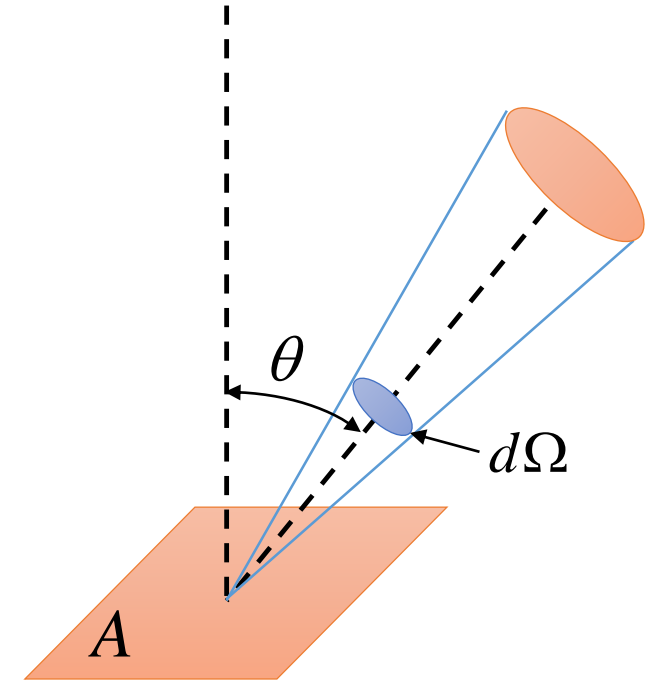


Figure 6.3. Power flow out of a black body surface.

Planck's Radiation Formula

- The spectral exitance
 - The power per surface area per frequency.

$$M_\nu = \frac{d^2 P}{dA d\nu}$$

$$M_\nu = \frac{1}{4} c p(\nu) = \frac{2\pi h}{c^2} \frac{\nu^3}{e^{\frac{h\nu}{kT}} - 1}$$

- The spectral exitance in term of the wavelength

$$M_\lambda = M_\nu(\nu = c/\lambda) \frac{d\nu}{d\lambda} = \frac{2\pi h c^2}{\lambda^5} \frac{1}{e^{\frac{hc}{\lambda kT}} - 1}$$

- The Jacobian factor $d\nu/d\lambda$ ensures that the M_λ is a distribution.

$$M_\lambda d\lambda = M_\nu d\nu$$

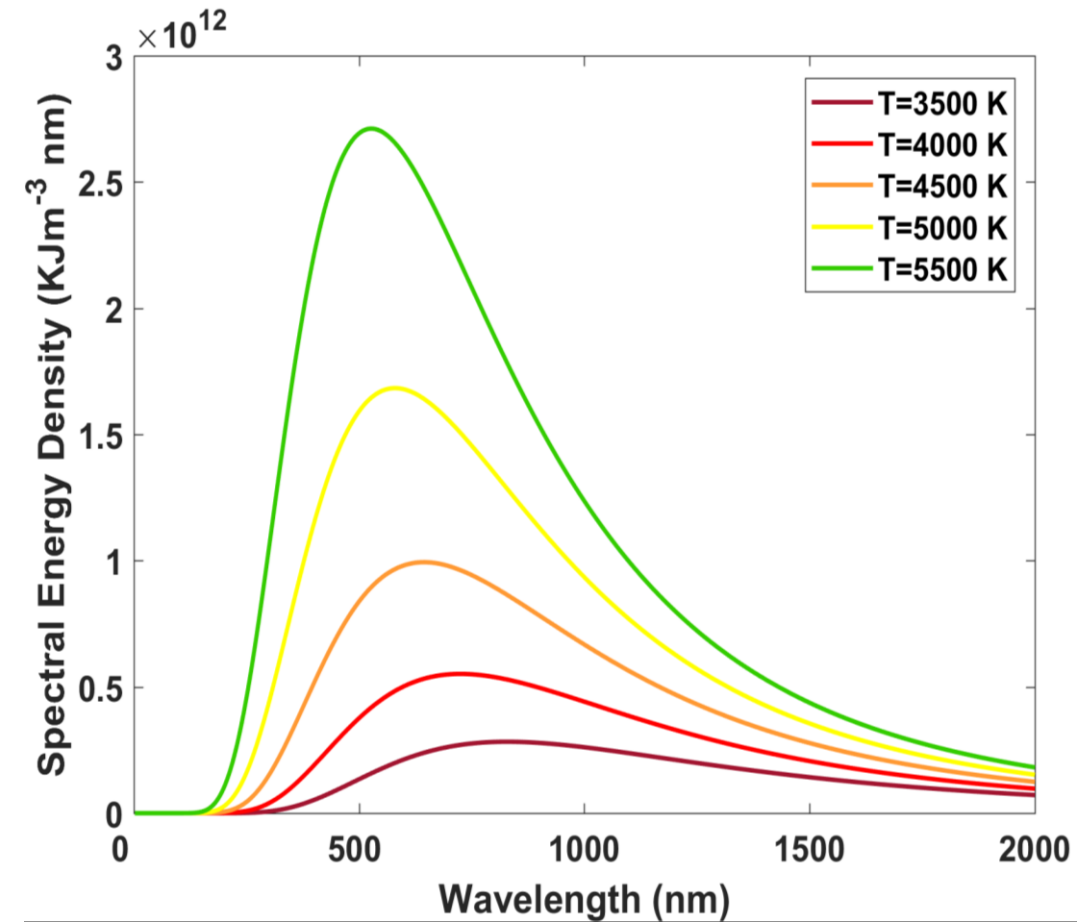


Figure 6.4. Spectral exitance of blackbodies at different temperatures.

Wien's Displacement Law

- A function of temperature
 - Both $p(\nu)$ and M_λ exhibit a maximum at a particular frequency ν_{max} .

$$\left. \frac{d\rho(\nu)}{d\nu} \right|_{\nu=\nu_{max}} = \left. \frac{dM_\nu}{d\nu} \right|_{\nu=\nu_{max}} = 0.$$

- Wien's displacement law
 - The relationship between the temperature of the source and the peak wavelength of its emission.

$$\nu_{max} \propto T \quad \lambda_{max} \propto \frac{a}{T} \quad \begin{array}{l} a \text{ --- constant} \\ a = 2,900 \mu mK \end{array}$$

- **Note:** λ_{max} is obtained by finding the maximum of function M_λ with respect to λ . $\lambda_{max} \neq c / \nu_{max}$
- Color temperature:
 - Expressing the “color” of thermal light by the temperature of the source.

Temperature	Source
1850 K	Candle flame, sunset/sunrise
2400 K	Standard incandescent lamps
2700 K	"Soft white" compact fluorescent and LED lamps
3000 K	“Warm white” compact fluorescent and LED lamps
3200 K	Studio lamps, photofloods, etc.
5000 K	Compact fluorescent lamps (CFL)
6200 K	Xenon short-arc lamp
6500 K	Daylight, overcast
6500 – 9500 K	LCD or CRT screen
15,000 – 27,000 K	Clear blue sky

Figure 6.5. Color temperature for various thermal sources.

Wien's Displacement Law

- Wien's displacement formula in daily activities
 - Humans evolved to gain maximum sensitivity of their visual system at the most dominant wavelength emitted by the Sun.
 - The Sun's effective temperature is 5800K, which places its peak emission at ~ 500 nm (green), near the maximum sensitivity of our eye.
 - Dimming the light on an incandescent light bulb will result in shifting the color toward red (longer wavelengths).
 - Heating a piece of metal will eventually produce radiation, of red color at first and blue-white when the temperature increases further. One can say that "white-hot" is hotter than "red-hot".
 - Warm-blooded animals at, say, $T=310\text{K}$ (37°C), emit peak radiation at $\sim 10\text{ }\mu\text{m}$, in the infrared region of the spectrum, outside our eye sensitivity.
 - Some reptiles and specialized cameras can sense these wavelengths and, thus, detect the presence of such animals.
 - Most of the radiation is in the infrared spectrum, which we sense as heat, but only a small portion of the spectrum is visible.
 - Wood fire can have temperatures of 1500-2000K, with peak radiation at $\sim 2\text{-}2.5\text{ }\mu\text{m}$.

Stefan-Boltzmann Law

- The Stefan-Boltzmann law

- The frequency-integrated spectral exitance, meaning, the exitance (in W/m^2), is proportional to the 4th power of temperature. Stefan-Boltzmann constant $\sigma = 5.67 \times 10^{-8} Wm^{-2}K^{-4}$.

$$M = \int_0^{\infty} M_{\nu} d\nu = \sigma T^4$$

- The total power emitted by a black body is MA , where A is the area of the source.
 - Estimate the size of other stars: The total power emitted by the Sun (S) and the star of interest (X)

$$P_S = 4\pi R_S^2 \sigma T_S^4$$

$$P_x = 4\pi R_x^2 \sigma T_x^4$$

$$R_x = R_S \left(\frac{T_S}{T_x} \right)^2 \sqrt{\frac{P_x}{P_S}}$$

- Gray body

- A body that does not absorb all the incident radiation and emits less total energy than a black body, with an emissivity $\varepsilon < 1$.

$$M = \varepsilon \sigma T^4$$

Asymptotic Behaviors of Planck's Formula

- Wien approximation

- The asymptotic behavior of Planck's formula (blue curve) for low temperature (high-frequency)

$$h\nu \gg K_B T$$

$$f \approx e^{-\frac{h\nu}{k_B T}}$$

$$p(\nu) \approx \frac{8\pi h}{c^3} \nu^3 e^{-\frac{h\nu}{k_B T}}$$

- Rayleigh-Jeans law

- At high temperatures (low-frequency) $h\nu \ll K_B T$

$$f \approx \frac{1}{1 + \frac{h\nu}{k_B T} - 1} = \frac{k_B T}{h\nu}$$

$$p(\nu) \approx \frac{8\pi \nu^2}{c^3} k_B T$$

- Rayleigh-Jeans law is known as classic limit formula.
- “Ultraviolet catastrophe”: The amount of energy radiated over the entire spectral range diverges.

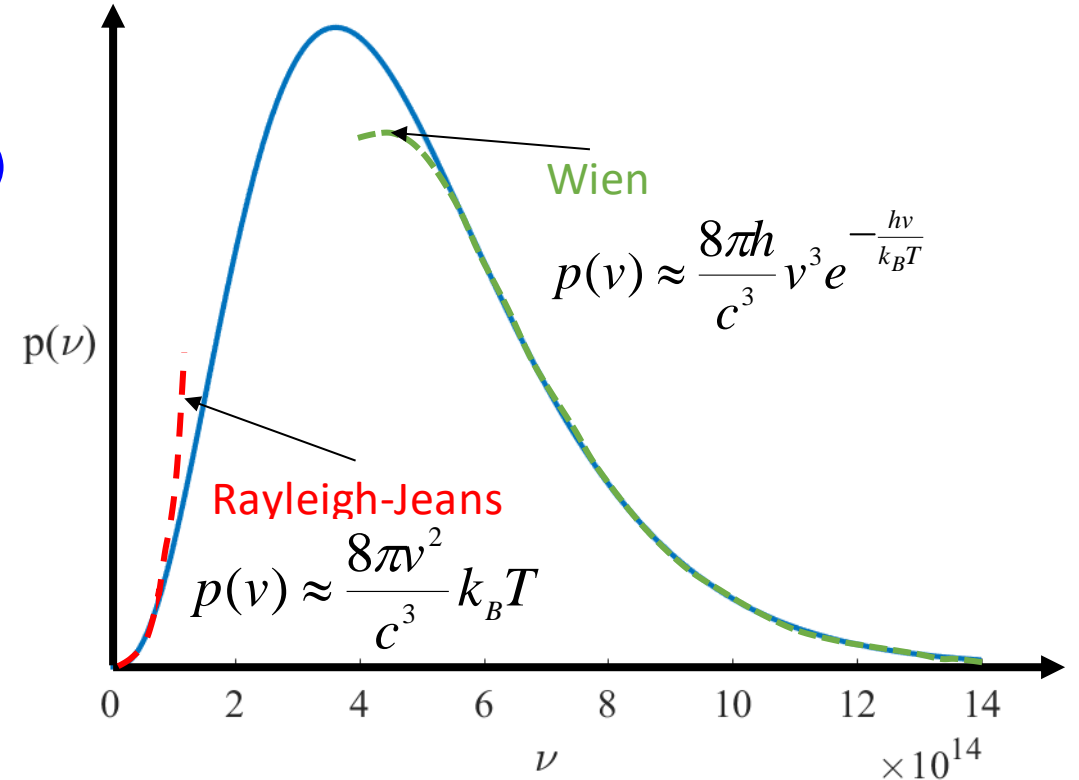


Figure 6.6. The asymptotic behavior of Planck's formula (blue curve) for high temperature (low-frequency, Rayleigh-Jeans, red curve) and low-temperature (high-frequency, Wien, green curve).

Einstein's Derivation of Planck's Formula

- The quantum of energy is assumed to be the difference between two atomic energy levels.

$$E_2 - E_1 = h\nu$$

- The atomic system exchange energy with the environment by 3 fundamental processes .
 - Absorption:** An atom in state 1 absorbs an incident photon and is excited to energy level 2.

$$\frac{dN_2}{dt} = B_{12}N_1\rho(\nu)$$

N_1, N_2 — the number density of each level

ρ — the incident energy density

B_{12} — the absorption rate, $[B_{12}] = s^{-1}$

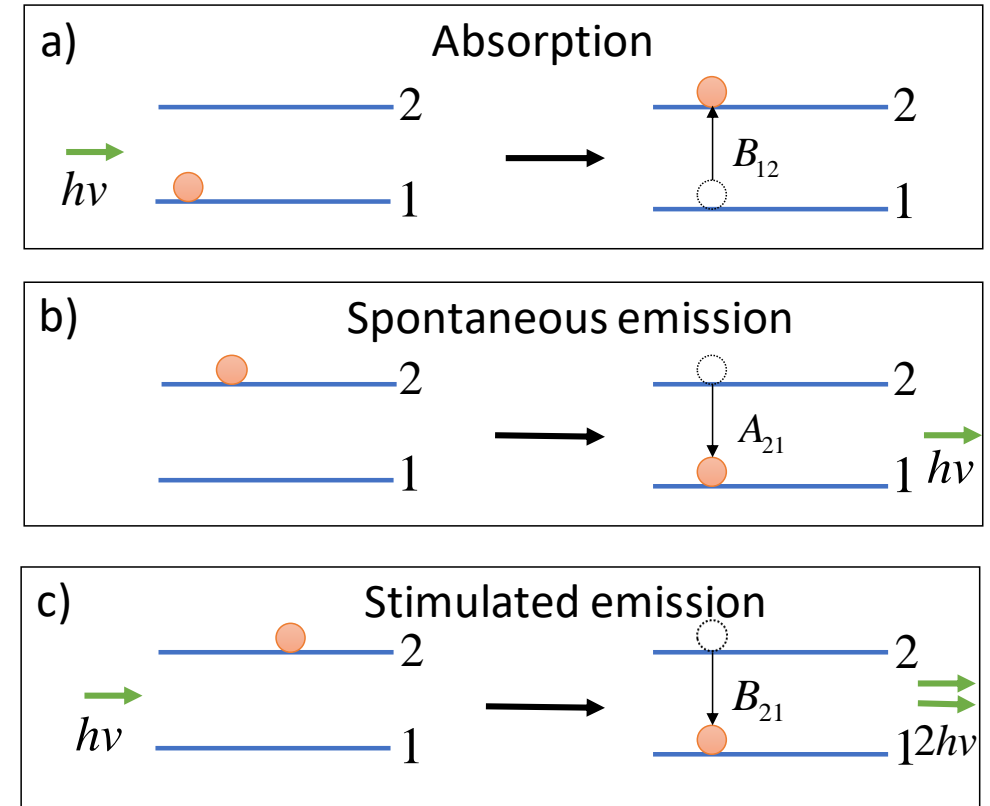


Figure 6.7. Radiative processes in a two-level atomic system: **a)** absorption, **b)** spontaneous emission, **c)** stimulated emission. Note how the stimulated rather than spontaneous emission is the reversed process to absorption.

Einstein's Derivation of Planck's Formula

- Spontaneous emission: An atom from level 2 decays radiatively (with emission of a photon) to the lower state.

$$\frac{dN_2}{dt} = -A_{21}N_2$$

A_{12} — the spontaneous emission rate constant.

- Note:** The inverse of A_{12} can be interpreted as the decay time constant, or natural lifetime $\tau=1/A_{12}$.
- Stimulated emission: Can be regarded as the exact reverse of absorption

$$\frac{dN_2}{dt} = B_{12}N_1\rho(\nu)$$

B_{12} — the absorption rate, $[B_{12}]=s^{-1}$

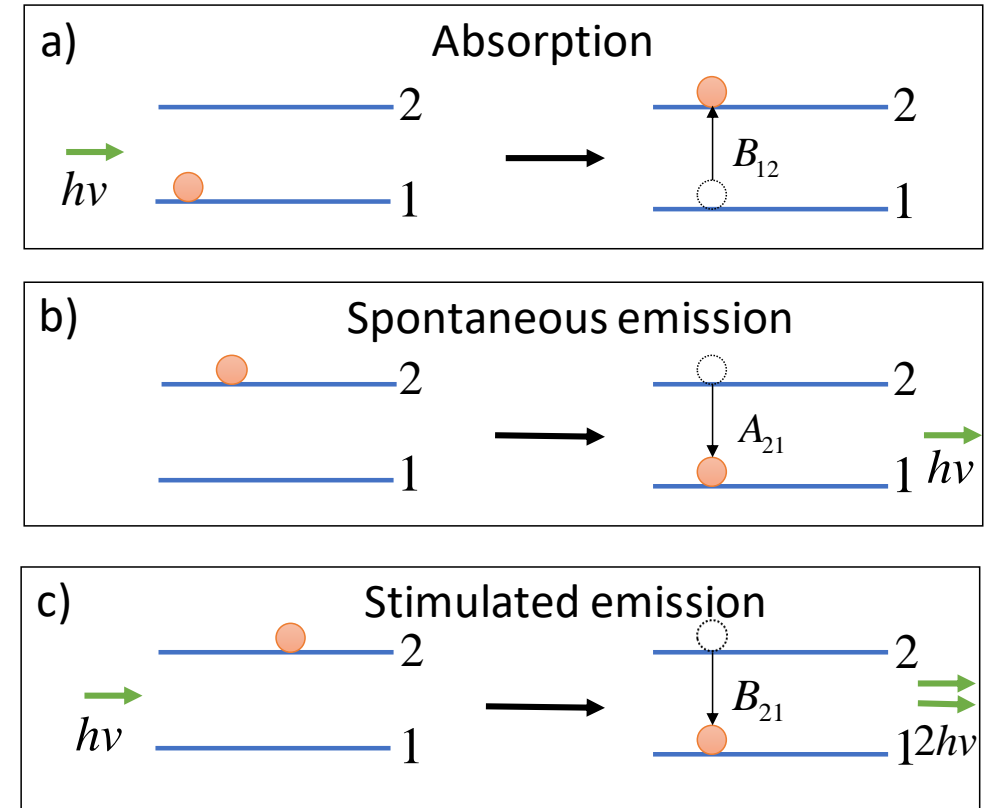


Figure 6.7. Radiative processes in a two-level atomic system: **a)** absorption, **b)** spontaneous emission, **c)** stimulated emission. **Note how the stimulated rather than spontaneous emission is the reversed process to absorption.**

Einstein's Derivation of Planck's Formula

- Einstein combined all these processes to express the rate equations.

$$\frac{dN_2}{dt} = -A_{21}N_2 + B_{12}N_1\rho(\nu) - B_{21}N_2\rho(\nu) = -\frac{dN_1}{dt}$$

- At thermal equilibrium, the excitation and decay mechanisms must balance each other completely. Using the classic Boltzmann statistics to get the ratio of the two populations.

$$\frac{dN_2}{dt} = \frac{dN_1}{dt} = 0 \qquad \frac{N_2}{N_1} = \frac{B_{12}\rho(\nu)}{A_{21} + B_{21}\rho(\nu)} = \frac{g_2}{g_1} \cdot e^{-\frac{h\nu}{k_B T}}$$

$$\rho(\nu) = \frac{A_{21}}{B_{21}} \frac{1}{\frac{B_{12}g_1}{B_{21}g_2} e^{\frac{h\nu}{k_B T}} - 1} \qquad g_1, g_2 \text{ — the degeneracy factors for the two states}$$

- $\rho(\nu)$ and Planck's formula are identical, provided two conditions are met

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

LASER: Light Amplification by Stimulated Emission of Radiation

Population inversion, Optical Resonator, and Narrow Band Radiation

- Laser radiation can be highly monochromatic and collimated.
 - **Note:** It is highly dissipative for thermal sources (e.g. incandescent filaments) to be filtered to approach the collimation and monochromaticity of a laser.
- Pumping
 - Delivering energy to the atomic system, by electrically, optically, chemically, etc.
 - A laser is an out-of-equilibrium system.
 - Pumping need an active medium, which acts as an optical amplifier.
 - Population inversion: An atomic system in which the population of the excited level (N_1) is larger than that of the lower level (N_2)

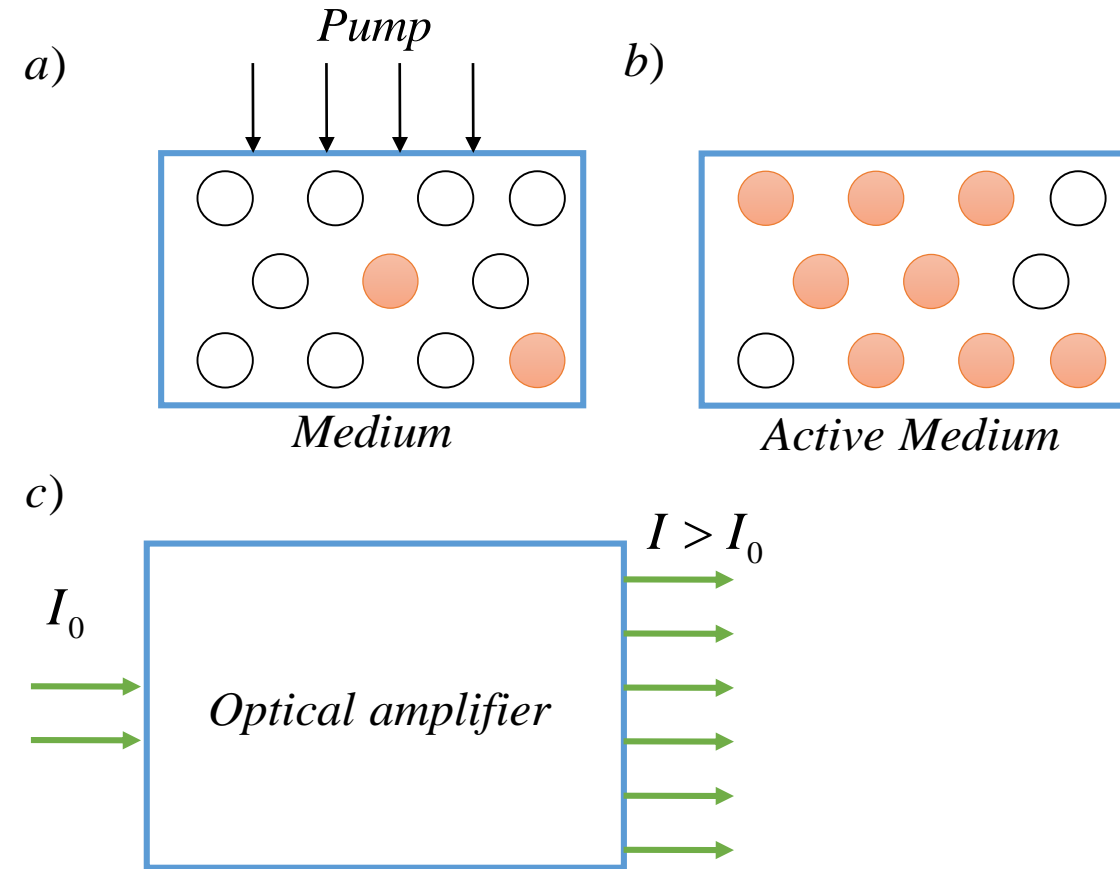


Figure 7.1. *a) Pumping: empty circles represent atoms on ground energy levels and solid circles denote excited atoms. b) Active medium: population inversion is achieved. c) Active medium acts as an optical amplifier of the incident radiation.*

Population inversion, Optical Resonator, and Narrow Band Radiation

- Positive feedback mechanism
 - Amplifying the light characterized by narrow spatial and temporal frequency bands.
- The optical resonator (cavity)
 - Converting the pump energy into a small number of modes: both longitudinal (temporal frequencies) and transverse (spatial frequencies).
- Examples
 - Positive feedback phenomenon
 - When a microphone is brought close to a speaker, a very narrow sound frequency band is amplified by the electronic circuit.
 - Spatial, or transverse mode feedback
 - Vibrations of broad frequencies are excited at the liquid surface, yet only those favored by the resonator (boundary conditions) become dominant.

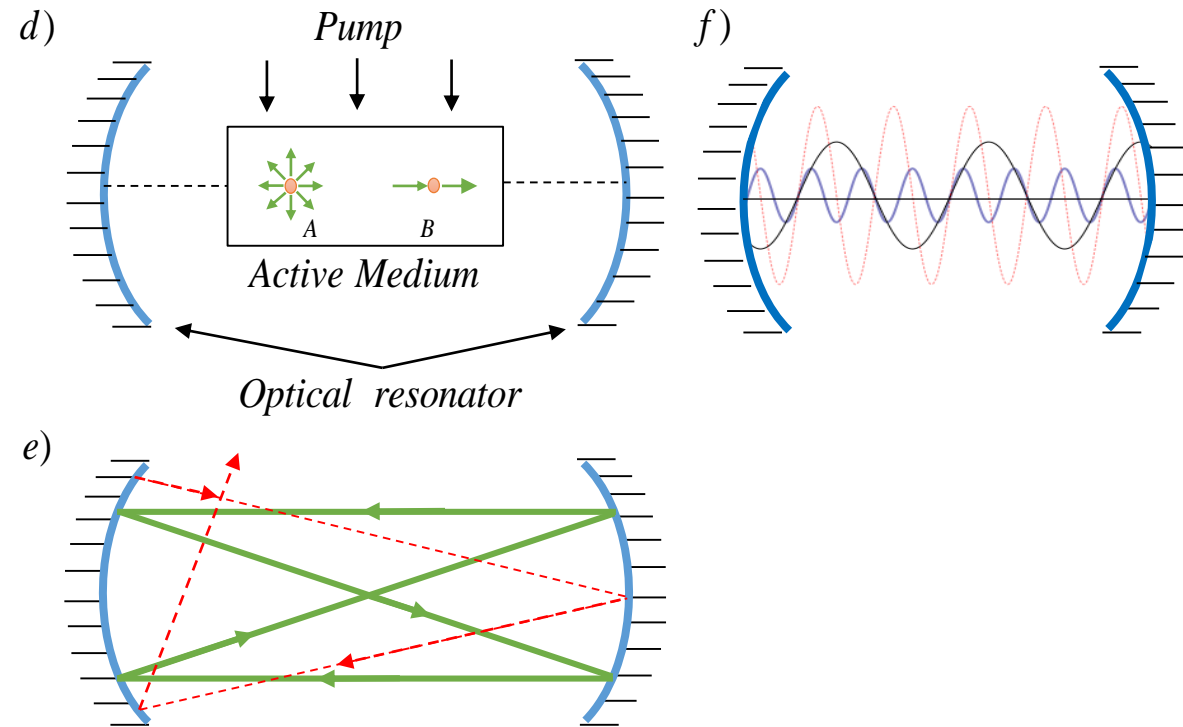


Figure 7.1. *d)* Active medium in a resonator: A, spontaneous emission, B, stimulated emission. *e)* Spatial frequency feedback: the path in green is stable, while the one in red is not (exits the resonator). *f)* Temporal frequency feedback: only the modes with zeros at the boundary survive in the resonator: the mode in blue line survives, the black and red are suppressed.

Gain

- Power gain in spectral irradiance, I_ν
 - Due to stimulated emission
 - The amplification is proportional to the volume of active medium, thus, distance dz .

$$dI_\nu = \gamma(\nu) I_\nu dz$$

- Gain coefficient, γ
 - For small signals, or weak amplification, γ does not depend on I_ν . The small signal gain is denoted by γ_0 .

$$I_\nu(L) = I_\nu(0) e^{\gamma_0(\nu)L}$$

- $\gamma_0 < 0$, denoting an exponential attenuation rather than gain.

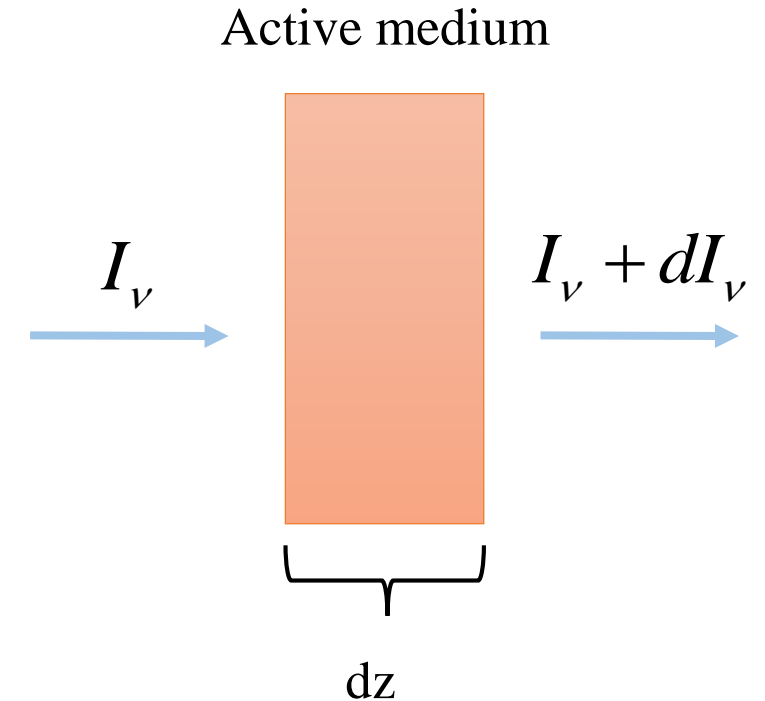


Figure 7.2. Gain through an active medium.

Gain

- Taking the rate equation for the populations of the two levels into account.

$$\frac{dN_2}{dt} = \int_0^\infty [-A_{21}N_2g(\nu) - B_{21}N_2\rho(\nu)g(\nu) + B_{12}N_1\rho(\nu)g(\nu)]d\nu$$

$p(\nu)$ —the spectral energy density of the pump

$p(\nu)d\nu$ —the probability of emission of light in $d\nu$

$g(\nu)$ —spectral line shape, probability density (emission & absorption)

- The line shape of the transition, where $g_{1,2}$ denote the spectral distribution for each electronic level.

$$g(\nu) = \int g_1(\nu')g_2(\nu' - \nu)d\nu'$$

- Standard deviation of $g(\nu)$, $\Delta\nu_{12}$.

$$\begin{aligned}\Delta\nu_{12}^2 &= \langle \nu_{12}^2 \rangle - \langle \nu_{12} \rangle^2 = \langle \nu_1^2 \rangle + \langle \nu_2^2 \rangle + 2\langle \nu_1 \rangle \langle \nu_2 \rangle - \langle \nu_1 + \nu_2 \rangle^2 \\ &= \langle \nu_1^2 \rangle - \langle \nu_1 \rangle^2 + \langle \nu_2^2 \rangle - \langle \nu_2 \rangle^2 = \Delta\nu_1^2 + \Delta\nu_2^2\end{aligned}$$

- The emission spectrum is broader than either of the individual levels, as the variances add up.

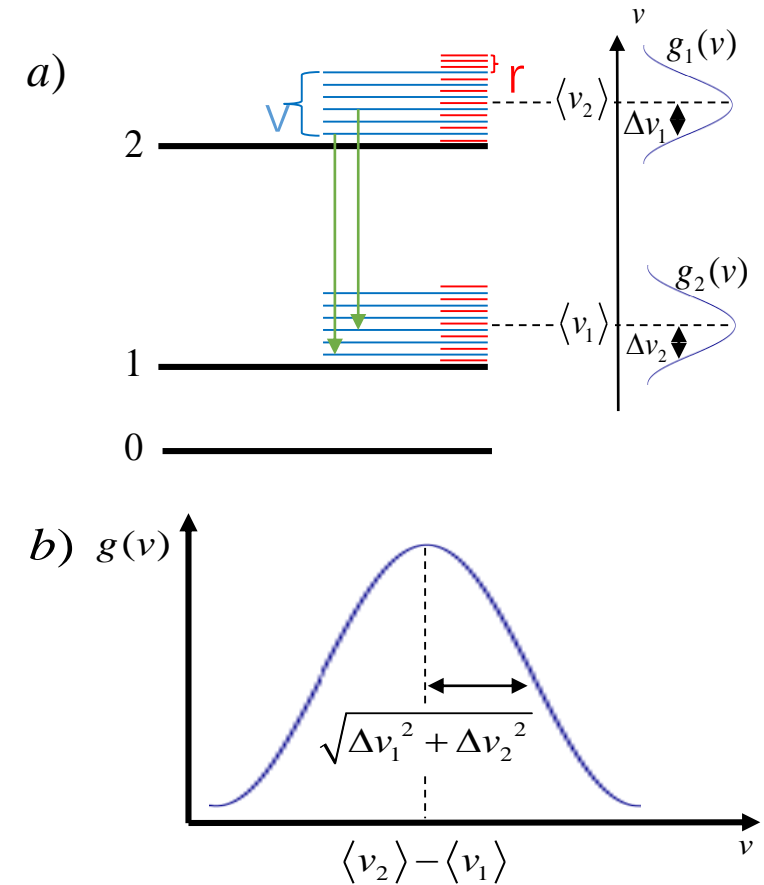


Figure 7.3. a) Electronic states, 0, 1, 2, each containing vibrational level (ν , blue lines) and respective rotational levels (r , red lines). The energy distribution of the upper levels 1 and 2 are g_1 , g_2 . **b)** The transition lineshape, g , is the cross-correlation function of g_1 and g_2 , with the average and standard deviation as indicated.

Gain

- The energy radiated per unit time and volume

$$d^2Q / (dtdV) = d^2Q / (dtAdz)$$

A — the area normal to direction z

dV — the infinitesimal volume of interest

$$\frac{dI_v}{dz} = \frac{d^2Q}{Adtdz} = \frac{d^2Q}{dtdV} = h\nu \frac{dN_2}{dt} = h\nu \left[-A_{21}N_2 - \int_0^\infty [B_{21}N_2\rho(\nu)g(\nu) - B_{12}N_1\rho(\nu)g(\nu)]d\nu \right]$$

$$\text{As } \int_0^\infty g(\nu)d\nu = 1, \text{ then } -A_{21}N_2 = -A_{21}N_2 \int_0^\infty g(\nu)d\nu$$

- Assume that the pump spectral density, $\rho(\nu)$, is much narrower than the absorption or emission linewidth, $g(\nu)$.

$$\rho(\nu') \simeq \rho(\nu)\delta(\nu - \nu')$$

$$\begin{aligned} & \int_0^\infty [B_{21}N_2\rho(\nu')g(\nu') - B_{12}N_1\rho(\nu')g(\nu')]d\nu' \\ &= \int_0^\infty [B_{21}N_2\rho(\nu)\delta(\nu - \nu')g(\nu') - B_{12}N_1\rho(\nu)\delta(\nu - \nu')g(\nu')]d\nu' \\ &= B_{21}N_2\rho(\nu)g(\nu) - B_{12}N_1\rho(\nu)g(\nu) \end{aligned}$$

Gain

- Invoke the relationships between Einstein's coefficients

$$\frac{1}{h\nu} \frac{dI_\nu}{dz} = -A_{21}N_2 - A_{21} \frac{c^3}{8\pi h\nu^3} \rho(\nu) g(\nu) \left[N_2 - \frac{g_2}{g_1} N_1 \right].$$

- For propagation along the z-direction

$$I_\nu = \rho(\nu)c \qquad \frac{1}{h\nu} \frac{dI_\nu}{dz} = -A_{21} \cdot N_2 - \frac{\sigma(\nu) I_\nu}{h\nu} \Delta N$$

$$\sigma(\nu) = A_{21} \frac{c^2}{8\pi\nu^2} g(\nu) = A_{21} \frac{\lambda^2}{8\pi} g(\nu) \qquad \sigma \text{—stimulated emission cross section}$$

$$\Delta N = N_2 - \frac{g_2}{g_1} N_1 \qquad \Delta N \text{—population inversion}$$

- σ quantifies how much stimulated emission power (in W) is emitted by each atom exposed to a certain irradiance (W/m^2)
- Note that the spontaneous emission term, $-A_{21}N_2$, represents noise in the laser system.

Gain

- During normal laser operation, the spontaneous emission term becomes subdominant and can be neglected.

$$\frac{dI_\nu}{dz} = \gamma(\nu) I_\nu = \sigma(\nu) I_\nu \Delta N$$

$$\gamma(\nu) = A_{21} \frac{\lambda^2}{8\pi} g(\nu) \left[N_2 - \frac{g_2}{g_1} N_1 \right] = \sigma(\nu) \Delta N$$

- The gain reduces or saturates if I_ν continues to increase via amplification.
- The small signal gain, γ_0

- The gain coefficient is positive only if there is a population inversion.
- For positive gain

$$I_\nu(L) = I_\nu(0) G_0(\nu, L) \quad G_0(\nu, L) = e^{\gamma_0(\nu)L}$$

- G_0 denotes power gain, which depends on the length of the medium and acts as a band-pass filter on the initial irradiance I_ν .

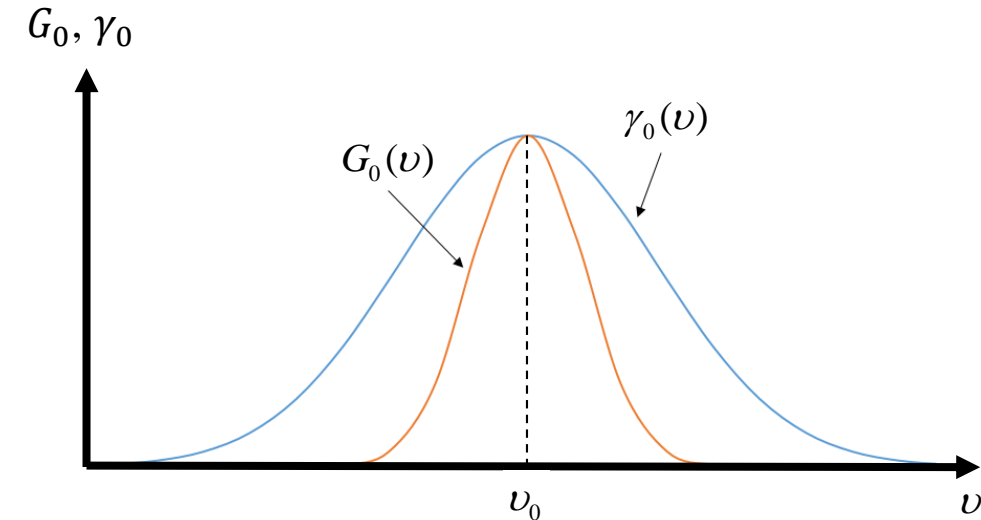


Figure 7.4. The (small signal) power gain, G_0 , is narrower in frequency than the gain coefficient, γ_0 .

Spectral Line Broadening

- Uncertainty principle
 - The line width of any transition has a finite bandwidth, simply because the light transit in the cavity is finite in time.
- Broadening the spectral line
 - Homogeneous broadening, when the mechanism is the same for all atoms
 - Inhomogeneous broadening, when different subgroups of atoms broaden the line differently.

Homogeneous Broadening

- Natural (lifetime) broadening
 - This broadening is due to the natural lifetime, i.e. without nonradiative decay like collisions.
 - The natural lifetime is the largest possible, the natural line shape is the narrowest.

Homogeneous Broadening

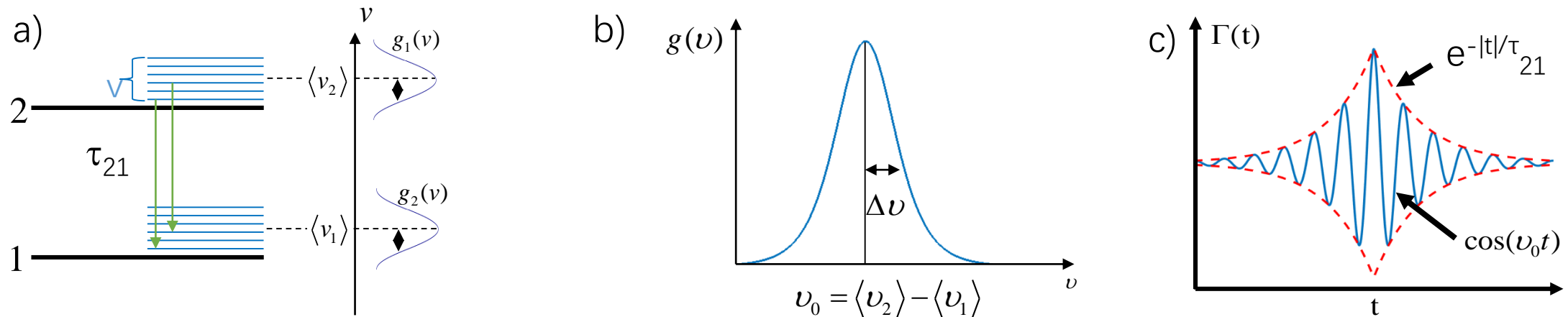


Figure 7.5. *a) Transition between two levels, with the lifetime as indicated. b) Spectral line of the emission. c) Temporal autocorrelation function associated with spontaneous emission, i.e., the Fourier transform of the power spectrum in b).*

- The natural line shape is a Lorentzian distribution, whose standard deviation diverges and, thus, cannot be used as a measure of bandwidth.

$$g(\nu) = \frac{1}{\pi} \frac{\Delta \nu / 2}{1 + \frac{(\nu - \nu_0)^2}{(\Delta \nu / 2)^2}}$$

$$\int_0^{\infty} g(\nu) d\nu = 1$$

$$\Gamma(t) = e^{-i2\pi\nu_0 t} e^{-2\pi\Delta\nu t}$$

- The temporal behavior of spontaneous emission (inverse Fourier transform of $g(\nu)$).

Homogeneous Broadening

- Collision broadening
 - The process of collisions between atoms is essential in gas lasers. In solids, pressure broadening is absent.
 - Assuming each atom experiences collisions at frequency ν_{col} . Collisions interrupt the emission process, essentially shortening the lifetime of both levels, 1 and 2, by the same amount.

$$A_{21}^{col} = A_{21} + \nu_{col}$$

$$A_{10}^{col} = A_{10} + \nu_{col}$$

$$\Delta\nu_{col} = \frac{1}{2\pi} [A_{21} + A_{10} + 2\nu_{col}]$$

$$\text{Often, } \nu_{col} \gg A_{21}, A_{10}, \quad \text{then we get } \Delta\nu_{col} \simeq \nu_{col}/\pi$$

- Typically, collision broadening is expressed as MHz of broadening per unit of pressure, and is homogeneous.

Inhomogeneous Broadening

- Inhomogeneous broadening
 - Doppler broadening (velocity related)
 - Isotope broadening (mass related)
 - Zeeman splitting (nuclear spins in magnetic fields)
 - Stokes splitting (nuclear spins in electric fields)
- Doppler broadening
 - At thermal equilibrium, the atoms in a gas have a Gaussian distribution of velocities along one axis (say, z), v_z .

$$p(v_z) = \frac{1}{\sqrt{2\pi}\Delta v} \cdot e^{-\frac{Mv_z^2}{2k_B T}} = \frac{1}{\sqrt{2\pi}\Delta v} \cdot e^{-\frac{v_z^2}{2(\Delta v)^2}} \quad \Delta v = \sqrt{\frac{k_B T}{M}} \quad \int_{-\infty}^{\infty} p(v_z) dv_z = 1$$

M is the atomic mass, T is the absolute temperature, k_B is the Boltzmann constant and Δv is the standard deviation of the Gaussian distribution.

Inhomogeneous Broadening

- Doppler frequency, ν_D

$$\nu_D - \nu_0 = \frac{v_z}{c} \nu_0.$$

- Natural line under Doppler effect

$$g\left(\nu - \nu_0 - \frac{v_z}{c} \nu_0\right) = \frac{1}{2\pi} \frac{\Delta\nu_h}{1 + \left(\frac{\nu - \nu_0 - \nu_0 \frac{v_z}{c}}{\frac{\Delta\nu_h}{2}}\right)^2}$$

- Inhomogeneous Doppler line broadening, which is the convolution between the Lorentzian associated with the homogeneous line, and the Gaussian velocity distribution.

Inhomogeneous Broadening

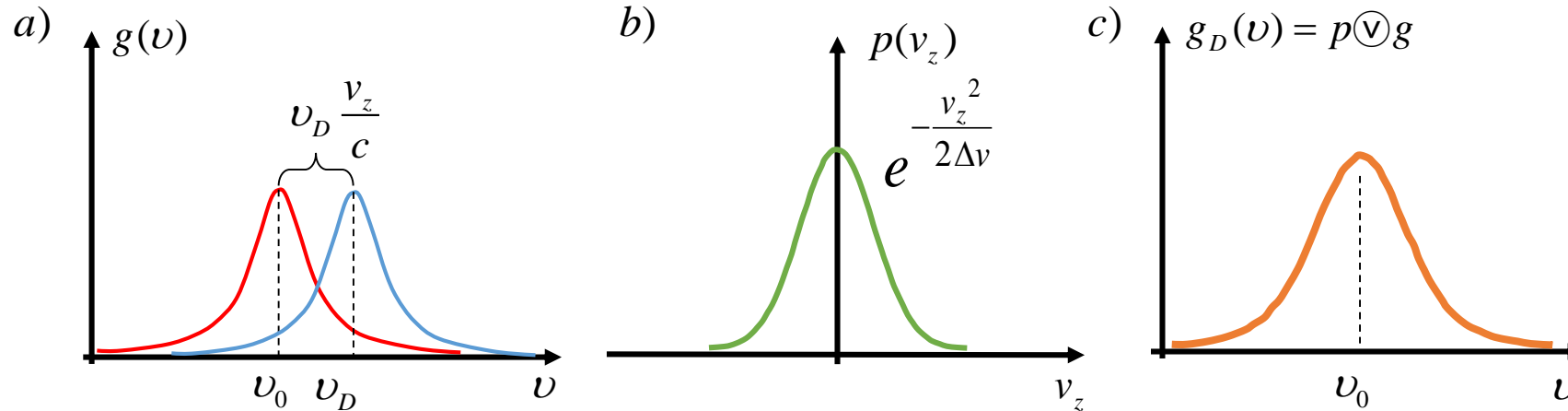


Figure 7.6. a) Doppler frequency shift of the “natural” transition line, for a single velocity v_z . b) Maxwell-Boltzmann distribution of velocities. c) Voigt distribution: the Doppler-broadened spectral line, averaged over all velocities.

- Voigt distribution

$$g_D(v) = \int_{-\infty}^{\infty} p(v_z) g\left(v - v_0 \frac{v_z}{c}\right) dv_z = p \odot g \qquad \tilde{g}_D(t) \propto e^{-a|t| - bt^2} e^{iv_0 t}$$

- The Doppler broadening is dominant over the natural broadening when g approaches a δ -function.
- Doppler broadening is reduced in low-temperature gases and is absent in solid state lasers.

Inhomogeneous Broadening

- Isotopic Broadening
 - The active medium contains isotopes of the same chemical element.
 - The helium-neon (He-Ne) laser, as neon occurs naturally in two isotopes ^{20}Ne and ^{22}Ne .
 - The spectral line is slightly shifted depending on which isotope emits light.
- Stokes and Zeeman Splitting
 - Stokes and Zeeman effects describe the splitting of the line due to, respectively, electric and magnetic fields present.
 - These phenomena are important in solid state lasers, where atoms in the lattice are exposed to inhomogeneous (local) fields.

Threshold for Laser Oscillation

- Population inversion is not sufficient for laser oscillation
 - The resonator introduces losses which may overwhelm the gain
- The threshold condition
 - Upon a round trip propagation in the resonator, the irradiance experiences a net gain.

$$e^{2\gamma_0(\nu)L} R_1 R_2 \geq 1.$$

- Threshold gain coefficient

$$\gamma_{th} = -\frac{1}{2L} \ln(R_1 R_2).$$

- The threshold condition acts as a filter in the frequency domain.

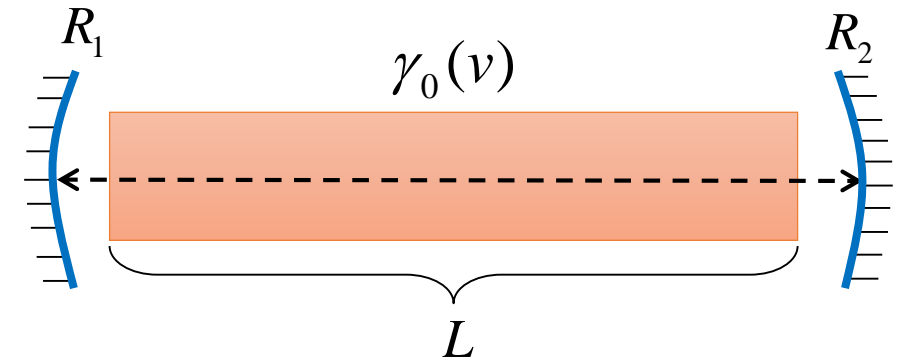


Figure 7.7. Losses in the resonator due to mirror reflection.

- For calculating the threshold gain, the stimulated emission can be ignored.
- As the power increases, spontaneous emission can be ignored.

Laser Kinetics

- The time evolution of laser radiation is dictated by the kinetics of the population in each level.
- Three-level system
 - The rate equations for the upper two levels of interest.

$$\frac{dN_2(t)}{dt} = P_2(t) - \frac{N_2(t)}{\tau_2} - \frac{\sigma(\nu)I(\nu)}{h\nu} [N_2(t) - N_1(t)]$$

$$\frac{dN_1(t)}{dt} = P_1(t) - \frac{N_1(t)}{\tau_1} + \frac{N_2(t)}{\tau_{21}} + \frac{\sigma(\nu)I(\nu)}{h\nu} [N_2(t) - N_1(t)]$$

$$\frac{1}{\tau_2} = \frac{1}{\tau_{20}} + \frac{1}{\tau_{21}} \text{ is the inverse lifetime (decay rate) of level 2.}$$

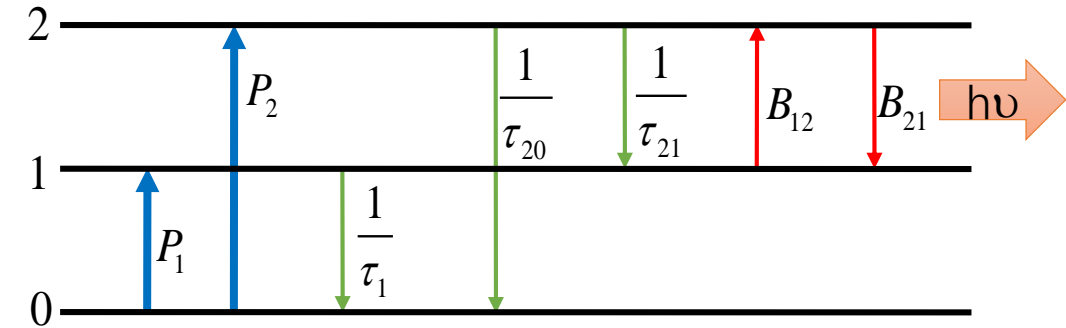


Figure 7.8. Three-level system: laser emission takes place due to radiative transition between levels 2 and 1.

$1/\tau_{20}$ — decay rate to ground state

$1/\tau_{21}$ — rate of spontaneous emission

P_1, P_2 — the pump rates of levels 1 and 2

σ — spontaneous emission cross section

$I(\nu)$ —spectral irradiance

$N_1 - N_2$ — population inversion

τ_1 — lifetime of level 1

Laser Kinetics

- Using Laplace transform to solve $N_1(t)$ and $N_2(t)$
 - The pumps $P_{1,2}$ turn on at $t=0$ and staying constant for $t>0$, i.e. a step function, $\Gamma(t)$

$$P_{1,2}(t) = \begin{cases} P_{1,2}, & t > 0 \\ \frac{1}{2} P_{1,2}, & t = 0 \\ 0, & \text{rest} \end{cases} = P_{1,2} \Gamma(t)$$

- Laplace Transform

$$\Gamma(t) \leftrightarrow \frac{1}{s}$$

$$\frac{df(t)}{dt} \leftrightarrow s\tilde{f}(s)$$

$$s\tilde{N}_2(s) = \frac{P_2}{s} - \frac{\tilde{N}_2(s)}{\tau_2} - \frac{\sigma I}{h\nu} [\tilde{N}_2(s) - \tilde{N}_1(s)]$$

$$s\tilde{N}_1(s) = \frac{P_1}{s} - \frac{\tilde{N}_1(s)}{\tau_1} + \frac{\tilde{N}_2(s)}{\tau_{21}} + \frac{\sigma I}{h\nu} [\tilde{N}_2(s) - \tilde{N}_1(s)]$$

Laser Kinetics

- Various particular cases can be solved, depending on which terms can be safely neglected.

$$s\tilde{N}_2(s) = \frac{P_2}{s} - \frac{\tilde{N}_2(s)}{\tau_2} - \frac{\sigma I}{h\nu} [\tilde{N}_2(s) - \tilde{N}_1(s)]$$
$$s\tilde{N}_1(s) = \frac{P_1}{s} - \frac{\tilde{N}_1(s)}{\tau_1} + \frac{\tilde{N}_2(s)}{\tau_{21}} + \frac{\sigma I}{h\nu} [\tilde{N}_2(s) - \tilde{N}_1(s)]$$

- $P_1=0$, no pumping of level 1.
- $1/\tau_2=0$, no spontaneous decay of level 2 (large signal gain).
- $\sigma=0$, no stimulated emission (weak signal).
- $1/\tau_{21}=0$, no spontaneous emission.
- $dN_1/dt = dN_2/dt = 0$, steady state.

Laser Kinetics

- Example 1: $P_1=0, \sigma=0$.

$$s\tilde{N}_2(s) = \frac{P_2}{s} - \frac{\tilde{N}_2(s)}{\tau_2} - \frac{\sigma I}{h\nu} [\tilde{N}_2(s) - \tilde{N}_1(s)]$$

$$s\tilde{N}_1(s) = \frac{P_1}{s} - \frac{\tilde{N}_1(s)}{\tau_1} + \frac{\tilde{N}_2(s)}{\tau_{21}} + \frac{\sigma I}{h\nu} [\tilde{N}_2(s) - \tilde{N}_1(s)]$$

$$\left(s + \frac{1}{\tau_2}\right) \tilde{N}_2(s) = \frac{P_2}{s}$$

$$\left(s + \frac{1}{\tau_1}\right) \tilde{N}_1(s) = \frac{\tilde{N}_2(s)}{\tau_{21}}$$

- Using partial fraction decomposition (or expansion)

$$\tilde{N}_2(s) = \frac{P_2}{s\left(s + \frac{1}{\tau_2}\right)} = P_2\tau_2 \left[\frac{1}{s} - \frac{1}{s + \frac{1}{\tau_2}} \right]$$

- The shift property of the Laplace transform

$$\tilde{f}(s+a) \rightarrow e^{-at} f(t) \qquad N_2(t) = P_2\tau_2 \left(1 - e^{-\frac{t}{\tau_2}} \right)$$

Laser Kinetics

- Expressing $N_1(s)$ as a sum of simple fractions, of the form $a/(s+b)$.

$$N_1(s) = \frac{P_2}{\tau_{21}} \frac{1}{s \left(s + \frac{1}{\tau_2} \right) \left(s + \frac{1}{\tau_1} \right)}$$

$$N_1(s) = \frac{P_2}{\tau_{21}} \left[\frac{A}{s} + \frac{B}{s + \frac{1}{\tau_2}} + \frac{C}{s + \frac{1}{\tau_1}} \right]$$

$$A \left(s + \frac{1}{\tau_2} \right) \left(s + \frac{1}{\tau_1} \right) + B \cdot s \left(s + \frac{1}{\tau_1} \right) + C \cdot s \left(s + \frac{1}{\tau_2} \right) = 1$$

$$A = \frac{1}{\left(s + \frac{1}{\tau_2} \right) \left(s + \frac{1}{\tau_1} \right)} \Bigg|_{s=0} = \tau_1 \tau_2, \quad B = \frac{1}{s \left(s + \frac{1}{\tau_1} \right)} \Bigg|_{s + \frac{1}{\tau_2} = 0} = \tau_1 \tau_2 \frac{1}{\frac{\tau_1}{\tau_2} - 1}, \quad C = \frac{1}{s \left(s + \frac{1}{\tau_2} \right)} \Bigg|_{s + \frac{1}{\tau_1} = 0} = \tau_1 \tau_2 \frac{\tau_1 / \tau_2}{1 - \frac{\tau_1}{\tau_2}}$$

Laser Kinetics

- Expressing $N_I(s)$ as a sum of simple fractions, of the form $a/(s+b)$.

$$N_1(t) = P_2 \frac{\tau_1 \tau_2}{\tau_2} \left[1 + \frac{\tau_1 / \tau_2}{1 - \tau_1 / \tau_2} e^{-\frac{t}{\tau_1}} - \frac{1}{1 - \tau_1 / \tau_2} e^{-\frac{t}{\tau_2}} \right]$$

- If $\tau_2 > \tau_1$, the density N_2 is greater than N_1 and gain is obtained across all values of t . If $\tau_1 > \tau_2$, the excited level is depleted and gain quickly diminishes.
- Note:** The two steady states are obtained as the limit of $N_1(t)$, $N_2(t)$, for $t \rightarrow \infty$.

$$N_1(t \rightarrow \infty) = P_2 \frac{\tau_1 \tau_2}{\tau_{21}}$$

$$N_2(t \rightarrow \infty) = P_2 \tau_2$$

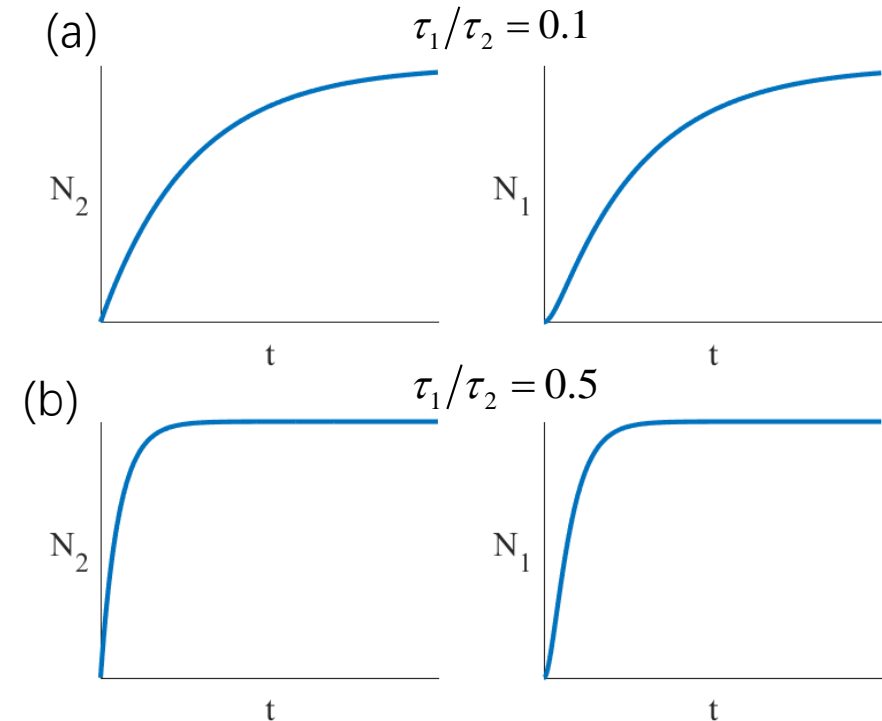


Figure 7.9. Population dynamics for the two levels expressed in Eqs. 7.35 (N_2) and 7.39 (N_1) for two ratios of the lifetimes, as indicated.

Laser Kinetics

- Partial fraction decomposition

$$f(s) = g(s) / h(s)$$

- g and h have no common factors and g of lower degree than h , we can expand f as

$$f(s) = \sum_n \frac{b_n}{s - a_n} = g(s)/h(s)$$

$$f(t) = \sum_n b_n e^{a_n t}$$

- a_n are the roots of h , b_n are constants that result from the identity $g(s)/h(s)$.
- A certain root, a_1 , has a multiplicity m .

$$\frac{1}{(s - a_1)^m}$$

$$f(s) = \sum_{n \neq 1} \frac{b_n}{s - a_n} + \sum_{k=1}^m \frac{b_{1k}}{(s - a_1)^k}$$

- Combining shift theorem with the Laplace transform pair.

$$\frac{1}{s^n} \leftrightarrow \frac{t^{n-1}}{(n-1)!}$$

$$\frac{b_{1k}}{(s - a_1)^k} \leftrightarrow \frac{b_{1k}}{(k-1)!} t^{k-1} e^{a_1 t}$$

- Suitable for the polynomial in the denominator that has roots of multiplicity greater than 1.

Gain Saturation

- The effect of stimulated emission ($\sigma \neq 0$)

$$s\tilde{N}_2(s) = \frac{P_2}{s} - \frac{\tilde{N}_2(s)}{\tau_2} - \frac{\sigma I}{h\nu} [\tilde{N}_2(s) - \tilde{N}_1(s)]$$

- Assume $\tau_1=0$, level 1 decays infinitely fast, i.e., $N_1=0$
- The population dynamics of level 2 in the Laplace domain.

$$\tilde{N}_2(s) \left[s + \frac{1}{\tau_2} + \frac{\sigma I}{h\nu} \right] = \frac{P_2}{s}$$

- New lifetime τ_2' , adjusted for the effects of stimulated emission.

$$\frac{1}{\tau_2'} = \frac{1}{\tau_2} \left[1 + \frac{\sigma I \tau_2}{h\nu} \right] = \frac{1}{\tau_2} \left(1 + \frac{I}{I_s} \right)$$

$$I_s = \frac{h\nu}{\sigma \tau_2} \text{ saturation irradiance} \quad N_2(t) = P_2 \tau_2' \left(1 - e^{-\frac{t}{\tau_2'}} \right)$$

- Whenever I approaches I_s , the gain saturates. ($I=I_s$, $\tau_2' = \tau_2/2$, faster depletion of level 2)

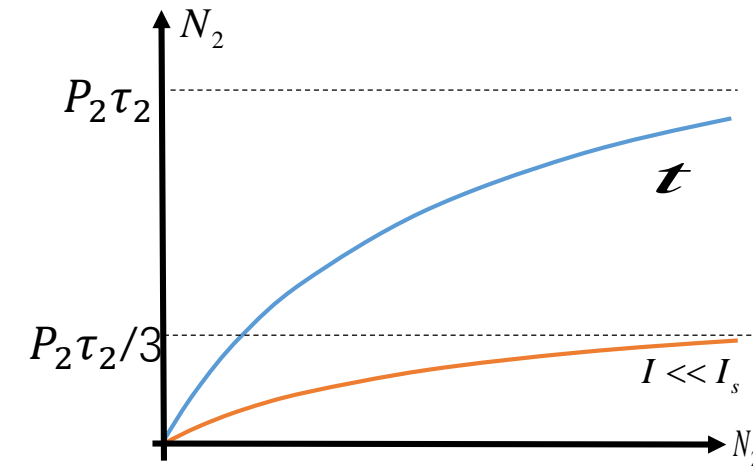


Figure 7.10. Effects of the saturation intensity on the N_2 kinetics.

Gain Saturation

- Saturation at steady state
 - The general equations at steady state.

$$P_2 - \frac{N_2}{\tau_2} - \frac{\sigma I}{h\nu} (N_2 - N_1) = 0$$

$$P_1 + \frac{N_2}{\tau_{21}} + \frac{\sigma I}{h\nu} (N_2 - N_1) - \frac{N_1}{\tau_1} = 0$$

$$N_2 - N_1 = \frac{P_2 \tau_2 \left(1 - \frac{\tau_1}{\tau_{21}}\right) - P_1 \tau_1}{1 + \left(\tau_1 + \tau_2 - \frac{\tau_1 \tau_2}{\tau_{21}}\right) \frac{\sigma I}{h\nu}}$$

- The gain is obtained as $\sigma(N_2 - N_1)$.

$$\gamma(v) = \frac{\gamma_0(v)}{1 + I/I_s} \quad \gamma_0(v) = \sigma(v) \left[P_2 \tau_2 \left(1 - \frac{\tau_1}{\tau_{21}}\right) - P_1 \tau_1 \right] \quad I_s = \frac{h\nu}{\sigma(v) \tau_2} \cdot \frac{1}{1 + \frac{\tau_1}{\tau_2} \left(1 - \frac{\tau_2}{\tau_{21}}\right)}$$

- Note: γ_0 is small signal gain, i.e. $I \rightarrow 0$, $\gamma \rightarrow \gamma_0$.
- For $\tau_2 \gg \tau_1$, or $\tau_{21} = \tau_2$, $I_s = h\nu/\sigma\tau_2$, the gain drops to $1/2 \gamma_0$.