

## Chapter 5: Radiative Transitions

5.1 Time-dependent perturbation theory

5.2 Radiative transitions, and selection rules

5.3 Einstein coefficients and basic principle of lasing

In this chapter, we examine how atoms respond to electromagnetic fields. We begin by discussing time-dependent perturbation theory and apply its first-order approximation to explore transition probabilities and selection rules. Additionally, we will introduce Einstein coefficients and study the basic principle of lasing.

## 5.1 Time-dependent perturbation theory

### 5.1a Time-dependent Schrödinger equation

As we have learned in PHYS20101, the state wave function of a quantum system of Hamiltonian  $\hat{H}$  is obtained, in general, by solving the time-dependent Schrödinger equation (TDSE)

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

or in Dirac notation

$$\hat{H}|\Psi(t)\rangle = i\hbar \frac{\partial}{\partial t} |\Psi(t)\rangle. \quad (1)$$

However, it may be that Eq. (1) is difficult to solve and we need to develop an approximation method to solve this equation. Assuming that the Hamiltonian  $\hat{H}$  can be written in two parts (similar to the time-independent perturbation theory we learned in PHYS20101),

$$\hat{H} = \hat{H}_0 + \hat{V}(t), \quad (2)$$

where the time-independent Hamiltonian  $\hat{H}_0$  was solved,

$$\hat{H}_0|m\rangle = E_m|m\rangle \quad (3)$$

with eigenvalues  $E_m$  and eigenstates  $|m\rangle$ ,  $m$  being the nominal index for all the quantum numbers of  $\hat{H}_0$ . We can take the time-dependent potential  $\hat{V}(t)$  as a perturbation and try to obtain the *approximate* eigenvalues and eigenfunctions of  $\hat{H}$  using  $E_m$  and  $|m\rangle$ . To this purpose, we write the exact eigenstate of  $\hat{H}$  as a linear combination of  $|m\rangle$  as

$$|\Psi(t)\rangle = \sum_m a_m(t)|m\rangle = \sum_m e^{-iE_m t/\hbar} c_m(t)|m\rangle, \quad (4)$$

where  $a(t)$  is re-written with the exponential factor for convenience. It represents the probability amplitude of the system in the eigenstate  $|m\rangle$  of  $\hat{H}_0$  at time  $t$ .

Substitute  $|\Psi(t)\rangle$  into the TDSE of Eq. (1), using Eq. (3), we have

$$\sum_m \left( E_m + \hat{V}(t) \right) e^{-iE_m t/\hbar} c_m(t)|m\rangle = \sum_m \left( E_m c_m(t) + i\hbar \frac{d}{dt} c_m(t) \right) e^{-iE_m t/\hbar} c_m(t)|m\rangle$$

or, after cancelling the same first term on both sides

$$\sum_m \hat{V}(t) e^{-iE_m t/\hbar} c_m(t) |m\rangle = i\hbar \sum_m \dot{c}_m(t) e^{-iE_m t/\hbar} c_m(t) |m\rangle, \quad (5)$$

with  $\dot{c}_m(t) = dc_m(t)/dt$ . In order to solve for  $c(t)$ , we take inner product of Eq. (5) on the both sides with  $\langle n|$ , using the orthonormal relations  $\langle n|m\rangle = \delta_{nm}$ , we obtain, switching the sides

$$i\hbar \dot{c}(t) = \sum_m V_{nm} e^{i\omega_{nm}t} c_m(t), \quad (6)$$

where

$$\omega_{nm} = \frac{E_n - E_m}{\hbar}, \quad V_{nm}(t) = \langle n|\hat{V}(t)|m\rangle.$$

Note that the TDSE of Eq. (1) is now reduced to Eq. (6) for  $c(t)$ . We next will develop a systematic approximation - the time-dependent perturbation theory - for solving for  $c(t)$ .

### 5.1b Perturbation theory

As our primary goal is to explore how the system responds to an external field, we make two assumptions about the initial condition here:

- a. We assume that the external field, represented by the perturbation potential  $\hat{V}(t)$ , is switched on at time  $t = 0$ ,

$$\hat{V}(t) \begin{cases} = 0, & t \leq 0 \\ \neq 0, & t > 0. \end{cases} \quad (7)$$

- b. Secondly, we assume that the quantum system under consideration was initially in an eigenstate of  $\hat{H}_0$ , say, state  $|1\rangle$ , before the external field  $\hat{V}(t)$  was applied. This implies that the coefficient, as described in Eq. (4), is

$$c_m(0) = \delta_{1,m} \quad \text{for } t \leq 0. \quad (8)$$

Now we are ready to introduce perturbation theory. In order to make a systematic approximation, we rewrite the Hamiltonian of Eq. (2) by inserting a book-keeping parameter  $\lambda$  as

$$\hat{H}(\lambda) = \hat{H}_0 + \lambda \hat{V}(t), \quad 0 \leq \lambda \leq 1,$$

and setting  $\lambda = 1$  in the end. We expand  $c(t)$  as a power series of  $\lambda$

$$c(t) = c_n^{(0)} + c_n^{(1)}\lambda + c_n^{(2)}\lambda^2 + \dots$$

and substitute into Eq. (6), replacing  $V_{nm}$  by  $\lambda V_{nm}$

$$i\hbar \left( \dot{c}_n^{(0)} + \dot{c}_n^{(1)}\lambda + \dot{c}_n^{(2)}\lambda^2 + \dots \right) = \sum_m \left( c_m^{(0)} + c_m^{(1)}\lambda + c_m^{(2)}\lambda^2 + \dots \right) \lambda V_{nm} e^{i\omega_{nm}t}. \quad (9)$$

By equating the coefficients of the same order of  $\lambda$  on both sides of Eq. (9), we obtain

$$\begin{aligned} \text{0th - order} \quad & i\hbar \dot{c}_n^{(0)} = 0 \\ \text{1st - order} \quad & i\hbar \dot{c}_n^{(1)} = \sum_m c_m^{(0)} V_{nm} e^{i\omega_{nm}t} \\ \text{2nd - order} \quad & i\hbar \dot{c}_n^{(2)} = \sum_m c_m^{(1)} V_{nm} e^{i\omega_{nm}t} \\ & \dots \end{aligned}$$

The 0th-order equation is easily solved,

$$c_n^{(0)} = \text{const.} = \delta_{1,n} \quad (10)$$

where the last equation is derived from the initial condition of Eq. (8). Substitute this into the 1st-order equation we have

$$i\hbar \dot{c}_n^{(1)} = V_{n1} e^{i\omega_{n1}t}. \quad (11)$$

Integrate over time  $t$ , we get

$$n = 1, \quad c_1^{(1)}(t) = \frac{1}{i\hbar} \int_0^t V_{11}(t') dt' \quad (12)$$

$$n \neq 1, \quad c_n^{(1)}(t) = \frac{1}{i\hbar} \int_0^t V_{n1}(t') e^{i\omega_{n1}t'} dt' \quad (13)$$

Together with the 0th-order solution of Eq. (10), and setting  $\lambda = 1$ , we obtain the 1st-order approximation:

- a. the probability for the system to remain in the initial state  $|1\rangle$  after applying the external field is

$$P_1(t) = |1 + c_1^{(1)}(t)|^2; \quad (14)$$

- b. the probability to make transition to a final state  $|n\rangle$  ( $n \neq 1$ ) is

$$P_n(t) = |c_n^{(1)}(t)|^2. \quad (15)$$

### 5.1c Example

Consider that a Hydrogen atom in its ground state  $\psi_{100}$  is in a uniform electric field in the  $z$  direction. The field is switched on at the time  $t = 0$ ,

$$E(t) = \begin{cases} 0, & t \leq 0, \\ E_0 e^{-t/\tau}, & t > 0, \end{cases}$$

where  $E_0$  and  $\tau (> 0)$  are constants. Find the probability that the Hydrogen atom ends up in the  $2p$  excited state  $\psi_{210}$  in the limit  $t \rightarrow \infty$ . Given that the ground and excited states of Hydrogen atom are

$$\psi_{100}(r, \theta, \phi) = \frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0}, \quad \psi_{210}(r, \theta, \phi) = \frac{r}{\sqrt{32\pi a_0^5}} e^{-r/2a_0} \cos \theta,$$

where  $a_0$  is the Bohr radius.

**Solution:** The transition amplitude in the 1st-order approximation is, according to Eq. (13)

$$c(t) = \frac{1}{i\hbar} \int_0^t V_{2p,1s}(t') e^{i\omega_{2p,1s} t'} dt'$$

where we have dropped the indices in  $c$  for simplicity. Since

$$\hbar\omega_{2p,1s} = E_{2p} - E_{1s} = -\frac{13.6}{2^2} + 13.6 = 10.2 \text{ eV}$$

and

$$V(t') = -(-e)zE_z = er \cos \theta E_0 e^{-t'/\tau}, \quad \tau > 0$$

we have

$$V_{2p,1s}(t') = \langle 2p|V(t')|1s\rangle = eE_0 e^{-t'/\tau} \langle 2p|r \cos \theta|1s\rangle,$$

where the integral is calculated as

$$\begin{aligned} \langle 2p|r \cos \theta|1s\rangle &= \frac{1}{4\pi\sqrt{2}a_0^4} \int_0^\infty dr r^4 e^{-3r/2a_0} \int_0^\pi d\theta \cos^2 \theta \sin \theta \int_0^{2\pi} d\phi \\ &= \frac{1}{4\pi\sqrt{2}a_0^4} \left[ \left( \frac{2a_0}{3} \right)^4 \right] \left( \frac{2}{3} \right) 2\pi = A. \end{aligned}$$

Hence

$$V_{2p,1s}(t') = eE_0 A e^{-t'/\tau}$$

The probability amplitude is

$$c(t) = \frac{eE_0 A}{i\hbar} \int_0^t e^{i(\omega_{2p,1s} - 1/\tau)t'} dt' = \frac{eE_0 A}{i\hbar} \frac{e^{i(\omega_{2p,1s} - 1/\tau)t}}{i(\omega_{2p,1s} - 1/\tau)}.$$

The transition probability is

$$P(t) = |c(t)|^2 = \left( \frac{eE_0A}{\hbar} \right)^2 \frac{1 + e^{-2t/\tau} - 2e^{-t/\tau} \cos(\omega_{2p,1s}t)}{\omega_{2p,1s}^2 + 1/\tau^2},$$

and in the limit  $t \rightarrow \infty$ ,

$$P = \frac{(eE_0A)^2}{\hbar^2(\omega_{2p,1s}^2 + 1/\tau^2)} = \frac{2^{15}(eE_0a_0)^2}{3^{10}(\omega_{2p,1s}^2 + 1/\tau^2)}.$$

## 5.2 Radiative transitions, and selection rules

### 5.2a Fermi Golder rule

Now we consider a geararl step-like perturbation potential  $\hat{V}(t)$

$$\hat{V}(t) = \begin{cases} 0, & t \leq 0, \\ \hat{V}, & t > 0 \end{cases} \quad (16)$$

where  $\hat{V}$  is time-independent. We assume that the system was in an (initial) eigenstate of  $\hat{H}_0$ ,  $|i\rangle$ . We need to find the probability for the system to make transition to a final eigenstate  $|f\rangle$  in the 1st-order approximation after the perturbation switching on. Using Eq. (13), noting that  $V_{f,i}$  is independent of time, we have

$$c(t) = \frac{1}{i\hbar} \int_0^t V_{f,i} e^{i\omega_{f,i}t'} dt' = \frac{V_{f,i}}{i\hbar} \frac{1 - e^{i\omega_{f,i}t}}{\omega_{f,i}}, \quad V_{f,i} = \langle f | \hat{V} | i \rangle.$$

Hence, the transition probability in the 1st-order approximation is

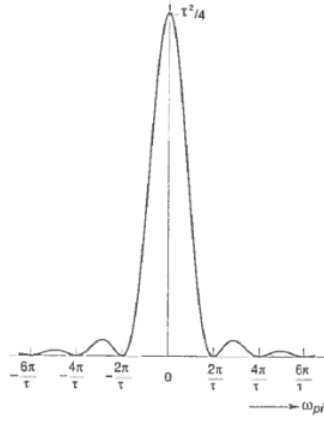
$$P(t) = |c(t)|^2 = \frac{4|V_{f,i}|^2 \sin^2(\omega_{f,i}t/2)}{\hbar^2 \omega_{f,i}^2} = \frac{2\pi t |V_{f,i}|^2}{\hbar^2} D(\omega_{f,i}, t), \quad (17)$$

where we have introduced  $D(x, t)$  defined as

$$D(x, t) = \frac{2}{\pi t} \frac{\sin^2(xt/2)}{x^2},$$

shown in following figure, and satisfying a normalization integral

$$\int_{-\infty}^{\infty} D(x, t) dx = 1.$$



Note that  $D(x, t)$  behaves as the Dirac-delta function in the limit  $t \rightarrow \infty$ ,

$$D(x, t) \rightarrow \delta(x), \quad \text{as } t \rightarrow \infty.$$

We summarize our result as the Fermi Golden Rule: the transition probability is given by

$$P(t) \propto \frac{2\pi t}{\hbar^2} |V_{f,i}|^2 \delta(\omega_{f,i}), \quad \text{when } t \rightarrow \infty, \quad (18)$$

**nonzero only when the final energy  $E_f$  equal the initial energy  $E_i$ .**

Next, we extend the step-like potential of Eq. (16) to a case with an oscillatory time dependence at an angular frequency  $\omega$

$$\hat{V} \rightarrow \hat{V} e^{-i\omega t}.$$

Hence the limiting probability now reads

$$P(t) \propto \frac{2\pi t}{\hbar^2} |V_{f,i}|^2 \delta(\omega_{f,i} - \omega), \quad \text{when } t \rightarrow \infty.$$

The probability per unit time, or the transition rate, is then

$$\frac{dP}{dt} = \frac{2\pi}{\hbar^2} |V_{f,i}|^2 \delta(\omega_{f,i} - \omega), \quad \text{when } t \rightarrow \infty. \quad (19)$$

## 5.2b Emission and absorption of EM radiations

We are now ready to discuss the response of a hydrogen atom to applied electromagnetic radiation. The magnetic field component of the radiation can be neglected, as it is much weaker (as  $B \propto E/c$ ). Using the dipole approximation, we focus on the potential of the electric field

$$\hat{V}(t) = -eE_0 \cos(\omega t) \hat{\mathbf{e}} \cdot \mathbf{r}, \quad (20)$$

where  $\hat{\epsilon}$  is the polarization direction of the  $\mathbf{E}$  field. Writing

$$\cos(\omega t) = \frac{1}{2} (e^{i\omega t} + e^{-i\omega t})$$

and using the Fermi Golden Rule of Eq. (19), we obtain the transition rate from the initial state  $|i\rangle$  to the final state  $|f\rangle$  in the limit  $t \rightarrow \infty$ ,

$$\frac{dP}{dt} = \frac{2\pi}{\hbar^2} \left( \frac{eE_0}{2} \right)^2 |\langle f | \hat{\epsilon} \cdot \mathbf{r} | i \rangle|^2 [\delta(\omega_{f,i} - \omega) + \delta(\omega_{f,i} + \omega)] . \quad (21)$$

Here, the first term represents the absorption rate, while the second term corresponds to the emission rate. In particular, the matrix element factor  $\langle f | \hat{\epsilon} \cdot \mathbf{r} | i \rangle$  will give us the selection rules for the transitions.

Recall that the states of hydrogen, including spin-orbit coupling as studied in Chapter 3, are characterized by four quantum numbers  $|n, l, j, m_j\rangle$  with  $j = l \pm 1/2$ . Denoting the initial state as  $|i\rangle = |n, l, j, m_j\rangle$  and the final state as  $|f\rangle = |n', l', j', m'_j\rangle$  with the primed quantum numbers. We need to evaluate the matrix element

$$\langle n', l', j', m'_j | \hat{\epsilon} \cdot \mathbf{r} | n, l, j, m_j \rangle .$$

Assuming a linear polarization of the radiation along the  $z$  direction,

$$\hat{\epsilon} \cdot \mathbf{r} = z = \cos \theta \propto Y_{1,0}(\theta, \phi)$$

where  $Y_{l,m_l}(\theta, \phi)$  is a spherical harmonic function. For a circular polarized field,

$$\hat{\epsilon} \cdot \mathbf{r} = \frac{1}{\sqrt{2}}(x + iy) \propto Y_{1,\pm 1}(\theta, \phi) .$$

Therefore in a general dipole approximation,

$$\hat{\epsilon} \cdot \mathbf{r} \propto Y_{1,m_1}(\theta, \phi), \quad m_1 = 0, \pm 1 .$$

Using the following identity for the spherical harmonics,

$$Y_l^{m_1} Y_l^{m_2} = a Y_{l+1}^{m_1+m_2} + b Y_{l-1}^{m_1+m_2}$$

with constants  $a$  and  $b$ , we conclude that the matrix element

$$\langle n', l', j', m'_j | \hat{\epsilon} \cdot \mathbf{r} | n, l, j, m_j \rangle \neq 0$$

if and only if  $\Delta l = l' - l = \pm 1$ . Therefore we obtain the selection rules for the electric dipole radiations as

$$\Delta l = \pm 1, \quad \Delta j = 0, \pm 1, \quad \Delta m_j = 0, \pm 1 . \quad (22)$$



Extension to a multi-electron atom under EM radiation, the dipole potential is

$$\hat{V} \propto eE_0 \cos(\omega t) \hat{\mathbf{e}} \cdot \mathbf{R},$$

where  $\mathbf{R} = \sum_i \mathbf{r}_i$  is the sum of all electrons' position vectors,  $\hat{\mathbf{L}} = \sum_i \hat{\mathbf{L}}_i$  is the total orbital angular momentum,  $\hat{\mathbf{S}} = \sum_i \hat{\mathbf{S}}_i$  the total spin,  $\hat{\mathbf{J}} = \sum_i \hat{\mathbf{J}}_i$  the total angular momentum, the selection rules for light multi-electron atoms with good quantum numbers ( $S, L, J, M_J$ ) are

$$\Delta S = 0, \quad \Delta L = 0, \pm 1, \quad J = 0, \pm 1, \quad \Delta M_J = 0, \pm 1, \quad (23)$$

and  $L_i = 0 \leftrightarrow L_f = 0$  is not allowed. In addition, if we are given the electronic configuration of the state of the  $Z$ -electron atom

$$(n_1 l_1)(n_2 l_2) \cdots (n_Z l_Z),$$

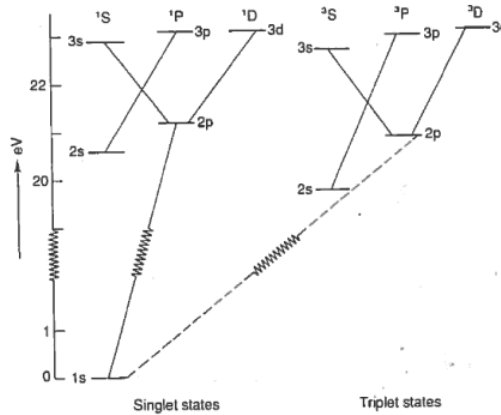
we can add another rule about the parity:

$$\pi^i = -\pi^f \quad (24)$$

where  $\pi$  is the total parity of the states

$$\pi = (-1)^{\sum_{i=1}^Z l_i}$$

because the dipole potential is an odd function of  $\mathbf{r}$ . The allowed dipole transition for a Helium atom is shown in the following figure, we have also included the very weak non-dipole transitions with  $\Delta S = 1$ .

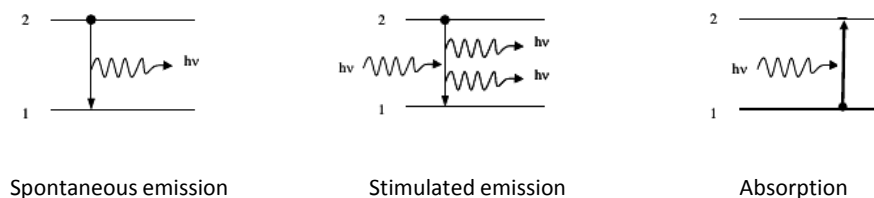


### 5.3 Einstein coefficients and basic principle of lasing

### 5.3a Einstein coefficients and population inversion

In the previous section, we discussed radiative transitions involving the emission and absorption of a single photon. Here, we focus on radiative transitions in multi-photon states involving many atoms. Specifically, we explore the fundamental principles underlying laser action. A few basic formulae from PHYS20352 Statistical Physics will be needed.

Consider first for simplicity that a gas of “atoms” has only two energy levels, the ground state with  $E_1$  and number density  $N_1$ , and the excited state with  $E_2$  and number density  $N_2$ . The atoms in a cavity will interact with the black-body radiation field, emitting and absorbing quanta of energy of frequency  $\nu$ , where  $h\nu = E_2 - E_1$ .



There are three types of transitions between these two energy levels: spontaneous emission, stimulated emission, and absorption:

- i. **Spontaneous emission:** The change rate is given by

$$\frac{dN_2}{dt} = -A_{21}N_2 \quad \rightarrow \quad N_2(t) = N_2(0) e^{-A_{21}t},$$

where  $A_{21}$  is the Einstein  $A$  coefficient.

- ii. **Stimulated emission:** The change rate in this case is given by

$$\frac{dN_2}{dt} = -B_{21}\rho N_2,$$

where  $\rho = I/c$  is the energy density at the transition frequency (with dimensions  $\text{Hz}^{-1}$ ) in the radiation field and  $B_{21}$  is the Einstein  $B$  coefficient for stimulated emission.

- iii. **Absorption:** The change rate

$$\frac{dN_1}{dt} = -B_{12}\rho N_1,$$

where  $B_{12}$  is the Einstein  $B$  coefficient for absorption.

Note that the stimulated coefficients  $B_{21}$  (or  $B_{12}$ ) is in fact related to the transition probability in the radiation potential and is proportional to the matrix element  $|\langle 1|\hat{V}|2\rangle|^2$  (see Eq. (21)). But how do we determine the spontaneous coefficient  $A_{21}$ ?

In general all three processes are operating, hence we write

$$\frac{dN_2}{dt} = -B_{21}\rho N_2 - A_{21}N_2 + B_{12}\rho N_1. \quad (25)$$

At thermal equilibrium, we have the following three conditions:

1. Zero rate

$$\frac{dN_2}{dt} = 0;$$

2. The blackbody radiation

$$\rho = \frac{8\pi h\nu^3}{c^3} \frac{1}{\exp(h\nu/k_B T) - 1}, \quad (26)$$

i.e. product of density of states for photons and boson occupation function;

3. The Boltzmann distribution

$$\frac{N_2}{N_1} = e^{-h\nu/k_B T}. \quad (27)$$

Hence, by substituting and some rearrangement we get,

$$\left( A_{21} - B_{21} \frac{8\pi h\nu^3}{c^3} \right) + \left( B_{12} \frac{8\pi h\nu^3}{c^3} - A_{21} \right) e^{h\nu/k_B T} = 0.$$

This must hold true for any temperature; therefore, both brackets must equal zero, leading to:

$$B_{12} = B_{21}, \quad A_{21} = \frac{8\pi h\nu^3}{c^3} B_{21}. \quad (28)$$

We already know the first equation in earlier discussion (see Eq. (21)). The 2nd equation expresses  $A_{21}$  in terms of  $B_{21}$ .

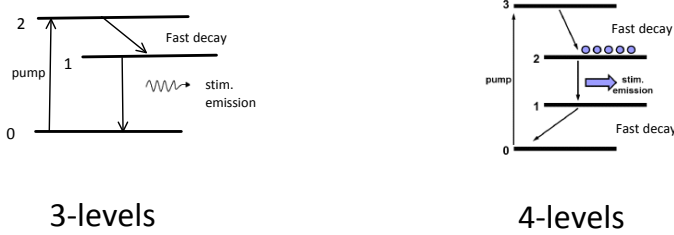
At thermal equilibrium, we always have  $N_2 < N_1$  from Eq. (27). To achieve  $N_2 > N_1$ , which is a fundamental requirement for a laser (light amplification through stimulated emission), we must use pumping to create an excess population of atoms in the excited states – this process is known as population inversion. Consequently, Eq. (25) is modified as

$$\frac{dN_2}{dt} = -B_{21}\rho N_2 - A_{21}N_2 + B_{12}\rho N_1 + R, \quad (29)$$

where  $R$  is the pump rate. Ways of doing this is described below.

### 5.3b Energy-level systems for practical lasers

As mentioned, to achieve population inversion in a laser system, pumping is required. In practice, this is typically implemented in laser systems with more than two energy levels, such as three-level or four-level systems. Consider a four-level system: in this case, pumping excites electrons from the ground state (level 0) to the top level (pump band, level 3), followed a transition to the upper laser level (level 2). Laser action occurs between the two middle levels (levels 2 and 1). For efficient operation, the transitions from level 3 to level 2 and from level 1 to level 0 must have lifetimes significantly shorter than that of the laser transition, to keep  $N_2 \gg N_1$ .



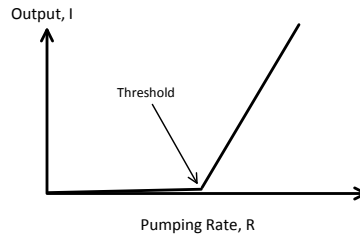
The rate equation of Eq. (29) is now, taking  $N = N_2 - N_1 \approx N_2$ ,

$$\frac{dN}{dt} = R - N(B_{21}\rho + A_{21}).$$

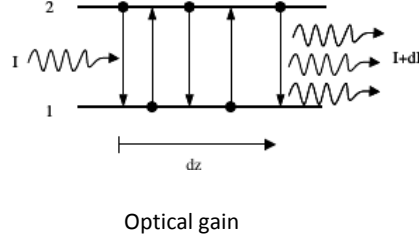
At the steady state, this is zero and  $N = N_{th}$ , so

$$\rho = \frac{1}{N_{th}B_{21}} (R - R_{th}), \quad (30)$$

where  $R_{th} = N_{th}A_{21} = N_{th}/\tau$  is the threshold pump rate,  $\tau = 1/A_{21}$  is the life-time of the state 2.



### 5.3c\* Optical gain



After achieving population inversion, we can calculate the optical gain as follow. Consider a system of the gas atoms in a cylindrical structure for the cavity, a typical structure for production of narrow beam of photons in a laser. In a length  $dz$ , the gain in intensity of the light  $dI$  is given by

$$dI = s(N_2 B_{21} - N_1 B_{12}) \frac{I}{c} h\nu dz ,$$

where  $s$  is known as the “lineshape”, related to the transition linewidth. But  $B_{21} = B_{12}$ , so

$$I(z) = I(0) e^{\gamma z} ,$$

where

$$\gamma = s(N_2 - N_1) B_{21} \frac{h\nu}{c} = (N_2 - N_1) \sigma ,$$

$\sigma$  is known as the stimulated emission cross section, and  $\gamma$  with dimensions  $\text{m}^{-1}$  as the gain coefficient. As we see, the system has optical gain if  $\gamma > 0$ , which happens in population inversion  $N_2 > N_1$ .