

Radiative transitions

- Einstein coefficients
- Radiative transitions
- Transition rates
- Selection rules
- Line profiles and curve of growth. Line broadening.

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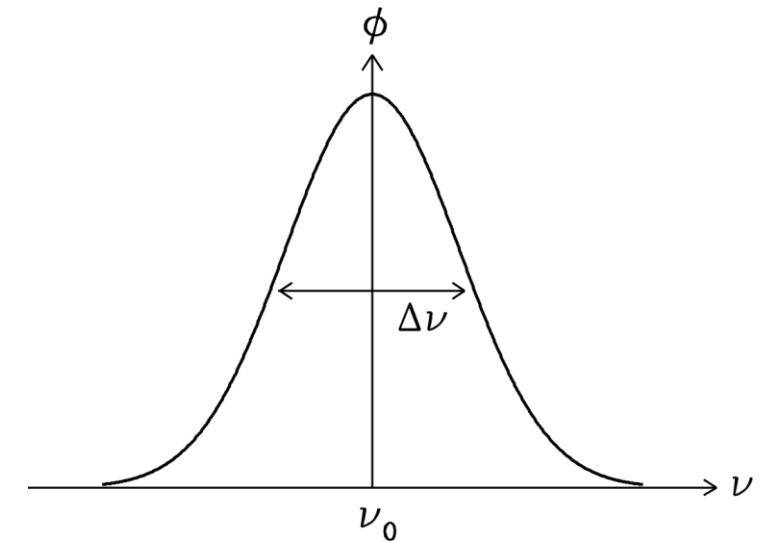
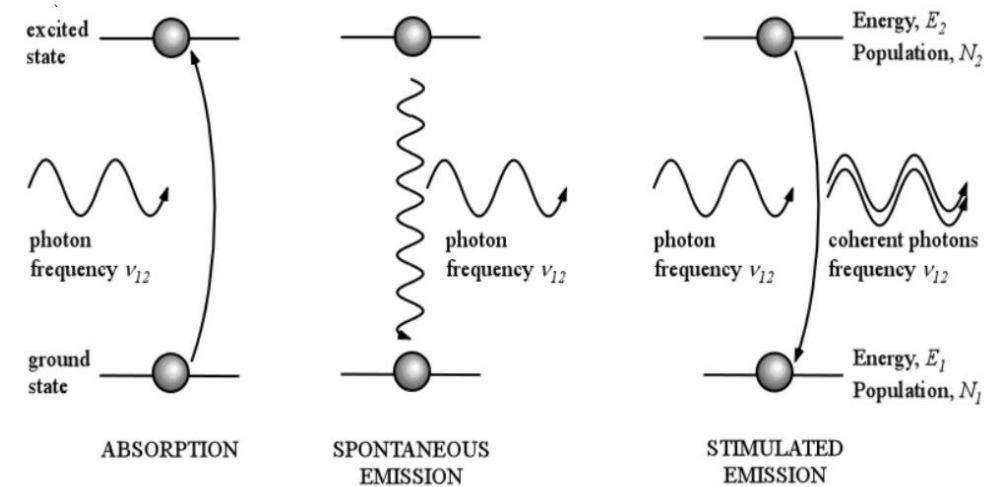
Einstein's coefficients

Kirchhoff's law, relating emission and absorption for a **thermal emitter**, must imply a relationship between emission and absorption at a microscopic level. Discovered by Einstein with a simple analysis. Suppose we have an atom with **two energy levels** with an energy difference of $\Delta E = h\nu_0$. Einstein coefficients describe the transition rates caused by the interaction of radiation with these discrete energy levels. Einstein identified three processes:

1) **Spontaneous emission**: this occurs when the system in level 2 drops in level 1 by emitting a photon, and it occurs even in the absence of a radiation field. We define the Einstein-A coefficient by:

A_{21} = transition probability per unit time for spontaneous emission (sec^{-1}).

2) **Absorption**: this occurs in the presence of photons of energy $h\nu_0$. The system makes a transition from level 1 to level 2 by absorbing a photon. To describe the background radiation field, we use the spherically averaged specific intensity J_ν (absorption does not depend on direction). However, there are uncertainties in the energy-level separations, i.e. atoms absorb photons that are not perfectly tuned to ΔE . To incorporate this, we use the **line profile function**, $\phi(\nu)$, the relative absorption probability around ν_0 , subject to the requirement $\int_{-\infty}^{+\infty} \phi(\nu) d\nu = 1$.



Note, the line profile function has dimension of the inverse of a frequency, i.e. time

Einstein's coefficients

We can approximate the width of $\Phi(\nu)$ as an effective width $\Delta\nu$ which is affected by many factors (to be discussed later).

The transition probability per unit time associated with spontaneous absorption is then the Einstein B-coefficient:

$B_{12}\bar{J}$ = transition probability per unit time for absorption (sec^{-1}) , where $\bar{J} \equiv \int_0^\infty J_\nu \Phi(\nu) d\nu$

3)**Stimulated emission** : Einstein found that to derive Planck's law another process is required, that is proportional to \bar{J} and causes emission of a photon. As before, we define:

$B_{21}\bar{J}$ = transition probability per unit time for stimulated emission (sec^{-1}).

Relations between Einstein coefficients

In thermodynamic equilibrium, the number of transitions per unit time per unit volume out of state 1 must equal the number of transitions per unit time per unit volume into state 1. Being n_1 and n_2 the number densities of atoms in levels 1 and 2,

$$n_1 B_{12} \bar{J} = n_2 A_{21} + n_2 B_{21} \bar{J}$$

Solving for \bar{J} ,

$$\bar{J} = \frac{n_2 A_{21}}{n_1 B_{12} - n_2 B_{21}}$$

Multiplicity of the level

Using the Boltzmann distribution (thermodynamic equilibrium), $\frac{n_2}{n_1} = \frac{g_2}{g_1} e^{\frac{-h\nu_0}{kT}}$ and $\bar{J} = \frac{\frac{A_{21}}{B_{21}}}{\frac{g_1 B_{12}}{g_2 B_{21}} e^{\frac{h\nu_0}{kT}} - 1}$

In thermal equilibrium, $J_\nu = (\text{for isotropy}) = I_\nu = B_\nu$ (Planck function).

Since J_ν varies slowly on the scale of $\Delta\nu$, then $\bar{J} = J_\nu \int_0^\infty \Phi(\nu) d\nu = J_\nu = B_\nu$

Einstein's coefficients

$$\bar{J} = \frac{\frac{A_{21}}{B_{21}}}{\frac{g_1 B_{12}}{g_2 B_{21}} e^{\frac{h\nu_0}{kT}} - 1} = B_\nu(T)$$

In order this equation to hold for every temperature, we must have the following **Einstein relations**:

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

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

Connect atomic properties and have no reference to T (unlike Kirchhoff's law, which hold in LTE): they must hold whether or not the atoms are in thermodynamic equilibrium. They extend Kirchhoff's law to include nonthermal emission. Example of detailed balance relation, connecting a microscopic process to its inverse.

Rewriting j_ν and α_ν in terms of the Einstein coefficients.

- In a small volume dV , the energy **emitted** per unit solid angle, frequency and time is $dE = j_\nu dV d\Omega dt d\nu$. Since each atom contributes an energy

$h\nu_0$ distributed over a solid angle 4π for each transition, this may also be expressed as : $dE = \frac{h\nu_0}{4\pi} \Phi(\nu) n_2 A_{21} dV d\Omega d\nu dt$, implying:

$$j_\nu = \frac{h\nu_0}{4\pi} \Phi(\nu) n_2 A_{21}$$

- The energy **absorbed** in time dt and volume dV is : $dE = dV dt h\nu_0 n_1 B_{12} \bar{J}$, so the energy absorbed out of a beam in a frequency range $d\nu$, solid angle $d\Omega$ time dt and volume dV is :

$$dE = \Phi(\nu) d\nu dV dt h\nu_0 n_1 B_{12} \frac{I_\nu d\Omega}{4\pi}$$

\bar{J} is averaged on solid angle and integrated on the line profile!

Einstein's coefficients

It follows that $\alpha_\nu = \frac{h\nu_0}{4\pi} \phi(\nu) n_1 B_{12}$

The stimulated emission is proportional to the intensity and only affects the photons along the given beam, in close analogy to the absorption process.

It is then convenient to treat it as a negative absorption. These two processes always occur together. Correcting for stimulated emission,

$$\alpha_\nu = \frac{h\nu_0}{4\pi} \phi(\nu) (n_1 B_{12} - n_2 B_{21})$$

Using the Einstein's relations, the absorption coefficient can be rewritten as

$$\alpha_\nu = \frac{h\nu_0}{4\pi} \phi(\nu) n_1 B_{12} \left(1 - \frac{g_1 n_2}{g_2 n_1}\right)$$

The source function $S_\nu = j_\nu / \alpha_\nu$ can also be rewritten in terms of the Einstein coefficients,

$$S_\nu = \frac{n_2 A_{21}}{n_1 B_{12} - n_2 B_{21}} = \frac{2h\nu^3}{c^2} \left(\frac{g_2 n_1}{g_1 n_2} - 1 \right)^{-1}$$

Generalized Kirchhoff's law

Problem.

If we neglect the stimulated emission, we do not find the Planck's law, but only the Wien law (BB part of the spectrum for $h\nu \gg kT$).

Why?

Hint: stimulated emission is proportional to n_2 , while absorption to n_1 .

Einstein's coefficients

Three interesting cases can be identified.

1- **Thermal emission.** If the matter is in equilibrium with itself (but not necessarily with radiation) (LTE), then

$\frac{n_1}{n_2} = \frac{g_1}{g_2} \exp\left(\frac{h\nu}{kT_{ex}}\right)$. In this case,

$$\alpha_\nu = \frac{h\nu_0}{4\pi} \phi(\nu) n_1 B_{12} \left[1 - \exp\left(-\frac{h\nu}{kT_{ex}}\right)\right] , \quad S_\nu = B_\nu(T_{ex})$$

This thermal value for the source function is just a statement of the Kirchhoff's law. The new result is the exponential correction in the absorption coefficient, which is due to the stimulated emission.

2- **Nonthermal emission.** $\frac{n_1}{n_2} \neq \exp\left(\frac{h\nu}{kT}\right)$. This occurs in a plasma, for example, if the radiating particles have a non-Maxwellian velocity distribution (e.g., they have a power law distribution of energies), or if the atomic populations do not obey the Maxwell-Boltzmann distribution. The generalized law can also be applied when scattering is present.

3- **Inverted populations: Masers.** For system in thermal equilibrium, $\frac{n_2 g_1}{n_1 g_2} = \exp\left(-\frac{h\nu}{kT}\right) < 1$ so that $\frac{n_1}{g_1} > \frac{n_2}{g_2}$, usually satisfied even when the material is out of equilibrium. In that case we say there are normal populations. It is possible to have inverted populations by putting enough atoms in the upper state, so to have $\frac{n_1}{g_1} < \frac{n_2}{g_2}$. In this case, the absorption coefficient is negative, $\alpha_\nu < 0$: the intensity increases along a ray. The amplification can be very large. A negative optical depth of ~ 100 can, for example, lead to amplifications by a factor 10^{43} .

Radiative transitions

Transition: a particle change its (position from one) quantum state to another. Here, we refer to electrons. There are two types of transitions: **radiative** and **non radiative**. In radiative transitions, energy is delivered as photons during the transition between different quantum states. According to Bohr's theory of atoms, when an electron drops from an higher energy level E_m to a lower energy level E_n , a photon of frequency

$$\nu = \frac{E_m - E_n}{h} \text{ is emitted.}$$

When the electron is in a given quantum state, it doesn't release any photon.

For simplicity, consider a system in which the electron moves in the x-direction only. The one-dimensional wave function for any **free** particle having energy E is given by:

$$\Psi = A e^{-\frac{i}{\hbar}(Et - px)} = \underbrace{A e^{-\frac{i}{\hbar}Et}}_{\text{Independent of time}} \underbrace{e^{+\frac{i}{\hbar}px}}_{\psi(x)} \equiv \psi e^{-\frac{i}{\hbar}Et}$$

Independent of time

$\Psi(x, t)$ is the product of the time dependent function $e^{-\frac{i}{\hbar}Et}$ and the position dependent function $\psi(x) = A e^{+\frac{i}{\hbar}px}$.

For an electron in a state of quantum number n and energy E_n , the time dependent wave function $\Psi_n(x, t) = \psi_n(x) e^{-\frac{iE_n t}{\hbar}}$; $\nu_n \equiv \frac{E_n}{h}$.

The complex conjugate of $\Psi(x, t)$ is :

$$\Psi_n^*(x, t) = \psi_n^*(x) e^{+\frac{iE_n t}{\hbar}}.$$

Now we have to find the position of the electron. We calculate the expectation value of the position of the electron in quantum state n and energy E_n :

$$\langle x \rangle = \int_{-\infty}^{+\infty} x \Psi_n^* \Psi_n dx = \int_{-\infty}^{+\infty} x \psi_n^* \psi_n \cancel{e^{+\frac{iE_n t}{\hbar}}} \cancel{e^{-\frac{iE_n t}{\hbar}}} dx = \int_{-\infty}^{+\infty} x \psi_n^* \psi_n dx \text{ *independent of time*.}$$

the expectation value of its position does not change in time: the position of the electron **does not oscillate** – **the electron does not radiate any photon, energy stays constant.**

Now consider an electron that goes from one energy state to another, say $E_n \rightarrow E_m$ because of some interaction.

During the transition, the electron exists in both states; the composite wavefunction is a linear combination of the initial and final states:

$$\Psi = a\Psi_n + b\Psi_m \quad ; \text{ its complex conjugate is } \Psi^* = a^*\Psi_n^* + b^*\Psi_m^*$$

$a^*a = |a|^2$ gives the probability for the electron to be in state Ψ_n , $b^*b = |b|^2$ gives the probability for the electron to be in state Ψ_m . The total probability is always 1 : $|a|^2 + |b|^2 = 1$.

When the electron is in the state n , $a = 1, b = 0$. In the state m , $a = 0, b = 1$. In either state, no radiation emitted.

But when the electron is *in the middle of the transition*, a and b have both non zero values: that is the time in which electromagnetic fields are produced and emitted in the form of photons

The expectation value of the position during the transition is

$$\langle x \rangle = \int_{-\infty}^{+\infty} x \Psi^* \Psi dx = \int_{-\infty}^{+\infty} x (a^*\Psi_n^* + b^*\Psi_m^*) (a\Psi_n + b\Psi_m) dx = \int_{-\infty}^{+\infty} x \underbrace{(|a|^2\Psi_n^*\Psi_n + |b|^2\Psi_m^*\Psi_m)}_{\text{Constant in time (expectation values of } x \text{ in the } n \text{ or } m \text{ quantum states)}} + \underbrace{b^*a\Psi_m^*\Psi_n + a^*b\Psi_n^*\Psi_m}_{\text{Time dependent}} dx =$$

$$\begin{aligned} &= |a|^2 \int_{-\infty}^{+\infty} x \psi_n^* \psi_n dx + |b|^2 \int_{-\infty}^{+\infty} x \psi_m^* \psi_m dx + b^*a \int_{-\infty}^{+\infty} x \psi_m^* e^{+\frac{iE_m t}{\hbar}} \psi_n e^{-\frac{iE_n t}{\hbar}} dx + a^*b \int_{-\infty}^{+\infty} x \psi_n^* e^{+\frac{iE_n t}{\hbar}} \psi_m e^{-\frac{iE_m t}{\hbar}} dx = \\ &= |a|^2 \int_{-\infty}^{+\infty} x \psi_n^* \psi_n dx + |b|^2 \int_{-\infty}^{+\infty} x \psi_m^* \psi_m dx + b^*a \int_{-\infty}^{+\infty} x \psi_m^* \psi_n e^{\frac{i(E_m - E_n)t}{\hbar}} dx + a^*b \int_{-\infty}^{+\infty} x \psi_n^* \psi_m e^{-\frac{i(E_m - E_n)t}{\hbar}} dx = \\ &= |a|^2 \int_{-\infty}^{+\infty} x \psi_n^* \psi_n dx + |b|^2 \int_{-\infty}^{+\infty} x \psi_m^* \psi_m dx + b^*a \int_{-\infty}^{+\infty} x \psi_m^* \psi_n [\cos \theta t + i \sin \theta t] dx + a^*b \int_{-\infty}^{+\infty} x \psi_n^* \psi_m [\cos \theta t + i \sin \theta t] dx \end{aligned}$$

$$\text{with } \theta \equiv \frac{(E_m - E_n)}{\hbar} \quad \text{and} \quad \cos \theta t = \cos 2\pi \frac{(E_m - E_n)t}{h} = \cos 2\pi \nu_{mn} t = \cos \omega_{mn} t \quad .$$

The expectation value of the electron position **oscillates with frequency** $\nu_{mn} = (E_m - E_n)/h$. *Dipole oscillation producing radiation.*

Time-dependent perturbation theory

Consider a system whose Hamiltonian can be written

$$H(t) = H_0 + H_1(t)$$

Here, H_0 is a simple time-independent Hamiltonian whose eigenvalues and eigenstates are known exactly. H_1 represents a small time-dependent external perturbation. Let the eigenstates of H_0 take the form

$$H_0\psi_m = E_m\psi_m$$

If the system is in one of these eigenstates, in the absence of an external perturbation, it remains in this state for ever.

However, a small time-dependent perturbation can give rise to **a finite probability** that if the system is initially in some eigenstate ψ_n of the unperturbed Hamiltonian, it will be in some other eigenstate at a subsequent time (because ψ_n is no longer an exact eigenstate of the total Hamiltonian).

A time-dependent perturbation allows the system to make **transitions between its unperturbed energy eigenstates**. Let us investigate such transitions.

Suppose that at $t=0$ the state of the system is represented by is some linear superposition of the unperturbed energy eigenstates ψ_m (independent of time) , with complex coefficients c_m :

$\psi(0) = \sum_m c_m \psi_m$. In the absence of the time-dependent perturbation, the time evolution of the system is simply

$$\psi(t) = \sum_m c_m \exp\left(-\frac{iE_m t}{\hbar}\right) \psi_m$$

Assuming the unperturbed eigenstates to be orthonormal, that is, $\langle n|m \rangle = \delta_{nm}$, the probability of finding the system in state n at time t is

$$P_n(t) = |\langle \psi_n | \psi \rangle|^2 = |c_n \exp(-iE_n t / \hbar)|^2 = |c_n|^2 = P_n(0)$$

When $H_1 \neq 0$, P_n and c_m vary in time: $\psi(t) = \sum_m c_m(t) \exp\left(-\frac{iE_m t}{\hbar}\right) \psi_m \Rightarrow P_n(t) = |c_n(t)|^2 \neq P_n(0)$

Here, we have separated the **fast phase oscillation of the eigenstates**, which depends on the unperturbed Hamiltonian, from the **slow (*) variation of the amplitudes $c_m(t)$** which depends entirely on the perturbation. The **time-dependent Schrödinger equation** yields:

$$i\hbar \frac{\partial \psi(t)}{\partial t} = H(t) \psi(t) = [H_0 + H_1(t)] \psi(t) = \sum_m c_m(t) \exp\left(-\frac{iE_m t}{\hbar}\right) (E_m + H_1) \psi_m$$

We also have

$$i\hbar \frac{\partial \psi(t)}{\partial t} = \sum_m \left(i\hbar \frac{dc_m}{dt} + c_m(t) E_m \right) \exp\left(-\frac{iE_m t}{\hbar}\right) \psi_m$$

Equating the right-hand sides of the previous two equations,

$$\sum_m i\hbar \frac{dc_m}{dt} \exp\left(-\frac{iE_m t}{\hbar}\right) \psi_m = \sum_m c_m(t) \exp\left(-\frac{iE_m t}{\hbar}\right) H_1 \psi_m$$

(*) $\hbar = 4.1357 \times 10^{-15} \text{ eV s}$

Projecting out the component of the previous equation which is proportional to ψ_n , we see that **only the off-diagonal matrix elements** give rise to the time variation of the coefficients c_n :

$$i\hbar \frac{dc_n}{dt} = \sum_m H_{nm}(t) \exp(i\omega_{nm}t) c_m(t) \quad \text{where } H_{nm}(t) = \langle n|H_1(t)|m\rangle \text{ and } \omega_{nm} = \frac{E_n - E_m}{\hbar}$$

Suppose that there are N linearly independent eigenstates of the unperturbed Hamiltonian: the time dependence of the set of N coefficients c_n , which specify the probabilities of finding the system in these eigenstates at time t , is determined by N coupled first-order differential equations. We cannot generally find exact solutions to these equations. Instead, we have to obtain approximate solutions via suitable expansions in small quantities. However, for the simple (but important) case of a two-state system (i.e., $N=2$), it is actually possible to solve the system without approximation.

Two-state systems.

Consider a system in which the time-independent Hamiltonian possesses two eigenstates:

$$H_0\psi_1 = E_1\psi_1 \quad ; \quad H_0\psi_2 = E_2\psi_2 \quad (\text{suppose } E_2 > E_1)$$

Suppose, for simplicity, that the diagonal elements of the time-dependent perturbation Hamiltonian are zero: $\langle 1|H_1|1\rangle = \langle 2|H_1|2\rangle = 0$

The off-diagonal elements are assumed to **oscillate sinusoidally at some frequency**:

$\langle 1|H_1|2\rangle = \langle 2|H_1|1\rangle^* = \gamma\hbar e^{i\omega t}$, where γ and $\omega > 0$ are real. Again, only the off-diagonal matrix elements give rise to the effect which we are interested in (transitions between states 1 and 2). The time evolution of the two c_n becomes:

$$i\frac{dc_1}{dt} = \gamma \exp[+i(\omega - \omega_{12})] c_2(t)$$

$$i\frac{dc_2}{dt} = \gamma \exp[-i(\omega - \omega_{21})] c_1(t) \quad \text{with } \omega_{21} = \frac{E_2 - E_1}{\hbar} > 0$$

The previous two equations can be combined into one second order equation for c_2 :

$$\frac{d^2 c_2}{dt^2} + i(\omega - \omega_{21}) \frac{dc_2}{dt} + \gamma^2 c_2 = 0 \quad . \text{ Once we solve for } c_2, \text{ we find } c_1 \text{ directly from the system of diff. equations.}$$

Let us search for a solution in which the **system at time $t=0$ is certain to be in state 1** : $c_1(t=0) = 1$, $c_2(t=0) = 0$ (remember that the sum over all the $|c_n|^2 = 1$ for the probabilistic meaning of these coefficients). With these initial conditions, it is easily demonstrated that the solutions are:

$$c_2(t) = \left(\frac{-i\gamma}{\Omega} \right) \exp \left[\frac{-i(\omega - \omega_{21})t}{2} \right] \sin(\Omega t)$$

$$c_1(t) = \exp \left[\frac{+i(\omega - \omega_{21})t}{2} \right] \cos(\Omega t) - \left[\frac{+i(\omega - \omega_{21})t}{2\Omega} \right] \exp \left[\frac{+i(\omega - \omega_{21})t}{2} \right] \sin(\Omega t)$$

$$\text{where } \Omega = \sqrt{\gamma^2 + (\omega - \omega_{21})^2/4}$$

$$\text{Now, the probabilities for each state at time } t \text{ are: } P_2(t) = |c_2(t)|^2 = \left[\frac{\gamma^2}{\gamma^2 + (\omega - \omega_{21})^2/4} \right] \sin^2(\Omega t) ; P_1(t) = |c_1(t)|^2 = 1 - P_2(t) .$$

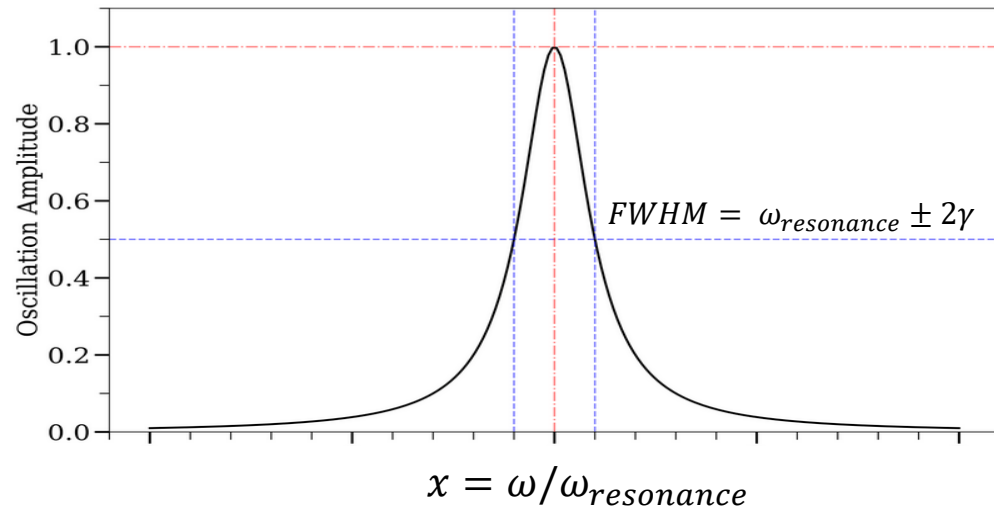
This result is known as *Rabi's formula*. It exhibits all the feature of the classical resonance: when the frequency of the perturbation ω matches the frequency ω_{21} , we find that : $P_2(t) = \sin^2(\gamma t)$; $P_1(t) = \cos^2(\gamma t)$. ($\Omega \rightarrow \gamma$ when $\omega \rightarrow \omega_{21}$)

Thus: the system starts at time $t=0$ in state 1. After a time interval $\Delta t = \frac{1}{\gamma} \frac{\pi}{2}$, the system is in state 2. After a further time interval $\Delta t = \frac{1}{\gamma} \frac{\pi}{2}$, i.e. at

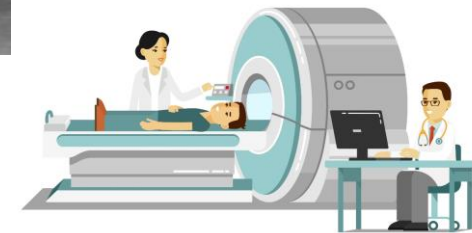
$t = \frac{\pi}{\gamma}$, the system is again in state 1. Thus, the system **periodically flip-flops between states 1 and 2 under the influence of the time-dependent perturbation**. This implies that the system **alternatively absorbs and emits energy** from the source of the perturbation.

The absorption-emission cycle **also takes place away from the resonance**, i.e. $\omega \neq \omega_{21}$. However, in this case the amplitude of the oscillations of $c_1(t)$ and $c_2(t)$ is **reduced**, since $\text{Amplitude} = \left[\frac{\gamma^2}{\gamma^2 + (\omega - \omega_{21})^2/4} \right] < 1$. This means that the maximum value of $P_2(t)$ is no longer unity, nor is the minimum of $P_1(t)$ zero.

In fact, if we plot the *maximum* value of $P_2(t)$ as a function of the applied frequency ω , we obtain a resonance curve whose maximum (=1) lies at the resonance ($\omega = \omega_{21}$) and whose full-width half-maximum (in frequency) is 4γ . Thus, if the applied frequency differs from the resonance frequency by more than 2γ , the transition probability from the state 1 to state 2 is always very small. The time-dependent perturbation is effective at causing transitions between 1 and 2 only if its frequency lies in the approximate range $\omega_{21} \pm 2\gamma$. Of course, the weaker the perturbation (i.e. the smaller γ becomes) the narrower the resonance.



*Isidor Rabi (1898-1988)
Nobel Prize in Physics in
1944 for NMR discovery.*



The amplitude of Rabi oscillations (*maximum* value of $P_2(t)$) as a function of the frequency ω of the external driving field. The maximum amplitude occurs at $\omega = \omega_{resonance}$. The resonance width is defined to be the difference of the two ω values at which the amplitudes are $1/2$. Symmetric w.r.t. $x=1$ ($x>0$)

Perturbation expansion

In the presence of a **small** time-dependent perturbation $H_1(t)$ to the time-independent unperturbed Hamiltonian H_0 , we can attempt a perturbative solutions of the system:

$$i\hbar \frac{dc_n}{dt} = \sum_m H_{nm}(t) \exp(i\omega_{nm}t) c_m(t) . \quad (**)$$

Suppose that at time $t=0$ the system is in some initial energy eigenstate labeled i . The initial conditions are then $c_n(t=0) = \delta_{ni}$. Since these coefficients are constant in time in the absence of perturbations, the zero-th order solution is simply:

$$c_n^{(0)}(t) = \delta_{ni}$$

The first-order solution is obtained, via iteration, by substituting the zeroth-order solution into the right-hand side of (**):

$$i\hbar \frac{dc_n^{(1)}}{dt} = \sum_m H_{nm}(t) \exp(i\omega_{nm}t) c_m^{(0)}(t) = H_{ni} \exp(i\omega_{ni}t) \quad \text{subject to the boundary condition } c_n^{(1)}(0) = 0$$

The solution to the previous equation is

$$c_n^{(1)}(t) = -\frac{i}{\hbar} \int_0^t H_{ni}(t') \exp(i\omega_{ni}t') dt'$$

It follows that, up to first-order in our perturbation expansion,

$$c_n(t) = c_n^{(0)}(t) + c_n^{(1)}(t) + \dots = \delta_{ni} - \frac{i}{\hbar} \int_0^t H_{ni}(t') \exp(i\omega_{ni}t') dt' + \dots \quad (\text{terms of higher order in } H_{nm})$$

Hence, the probability of finding the system in a final energy eigenstate labeled f at time t , given that it is in the energy level i at time zero, is:

$$P_{i \rightarrow f}(t) = |c_f(t)|^2 = \left| -\frac{i}{\hbar} \int_0^t H_{fi}(t') \exp(i\omega_{fi}t') dt' \right|^2$$

Note, finally, that the perturbative solution is clearly only valid provided $P_{i \rightarrow f}(t) \ll 1$.

Harmonic Perturbations

Hermitian adjoint of $V(*)$

$H_1(t) = V \exp(i\omega t) + V^\dagger \exp(-i\omega t)$ where V is in general a function of position, momentum and spin operators, with $\omega > 0$.

It follows, from the first-order perturbative calculations, that

$$c_f(t) = \delta_{fi} - \frac{i}{\hbar} \int_0^t [V_{fi} \exp(i\omega t') + V_{fi}^\dagger \exp(-i\omega t')] \exp(i\omega_{fi} t') dt'$$

where $V_{fi} = \langle f|V|i \rangle$, $V_{fi}^\dagger = \langle f|V^\dagger|i \rangle = \langle i|V|f \rangle^*$. Integrating in dt' ,

$$c_f(t) = \delta_{fi} - \frac{it}{\hbar} \left\{ V_{fi} \exp \left[i(\omega + \omega_{fi}) \frac{t}{2} \right] \text{sinc} \left[(\omega + \omega_{fi}) \frac{t}{2} \right] + V_{fi}^\dagger \exp \left[-i(\omega - \omega_{fi}) \frac{t}{2} \right] \text{sinc} \left[(\omega - \omega_{fi}) \frac{t}{2} \right] \right\}$$

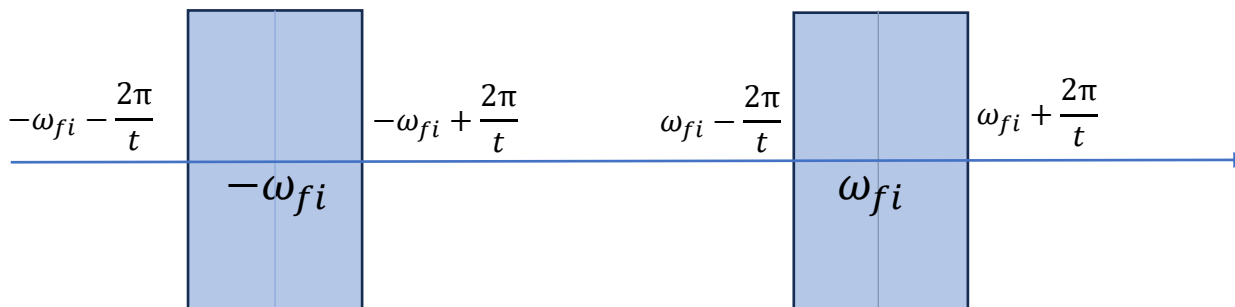
where $\text{sinc } x \equiv \frac{\sin x}{x}$

The function $\text{sinc}(x)$ takes large values only for $|x| \lesssim \pi$ and is negligible when $x \gg \pi$.

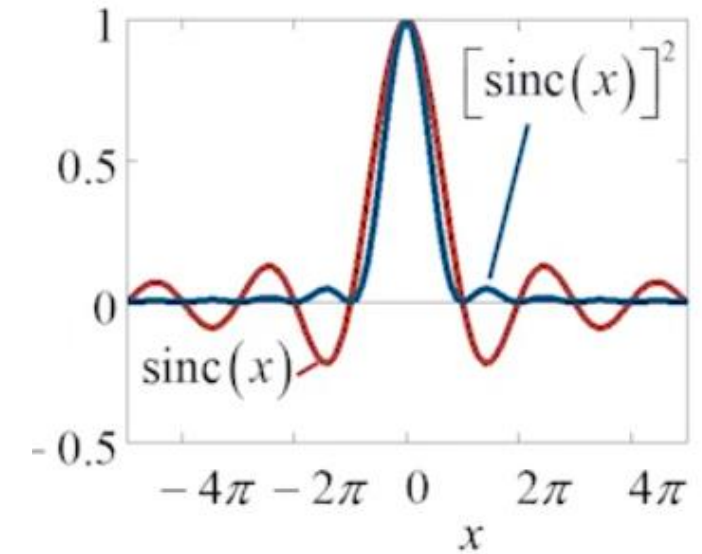
The two $\text{sinc}(x)$ terms in $c_f(t)$ are, respectively, non negligible only when:

$$|(\omega + \omega_{fi})| \lesssim \frac{2\pi}{t} \quad \text{and} \quad |(\omega - \omega_{fi})| \lesssim \frac{2\pi}{t}$$

Eventually, when t increases, the range in ω in which the two terms are non negligible gradually **shrinks in size**. When $t \gg \frac{2\pi}{|\omega_{fi}|}$ the two ranges becomes strongly peaked and non-overlapping.



For $t \rightarrow \infty$, non negligible only if $\omega = -\omega_{fi}$ or if $\omega = \omega_{fi}$



(*) The adjoint operator is defined as $\langle v|V|w \rangle = \langle w|V^\dagger|v \rangle^*$

Harmonic Perturbations

Hermitian adjoint of V

$H_1(t) = V \exp(i\omega t) + V^\dagger \exp(-i\omega t)$ where V is in general a function of position, momentum and spin operators, with $\omega > 0$.

It follows, from the first-order perturbative calculations, that

$$c_f(t) = \delta_{fi} - \frac{i}{\hbar} \int_0^t [V_{fi} \exp(i\omega t') + V_{fi}^\dagger \exp(-i\omega t')] \exp(i\omega_{fi} t') dt'$$

where $V_{fi} = \langle f|V|i \rangle$ $V_{fi}^\dagger = \langle f|V^\dagger|i \rangle = \langle i|V|f \rangle^*$. Integrating in dt' ,

$$c_f(t) = \delta_{fi} - \frac{it}{\hbar} \left\{ V_{fi} \exp \left[i(\omega + \omega_{fi}) \frac{t}{2} \right] \text{sinc} \left[(\omega + \omega_{fi}) \frac{t}{2} \right] + V_{fi}^\dagger \exp \left[-i(\omega - \omega_{fi}) \frac{t}{2} \right] \text{sinc} \left[(\omega - \omega_{fi}) \frac{t}{2} \right] \right\}$$

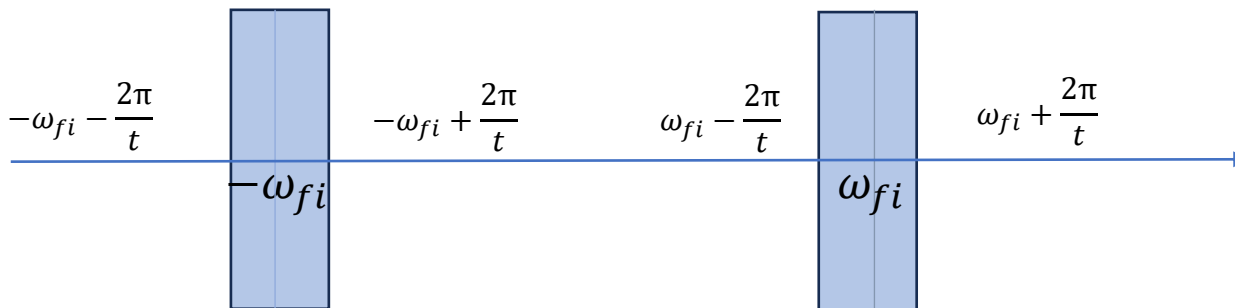
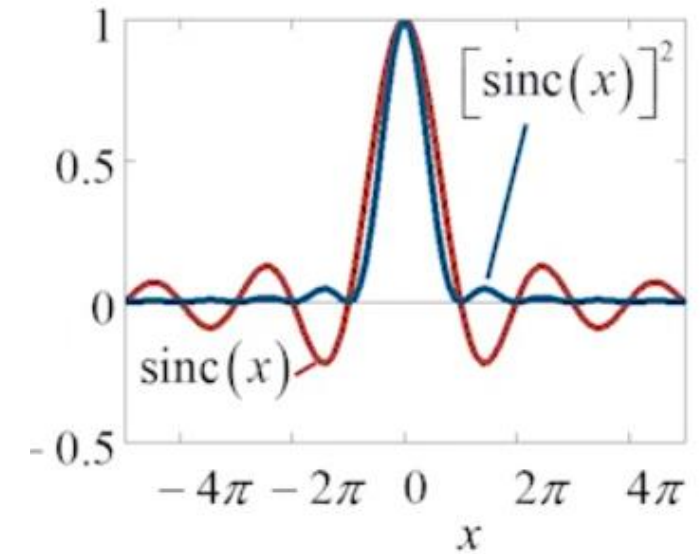
where $\text{sinc } x \equiv \frac{\sin x}{x}$

The function $\text{sinc}(x)$ takes large values only for $|x| \lesssim \pi$ and is negligible when $x \gg \pi$.

The two $\text{sinc}(x)$ terms in $c_f(t)$ are, respectively, non negligible only when:

$$|(\omega + \omega_{fi})| \lesssim \frac{2\pi}{t} \quad \text{and} \quad |(\omega - \omega_{fi})| \lesssim \frac{2\pi}{t}$$

Eventually, when t increases, the range in ω in which the two terms are non negligible gradually **shrinks in size**. When $t \gg \frac{2\pi}{|\omega_{fi}|}$ the two ranges becomes strongly peaked and non-overlapping.



For $t \rightarrow \infty$, non negligible only if $\omega = -\omega_{fi}$ or if $\omega = \omega_{fi}$

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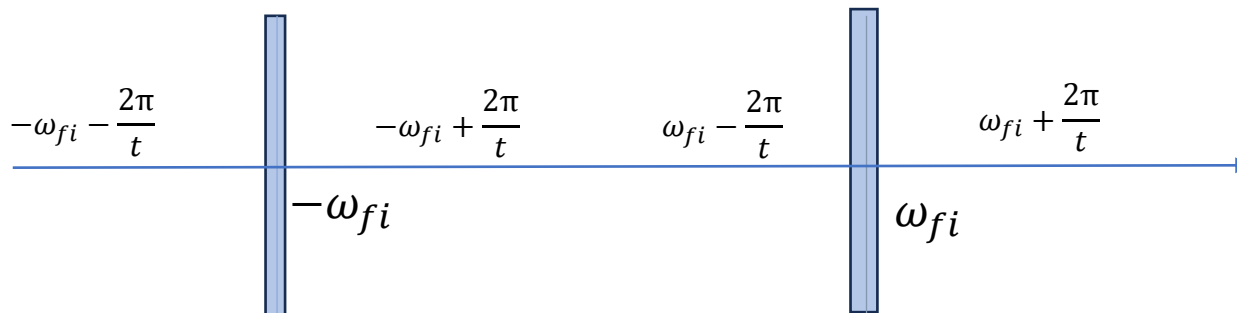
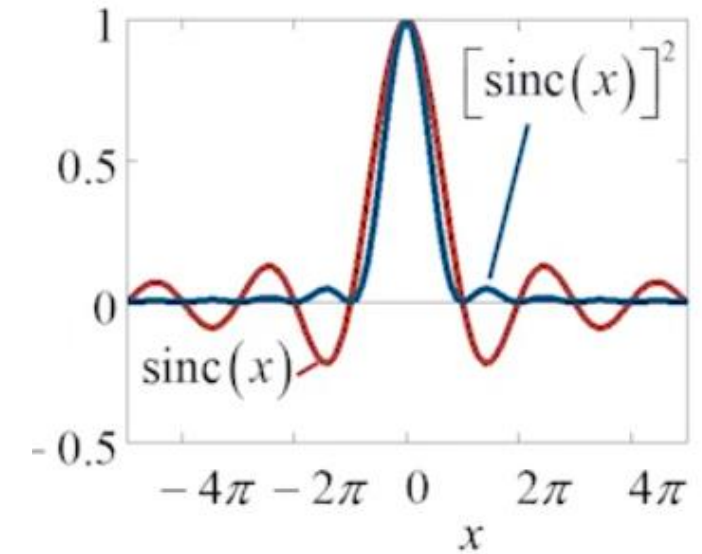
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For $t \rightarrow \infty$, non negligible only if $\omega = -\omega_{fi}$ or if $\omega = \omega_{fi}$

When $t \gg \frac{2\pi}{|\omega_{fi}|}$ the two ranges becomes **strongly peaked and non-overlapping**. In this limit and with $f \neq i$,

$$P_{i \rightarrow f}(t) = |c_f(t)|^2 = \frac{t^2}{\hbar^2} \left\{ \underbrace{|V_{fi}|^2 \operatorname{sinc}^2 \left[(\omega + \omega_{fi}) \frac{t}{2} \right]}_{\text{Stim. emission}} + \underbrace{|V_{fi}^\dagger|^2 \operatorname{sinc}^2 \left[(\omega - \omega_{fi}) \frac{t}{2} \right]}_{\text{absorption}} \right\}$$

For $t \rightarrow \infty$, non negligible only if $\omega = -\omega_{fi}$ or if $\omega = \omega_{fi}$

This expression exhibits a resonant behavior at $\omega = \pm\omega_{fi}$. At each of the resonant frequencies ($\pm\omega_{fi}$), the transition probability goes at t^2 (because $\operatorname{sinc}(0)=1$). The resonance at $\omega = -\omega_{fi}$ corresponds to $E_f - E_i = -\hbar\omega$: the system loses energy $\hbar\omega$ to the perturbing field while decaying to a final state with $E_f < E_i$. This process is known as **stimulated emission**.

The resonance at $\omega = \omega_{fi}$ corresponds to $E_f - E_i = \hbar\omega$: the system gains energy $\hbar\omega$ from the perturbing field while making a transition to a final state with $E_f > E_i$. This process is known as **absorption**.

Stimulated emission and absorption are **mutually exclusive processes**, because the first requires $\omega_{fi} < 0$ whereas the second requires $\omega_{fi} > 0$.

Hence, we can write the transition probabilities for both processes separately:

$$P_{i \rightarrow f}^{stim}(t) = \frac{t^2}{\hbar^2} |V_{fi}^\dagger|^2 \operatorname{sinc}^2 \left[(\omega + \omega_{fi}) \frac{t}{2} \right]$$

$$P_{i \rightarrow f}^{abs}(t) = \frac{t^2}{\hbar^2} |V_{fi}|^2 \operatorname{sinc}^2 \left[(\omega - \omega_{fi}) \frac{t}{2} \right]$$

Since $\omega_{fi} = -\omega_{if}$, the two probabilities have the same values.

If the perturbation has pulsation $\omega = |\omega_{fi}|$, non-null probability that the system absorbs a photon (if $\omega_{fi} > 0$) or emits a photon (if $\omega_{fi} = \frac{E_f - E_i}{\hbar} < 0$)

Electromagnetic Hamiltonian: matter-radiation interaction.

In the **semiclassical** theory of radiative transitions, the atom is treated quantum mechanically, but the radiation field is treated classically, no feedback of atom on the electromagnetic field.

The Hamiltonian of **an atomic electron** in an external electromagnetic field is: $H = \frac{\left(\mathbf{p} - \frac{e\mathbf{A}}{c}\right)^2}{2m_e} + e\varphi + V_0(r)$ where \mathbf{A} and φ are the vector and scalar potentials, functions of the position operator related to \mathbf{E} and \mathbf{B} :

$$\mathbf{E} = -\nabla\varphi - \frac{\partial\mathbf{A}}{c\partial t} ; \quad \mathbf{B} = \nabla \times \mathbf{A} .$$

Choosing the the Coulomb gauge, $\nabla \cdot \mathbf{A} = 0$, and $\mathbf{p} \cdot \mathbf{A} = \mathbf{A} \cdot \mathbf{p}$. Hence,

$$H = \frac{p^2}{2m_e} - \frac{e\mathbf{A} \cdot \mathbf{p}}{m_e c} + \frac{e^2 A^2}{2m_e c^2} + e\varphi + V_0(r)$$

In the case of a perturbation given by a linearly polarized, monochromatic, plane-wave,

$$\varphi = 0 \text{ and } \mathbf{A} = A_0 \boldsymbol{\epsilon} \cos(\mathbf{k} \cdot \mathbf{r} - \omega t) \quad \boldsymbol{\epsilon} = \text{unit vector of polarization direction, } \mathbf{k} = \frac{2\pi}{\lambda} \mathbf{n} .$$

Neglecting A^2 (second order in A_0), the Hamiltonian becomes:

$$H = H_0 + H_1(t) \text{ where}$$

$$H_0 = \frac{p^2}{2m_e} + V_0(r)$$

$$V^\dagger$$

$$V$$

$$\text{and } H_1(t) \cong -\frac{e\mathbf{A} \cdot \mathbf{p}}{m_e c} = -\frac{eA_0 \boldsymbol{\epsilon} \cdot \mathbf{p}}{2m_e c} [\exp(i\mathbf{k} \cdot \mathbf{r} - i\omega t) + \exp(-i\mathbf{k} \cdot \mathbf{r} + i\omega t)] = \text{perturbation} \quad \left(\mathbf{k} = \frac{2\pi}{\lambda} \mathbf{n} = \frac{2\pi\nu}{c} \mathbf{n} = \frac{\omega}{c} \mathbf{n} \right)$$

This has **the same form as our previous harmonic perturbation**, provided that

$$V = -\frac{eA_0 \boldsymbol{\epsilon} \cdot \mathbf{p}}{2m_e c} \exp(-i\mathbf{k} \cdot \mathbf{r}) \text{ and } V^\dagger = -\frac{eA_0 \boldsymbol{\epsilon} \cdot \mathbf{p}}{2m_e c} \exp(i\mathbf{k} \cdot \mathbf{r})$$

It follows that:

$$P_{i \rightarrow f}^{abs}(t) = \frac{t^2}{\hbar^2} \frac{e^2 |A_0|^2}{4m_e^2 c^2} |\langle f | \boldsymbol{\epsilon} \cdot \mathbf{p} \exp(i\mathbf{k} \cdot \mathbf{r}) | i \rangle|^2 \text{sinc}^2 \left[(\omega - \omega_{fi}) \frac{t}{2} \right]$$

In terms of the **energy density** of the electromagnetic wave, since $E_0 = \frac{\omega}{c} A_0$ and $U = \frac{1}{8\pi} |E_0|^2 \Rightarrow |A_0|^2 = \frac{c^2 8\pi U}{\omega^2}$ (CGS)

$$P_{i \rightarrow f}^{abs}(t) = \frac{t^2}{\hbar^2} \frac{e^2}{m_e^2} \frac{2\pi U}{\omega^2} |\langle f | \boldsymbol{\epsilon} \cdot \mathbf{p} \exp(i\mathbf{k} \cdot \mathbf{r}) | i \rangle|^2 \text{sinc}^2 \left[(\omega - \omega_{fi}) \frac{t}{2} \right] \quad (\text{proportional to the incident radiation density})$$

If the incident radiation is not monochromatic, but extends over a range of frequencies,

$U = \int_{-\infty}^{+\infty} \rho(\omega) d\omega$ and, for incoherent radiation, we add the intensities of the uncorrelated frequency waves:

$$P_{i \rightarrow f}^{abs}(t) = \int_{-\infty}^{+\infty} \frac{t^2}{\hbar^2} \frac{e^2}{m_e^2} \frac{2\pi}{\omega^2} |\langle f | \boldsymbol{\epsilon} \cdot \mathbf{p} \exp(i\mathbf{k} \cdot \mathbf{r}) | i \rangle|^2 \text{sinc}^2 \left[(\omega - \omega_{fi}) \frac{t}{2} \right] \rho(\omega) d\omega$$

For $t \gg \frac{2\pi}{|\omega_{fi}|}$, the sinc function is strongly **peaked** about $\omega = \omega_{fi}$ and $\int_{-\infty}^{+\infty} \text{sinc}^2 x dx = \pi$.

$$P_{i \rightarrow f}^{abs}(t) = \frac{t}{\hbar^2} \frac{e^2}{m_e^2} \frac{4\pi^2}{\omega_{fi}^2} \rho(\omega_{fi}) |\langle f | \boldsymbol{\epsilon} \cdot \mathbf{p} \exp(i\mathbf{k} \cdot \mathbf{r}) | i \rangle|^2$$

We see that the spectral integration transformed the probability into **a function of t instead than t^2** . While this expression holds as long as $P_{i \rightarrow f}^{abs}(t) \ll 1$, a universal result is that:

$$w_{i \rightarrow f}^{abs} \equiv \frac{dP_{i \rightarrow f}^{abs}(t)}{dt} = \frac{e^2 4\pi^2}{\hbar^2 \omega_{fi}^2 m_e^2} \rho(\omega_{fi}) |\langle f | \boldsymbol{\epsilon} \cdot \mathbf{p} \exp(i\mathbf{k} \cdot \mathbf{r}) | i \rangle|^2 \quad \text{is constant in time.}$$

The transition probability per unit time, $w_{i \rightarrow f}^{abs}$, is called **transition rate**: probability for transition between t and $t + dt$. In the same way,

$$w_{i \rightarrow f}^{stim} \equiv \frac{dP_{i \rightarrow f}^{stim}(t)}{dt} = \frac{e^2 4\pi^2}{\hbar^2 \omega_{fi}^2 m_e^2} \rho(\omega_{fi}) |\langle f | \boldsymbol{\epsilon} \cdot \mathbf{p} \exp(i\mathbf{k} \cdot \mathbf{r}) | i \rangle|^2$$

Electric dipole approximation

In general, the wavelength of the electromagnetic radiation that induces, or is emitted during, transitions between different atomic energy levels is much larger than the typical size of an atom. Thus,

$$\exp(i\mathbf{k} \cdot \mathbf{r}) = 1 + i\mathbf{k} \cdot \mathbf{r} + \dots \sim 1 \quad \text{electric dipole approximation}$$

$$\langle f | \boldsymbol{\epsilon} \cdot \mathbf{p} \exp(i\mathbf{k} \cdot \mathbf{r}) | i \rangle \sim \boldsymbol{\epsilon} \cdot \langle f | \mathbf{p} | i \rangle \quad (\text{neglects the spatial variations of the wave, on the small distances of atoms}).$$

$$\text{Now, } [\mathbf{r}, H_0] = \left[\mathbf{r}, \frac{p^2}{2m_e} + V_0(r) \right] = \frac{1}{2m_e} [\mathbf{r}, p^2] = \frac{2\hbar i \mathbf{p}}{2m_e} = \frac{\hbar i \mathbf{p}}{m_e} \quad (\text{Note: we used the properties } [\mathbf{x}, \mathbf{p}] = i\hbar \text{ and } [\mathbf{x}, \mathbf{p}^2] = 2i\hbar \mathbf{p})$$

Thus:

$$\langle f | \mathbf{p} | i \rangle = -\frac{im_e}{\hbar} \langle f | [\mathbf{r}, H_0] | i \rangle = im_e \omega_{fi} \langle f | \mathbf{r} | i \rangle$$

$$w_{i \rightarrow f}^{abs} \equiv \frac{dP_{i \rightarrow f}^{abs}(t)}{dt} = \frac{4\pi^2}{\hbar^2} \rho(\omega_{fi}) |\boldsymbol{\epsilon} \cdot \mathbf{d}_{if}|^2 \quad \text{where } \mathbf{d}_{if} \equiv \langle f | e\mathbf{r} | i \rangle = \text{effective atomic electric dipole during a transition } i \leftrightarrow f.$$

For unpolarized isotropic radiation, we average the above formula over all angles, which gives:

$$\langle |\boldsymbol{\epsilon} \cdot \mathbf{d}_{if}|^2 \rangle = \frac{d_{if}^2}{3}, \quad \text{since } \langle \cos^2 \theta \rangle = \frac{1}{3} \quad \text{and having defined } d_{if}^2 = |\langle f | ex | i \rangle|^2 + |\langle f | ey | i \rangle|^2 + |\langle f | ez | i \rangle|^2.$$

Hence, the transition rates for absorption and stimulated emission induced by unpolarized isotropic radiation are (in CGS):

$$w_{i \rightarrow f}^{abs} = \frac{4\pi^2}{3\hbar^2} \rho(\omega_{fi}) d_{if}^2 \quad w_{i \rightarrow f}^{stim} = \frac{4\pi^2}{3\hbar^2} \rho(\omega_{fi}) d_{if}^2$$

Short recap on Fourier transforms (from Ribicki Lightman chapter 2 and chapter 10)

$S = \frac{c}{4\pi} E \times B$ The time averaged Poynting vector is $\langle S \rangle = \frac{c}{8\pi} |E|^2$, and $\langle U \rangle = \frac{1}{8\pi} |B|^2$ = time averaged energy density.

If the radiation is in the form of a finite pulse, that vanishes at $t \rightarrow \pm\infty$, we can express $E(t)$ in terms of a Fourier integral:

$$\hat{E}(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} E(t) e^{i\omega t} dt$$

The inverse of this is: $E(t) = \int_{-\infty}^{\infty} \hat{E}(\omega) e^{-i\omega t} d\omega$

$\hat{E}(\omega)$ is complex while $E(t)$ is real. Thus, $\hat{E}(-\omega) = \hat{E}^*(\omega)$, so that **the negative frequencies can be eliminated**.

We want to have information about the **energy**. The energy per unit area per unit time, in terms of Poynting vector, is $\frac{d\mathcal{E}}{dt dA} = \frac{c}{4\pi} E^2(t)$

The total energy per unit area in the pulse is $\frac{d\mathcal{E}}{dA} = \frac{c}{4\pi} \int_{-\infty}^{\infty} E^2(t) dt$

From Parseval's theorem for Fourier transforms, we know that $\int_{-\infty}^{\infty} E^2(t) dt = 2\pi \int_{-\infty}^{\infty} |\hat{E}(\omega)|^2 d\omega = 4\pi \int_0^{\infty} |\hat{E}(\omega)|^2 d\omega \Rightarrow \frac{d\mathcal{E}}{dA} = c \int_0^{\infty} |\hat{E}(\omega)|^2 d\omega$

and we identify the energy per unit area per unit frequency: $\frac{d\mathcal{E}}{dA d\omega} = c |\hat{E}(\omega)|^2$ = energy/area/frequency **in the entire pulse**, NOT per unit time!

Writing both dt and $d\omega$ would violate the uncertainty relation between ω and t . However, **if the pulse has a timescale T** , we may *formally* write

$$\mathfrak{I}(\omega) \equiv \frac{d\mathcal{E}}{dA d\omega dt} = \frac{1}{T} \frac{d\mathcal{E}}{dA d\omega} = \frac{c}{T} |\hat{E}(\omega)|^2 \quad ; \quad \langle U(\omega) \rangle = \frac{d\mathcal{E}}{c dA d\omega dt} = \frac{1}{T} |\hat{E}(\omega)|^2. \text{ In the Coulomb gauge, } \hat{E}(\omega) = -\frac{1}{c} \frac{\partial A}{\partial t} = \frac{\omega}{c} A(\omega) \Rightarrow \langle U(\omega) \rangle = \frac{\omega^2}{T c^2} |\hat{A}(\omega)|^2 \equiv \rho(\omega)$$

which is what we define $\langle U(\omega) \rangle \equiv \rho(\omega)$ = spectral energy density (the total, bolometric energy density is, of course, $\langle U \rangle = \int_{-\infty}^{\infty} \rho(\omega) d\omega$.)

$\frac{\mathfrak{I}(\omega)}{c} = \rho(\omega)$ is the correspondence with the notation of the book Rybicki-Lightman chapter 10

Spontaneous emission

In the absence of any external radiation, we would not expect an atom in a given state to spontaneously jump into a state with a higher energy. However, it is possible for such an atom to spontaneously jump into a state with a lower energy via the emission of a photon whose energy is equal to the difference between the energies of the initial and final states. This process is known as *spontaneous emission*.

The rate of spontaneous emission between two atomic states can be derived using a famous thermodynamic argument due to Einstein . Consider a very large ensemble of similar atoms placed inside a closed cavity whose walls are perfect absorbers/emitters held at temperature T . At thermodynamic equilibrium, this cavity is filled with Blackbody radiation. Consider two atomic states labeled u and ℓ with $E_u > E_\ell$. From statistical mechanics, in thermal equilibrium the rate at which atoms from the ensemble leave state u due to transitions to state ℓ must be balanced by the rate at which atoms enter state ℓ due to transitions from state u , irrespective of any other atomic states. This is the **detailed balance principle**.

The former rate is: $W_{u \rightarrow \ell} = N_u (w_{u \rightarrow \ell}^{spont} + w_{u \rightarrow \ell}^{stim})$, where we introduced a **spontaneous emission rate** $w_{u \rightarrow \ell}^{spont}$.

The latter rate will be: $W_{\ell \rightarrow u} = N_\ell w_{\ell \rightarrow u}^{abs}$

$$\text{In thermal equilibrium,} \quad N_\ell w_{\ell \rightarrow u}^{abs} = N_u (w_{u \rightarrow \ell}^{spont} + w_{u \rightarrow \ell}^{stim}) \quad (*)$$

If the levels are degenerate, the transition rates are found counting all the initial states and summing over the final states. In practice, the relation we obtained for non degenerate states has to be corrected :

$$g_\ell w_{\ell \rightarrow u}^{abs} = g_u w_{u \rightarrow \ell}^{stim} \quad \text{Replacing } w_{u \rightarrow \ell}^{stim} \text{ in equation } (*),$$

$$w_{u \rightarrow \ell}^{spont} = \frac{g_\ell}{g_u} \left(\frac{N_\ell g_u}{N_u g_\ell} - 1 \right) w_{\ell \rightarrow u}^{abs} = \frac{g_\ell}{g_u} \left(\frac{N_\ell g_u}{N_u g_\ell} - 1 \right) \cdot \frac{4\pi^2}{3\hbar^2} \rho(\omega_{u\ell}) d_{u\ell}^2$$

Known from statistical thermodynamics!

From statistical thermodynamics, we know that, *in thermal equilibrium*, the number of atoms in an ensemble occupying a state of energy E is proportional to $\exp(-E/k_B T)$. This implies that $\frac{N_\ell}{N_u} = \frac{g_\ell}{g_u} \exp(\hbar\omega_{u\ell}/k_B T)$.

We use the Planck law to derive this exponential, since the BB spectrum is $\rho(\omega) = \frac{\hbar}{\pi^2 c^3} \frac{\omega^3}{\exp(\hbar\omega/k_B T) - 1}$, and obtain:

$$w_{u \rightarrow \ell}^{spont} = \frac{g_\ell}{g_u} \frac{4 \omega_{u\ell}^3 d_{u\ell}^2}{3 \hbar c^3}$$

Although this result has been derived for an atom in a radiation-filled cavity, it remains correct even in the absence of radiation.

Finally, the corresponding absorption and stimulated emission rates for an atom in a radiation-filled cavity are

$$w_{\ell \rightarrow u}^{abs} = \frac{g_u}{g_\ell} \cdot \frac{\pi^2 c^3}{\hbar \omega_{u\ell}^3} \rho(\omega_{u\ell}) \cdot w_{u \rightarrow \ell}^{spont} = \rho(\omega_{u\ell}) \frac{4\pi^2}{3 \hbar^2} d_{u\ell}^2 ;$$

$$w_{u \rightarrow \ell}^{stim} = \frac{\pi^2 c^3}{\hbar \omega_{u\ell}^3} \rho(\omega_{u\ell}) \cdot w_{u \rightarrow \ell}^{spont} = \frac{g_\ell}{g_u} \rho(\omega_{u\ell}) \frac{4\pi^2}{3 \hbar^2} d_{u\ell}^2 .$$

Spontaneous emission is a **quantum effect**, which in a semiclassical picture can be described as an emission which is stimulated by vacuum noise. It results from an interaction with the quantum-mechanical electromagnetic field, which is influenced by the atomic or ionic environment. Spontaneous transitions are **not explainable within the framework of the Schrödinger equation**, in which the electronic energy levels are quantized, but the electromagnetic field is not. Given that the eigenstates of an atom are properly diagonalized, the overlap of the wavefunctions between the excited state and the ground state of the atom is zero. Thus, in the absence of a quantized electromagnetic field, the excited state atom cannot decay to the ground state. In order to explain spontaneous transitions, quantum mechanics must be extended to a quantum field theory, where the electromagnetic field is quantized at every point in space. The quantum field theory of electrons and electromagnetic fields is known as *quantum electrodynamics*.

Einstein coefficients

Be $J_{\nu_{ul}}$ the averaged (over solid angle) radiation intensity at frequency ν_{ul} , and using $J_{\nu_{ul}} = \frac{1}{4\pi} I(\nu_{ul}) = \frac{2\pi}{4\pi} I(\omega_{ul}) = \frac{1}{2} I(\omega_{ul}) = \frac{c}{2} \rho(\omega_{ul})$, we can relate the average values of the transition probabilities to the *Einstein coefficients*, so defined:

$$A_{u\ell} \equiv \frac{1}{g_u} w_{u \rightarrow \ell}^{spont} = \frac{4 \omega_{u\ell}^3}{3 g_u \hbar c^3} d_{u\ell}^2$$

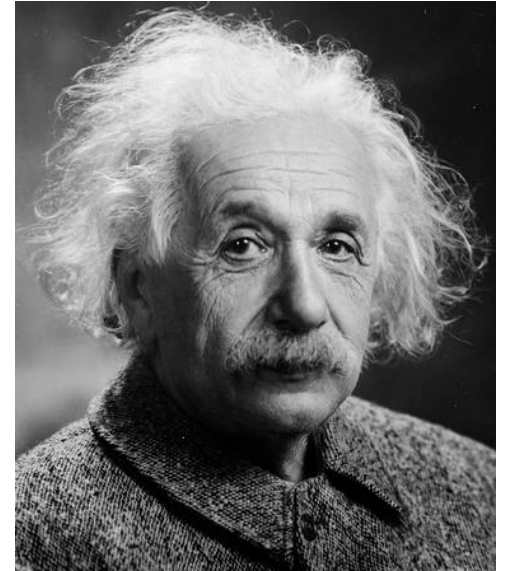
$$B_{\ell u} \equiv \frac{1}{g_\ell J_{\nu_{ul}}} w_{u \rightarrow \ell}^{abs} = \frac{8\pi^2}{3 g_\ell c \hbar^2} d_{u\ell}^2$$

$$B_{u\ell} \equiv \frac{1}{g_u J_{\nu_{u\ell}}} w_{u \rightarrow \ell}^{stim} = \frac{8\pi^2}{3 g_u c \hbar^2} d_{u\ell}^2$$

$$g_\ell B_{\ell u} = g_u B_{u\ell}$$

$$A_{u\ell} = \frac{2\hbar \nu_{u\ell}^3}{c^2} B_{\ell u}$$

Einstein relations



Albert Einstein, 1879-1955

Notice that $A_{u\ell} \propto \nu_{u\ell}^3$. Spontaneous emission is expected to dominate at high frequencies.

Example. For Hydrogen atom $A_{n+1,n} \approx 5.3 \times 10^9 \left(\frac{1}{n^5} \right) \text{ s}^{-1}$.

For example, the 5.0089 GHz H109 α transition rate is $A_{110,109}$ is $\sim 0.3 \text{ s}^{-1}$

Selection rules: which transitions are possible?

Recall the definition of dipole matrix element between a final and an initial state: $\mathbf{d}_{fi} \equiv -e \int \phi_f^* \sum_j \mathbf{r}_j \phi_i d^3\mathbf{r}$. In a multielectron system, the following rules apply to the jumping electron, and completely determine the spectrum for one-electron atoms such as H I and He II, and the alkali metals.

1) For the «jump» of a single electron, we can consider the single electron position vector: since the dipole operator $\mathbf{d} = -e\mathbf{r}$ changes sign under parity ($\mathbf{r} \rightarrow -\mathbf{r}$), matrix element $\langle f|\mathbf{d}|i\rangle$ will vanish if $|i\rangle$ and $|f\rangle$ have same parity. For states with a given configuration, the parity is $(-1)^{\sum \ell_i}$, where the sum is over the angular momenta quantum numbers of the individual orbitals: the configuration must change by at least one orbital.

The parity of the wavefunction must change in an electric dipole transition

2) Separating wavefunction into spatial and spin components, $|f\rangle = |\phi_f\rangle \otimes |\chi_f\rangle$. Since the dipole operator only acts on the spatial part, $\langle f|\mathbf{d}|i\rangle = -\langle \chi_f|\chi_i\rangle \int \phi_f^* e\mathbf{r} \phi_i d^3\mathbf{r}$ and the spin term vanishes unless $|\chi_f\rangle$ and $|\chi_i\rangle$ are identical, $\Delta s = 0, \Delta m_s = 0$.

The spin state is not altered in electric dipole transitions.

3) From the operator identity $[\mathbf{L}_i, \mathbf{r}_j] = i\hbar\epsilon_{ijk}\mathbf{r}_k$ it follows that $[\mathbf{L}_z, \mathbf{z}] = 0$.

Then $\langle n, \ell, m | [\mathbf{L}_z, \mathbf{z}] | n', \ell', m' \rangle = \hbar(m - m') \langle n, \ell, m | \mathbf{z} | n', \ell', m' \rangle = 0$ unless $m = m'$.

Now consider the linear combination $\mathbf{x}_{\pm} = \mathbf{x} \pm i\mathbf{y}$. It is easily demonstrated that $[\mathbf{L}_z, \mathbf{x}_{\pm}] = \pm\hbar\mathbf{x}_{\pm}$

Hence $\langle n, \ell, m | [\mathbf{L}_z, \mathbf{x}_+] - \hbar\mathbf{x}_+ | n', \ell', m' \rangle = \hbar(m - m' - 1) \langle n, \ell, m | \mathbf{x}_+ | n', \ell', m' \rangle = 0$ unless $m' = m - 1$

Similarly, $\langle n, \ell, m | [\mathbf{L}_z, \mathbf{x}_-] + \hbar\mathbf{x}_- | n', \ell', m' \rangle = \hbar(m - m' + 1) \langle n, \ell, m | \mathbf{x}_- | n', \ell', m' \rangle = 0$ unless $m' = m + 1$

Now, the electric dipole elements $\langle n, \ell, m | \mathbf{x} | n', \ell', m' \rangle$ and $\langle n, \ell, m | \mathbf{y} | n', \ell', m' \rangle$ are **both zero** if $\langle n, \ell, m | \mathbf{x}_+ | n', \ell', m' \rangle$ and $\langle n, \ell, m | \mathbf{x}_- | n', \ell', m' \rangle$ are both zero.

It follows that the dipole matrix element is not vanishing for $m' = m, m \pm 1$.

The dipole elements between two states are non vanishing for $\Delta m = 0, \pm 1$.

4) Using operator identity $[\mathbf{L}^2, [\mathbf{L}^2, \mathbf{r}]] = 2\hbar^2(\mathbf{r}\mathbf{L}^2 + \mathbf{L}^2\mathbf{r})$ we have:

$$\langle n, \ell, m | [\mathbf{L}^2, [\mathbf{L}^2, \mathbf{r}]] | n', \ell', m' \rangle = \hbar^2[\ell'(\ell' + 1) - \ell(\ell + 1)]^2 \langle n, \ell, m | \mathbf{r} | n', \ell', m' \rangle = 2\hbar^2[\ell'(\ell' + 1) + \ell(\ell + 1)] \langle n, \ell, m | \mathbf{r} | n', \ell', m' \rangle$$

i.e. $(\ell + \ell')(\ell + \ell' + 2)[(\ell - \ell')^2 - 1] \langle n, \ell, m | \mathbf{r} | n', \ell', m' \rangle = 0$. Since $\ell, \ell' \geq 0$, dipole matrix elements are not vanishing only if $\ell' = \ell \pm 1$ (note: $\ell = 0$ to $\ell' = 0$ is forbidden because of the parity condition).

To produce an electric dipole transition, we must have $\Delta\ell = \pm 1$.

There are also selection rules **for many electrons atoms**, that involve the total quantities L, S and J. One general result is that the transition from $J=0$ to $J=0$ is forbidden: the photon carries off one unit of angular momentum. In LS coupling, we find:

1. $\Delta J = 0, \pm 1$ with $J=0 \rightarrow J=0$ forbidden.
2. $\Delta M_J = 0, \pm 1$
3. Parity must change.

Additional set of rules, not rigorously satisfied by complex atoms (*“propensity rules”*):

4. $\Delta S = 0$ (but relativistic effects can mix spin states, especially for high Z ions.
5. Δn arbitrary, $\Delta l = \pm 1$ Only one electron jumps: the configuration of the two states must differ by only the movement of a single electron.
6. $\Delta L = 0, \pm 1$, with $L = 0 \rightarrow 0$ forbidden (Note: no direct relation between L and the parity!)

In many-electrons systems, there can be transitions that violate rule 4 and change the total spin (**semi-forbidden** transitions): they are called **intercombination lines** (e.g. CIII]). Semi-forbidden transitions, resulting in intercombination lines, are electric dipole transitions for which the selection rule of spin conservation is violated **as a result of the failure of LS coupling**.

Transitions which violate the propensity rule 5 and/or 6 are strictly **forbidden** and are labelled by two square brackets (e.g. [CIII]).

- Examples

Species	f	\leftarrow	i	$\lambda(\text{\AA})$	$A_{ul}(s^{-1})$	ΔJ	Parity [†]	ΔS	Δl
NII	$2p^2\ ^3P_0^e$	\leftarrow	$2p3s\ ^3D_1^o$	1084.0	2.18×10^8	-1	$o \rightarrow e$	0	-1
CIII]	$2s^2\ ^1S_0^e$	\leftarrow	$2s2p\ ^3P_1^o$	1908.7	114	+1	$o \rightarrow e$	-1	-1
[CIII]	$2s^2\ ^1S_0^e$	\leftarrow	$2s2p\ ^3P_2^o$	1906.7	0.0052	+2	$o \rightarrow e$	-1	-1

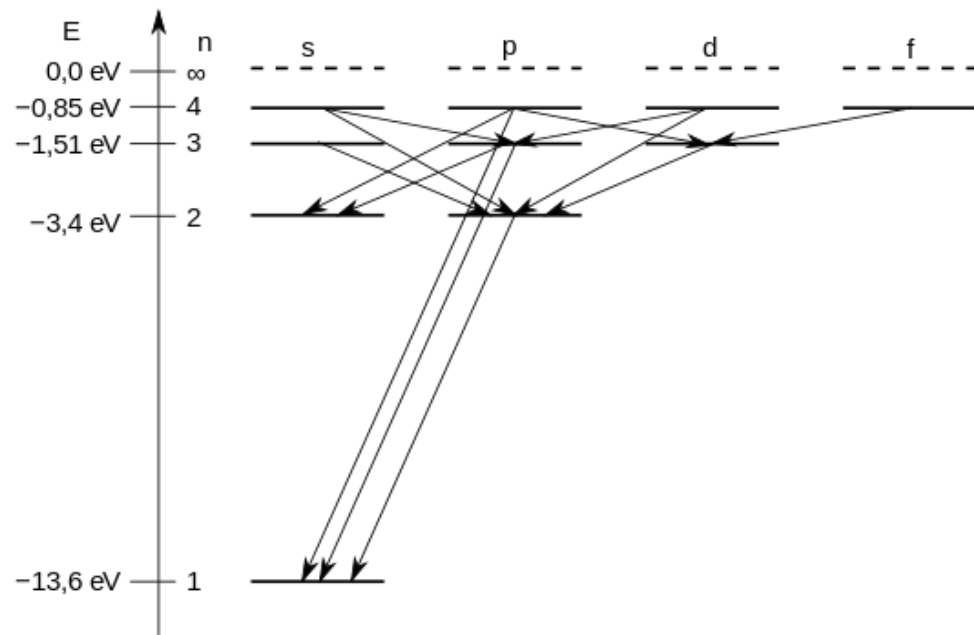
- The **quadrupole** term can be $\neq 0$ when the dipole is 0 (semi –forbidden transition, second term of expansion of potential vector A). Similar expression to the case of the dipole can be derived. But now we have to consider terms such as $\int \phi_f^* e\mathbf{r}^2 \phi_i d^3\mathbf{r}$. These transitions are termed (semi–) forbidden, but their probabilities ($A_{u\ell}$), although much smaller than in the dipole case, may be relevant.

Selection rules: Δn arbitrary, $\Delta l = 0, \pm 2$; $\Delta J = 0, \pm 1, \pm 2$; $\Delta L = 0, \pm 1, \pm 2$; $\Delta S = 0$; $\Delta M_J = 0, \pm 1, \pm 2$.

- The **magnetic dipole** refers to hyperfine structure transitions, where energy levels differ by very small quantities.

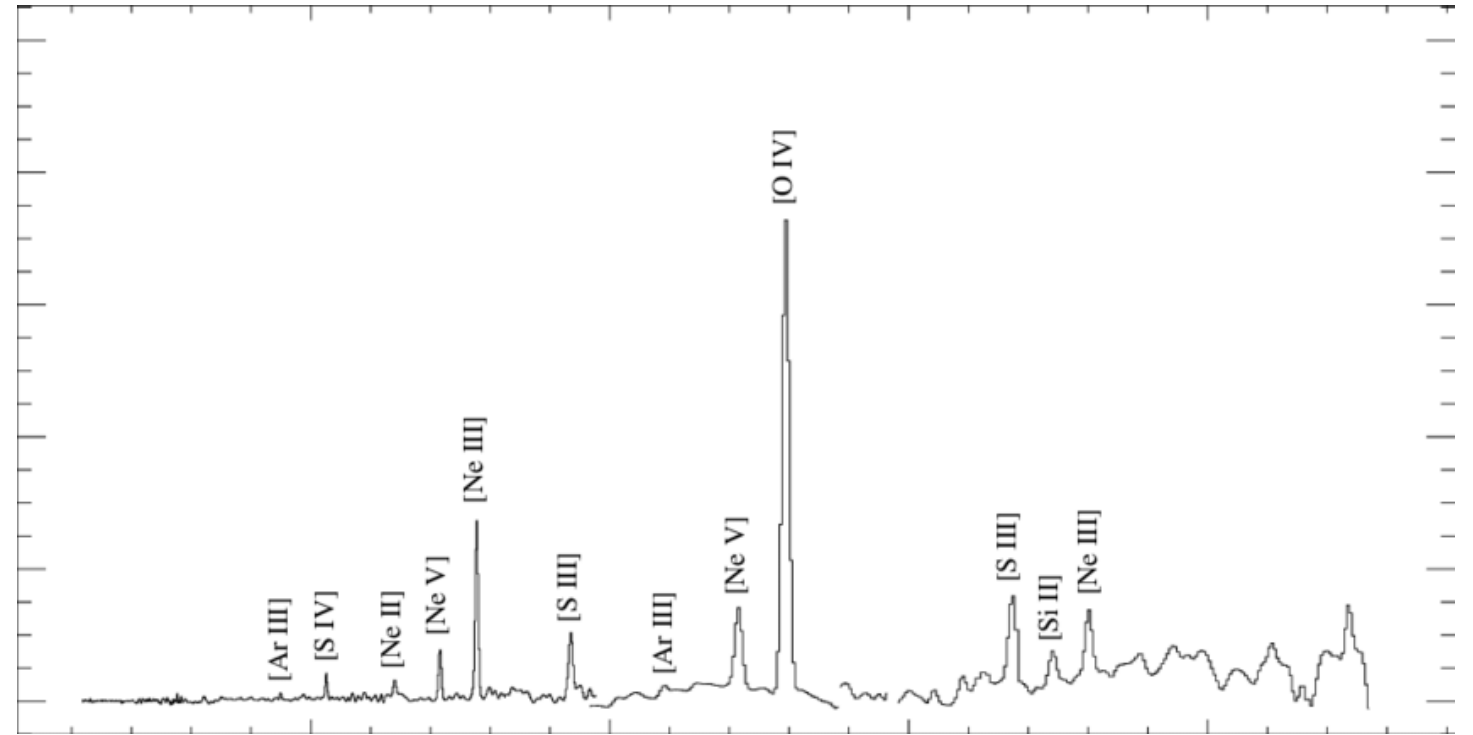
Selection rules: $\Delta n = \Delta l = \Delta L = 0$; $\Delta J = 0, \pm 1$; $\Delta M_J = 0, \pm 1$; $\Delta S = 0, \pm 1$.

Typically, a rough estimate gives $\frac{A_{u\ell\ quadrupole}}{A_{u\ell, dipole}} \sim 10^{-5}$ and $\frac{A_{u\ell\ magnetic}}{A_{u\ell, dipole}} \sim 10^{-8}$



Grotrian diagram for Hydrogen atom

Line	wavelength (Å)	oscillator strength	$A_{ul} (s^{-1})$
Lyman α	1215.67	0.41620	4.70E+008
Lyman β	1025.72	0.07910	5.58E+007
Lyman γ	972.54	0.02899	1.28E+007
Lyman limit	911.80		
H α	6562.80	0.64070	4.41E+007
H β	4861.32	0.11930	8.42E+006
H γ	4340.46	0.04467	2.53E+006
H δ	4101.73	0.02209	9.73E+005
H ϵ	3970.07	0.01270	4.39E+005
H limit	3646.00		
P α	18751.00	0.84210	8.99E+006
P β	12818.10	0.15060	2.20E+006
P γ	10938.10	0.05584	7.78E+005
P limit	8204.00		
B α	40512.00	1.03800	2.70E+006
B β	26252.00	0.17930	7.71E+005
B γ	21655.00	0.06549	3.04E+005
B limit	14584.00		



NGC 6445, also known as the **Little Gem Nebula** or **Box Nebula**, is a planetary nebula in the constellation Sagittarius.

Width of spectral lines

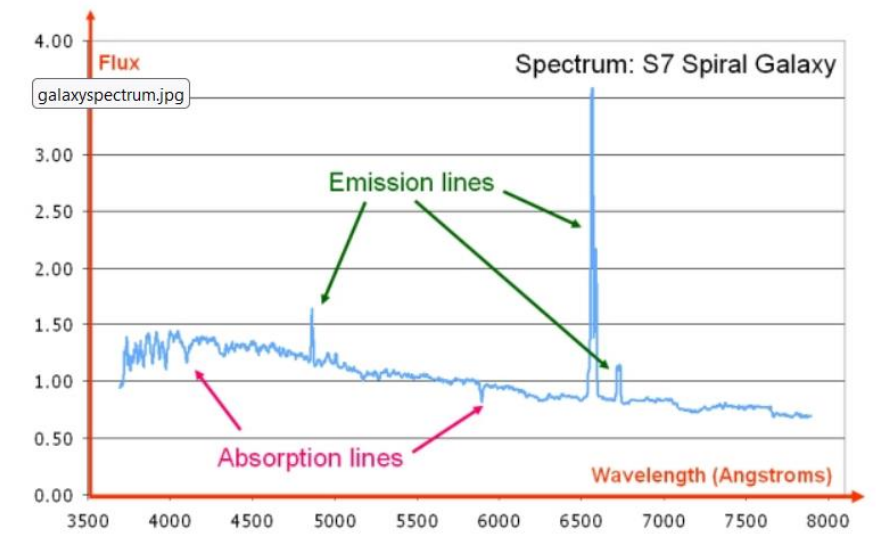
The set of emitted photons during radiative transitions IS NOT monochromatic. The energy difference between the two levels is not infinitely sharp, and it is described by the line profile function $\varphi(\nu)$:

$$\int_0^\infty \varphi(\nu) d\nu = 1 \quad .$$

The line profile, peaked around $\nu_{u\ell}$, represents how effectively photons with frequencies around $\nu_{u\ell}$ can cause transitions: $\bar{J} = \int_0^\infty J_\nu \varphi(\nu) d\nu$

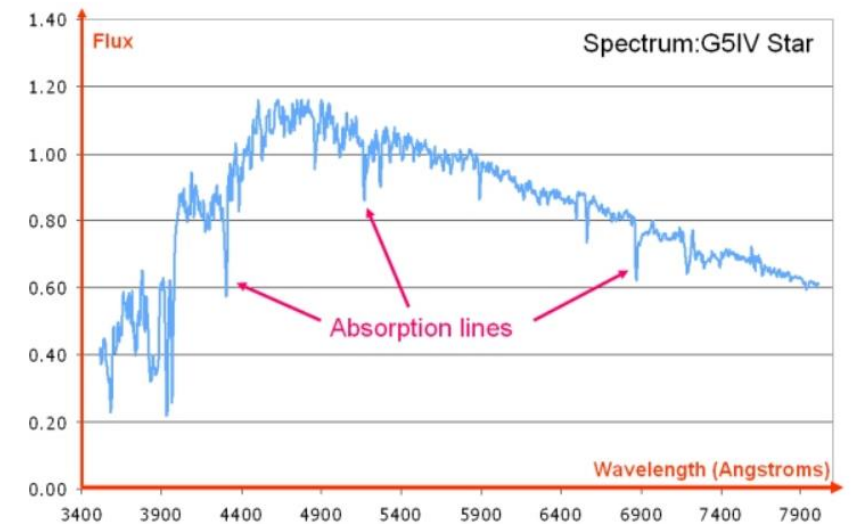
Real spectral lines are broadened because:

- Energy levels are not infinitely sharp.
- Atoms are moving relative to observer.
- Three mechanisms determine the line profile $\varphi(\nu)$:
 - **Quantum mechanical uncertainty in the energy of levels with finite lifetimes.** This determines the natural width of a line (generally very small).
 - **Collisional broadening.** Collisions reduce the effective lifetime of a state, leading to broader lines. High pressure gives more collisions (eg stars).
 - **Doppler or thermal broadening,** due to the thermal (or large-scale turbulent) motion of individual atoms in the gas relative to the observer.



The spectrum of an S7 Spiral Galaxy showing emission and absorption line features either side of the continuum. Wavelength is measured in angstroms, while the flux is in arbitrary units.

Dataset: VizieR catalogue III/219, *Spectral Library of Galaxies, Clusters and Stars* (Santos et al. 2002)



The spectrum of a G5IV star showing absorption line features below the level of the star's **blackbody** continuum spectrum. Wavelength is measured in angstroms, while the **flux** is in arbitrary units.

Dataset: VizieR catalogue III/219, *Spectral Library of Galaxies, Clusters and Stars* (Santos et al. 2002)

Natural broadening

Absorption of radiation always produces an excited state with a finite lifetime: $\Delta t \cong 1/A_{u\ell}$

The uncertainty principle relates the lifetime of a state to the energy width: the spread in energy, $\Delta\varepsilon$, and the duration Δt in the state must satisfy $\Delta\varepsilon\Delta t \sim \hbar$.

Define the rate of disappearance (depopulation) of an **excited** state n (with energy ε_n) as $\frac{\partial[\varepsilon_n]}{\partial t} = -\frac{[\varepsilon_n]}{\tau_n} \rightarrow \varepsilon_n(t) = \varepsilon_0 e^{-t/\tau_n}$ where τ_n is the lifetime of the state n . The lifetime τ_n determines the width of the line, or the spectrum (intensity of emitted/absorbed radiation vs. frequency), i.e. the range of possible frequencies at which the photon will be emitted.

Assume that the decay from a state n to other states proceed at a rate $\gamma_n = \sum_{m < n} A_{nm}$, so that $\tau_n = 1/\gamma_n$. (If radiation is present, we add also the induced processes). The conjugate energy width can be obtained from the Fourier transform of the life time function : $\hat{f}(\omega) \equiv \int_0^\infty e^{-t/\tau_n} e^{-i\omega t} dt$

This Fourier transform is easily solved: $\hat{f}(\omega) = \frac{1}{\frac{1}{\tau_n} - i\omega} = \frac{1/\tau_n}{(1/\tau_n)^2 + \omega^2} + \frac{i\omega}{(1/\tau_n)^2 + \omega^2}$ which is a complex function, whose real part is a **Lorentzian**.

It can be shown that the line shape that will be observed for transitions that have no inhomogeneous broadening is $\varphi(\nu) = \frac{\gamma/4\pi^2}{(\nu - \nu_{u\ell})^2 + (\gamma/4\pi)^2}$.

If both the upper and lower states are broadened, sum the γ values for the two states.

Natural linewidth isn't often directly observed, except in the line wings in low-pressure (nebular) environments.

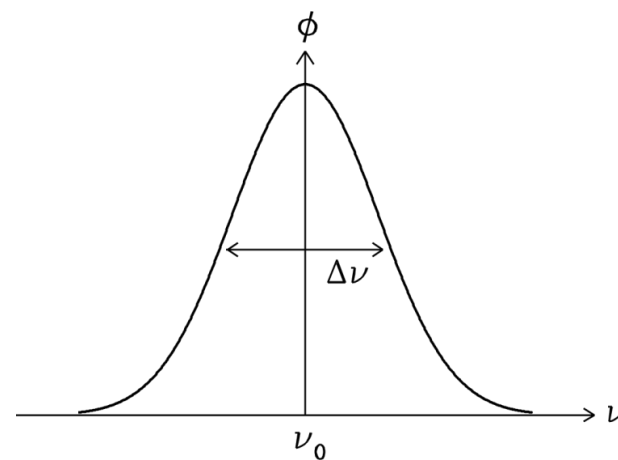
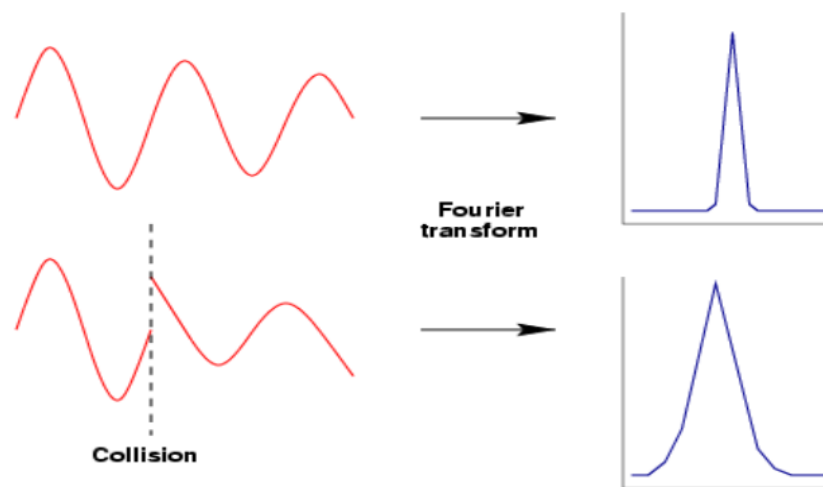
Other broadening mechanisms usually dominate.

Collisional broadening

Collisions randomize the phase of the emitted radiation. If frequent enough, they (effectively) shorten the lifetime further. If the frequency of collisions is ν_{col} , then the profile is still a Lorentzian, $\Gamma = \gamma + 2\nu_{col}$,

$$\phi(\nu) = \frac{\Gamma/4\pi^2}{(\nu - \nu_{ul})^2 + (\Gamma/4\pi)^2}.$$

Collisions dominate in high density environments, hence get broader lines in dwarfs than giants of the same spectral type.



Doppler (thermal) broadening

Atoms are in (thermal) motion wrt the observer, and the rest (atom) frame frequencies can be either red- or blue- shifted. If v_r is the radial velocity,

$$\Delta\nu = \nu_{obs} - \nu_{em} = \nu_{em} \frac{v_r}{c} \rightarrow v_r = c \frac{\nu_{obs} - \nu_{em}}{\nu_{em}}$$

Maxwell's Law of velocity distribution gives number of atoms with a given velocity. For one component of velocity (we only care about the motions along the line of sight),

$$dN(v_r) \propto \exp\left(-\frac{mv_r^2}{2kT}\right) dv_x$$

Combine Doppler shift with the v_r distribution:

$$\phi(\nu) = \frac{e^{-(\nu_{obs} - \nu_{em})^2 / \Delta\nu_D^2}}{\Delta\nu_D \sqrt{\pi}}, \text{ where the Doppler width is } \Delta\nu_D = \frac{v_{em}}{c} \sqrt{\frac{2kT}{m}}$$

This is a Gaussian, which falls off very rapidly away from the line center.

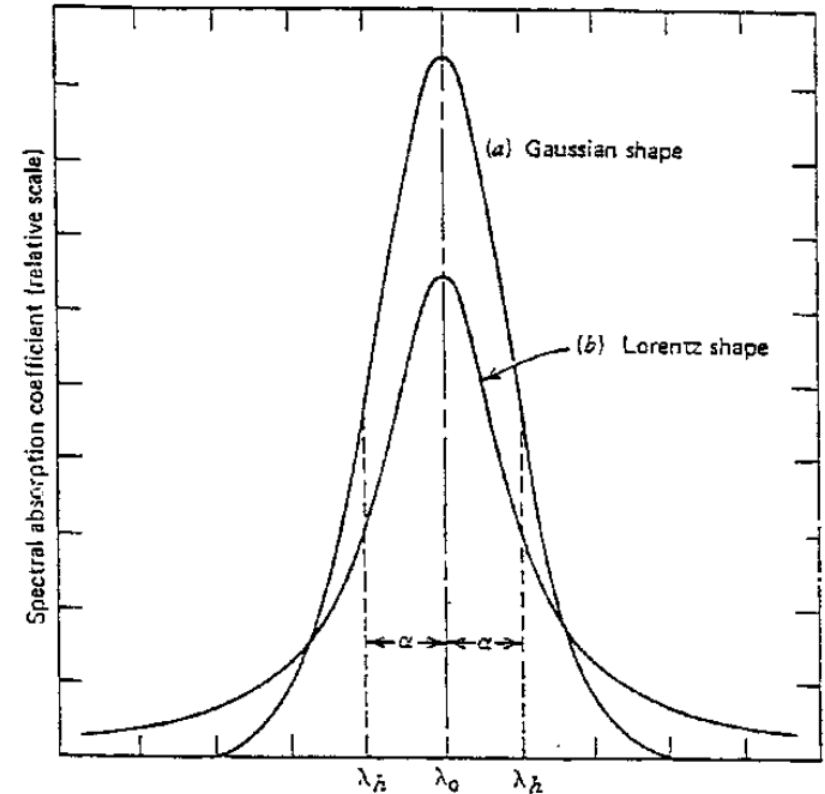
$$\text{Example, for Hydrogen atom, } \Delta\nu_D \frac{c}{v_{em}} = \sqrt{\frac{2kT}{m}} = 13 \left(\frac{T}{10^4 K}\right)^{1/2} \text{ km/s}$$

The centroid ("natural frequency") remains unchanged; only in the case that the whole cloud is moving, then also the centroid is (Doppler) shifted.

Valid also in case of **turbulence**, once modified the Doppler width by introducing ξ ,

$$\text{the rms of turbulent velocities (with Gaussian distribution): } \Delta\nu_D = \frac{v_{em}}{c} \sqrt{\frac{2kT}{m} + \xi}.$$

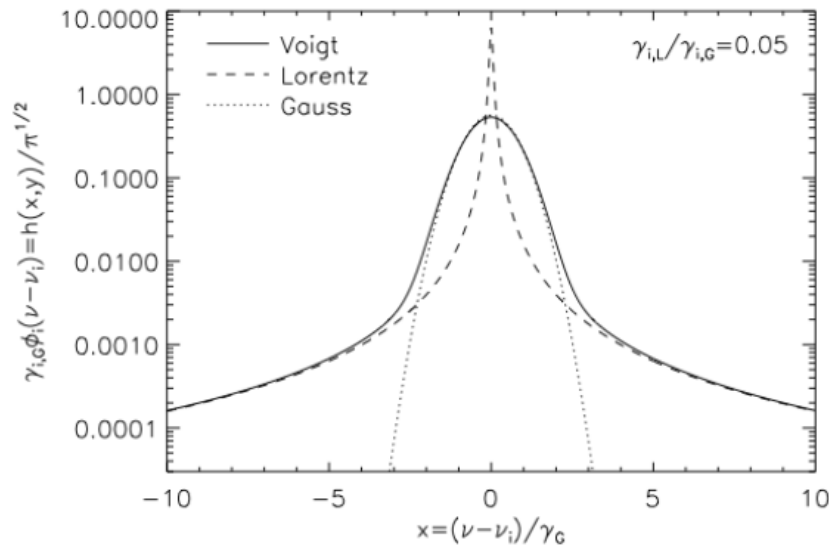
This situation occurs, e.g., in observations of star forming regions or in convective stellar photospheres.



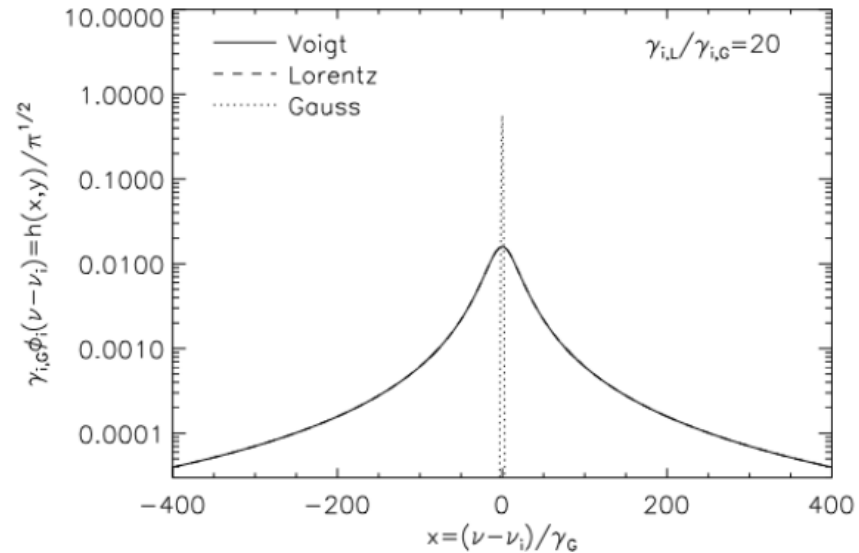
Lorentzian and Gaussian lines with the same integrated area. The gaussian shape has a higher maximum intensity, but the Lorentzian line shape has much more absorption (or emission) in the far line wings.

Voigt profile

All broadening mechanisms coexist, with Doppler and Lorentz broadenings being dominant. The combination of thermal broadening with the natural or collisionally broadened line profile is called the Voigt profile. This is the convolution of the Lorentz profile with a Doppler (Gaussian) profile. No simple analytic form. Lorentz profile falls off slower than Doppler profile, so core remains roughly Gaussian, while the wings look like a Lorentz profile.



If thermal/microturbulent Doppler broadening is large with respect to natural broadening, the Gaussian profile dominates near the line center, but wings of the Lorentzian profile can reappear far from the line center.



If thermal/microturbulent Doppler broadening is small with respect to natural broadening, the profile is similar to a Lorentzian.

Bound-free transitions (photoionization)

Bound-bound transitions occur only for photons with exactly the right amount of energy, but bound-free transitions can absorb ANY photon with more than a critical amount of energy. Therefore, the opacity of a material will increase at wavelengths shorter than one of these critical edges.

Bound-free transitions occur between atomic state and an unbound state, due to absorption in a continuous range of photon frequencies.

Free electron can have a range of kinetic energies => bound-free transitions produce continuous opacity (not just at lines).

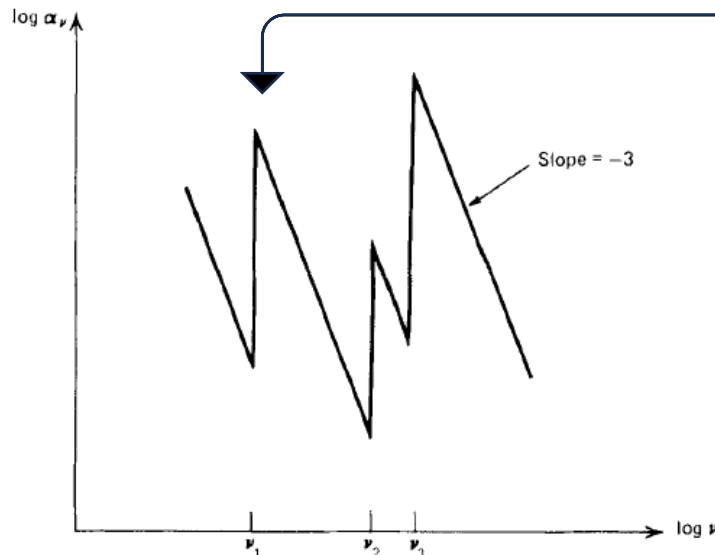
A minimum photon energy is needed to ionize an atom from a given level, e.g $\lambda \leq 91.2$ nm to ionize hydrogen from the $n = 1$ level.

For a hydrogen-like atom in a level with principal quantum number n , with ionization potential χ_n , the bound-free absorption cross-section is:

$$\sigma_{bf} = 0 \text{ for } \nu < \frac{\chi_n}{h} \text{ and } \sigma_{bf} \propto \frac{g(\nu, n, Z)}{n^5 \nu^3} \text{ otherwise.}$$

Here g is the bound-free Gaunt factor, a slowly varying correction factor to the simple scaling, and Z is the atomic number.

Absorption cross-section has sharp rises, absorption edges, at the frequency where the atom in a given level can be ionized.



Schematic illustration of the frequency dependence of the absorption coefficient. The sharp rises, absorption edges, occur at the frequency of ionization of each level.

Radiative transfer revisited

Integrating $I_\nu(\tau) = I_\nu^0 e^{-\tau_\nu} + S_\nu(1 - e^{-\tau_\nu})$ we have the well known cases:

$$1) \quad I_\nu(\tau) = I_\nu^0 + \tau_\nu(S_\nu - I_\nu^0) \quad \text{if } \tau_\nu \ll 1$$

$$2) \quad I_\nu(\tau) = S_\nu \quad \text{if } \tau_\nu \gg 1$$

We know that in LTE $\alpha_\nu = \frac{h\nu_0}{4\pi} \phi(\nu) n_1 B_{12} \left[1 - \exp\left(-\frac{h\nu}{kT_{ex}}\right) \right]$, $S_\nu = B_\nu(T_{ex})$

For a given frequency (transition), we can then express the intensity of the incoming radiation field in terms of its brightness temperature T_b and the population distribution of levels in atoms in terms of T_{ex} . Intensities are reopresented with temeprature scales:

$$\Delta T = \frac{h\nu}{k} \left\{ \frac{1}{\exp\left(\frac{h\nu}{kT_{ex}}\right) - 1} - \frac{1}{\exp\left(\frac{h\nu}{kT_b}\right) - 1} \right\} (1 - \exp(-\tau_\nu)) \quad \text{and, if } h\nu/kT \ll 1 \text{ the equation can be simplified further:}$$

$$\Delta T = (T_{ex} - T_b) \underbrace{(1 - \exp(-\tau_\nu))}_{\text{always } \geq 0 \text{ and } < 1}$$

For line transitions (Ly α , Ly β , H α , H β , CO, HI,...) the cloud is **fully transparent** ($\tau = 0$) for $\nu \neq \nu_0$, giving $I_\nu(\tau) = I_\nu^0$, while at the frequency of the line ($\nu = \nu_0$) we have $I(\nu_0)$.

The line is in emission if $I(\nu_0) > I^0(\nu_0)$ or $T_{ex} > T_b$

The line is in absorption if $I(\nu_0) < I^0(\nu_0)$ or $T_{ex} < T_b$