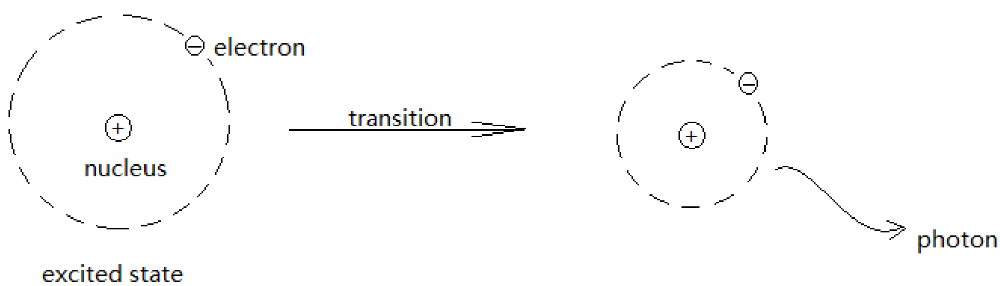
Lecture 6 Absorption

<u>Definition:</u> Absorption of EM radiation is the way by which the energy of a photon is taken up by matter, typically the electrons of an atom. Thus, the EM energy is transformed to other forms of energy, for example, heat, or chemical energy.

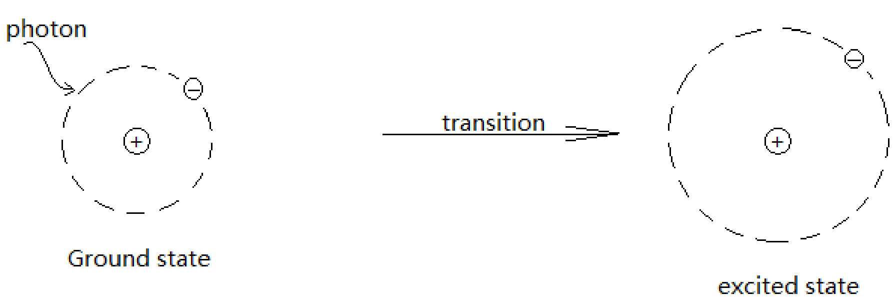
<u>Physical Explanation:</u>

Quantum theory predicts that the circular orbits of the electrons were quantized; that is, their angular momentum could have only integral multiples of a basic value. Radiation emission occurs only when an atom makes a transition from one energy state E_k to a state with lower energy E_j so that: $E_k - E_j = hf$ (h is the Planck's constant, f is the frequency of the EM radiation). The lowest energy state is called the <u>ground state</u> of and atom. Excited state: when an electron of an atom absorbs energy, the atom is said to be in an excited state.

Emission



Absorption



<u>Absorption and emission lines:</u>

Since an isolated molecule can only absorb and emit energy in discrete amounts, it can interact only with radiation having certain discrete wavelengths. Thus, the absorption and emission properties of an isolated molecule can be described in terms of a line spectrum. This is why you see those isolated absorption lines in the EM spectrum by the atmosphere gases.

Absorptivity (absorptance): is the ratio of radiation energy absorbed by an object to the incident total radiation energy. The absorptivity (a) is dependent on the wavelength λ, and viewing directions θ and φ. $a_\lambda(\theta, \varphi)$.

The graybody approximation:

- is to assume that the absorptivity of an object is not dependent on wavelengths.
- This is usually not a good assumption for the entire EM band.
- But a good approximation is to assign on constant absorptivity a_{sw} to the entire shortwave (solar) band, and another constant absorptivity a_{lw} to the longwave (thermal IR) band.
  - For most terrestrial surfaces, $a_{lw} \approx 1$;
  - a_{sw} is highly variable:
    $a_{sw} \approx 0$ for deep snow
    $a_{sw} \approx 1$ for forests and water bodies.

Kirchhoff's Law:

A substance emits radiation at each wavelength as efficiently as it absorbs it.

$$\varepsilon_\lambda(\theta, \varphi) = a_\lambda(\theta, \varphi)$$

This is strictly valid only for monochromatic radiation at a given wavelength λ and specified θ and φ (viewing angles).

Sometimes, it is ok to use graybody approximation. So that $\varepsilon(\lambda_1, \lambda_2) = a(\lambda_1, \lambda_2)$

Caveat:

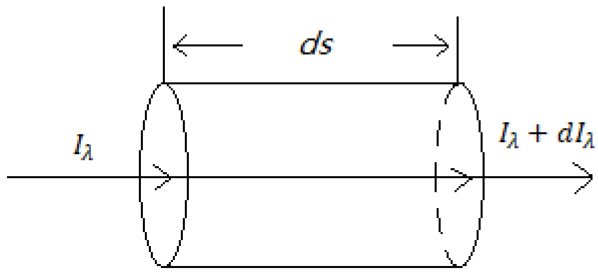
Kirchhoff's Law is only valid for conditions under local thermodynamic equilibrium (LTE).

LTE: in this condition, a material's temperature is uniform, and radiation is isotropic within a small volume. Those conditions are satisfied when energy transitions are dominated by molecular collisions.

- Below about 100 km in the atmosphere, LTE is a good assumption.
- In lightning discharges, the condition is non-LTE, therefore, both Kirchhoff's Law and Planck's Law do not apply.

No-scattering/no-emission radiative transfer equation:

Lambert's Law/Beer's Law: consider the passage of radiation through a layer of air or other material with infinitesimal thickness ds.



$$\frac{dI_\lambda}{I_\lambda} = -\beta_{a\lambda}\, ds \qquad (6.1)$$

Where I_λ is the incident radiant intensity (radiance) at wavelength λ. dI_λ is the reduction in I_λ due to absorption.

1. Absorption coefficient $\beta_{a\lambda}$:

In Eq. (6.1), $\beta_{a\lambda}$ is the absorption coefficient, which is the rate of power attenuated per unit distance due to absorption only. It has dimensions of inverse length (m^{-1}).

Integrating Lambert's Law (6.1) along the path of radiation from position *s = 0* to distance *s*:

$$I_\lambda(s) = I_\lambda(0)\exp\left(-\int_0^s \beta_{a\lambda} ds\right) \qquad (6.2)$$

For a uniform medium, $\beta_{a\lambda}$ is constant along the path. Then Eq. (6.2) becomes:

$$I_\lambda(s) = I_\lambda(0)\exp\left(-\beta_{a\lambda} s\right) \qquad (6.3)$$

The integrated form of Lambert's law in Eq. (6.3) shows that, for an initial intensity $I_\lambda(0)$ at position s=0 within a uniform medium, as the radiation propagates to distance s, the final intensity $I_\lambda(s)$ decreases exponentially. The rate at which the radiation falls off is proportional to $\beta_{a\lambda}$. The quantity $1/\beta_{a\lambda}$ gives the distance required for the wave's energy to be attenuated to *$e^{-1} \approx 37\%$* of its original values.

2. Mass Absorption coefficient $k_{a\lambda}$:

We know that Absorption coefficient $\beta_{a\lambda}$ is a measure of how strongly radiation is attenuated by absorption as it traverses a given geometric distance *s*. It is sometimes desirable to describe the strength of attenuation not by reference to a fixed geometric distance, but rather a fixed mass of material (medium). So we defined a new quantity called the **mass absorption coefficient** $k_{a\lambda}$, which relates to the volume absorption coefficient $\beta_{a\lambda}$ to the density ρ of the medium (air or other material):

$$\beta_{a\lambda} = \rho k_{a\lambda}$$

$k_{a\lambda}$ is the mass absorption coefficient (also referred to as the specific absorption cross section), which has units of area/mass (m^2/kg).

Using $k_{a\lambda}$, Eq (6.1) becomes:

$$\frac{dI_\lambda}{I_\lambda} = -\rho k_{a\lambda}\, ds \quad (6.4)$$

This form of Lambert's law in Eq. (6.4) shows that the fractional energy absorbed from a pencil of radiation is proportional to the mass traversed by the radiation.

3. Other Absorption Parameters:

- Relationship between absorption coefficient $\beta_{a\lambda}$, mass absorption coefficient $k_{a\lambda}$, and absorptivity (absorptance) a_λ:
  Differential absorptivity $da_\lambda = \frac{-dI_\lambda}{I_\lambda} = \rho k_{a\lambda}\, ds = \beta_{a\lambda}\, ds$
- Absorption coefficient $\beta_{a\lambda}$ for several gas species:
  $$\beta_{a\lambda} = \sum_i r_i \rho k_{a\lambda i}$$
  Where r_i denotes the mass mixing ratio of the i^{th} absorbing species.
- **Optical path length:** from Eq. (6.2), we defined optical path length as:
  $$u(s) = \int_0^s \rho k_{a\lambda} ds' = \int_0^s \beta_{a\lambda} ds'$$
  In absence of scattering and emission, the intensity inside a pencil of radiation decreases exponentially with the optical path length. For uniform medium,
  $$u(s) = \beta_{a\lambda} s = \rho k_{a\lambda} s$$
  Where *s* is the distance that the radiation traverses to. Optical path length is the dimensionless distance traversed by radiation weighted according to either absorption coefficient $\beta_{a\lambda}$ or the density ρ and mass absorption coefficient $k_{a\lambda}$ of the medium. **Optical path length** is similar to **optical depth (also known as optical thickness)**. In Lec. 7, you will see that we define optical thickness/depth as τ by including both absorption and scattering (extinction).
- **Transmissivity (transmittance)**: describes the fraction of incident radiation remaining in the pencil beam at a given distance:
  $$T_\lambda = \frac{I_\lambda(s)}{I_\lambda(0)} = e^{-u(s)}$$
  In absence of scattering and emission, since the absorptivity (absorptance) a_λ represents the function of incident radiation that has been absorbed from the pencil beam during the same traversal, so
  $$T_\lambda + a_\lambda = 1$$
  $$\Rightarrow\ a_\lambda = 1 - e^{-u(s)}$$
  ⇒ absorptivity exponentially approaches to 1 with increasing path length through an absorbing medium, which, in that limit, is said to be "optically thick".