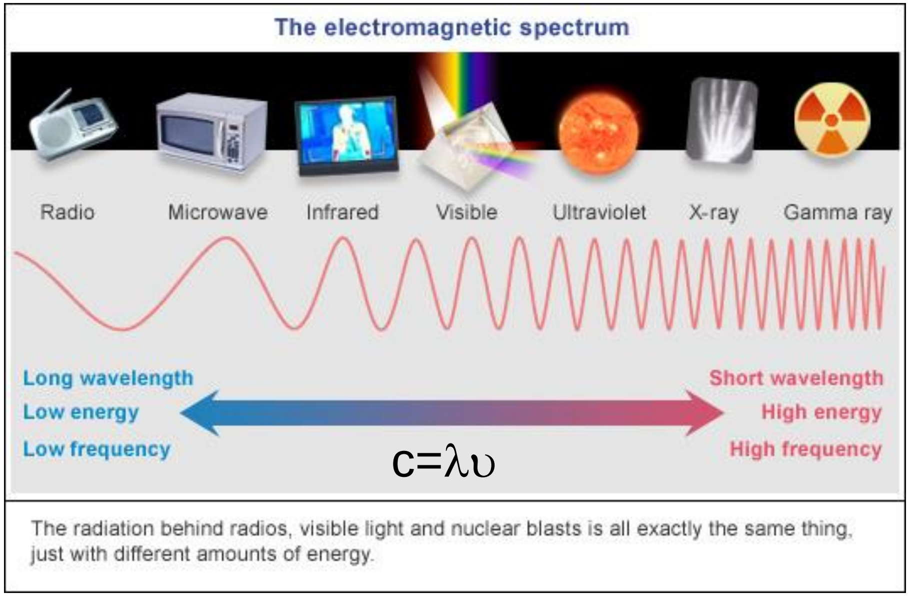
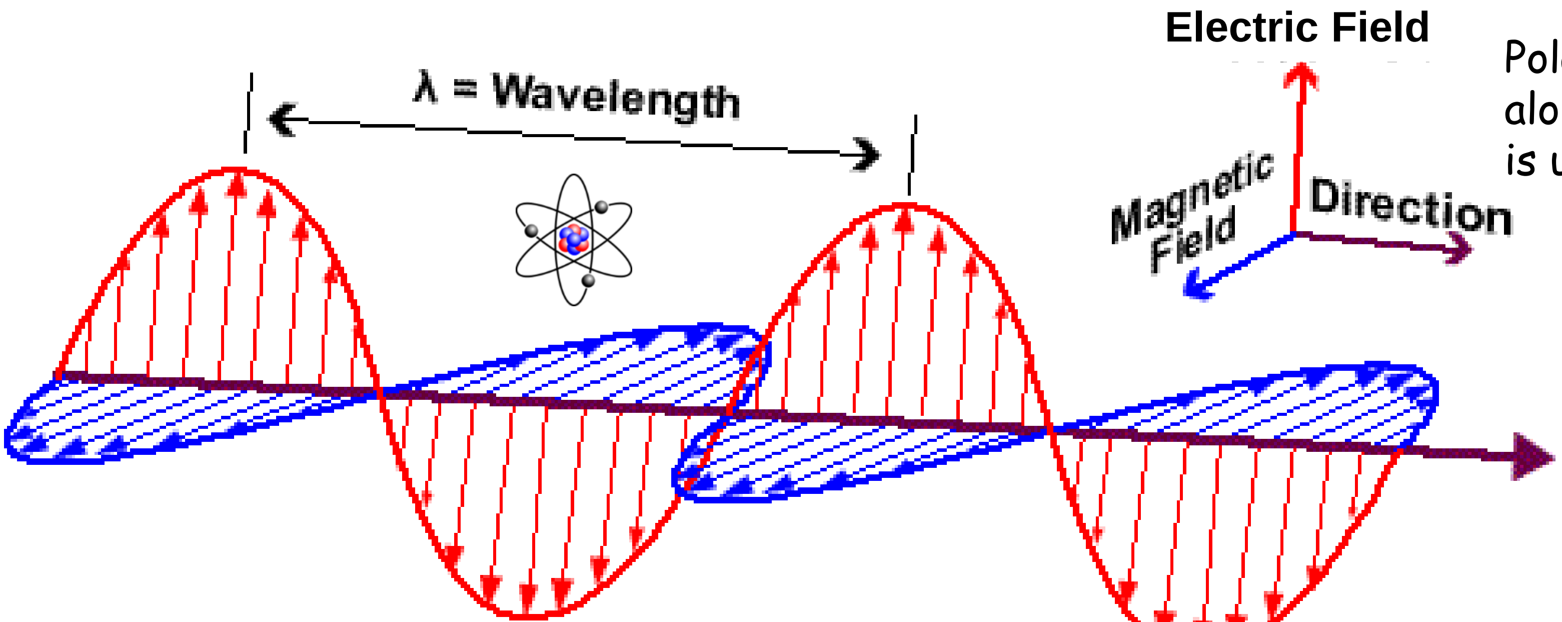
11.2: Emission and absorption of radiation

11.2.1: Electromagnetic waves





Polarized light along z axis (k is unit vector)

If atom is much smaller than wavelength, then the electric field is ~uniform inside atom.

$$\mathbf{E} = E_0 \cos(\omega t)\, \hat{k}$$

Visible light is ~5000 Å
while an atom is ~ 1 Å

$$H' = -qE_0 z\cos(\omega t)$$

$$\mathbf{E} = -\nabla H'(\mathbf{r})/q$$

$$\mathbf{E} = E_0\cos(\omega t)\,\hat{k}$$

We will see that diagonal matrix elements of *H'* vanish by symmetry for atoms such as hydrogen. Thus, the matrix elements that matter are (a≠b):

$$H'_{ba} = -\wp E_0 \cos(\omega t)$$

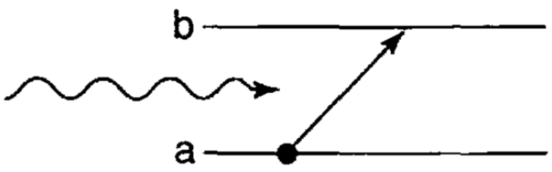
where the electric dipole moment →

$$\wp \equiv q\langle \psi_b | z | \psi_a \rangle$$

Relating with previous generic formulas thus only requires replacement →

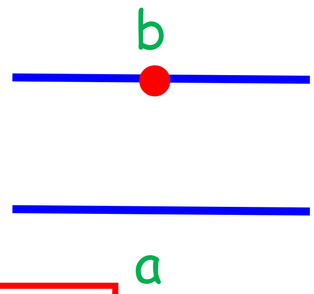
$$V_{ba} = -\wp E_0$$

$$P_{a\to b}(t) = \left(\frac{|\wp| E_0}{\hbar}\right)^2 \frac{\sin^2[(\omega_0-\omega)t/2]}{(\omega_0-\omega)^2}$$



$$c_a(0) = 0,\ c_b(0) = 1$$

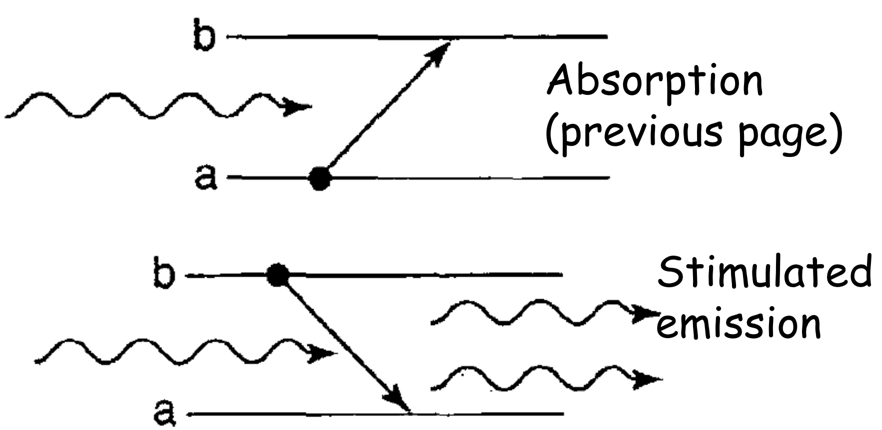
Suppose we repeat the same calculation as in the previous lecture, but with the electron first at *b*. It can be shown result is the same just switching *a* <--> *b*.



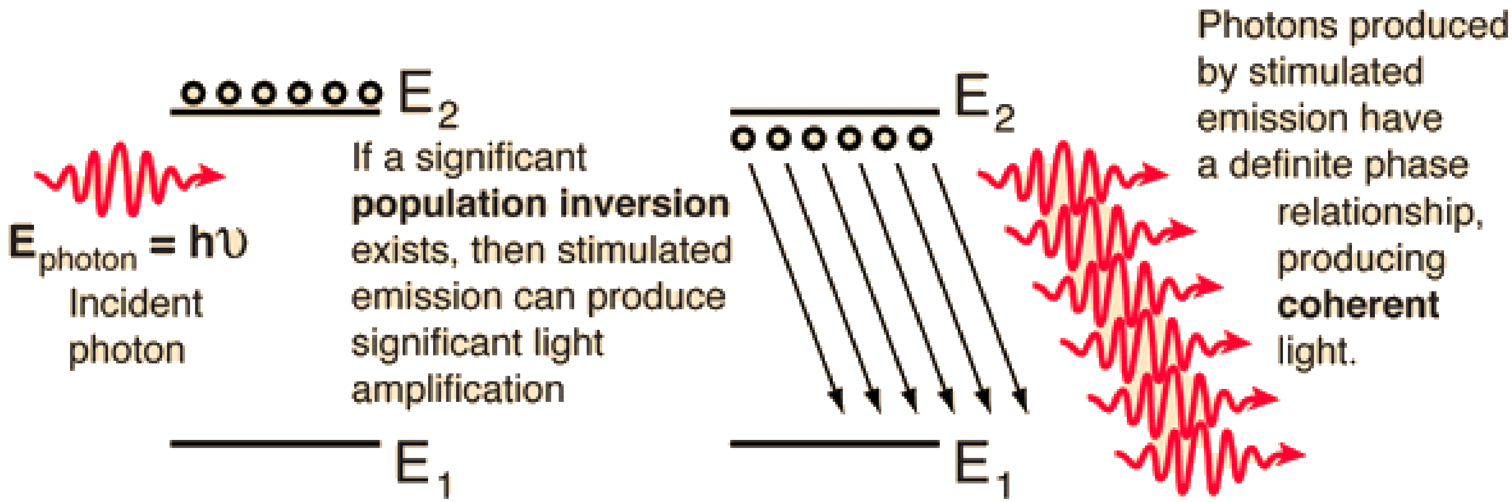
$$P_{b\to a}(t) = \left(\frac{|\wp| E_0}{\hbar}\right)^2 \frac{\sin^2[(\omega_0 - \omega)t/2]}{(\omega_0 - \omega)^2}$$

As expressed before, even though you are originally at "*b*", by merely being immersed in a radiation field (i.e. a lot of photons) the electron can **decay** to a lower energy.

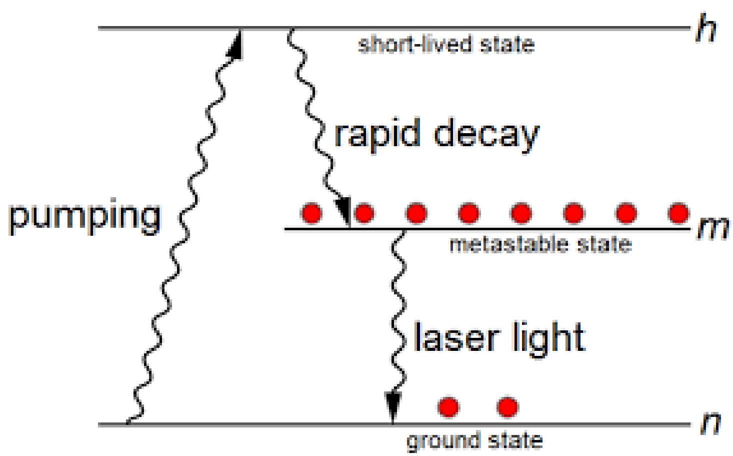
This is called **stimulated emission**. The electron in "*b*" is "unstable", and any perturbation (like a shower of photons) may **drop it** to "*a*". Actually the probability a->b and b->a is the same.



FYI only. Because of stimulated emission **amplification** can occur. Almost instantly a huge number of photons in phase can be produced:



You need three states in practice:

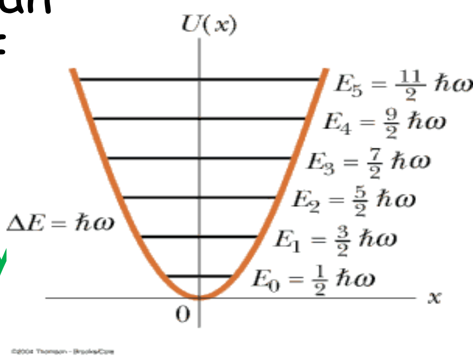


This is the basis of Light Amplification by Stimulated Emission of Radiation (LASER).

So far, in the presence of the **same** external field of the proper frequency, (1) we can either move an electron from a lower level to an upper level (**absorption**) or (2) we can lower an electron from an upper level to a lower level (**stimulated emission**).

Remarkably, there is a third possibility: **spontaneous emission**. This is when an electron is in a high energy level, there is NO obvious external field, and yet the electron decays to a lower level **spontaneously**.

This contradicts what I said at the start of Ch.11: that an electron in an upper level will remain there forever if if no disturbance shakes the electron. But in QUANTUM electrodynamics, like in a harmonic oscillator, **there is always some oscillation present.** The zero-point energy



Amazingly even in the best laboratory conditions there is **always** some radiation present even at zero temperature, similarly as in ANY quantum mechanics problem: **e.g. the particle never rests at the bottom of the infinite square well because the ground state energy is not 0 but larger than 0.**

11.2.3: Incoherent Perturbations

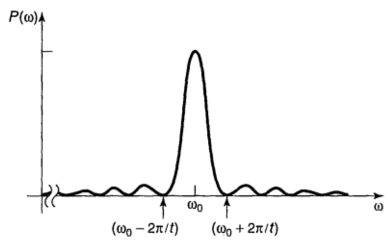
So far, we have assumed the "external" field has only one frequency.

However, radiation is never perfectly monochromatic. There are always many frequencies contributing (non-monochromatic).

It can be shown that in the presence of many frequencies ω with a particular energy density ρ(ω) the probability for the transition becomes:

$$P_{b\to a}(t) = \frac{2}{\epsilon_0 \hbar^2} |\wp|^2 \int_0^\infty \rho(\omega) \left\{ \frac{\sin^2[(\omega_0 - \omega)t/2]}{(\omega_0 - \omega)^2} \right\} d\omega$$

If {...} is sharply peaked, then:



$$P_{b\to a}(t) \cong \frac{2|\wp|^2}{\epsilon_0 \hbar^2} \rho(\omega_0) \int_0^\infty \frac{\sin^2[(\omega_0 - \omega)t/2]}{(\omega_0 - \omega)^2} d\omega$$

Using the mathematical identity $$\int_{-\infty}^{\infty} \frac{\sin^2 x}{x^2} dx = \pi$$

we arrive to $$P_{b\to a}(t) \cong \frac{\pi |\wp|^2}{\epsilon_0 \hbar^2} \rho(\omega_0) t$$

and taking time derivative to obtain a probability rate $R \equiv dP/dt$ $$R_{b\to a} = \frac{\pi}{\epsilon_0 \hbar^2} |\wp|^2 \rho(\omega_0)$$

This is a constant (no longer an oscillatory function).

So far we also assumed the radiation was polarized with electric field along *z*. If we average in all directions (unpolarized):

$$R_{b\to a} = \frac{\pi}{3\epsilon_0 \hbar^2} |\boldsymbol{\wp}|^2 \rho(\omega_0)$$

$$\wp \equiv q\langle \psi_b | z | \psi_a \rangle \Rightarrow \boldsymbol{\wp} \equiv q \langle \psi_b | \mathbf{r} | \psi_a \rangle$$

11.3.3 Selection rules

Very often the matrix elements $\langle\psi_b|\mathbf{r}|\psi_a\rangle$ that appear in the rate are zero by symmetry.

Consider the hydrogen atom. In this case the matrix elements are: $\langle n'l'm'|\mathbf{r}|nlm\rangle$

Commutators discussed time ago (Ch. 4)

$$[L_z, x] = i\hbar y, \quad [L_z, y] = -i\hbar x, \quad [L_z, z] = 0$$

or spherical harmonics ($Y_1^0 \sim \cos\theta$; $z = r\cos\theta$) allow us to arrive to the first rule (Ch. 6, page 259):

No transitions occur unless $\Delta m = \pm 1$ or 0

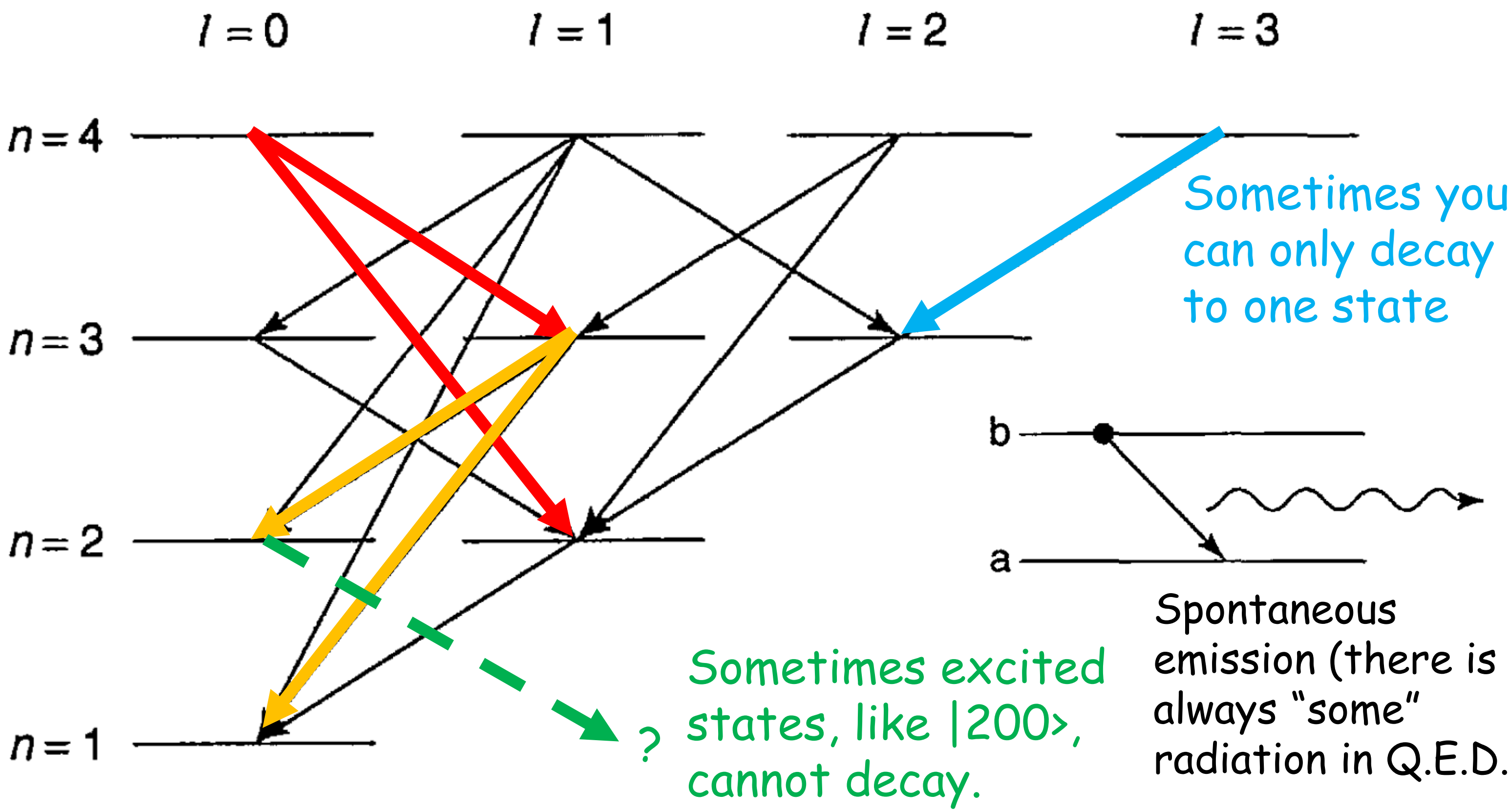
From many other commutators learned time ago, it can be derived the second rule:

No transitions occur unless $\Delta l = \pm 1$

Although for us the external field is not quantum, intuitively the results are in agreement with "photons" emitted or absorbed, because photons have spin s=1 (bosons) and projections are m_s = -1,0,1.

Conservation of angular momentum leads to these selections rules: whatever happens to the electron in the atom, must be compensated by the photon with regards to energy and angular momentum.

$\Delta l = \pm 1$



The states that cannot decay are "metastable" with long lifetimes. They eventually decay from atomic collisions or emitting two photons (much lower probability).