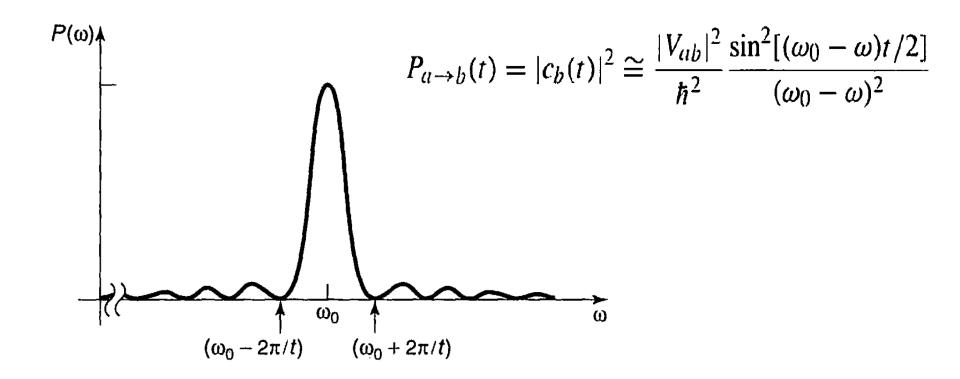
Plotting results at a fixed time, as a function of frequency, make more clear that near resonance the probability is maximized.



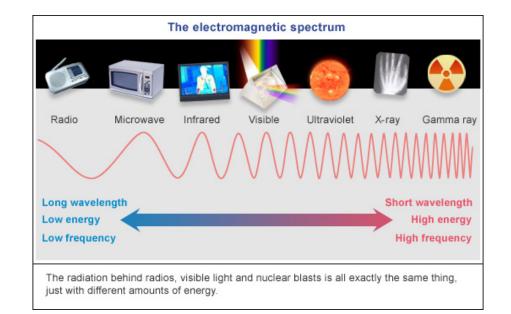
Near resonance, 
$$\sin^2[(\omega_0-\omega)t/2] \sim [(\omega_0-\omega)t/2]^2$$

At resonance, amplitude grows like  $t^2$  so eventually the transition will surely occur.

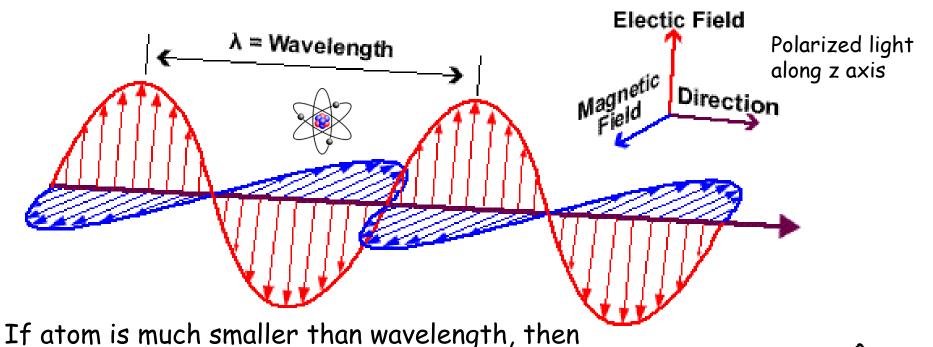
## 11.2: Emission and absorption of radiation

11.2.1: Electromagnetic waves

the electric field is ~ uniform inside atom



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



2

Visible light is  $\sim 5000 \text{ Å}$  while an atom is  $\sim 1 \text{ Å}$ 

$$H' = -q E_0 z \cos(\omega t)$$

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

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

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):

$$H'_{ba} = -pE_0\cos(\omega t)$$

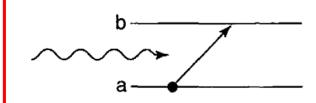
where the electric dipole moment  $\rightarrow$ 

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

Relating with previous generic formulas thus require replacement  $\rightarrow$ 

$$V_{ba} = -p E_0$$

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



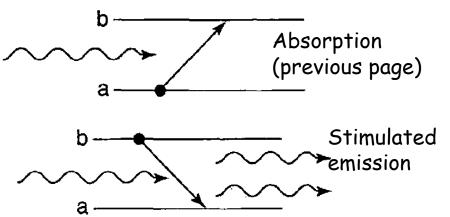
Suppose we repeat the same calculation as in the previous lecture but with the electron first at b. Result is the same just switching a < -- > b.

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

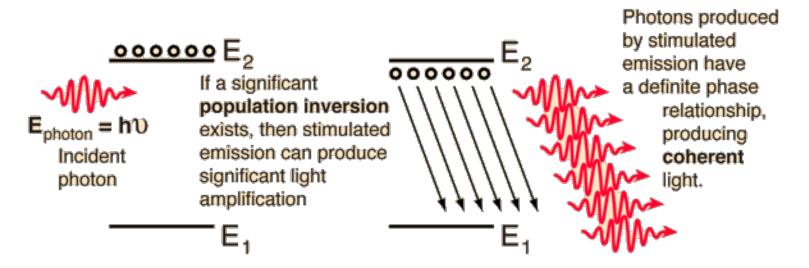
$$P_{b\to a}(t) = \left(\frac{|p|E_0}{\hbar}\right)^2 \frac{\sin^2[(\omega_0 - \omega)t/2]}{(\omega_0 - \omega)^2}$$

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.

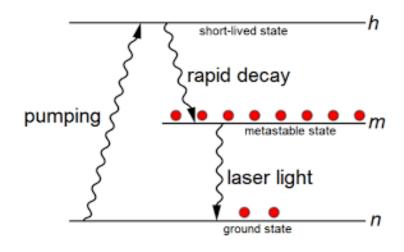
This is called **stimulated emission**. The electron in "b" is "unstable", and any perturbation (like a shower of photons) may **drop it** to "a". Actually the probability a->b and b->a is the same.



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 right 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 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 without any disturbance shacking 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.

U(x)

 $\Delta E = \hbar \omega$ 

## 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  $\omega$  with a particular energy density  $\rho(\omega)$  the probability for the transition becomes:

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

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

$$P(\omega)$$

$$(\omega_0 - 2\pi/t)$$

$$(\omega_0 + 2\pi/t)$$

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

Using the mathematical identity

$$\int_{-\infty}^{\infty} \frac{\sin^2 x}{x^2} \, dx = \pi$$

we arrive to 
$$P_{b o a}(t)\cong rac{\pi |p|^2}{\epsilon_0 \hbar^2} 
ho(\omega_0) t$$

and taking time derivative to obtain a probability rate  $R \equiv dP/dt$ 

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

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):

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

$$p \equiv q \langle \psi_b | z | \psi_a \rangle | \mathbf{p} \equiv q \langle \psi_b | \mathbf{r} | \psi_a \rangle$$

## 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:  $\langle n'l'm'|\mathbf{r}|nlm\rangle$ 

Commutators discussed time ago (Ch. 4)

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

allow us to arrive to the first rule:

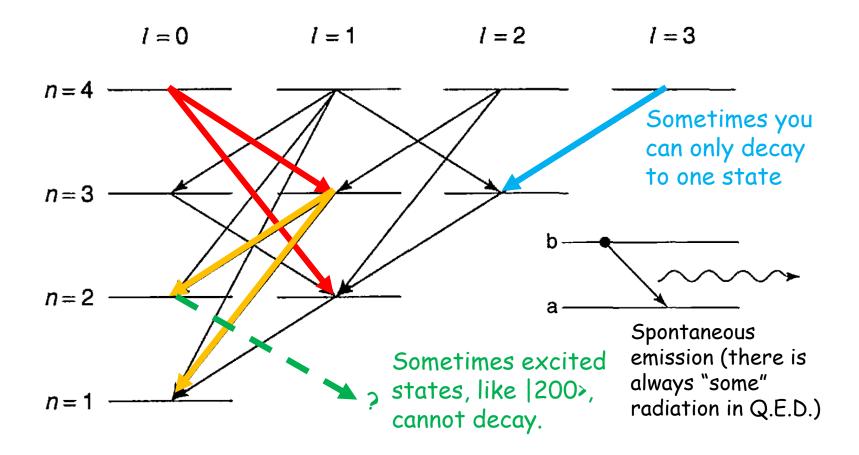
No transitions occur unless  $\Delta m = \pm 1$  or 0

From many other commutators learned time ago, we can derive 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  $m_s=-1,0,1$ .

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.



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