INCOHERENT PERTURBATIONS

Let us now look at a very common physics problem: the description of transitions between excited states in an atom. We can use perturbation theory by considering the following situation: if I put my atom in an electric (or magnetic) field, which in principle could vary as a function of time, what is the probability that I may have a transition? We know the solution of the unperturbed Hamiltonian: $\psi_{n\ell m}(\vec{r})$, our orbital wavefunctions.

Let us add an oscillating electric field (which reminds us of EM waves...):

$$\vec{E}' = E_z \cos(\omega t)\,\hat{z}$$

Then, the contribution to the Hamiltonian becomes:

$$H' = -e\,\vec{E}'\cdot\vec{r} = -e\cdot E_z'\cdot z\cos(\omega t)$$

Let us note that $\psi_{n\ell m}(\vec{r})$, wavefunctions in spherically symmetric Coulomb potential, all have definite inversion symmetry. Therefore:

$$\langle \psi_{n\ell m} | H' | \psi_{n\ell m} \rangle = 0$$

However, $\langle \psi_{n'\ell' m'} | H' | \psi_{n\ell m} \rangle$ may not be $\emptyset$ when the two states are different.

First-order perturbation theory tells me:

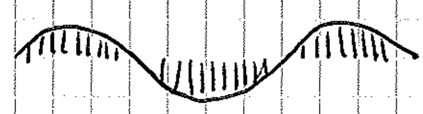
$$P_{a\to b}(t) = P_{b\to a}(t) = \left(\frac{e E_z' |\langle \psi_b | z | \psi_a \rangle|}{\hbar}\right)^2 \frac{\sin^2\left(\frac{\omega_0-\omega}{2}t\right)}{(\omega_0-\omega)^2}$$

where $\omega_0 = \dfrac{E_b - E_a}{\hbar}$. This formula shows the very interesting result of Rabi flopping: there are values of t for which the probability of a transition is zero, despite the perturbation having acted for a while.

What if, instead of having a single perturbation, with frequency ω, we had an incoherent radiation, over a range of frequencies?

Let us consider an electromagnetic wave. Its energy density is:

$$u = \frac{\varepsilon_0}{2} E_0^2$$

(imagine  $\vec{E}(x,t) = \underline{E_0} e^{i(kx-\omega t)} \hat{n}$)

direction of $\vec{E}$ field (polarization)

Then, we can write:

$$P_{a\to b}(t) = \frac{2 u e^2}{\varepsilon_0 \hbar^2} \cdot |\langle \psi_b | z | \psi_a \rangle|^2 \cdot \frac{\sin^2\left(\frac{\omega_0-\omega}{2}t\right)}{(\omega_0-\omega)^2}$$

Let me generalize the formula above to the case in which $\vec{E}$'s direction is not simply along $\hat{z}$. The Hamiltonian becomes $e\vec{E}\cdot\vec{r}$ and here above I can write:

$$P_{a\to b}(t) = \frac{2u}{\varepsilon_0 \hbar^2} \, |p|^2 \cdot \frac{\sin^2\left(\frac{\omega_0-\omega}{2}t\right)}{(\omega_0-\omega)^2}$$

where p is the electric dipole: $\langle \psi_b | e\vec{r} | \psi_a \rangle$

Now note that u describes the energy density of our impending radiation. In the case of a monochromatic wave, $u = \frac{1}{2}\varepsilon_0 E_0^2$.

In the case of incoherent radiation, we can write:

$$u(\omega) \to \rho(\omega)\, d\omega$$

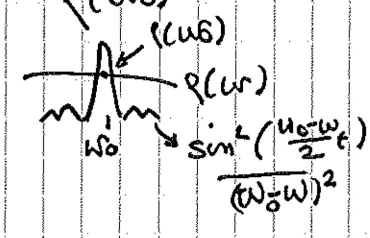
where $\rho(\omega)$ is the energy density per unit of frequency. When we shine incoherent radiation, we need to add all components to find transition probability $\Longrightarrow$ integrate over $d\omega$:

$$P_{a\to b}(t) = \frac{2}{\varepsilon_0 \hbar^2} |p|^2 \int d\omega \, \rho(\omega) \frac{\sin^2\left(\frac{\omega_0-\omega}{2}t\right)}{(\omega_0-\omega)^2}$$

Note that the expression $1/(\omega_0-\omega)^2$ is sharply peaked at $\omega=\omega_0$, while $\rho(\omega)$ is typically rather broadly distributed. We can use the following approximation:

$$P_{a\to b}(t) = \frac{2}{\varepsilon_0\hbar^2}|p|^2\int_{-\infty}^{\infty} d\omega\, \rho(\omega)\, \frac{\sin^2\left(\frac{\omega_0-\omega}{2}t\right)}{(\omega_0-\omega)^2} \approx$$

replace $\rho(\omega)$ with $\rho(\omega_0)$:



$$\approx \frac{2}{\varepsilon_0\hbar^2}|p|^2\rho(\omega_0)\underbrace{\int_{-\infty}^{\infty} d\omega\, \frac{\sin^2\left(\frac{\omega_0-\omega}{2}t\right)}{(\omega_0-\omega)^2}}_{\pi t/2}$$

$$P_{a\to b}(t) \approx \frac{\pi|p|^2}{\varepsilon_0\hbar^2}\rho(\omega_0)\cdot t$$

The probability of a transition does not oscillate any more: that behavior gets washed out when I use an incoherent wave with many components (i.e., not a monochromatic wave).

What is the transition rate, i.e., the probability of a transition per unit of time? It is CONSTANT:

$$R_{a\to b} = \frac{dP_{a\to b}(t)}{dt} = \frac{\pi|p|^2}{\varepsilon_0\hbar^2}\rho(\omega_0)$$

One additional small step. Here we are assuming that the $\vec{E}$ field is polarized in one direction (e.g.: $\vec{E}=E_0\hat{z}\cos(\omega t)$, then $\vec{p}=e\hat{z}\langle\psi_a|z|\psi_b\rangle$).

If $\vec{E}$ is <u>not</u> polarized, then I need to use the average $|\vec{p}\cdot\hat{n}|^2$ instead of $|p|^2$, above. $\hat{n}$ is a unit vector indicating the $\vec{E}$ field polarization, and we are assuming that any direction is equally probable. Hence:

$$\vec{p}\cdot\hat{n} = p\cos\theta \Rightarrow |\vec{p}\cdot\hat{n}|^2_{average} = \frac{1}{4\pi}\int_0^{2\pi}d\varphi\int_0^{\pi}d\theta\, p^2\cos^2\theta\,\sin\theta\, d\theta = \frac{|p|^2}{3}$$

Finally, for non-monochromatic, non-polarized incident $\vec{E}$ field:

$$\boxed{R_{a\to b} = \pi|p|^2\rho(\omega_0)/3\varepsilon_0\hbar^2}$$