Lecture 22 Highlights

We now consider the problem of how an atom makes a transition from one state to another when it is stimulated (perturbed) by an electromagnetic field. Consider a hydrogen atom in its 1s ground state. The light exerts a force on the electron dominated by the electric field, $\vec{E} = E_{0x}\hat{x}\cos(\omega t)$, which is arbitrarily assumed to be polarized along the x-direction. We assume that the wavelength of the (visible) light (λ ~ 500 nm) is much greater than the size of the atom, which is the scale of the Bohr diameter ~ 0.1 nm. Therefore the atom experiences a uniform-in-space electric field, as written above, to good approximation.

The potential associated with the (conservative) electric force is:

$V(x,t) = -(-e)\int_0^x E_x dx'$, which yields $V(x,t) = \frac{e}{2}E_{0x}x\left(e^{i\omega t} + e^{-i\omega t}\right)$. We treat this potential as the time-dependent perturbation. Assume that the hydrogen atom is left alone in the 1s state for all times before t=0. At t=0 the light turns on and the perturbation begins. At time t the light is turned off. Now the question is which state does the hydrogen atom find itself in, and with what probability? This is a job for time-dependent perturbation theory.

The transition probability can be calculated from the transition amplitude rate from state n to state j:

$$\dot{a}_{nj} = \frac{-i}{\hbar}e^{i(E_j^0 - E_n^0)t/\hbar}\int \psi_j^*(\vec{x})\mathrm{H}'(\vec{x},t)\psi_n(\vec{x})d^3x$$

In this case we get:

$$\dot{a}_{nj} = \frac{-ieE_{0x}}{2\hbar}\left[e^{i(E_j^0 - E_n^0 + \hbar\omega)t/\hbar} + e^{i(E_j^0 - E_n^0 - \hbar\omega)t/\hbar}\right]\int \psi_j^*(\vec{x})x\psi_n(\vec{x})d^3x$$

The last piece is the "dipole matrix element" $x_{jn} = \int \psi_j^*(\vec{x})x\psi_n(\vec{x})d^3x$, which will give rise to "selection rules" for the transitions.

Integrating up the transition amplitude rate gives the transition amplitude:

$$a_{nj}(t) = \frac{eE_{0x}}{2}\left[\frac{1 - e^{i(E_j^0 - E_n^0 + \hbar\omega)t/\hbar}}{E_j^0 - E_n^0 + \hbar\omega} + \frac{1 - e^{i(E_j^0 - E_n^0 - \hbar\omega)t/\hbar}}{E_j^0 - E_n^0 - \hbar\omega}\right]x_{jn}$$

This quantity has two terms that get very large when $E_j^0 - E_n^0 = \pm\hbar\omega$. The system starts in state n and makes a transition to state j. Hence the second term corresponds to absorption of energy $\hbar\omega$ by the atom in moving from state n to state j. The first term corresponds to the atom starting in a higher energy state n and giving up energy $\hbar\omega$ to the electromagnetic field and going into lower energy state j. This process is known as stimulated emission, and will be investigated in more detail later.

We focus on the case of absorption of energy by the atom from the electromagnetic field $E_j^0 - E_n^0 = +\hbar\omega$, which arises from the second term. After taking the absolute square and using the trigonometric identity $\cos z = 1 - 2\sin^2\frac{z}{2}$, we get the absorption probability:

$$\left|a_{nj}(t)\right|^2 = e^2 E_{0x}^2 \left|x_{jn}\right|^2 \frac{\sin^2\left(\frac{\left(E_j^0 - E_n^0 - \hbar\omega\right)t}{2\hbar}\right)}{\left(E_j^0 - E_n^0 - \hbar\omega\right)^2}$$

As a function of time this transition probability is sinusoidal. It increases initially from zero, as we would expect. However it returns to zero periodically in intervals of time given by $\frac{2\pi\hbar}{\left(E_j^0 - E_n^0 - \hbar\omega\right)}$. This is the phenomenon of Rabi flopping (Fig. 9.1), in which the system periodically has probability zero of having made a transition to the upper state, despite the fact that the perturbation has been acting for some time.

As a function of frequency offset (detuning) from resonant absorption, $\omega - \frac{E_j^0 - E_n^0}{\hbar}$, the transition probability (for fixed duration t) is a sinc^2-like function (Fig. 9.2). Recall that $\mathrm{sinc}(x) \equiv \frac{\sin x}{x}$. This means that there is non-zero probability for the atom to make the transition even though the frequency does not exactly satisfy the condition $\hbar\omega = E_j^0 - E_n^0$. Because the perturbation is on for a finite time interval, there is an uncertainty in the frequency of the light, and this uncertainty satisfies the energy-time uncertainty relation: $\Delta E \ \Delta t \geq \hbar$.