## Lecture 14 Highlights Phys 402

We are exploring time-dependent perturbation theory...

Consider the problem of how an atom makes a transition from one state to another when it is stimulated (perturbed) by a time-dependent electromagnetic field. Consider a hydrogen atom prepared 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. The electric field in the electromagnetic wave stretches the Hydrogen atom and gives it an electric dipole moment. This stretching happens  $\omega$  times per second, where  $\frac{\omega}{2\pi} \sim 10^{15}$ Hz for visible light. We assume that the wavelength of the (visible) light ( $\lambda \sim 500$  nm) is much greater than the size of the atom, which is the scale of the Bohr diameter  $\sim 0.1$  nm. Therefore the atom experiences a uniform-in-space but oscillating in time electric field, as written above, to good approximation. (Think about being on a small boat in the ocean with long wavelength swells going by. Locally you see a 'flat' sea surface that simply oscillates up and down sinusoidally with time.)

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 H'. 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 found in Eq. (1) of the last lecture:

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

In this case we get:

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

The last piece is the "dipole matrix element"  $x_{jn} \equiv \int \psi_j^*(\vec{x}) x \psi_n(\vec{x}) d^3 x$ , which will give rise to "selection rules" for the transitions. For the moment, we can consider this simply as a time-independent complex number, and we will return to this term later.

Integrating up the transition amplitude rate gives the transition amplitude for the time-dependent perturbation of duration *t*:

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

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' of radiation. Note that these two processes (absorption and stimulated emission) occur with the same probability pre-factor.

Recall that  $\omega$  is the frequency of the electromagnetic field that is perturbing the atom, and is a variable under our control. The energy difference  $E_j^0 - E_n^0$  is a fixed property of the quantum system (in this case a Hydrogen atom). We focus on the case of absorption of energy by the atom from the electromagnetic field  $E_j^0 - E_n^0 = +\hbar\omega$  (i.e.  $E_j^0 > E_n^0$ ), which arises from the second term. Last time we found that the absorption probability is:

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

As a function of time this transition probability is (a squared) 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. 11.4 in Griffiths), 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. This is quite surprising at first sight. It occurs because when the atom is excited in to the upper state and can emit a photon by means of the stimulated emission process and go back to the initial state.

When the electromagnetic driving frequency is "right on the money", namely  $\omega = \frac{E_j^0 - E_n^0}{\hbar}, \text{ one can find the following result for the transition probability:}$   $\lim_{\omega \to \frac{E_j^0 - E_n^0}{\hbar}} |a_{nj}(t)|^2 = \frac{e^2 E_{0x}^2 |x_{jn}|^2}{4\hbar^2} t^2.$  In other words the transition probability increases

quadratically in time, until the point where perturbation theory is no longer valid.

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*<sup>2</sup>-like function (Fig. 11.5 of Griffiths). Recall that 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:  $\Delta E \ \Delta t \ge \hbar$ . By examining the Fourier transform of the finite-duration (in time) perturbation one finds "sidebands" at frequencies nearby the central frequency of the cos  $\omega t$  perturbation. Some of these sidebands will be at the transition frequency of the quantum system  $\frac{E_j^0 - E_n^0}{\hbar}$ . (Note that the energy-time uncertainty relation:  $\Delta E \ \Delta t \ge \hbar$  does not arise from a pair of non-commuting operators, but is simply a consequence of the behavior of functions that are Fourier transform pairs.)

The phenomenon of Rabi oscillations is very different from our everyday experience of how macroscopic objects (i.e. those made up of many atoms) absorb electromagnetic radiation. When illuminated with broadband light (like French fries under an infrared lamp at McDonalds) objects tend to steadily absorb the light and heat up to a steady state temperature, showing no signs of oscillation with time. We did a calculation of the transition probability of an atom illuminated with a broad spectrum of light like that coming out of a blackbody radiator, like the sun. A black body radiation spectrum has an electromagnetic energy density (energy per unit volume per unit frequency) given by Planck's formula:

$$\rho(\omega) = \frac{\hbar}{\pi^2 c^3} \frac{\omega^3}{e^{\hbar\omega/k_B T} - 1},\tag{1}$$

where  $\omega$  is the angular frequency of the radiation,  $k_B$  is Boltzmann's constant, and T is temperature of the blackbody radiator. This source is emitting light over a broad range of frequencies. We co-opted the result from the last lecture that the probability of transition due to a monochromatic light source of strength  $E_{0x}$  is given by:

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

We replaced the energy density of this monochromatic wave  $(\frac{1}{2}\varepsilon_0 E_{0x}^2)$  with the energy density of a blackbody radiator ( $\rho(\omega) d\omega$ ) for a differential segment of frequency  $d\omega$ . The blackbody source illuminates the atom with many different frequencies and many different polarizations simultaneously. This excitation is **incoherent** in that there is no fixed phase relationship between the incoming light at different frequencies. As such, we will **incoherently** add up the probability (as opposed to amplitude) of transition for each differential segment of the frequency spectrum separately. The result is a transition probability that increases linearly with time, or in other words, a transition rate that is constant. This is consistent with our everyday experience that objects illuminated with light get steadily hotter (until they radiate or conduct some of that heat away and come in to a steady state condition). To see Rabi oscillations requires carefully prepared laboratory conditions where the Hamiltonian of the atom is controlled to be just the terms that we assume, and no others.

We found the rate of absorption of this type of radiation by a two-level atom (states a and b) assuming random polarization of the light:

$$R_{a\to b} = \frac{\pi e^2 \rho(\omega_{ab})}{3\varepsilon_0 \hbar^2} \Big( |x_{ab}|^2 + |y_{ab}|^2 + |z_{ab}|^2 \Big) \equiv \rho(\omega_{ab}) M_{ab},$$

where  $E_b - E_a = \hbar \omega_{ab}$ , and the term in parentheses contains the three Cartesian dipole matrix elements between states *a* and *b*.

A constant transition rate is very different from the oscillatory transition probability seen in the Rabi flopping case. This difference comes about because the many absorption processes at different frequencies produce a 'smeared-out' response that destroys the coherent Rabi oscillations and results in a classical incoherent absorption.