Lecture 15 Highlights
Phys 402

We continued with time-dependent perturbation theory applied to the Hydrogen atom.

Selection Rules

We have been considering a quantum system that is perturbed by a time-dependent perturbation and we have calculated the probability that the system makes a transition. All of the transition probabilities and rates we have calculated are proportional to "dipole matrix elements," such as x_{jn}. These are similar to dipole moment calculations for a charge distribution in classical physics, except that they involve the charge distribution in two different states, connected by the dipole operator for the transition. In many cases these integrals are zero because of symmetries of the associated wavefunctions. This gives rise to **selection rules** for possible transitions under the dipole approximation (atom size much smaller than the electromagnetic wave wavelength).

To make further progress we have to consider a specific quantum system. For example, consider the matrix element $z_{n,\ell,m;n',\ell',m'}$ between states of the Hydrogen atom labeled by the quantum numbers n, ℓ, m and n', ℓ', m':

$$z_{n,\ell,m;n',\ell',m'} = \iiint \psi_{n,\ell,m}(\vec{r})\, z \psi_{n',\ell',m'}(\vec{r}) d^3 r$$

Recall the properties of the Hydrogen atom wave functions as given in Eqs. [4.89] and [4.32] of Griffiths. Note the ortho-normality properties of the Hydrogen-atom wavefunctions (Eq. [4.90]) and the spherical harmonics (Eq. [4.33]). Also recall that all 3 quantum numbers n, ℓ, m are integers. To make progress, first consider just the ϕ integral in the matrix element. In this case, since $z = r\cos\theta$, the ϕ dependence comes entirely from the spherical harmonics in the Hydrogen atom wave-functions:

$$z_{n,\ell,m;n',\ell',m'} \propto \int_0^{2\pi} e^{-im\phi}\, e^{+im'\phi} d\phi$$

Since m and m' are integers, this integral will be zero unless $m = m'$ (use L'Hôpital's rule to prove this). This gives rise to a **selection rule** from this type of matrix element, namely $\Delta m \equiv m - m' = 0$, to get a non-zero transition probability.

After considering the ϕ integral for the other polarization directions, x and y (which are proportional to $\cos\phi$ and $\sin\phi$), one finds another possible selection rule: $\Delta m = \pm 1$. Note that any general polarization direction can be written as a linear superposition of x, y, and z-directed electric fields. By exploring all of these possibilities, we eliminate any bias or prejudice implied by our arbitrary choice of a coordinate system to describe the physics of atom-light interaction.

Examining the θ integrals, one finds that the Hydrogen atom wavefunctions are proportional to the associated Legendre polynomials $P_\ell^{|m|}(\cos\theta)$, while the dipole operators x, y, and z bring in factors of $\sin\theta$ and $\cos\theta$ in the matrix element integrals. One can use the identities (recurrence formulas):

$$\cos\theta \times P_\ell^m(\cos\theta) = \frac{(\ell - m + 1)P_{\ell+1}^m(\cos\theta) + (\ell + m)P_{\ell-1}^m(\cos\theta)}{2\ell + 1}$$ [see Wiki]

$$\sin\theta \times P_\ell^m(\cos\theta) = \frac{-P_{\ell+1}^{m+1}(\cos\theta) + P_{\ell-1}^{m+1}(\cos\theta)}{2\ell + 1}$$. For these identities, see the site http://functions.wolfram.com/Polynomials/LegendreP2/17/02/01/ .

Using the orthogonality of the spherical harmonics, one comes up with a new set of selection rules on the angular momentum quantum number: $\Delta\ell = \pm 1$.

Since both integrals (ϕ and θ) are done in sequence, both sets of selection rules must be satisfied to get a non-zero probability of transition. Thus the dipole approximation selection rules are: $\Delta m = 0$ or ± 1 and $\Delta\ell = \pm 1$.