Lecture 29 Phys 506

Hydrogen and light

Suppose Hydrogen interacts with light. We describe the light with a vector potential $\vec{A}(\vec{r},t)$ in the Coulomb gauge where $\nabla\cdot\vec{A}=0$ and we ignore the fine structure.

$$\hat{H} = \frac{1}{2m}\Big(\vec{p} + \frac{|e|}{c}\vec{A}\Big)^2 - \frac{e^2}{r} + \frac{|e|\hbar}{mc}\vec{S}\cdot\vec{B}(\vec{r},t)$$

canonical interaction with a field

interaction of a spin with a magnetic field $\vec{B} = \vec{\nabla}\times\vec{A}$

expand to get

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{|e|}{2mc}(\vec{p}\cdot\vec{A} + \vec{A}\cdot\vec{p}) + \frac{|e|^2}{2mc^2}\vec{A}\cdot\vec{A} - \frac{e^2}{r} + \frac{|e|\hbar}{mc}\vec{S}\cdot\vec{B}$$

$\vec{A}$ and $\vec{p}$ do commute due to the Coulomb gauge

neglect since small

$$\hat{H} = \hat{H}_0 + \hat{V} \qquad \hat{H}_0 = \frac{\hat{p}^2}{2m} - \frac{e^2}{r} \qquad \hat{V} = \frac{|e|}{mc}\vec{A}\cdot\vec{p} + \frac{|e|\hbar}{mc}\vec{S}\cdot(\vec{\nabla}\times\vec{A})$$

let $\vec{A} = \vec{A}_0 e^{i(\vec{k}\cdot\vec{r}-\omega t)} + \vec{A}_0^* e^{-i(\vec{k}\cdot\vec{r}-\omega t)}$

$$\hat{V}(t) = \hat{V}_\omega e^{i\omega t} + \hat{V}_{-\omega}e^{-i\omega t} \qquad \hat{V}_{-\omega} = \hat{V}_\omega^\dagger \Rightarrow \text{harmonic perturbation}$$

$$\hat{V}_{-\omega} = \frac{|e|}{mc}e^{i\vec{k}\cdot\vec{r}}\left[\vec{A}_0\cdot\vec{p} + i\hbar\vec{S}\cdot(\vec{k}\times\vec{A}_0)\right] \qquad \hat{V}_\omega = \text{same with } i\to -i \text{ and } \vec{A}_0\to\vec{A}_0^*$$

Usually $\vec{k}$ of a photon has a wavelength $\sim 100\,nm$

$\vec{r}$ of an atom $\sim 10^{-1}\,nm \Rightarrow \vec{k}\cdot\vec{r} \ll 1$ for optical processes

$\Rightarrow$ expand $e^{i\vec{k}\cdot\vec{r}}$ in powers of $\vec{k}\cdot\vec{r}$

$$\hat{V}_{-\omega} = \frac{|e|}{mc}\left[\vec{A}_0\cdot\vec{p} + i\hbar\vec{s}\cdot(\vec{k}\times\vec{A}_0) + i\vec{k}\cdot\vec{r}\,\vec{A}_0\cdot\vec{p} + O(k^2)\right]$$

But $\vec{k}\cdot\vec{r}\,\vec{A}_0\cdot\vec{p} = \sum_{ij} k_i A_{0j}\, r_i p_j$

$$= \sum_{ij} k_i A_{0j} \frac{1}{2}\left\{ r_i p_j + \underbrace{p_i r_j + r_i p_j - p_j r_i}_{i\hbar\delta_{ij}} + \underbrace{p_j r_i - p_i r_j}_{\epsilon_{ijk}\hbar L_k} \right\}$$

middle term $\sim \sum_i k_i A_{0i}\, i\hbar = i\hbar\,\vec{k}\cdot\vec{A}_0 = 0$ because of Coulomb gauge

So

$$\boxed{\hat{V}_{-\omega} = \frac{|e|}{mc}\left[\vec{A}_0\cdot\vec{p} + \frac{i\hbar}{2}(\vec{L}+2\vec{s})\cdot(\vec{k}\times\vec{A}_0) + \frac{i}{2}\sum_{ij} k_i A_{0j}(r_i p_j + p_i r_j)\right]}$$

We need to calculate matrix elements of $\hat{V}_{-\omega}$, which are simplified by the following tricks

$$\vec{p} = \frac{im}{\hbar}[\hat{H}_0, \vec{r}] \Rightarrow \langle n|\hat{\vec{p}}|m\rangle = \langle n|\frac{im}{\hbar}[\hat{H}_0,\hat{\vec{r}}]|m\rangle$$

$$= i m\, \omega_{mn} \langle n|\vec{r}|m\rangle \qquad \omega_{nm} = \frac{E_n - E_m}{\hbar}$$

with $\hat{H}_0|m\rangle = E_m|m\rangle$

$$\hat{r}_i\hat{p}_j + \hat{p}_i\hat{r}_j = \frac{im}{\hbar}\left[\hat{r}_i[H_0,\hat{r}_j] + [H_0,\hat{r}_i]\hat{r}_j\right] = \frac{im}{\hbar}[\hat{H}_0, \hat{r}_i\hat{r}_j]$$

so $\langle n|\hat{r}_i\hat{p}_j + \hat{p}_i\hat{r}_j|m\rangle = im\,\omega_{mn}\langle n|\hat{r}_i\hat{r}_j|m\rangle$

and

$$\langle n|\hat{V}_{-\omega}|m\rangle = \frac{-i\,\omega_{mn}}{c}\vec{A}_0\cdot\langle n|-|e|\vec{r}|m\rangle - i(\vec{k}\times\vec{A}_0)\cdot\langle n|\frac{-|e|\hbar}{2mc}(\vec{L}+2\vec{s})|m\rangle$$

$$+ \frac{\omega_{nm}}{6c}\sum_{ij} k_i A_{0j}\langle n|-|e|\left(3\hat{r}_i\hat{r}_j - \delta_{ij}\hat{\vec{r}}^{\,2}\right)|m\rangle + O(k^2)$$

vanishes since $\vec{k}\cdot\vec{A}_0 = 0$

Define $-|e|\hat{\vec{r}} = \hat{\vec{D}}$ = electric dipole moment

$-\frac{|e|\hbar}{2mc}(\vec{L}+2\vec{s}) = \hat{\vec{\mu}}$ = magnetic dipole moment and $-|e|\left(3\hat{r}_i\hat{r}_j - \delta_{ij}\hat{r}^2\right) = \hat{Q}_{ij}$ = electric quadrupole moment

Then

$$\boxed{\left(\hat{V}_{-\omega}\right)_{nm} = -\frac{i}{c}\omega_{nm}\vec{A}_0\cdot\left(\vec{D}\right)_{nm} - i\left(\vec{k}\times\vec{A}_0\right)\cdot\left(\vec{\mu}\right)_{nm} + \frac{\omega_{nm}}{6c}\sum_{ij}k_i A_j^0\left(Q_{ij}\right)_{nm} + O(k^2)}$$

This result also holds for many electron atoms.

The electric dipole moment transition, denoted E1, dominates unless its matrix element vanishes

The magnetic dipole (M1) and electric quadrupole (E2) transitions are the same order of magnitude and are usually called "forbidden" transitions. They are important only if E1 vanishes.

Selection rules

E1 $\quad \Delta J = \pm 1, 0$ but no $0 \to 0$ transitions

$\quad\Rightarrow \Delta S = 0 \quad \Delta L = \pm 1$ due to parity arguments

M1 $\quad \Delta J = \pm 1, 0 \quad$ no $0 \to 0 \quad \Delta L = \Delta S = 0$

E2 $\quad J_n + J_m \geq 2 \geq |J_n - J_m| \quad$ no $0 \to 0 \quad \Delta S = 0$

To correctly derive the interaction with the electromagnetic field we need to properly quantize the photons. We will discuss some of these issues later but for now, we note that a semiclassical approach and the full quantum analysis give the same results, so we will do the simpler one.

$$\vec{A}_0 = \vec{\varepsilon} \times \sqrt{\frac{2\pi\hbar c^2}{\omega_k}} * \begin{cases} \sqrt{n+1} & \leftarrow \text{emission} \\ \sqrt{n} & \leftarrow \text{absorption} \end{cases}$$

$\vec{\varepsilon}$: polarization vector of light. (unit vector $\perp$ to $\vec{k}$)

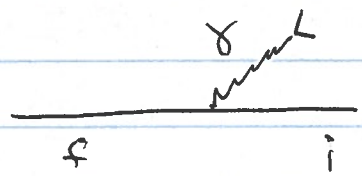
$\omega_k = ck$

n = # of photons with polarization $\vec{\varepsilon}$ and wave vector $\vec{k}$

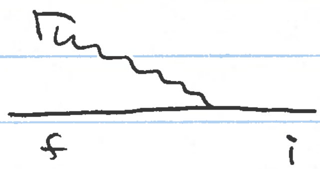
These terms come from simple-harmonic oscillator like raising and lowering operators multiplied by some constants.

Use the Fermi golden rule to calculate emission or absorption rates of photons

Absorption



Emission



Recall

$$\underbrace{\frac{d\Gamma}{d\Omega_\gamma}}_{\text{rate of change of probability}} = \int dE \, \frac{2\pi}{\hbar} \, \rho_\gamma(k) \, \left| M^{E1}(k) \right|^2 \delta(E_f - E_i)$$

$d\Omega_\gamma$: solid angle of photon

$\rho_\gamma(k)$: density of states from converting k integral to energy integral

$|M^{E1}(k)|^2$: matrix element $|U_{fi}(k)|^2$

$$\rho_\gamma(k) = \frac{1}{(2\pi)^3} k^2 \left(\frac{dE}{dk}\right)^{-1} \qquad E = \hbar\omega_k = \hbar ck$$

$$\Rightarrow \rho_\gamma(k) = \frac{1}{(2\pi)^3} \cdot \left(\frac{E}{\hbar c}\right)^2 \cdot \frac{1}{\hbar c} = \frac{1}{(2\pi)^3} \frac{\omega^2}{\hbar c^3}$$

For spontaneous emission $n = 0$ so $\frac{\omega}{c} \vec{A}_0 = \sqrt{2\pi\omega\hbar}\,\vec{\varepsilon}$

$$M^{E1}(k) = \langle f | \vec{D} | i \rangle$$

So we get

$$\frac{d\Gamma^{E1}}{d\Omega_\gamma} = \frac{\omega^3}{2\pi\hbar c^3} \left| \langle f | \vec{\epsilon} \cdot \vec{D} | i \rangle \right|^2 = \text{differential emission rate}$$

where we have the energy of the final atomic state $\langle f|$ plus $\hbar\omega$ equals the energy of the initial atomic state $|i\rangle$ from the delta function in the integral over energy.

$$\Rightarrow \quad \omega = \omega_k = \omega_{nm} = \omega_{if}$$

The total rate is found by integrating over the solid angle

$$\Gamma_{f\leftarrow i} = \sum_{\text{polarizations } \alpha} \int d\Omega_\gamma \frac{d\Gamma_{f\leftarrow i}}{d\Omega_\gamma} = \frac{\text{probability}}{\text{time}}$$

In the dipole approximation, we have

$$\Gamma_{f\leftarrow i} = \frac{\omega^3 e^2}{2\pi\hbar c^3} \int d\Omega_\gamma \sum_\alpha \left| \langle f | \vec{\epsilon}(\vec{k},\alpha) \cdot \hat{\vec{r}} | i \rangle \right|^2$$

Polarization vectors: $\vec{\epsilon} \cdot \vec{k} = 0$ in the Coulomb gauge

Completeness says $\displaystyle\sum_{\alpha=1}^{2} \varepsilon_i(k,\alpha)\, \varepsilon_j(k,\alpha) + \frac{k_i k_j}{|k|^2} = \delta_{ij}$

$$\Rightarrow \sum_\alpha \varepsilon_i(k,\alpha)\, \varepsilon_j(k,\alpha) = \delta_{ij} - \frac{k_i k_j}{|k|^2}$$

So we get

$$\Gamma_{f\leftarrow i} = \frac{\omega^3 e^2}{2\pi\hbar c^3} \sum_{ij} \int d\Omega_\gamma \left(\delta_{ij} - \frac{k_i k_j}{|k|^2} \right) \langle f | r_i | i \rangle \langle i | r_j | f \rangle$$

$$= \frac{\omega^3 e^2}{2\pi\hbar c^3} \sum_{ij} \left(\delta_{ij} \cdot 4\pi - \frac{k^2 \delta_{ij}}{k^2} \cdot \frac{4\pi}{3} \right) \langle f | r_i | i \rangle \langle i | r_j | f \rangle$$

$$\boxed{\Gamma_{f\leftarrow i} = \frac{4\omega^3 e^2}{3\hbar c^3} \left| \langle f | \vec{r} | i \rangle \right|^2}$$

Lifetime

If we assume the form $\dot{P} = cP$ for the fermi golden rule

Then $P_{any \leftarrow i} = e^{-\sum_{any} \Gamma_{any\leftarrow i}\, t} = e^{-t/\tau_i}$

$$\tau_i = \frac{1}{\sum_{any} \Gamma_{any\leftarrow i}} = \text{total lifetime of state } i$$

$$\tau_{f\leftarrow i} = \frac{1}{\Gamma_{f\leftarrow i}} = \text{partial lifetime of state } i \text{ decaying to state } f.$$

Orders of magnitude

Typical atomic frequency is $\omega \sim \frac{e^2}{a_0 \hbar}$

so $k a_0 = \frac{\omega}{c} a_0 \sim \frac{e^2}{\hbar c} = \alpha =$ fine structure constant $\cong \frac{1}{137} << 1$

$$\Gamma^{E1} \cong \frac{\omega^3 e^2}{\hbar c^3} \cdot a_0^2 \sim \frac{e^8}{a_0 \hbar^4 c^3} \sim \alpha^4 \frac{c}{a_0}$$

$$\sim \frac{\cancel{\ }\cdot 10^{-8}}{\cancel{\ }4} \cdot \frac{3\times10^8 \, m/s}{0.5\times10^{-10} \, m} \sim 1.5\times10^{10}/sec$$

$$\Rightarrow \tau_{E1} \sim \cancel{\ } 10^{-10} \text{ sec}$$

Forbidden rates are typically smaller by $(ka_0)^2 \sim \alpha^2$

so $\tau_{M1}, \tau_{E2} \sim 10^{-5} - 10^{-6}$ sec