Phys 506 lecture 33: Hydrogen and light

1 Introduction

Suppose hydrogen interacts with light. We describe the light with a vector potential $\mathbf{A}(\hat{\mathbf{r}}, t)$ in the Coulomb gauge, where $\nabla \cdot \mathbf{A} = 0$, and we ignore the fine structure. The Hamiltonian is given by:

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

where we have minimally coupled the momentum to include the canonical interaction with a field in the $\frac{1}{2m}\left(\hat{\mathbf{p}} + \frac{|e|}{c}\hat{\mathbf{A}}\right)^2$ term and we have included an interaction of the spin with a magnetic field $\mathbf{B} = \nabla \times \hat{\mathbf{A}}$ term as the last term. Expanding the Hamiltonian, we get:

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

Note here that we have neglect the $\hat{\mathbf{A}} \cdot \hat{\mathbf{A}}$ term since it is assumed to be small and the $\hat{\mathbf{A}}$ and $\hat{\mathbf{p}}$ commute in the Coulomb gauge. Thus, the Hamiltonian can be written in the form:

$$\hat{H} = \hat{H}_0 + \hat{V},$$

where:

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

Using the plane-wave ansatz, let:

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

Then, the perturbation potential is:

$$\hat{V}(t) = \hat{V}_\omega e^{-i\omega t} + \hat{V}_{-\omega} e^{i\omega t}$$

where we assume a harmonic perturbation with $\hat{V}_{-\omega} = \hat{V}_\omega^\dagger$ and:

$$\hat{V}_{-\omega} = \frac{e}{mc} e^{i\mathbf{k}\cdot\hat{\mathbf{r}}} \left(\mathbf{A}_0 \cdot \hat{\mathbf{p}} + i\hbar\mathbf{S} \cdot (\mathbf{k} \times \mathbf{A}_0)\right).$$

and $\hat{V}_\omega$ is the same with $i \to -i$ and $\mathbf{A}_0 \to \mathbf{A}_0^*$. To get a sense of the scales, note that usually $\mathbf{k}$ of a photon has a wavelength $\sim 100\,\text{nm}$ and $\mathbf{r}$ of an atom $\sim 10^{-1}\,\text{nm}$ which implies $|\mathbf{k}\cdot\mathbf{r}| \ll 1$ for optical processes. Thus, we can expand $e^{i\mathbf{k}\cdot\hat{\mathbf{r}}}$ in powers of $\mathbf{k}\cdot\hat{\mathbf{r}}$ as:

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

For the third term, note that:

$$\begin{aligned}\mathbf{k}\cdot\hat{\mathbf{r}}(\mathbf{A}_0\cdot\hat{\mathbf{p}}) &= \sum_{ij} k_i A_{0j}\hat{r}_i\hat{p}_j \\ &= \frac{1}{2}\sum_{ij} k_i A_{0j}\left(\hat{r}_i\hat{p}_j + \hat{p}_i\hat{r}_j + \hat{r}_i\hat{p}_j - \hat{p}_j\hat{r}_i + \hat{p}_j\hat{r}_i - \hat{p}_i\hat{r}_j\right),\end{aligned}$$

where we can simplify by noting $\hat{p}_i\hat{r}_j - \hat{p}_j\hat{r}_i = [\hat{p}_i, \hat{r}_j] = i\hbar\delta_{ij}$, but $\sum_i k_i A_{0i} i\hbar = i\hbar\mathbf{k}\cdot\mathbf{A}_0 = 0$ in the Coulomb gauge. Therefore, we have:

$$\hat{V}_{-\omega} = \frac{|e|}{mc}\left[\mathbf{A}_0\cdot\hat{\mathbf{p}} + \frac{i\hbar}{2}(\hat{\mathbf{L}} + 2\hat{\mathbf{S}})\cdot(\mathbf{k}\times\mathbf{A}_0) + \frac{i}{2}\sum_{ij} k_i A_{0j}(\hat{r}_i\hat{p}_j + \hat{p}_j\hat{r}_i)\right]$$

where we used the fact that $\hat{p}_j\hat{r}_i - \hat{p}_i\hat{r}_j = \epsilon_{ijk}\hbar\hat{L}_k$.

2 Calculating the matrix elements

To calculate the matrix elements of $\hat{V}_{-\omega}$, we use the following tricks:

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

where $\omega_{mn} = \frac{E_n - E_m}{\hbar}$ with $\hat{H}_0|m\rangle = E_m|m\rangle$. Further:

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

so:

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

and

$$\begin{aligned}\langle n|\hat{V}_{-\omega}|m\rangle = -i\frac{\omega_{nm}}{c}\mathbf{A}_0\cdot\langle n| - |e|\mathbf{r}|m\rangle - i(\mathbf{k}\times\mathbf{A}_0)\cdot\langle n| - \frac{|e|\hbar}{2mc}(\hat{\mathbf{L}} + 2\hat{\mathbf{S}})|m\rangle \\ + \frac{\omega_{nm}}{6c}\sum_{ij} k_i A_{0j}\langle n| - |e|\left(3\hat{r}_i\hat{r}_j - \delta_{ij}\hat{r}^2\right)|m\rangle + \mathcal{O}(k^2).\end{aligned}$$

The $\delta_{ij}\hat{\mathbf{r}}^2$ vanishes since $\mathbf{k}\cdot\mathbf{A}_0 = 0$. The above expression also motivates us to define three quantities: the **electric dipole moment** $\hat{\mathbf{D}} = -|e|\hat{\mathbf{r}}$ and the **magnetic dipole moment** $\hat{\mu} = -\frac{|e|\hbar}{2mc}(\hat{\mathbf{L}} + 2\hat{\mathbf{S}})$ and the **electric quadrupole moment**

$\hat{Q}_{ij} = -|e|\left(3\hat{r}_i\hat{r}_j - \delta_{ij}\hat{r}^2\right)$. Using these definitions, the expression for $\hat{V}_{-\omega}$ becomes:

$$(\hat{V}_{-\omega})_{nm} = -i\frac{\omega_{nm}}{c}\mathbf{A}_0\cdot\langle n|\hat{\mathbf{D}}|m\rangle - i(\mathbf{k}\times\mathbf{A}_0)\cdot\langle n|\hat{\mu}|m\rangle + \frac{\omega_{nm}}{c}\sum_{ij} k_i A_{0j}\langle n|\hat{Q}_{ij}|m\rangle + \mathcal{O}(k^2).$$

or equivalently:

$$\boxed{(\hat{V}_{-\omega})_{nm} = -i\frac{\omega_{nm}}{c}\mathbf{A}_0\cdot(\hat{\mathbf{D}})_{nm} - i(\mathbf{k}\times\mathbf{A}_0)\cdot(\hat{\mu})_{nm} + \frac{\omega_{nm}}{c}\sum_{ij} k_i A_{0j}(\hat{Q}_{ij})_{nm} + \mathcal{O}(k^2)}$$

This result also holds for many-electron atoms.

3 Selection rules

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. We thus have the **selection rules**:

1. E1: $\Delta J = \pm 1, 0$ but no $0 \to 0$ transitions $\implies$ $\Delta S = 0, \quad \Delta L = \pm 1$ due to parity arguments
2. M1: $\Delta J = \pm 1, 0$ no $0 \to 0$ transitions $\Delta S = \Delta L = 0$
3. E2: $J_n + J_m \geq 2 \geq |J_i - J_f| \leq 2$ no $0 \to 0$ transitions $\Delta S = 0$

4 Transition rates

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

$$\mathbf{A}_0 = \epsilon \times \sqrt{\frac{2\pi\hbar c^2}{\omega_k}} \times \begin{cases} \sqrt{n+1} & \text{for emission} \\ \sqrt{n} & \text{for absorption} \end{cases}$$

where ϵ is the polarization vector of light, i.e. a unit vector perpendicular to $\mathbf{k}$, $\omega_k = ck$ and n is the number of photons with polarization vector ϵ and wave vector $\mathbf{k}$. These terms come rom simple-harmonic oscillator like raising and lowering operators multiplied by some constants. We can use Fermi’s golden rule to calculate emission or absorption rates of photons, which are visually represented as:

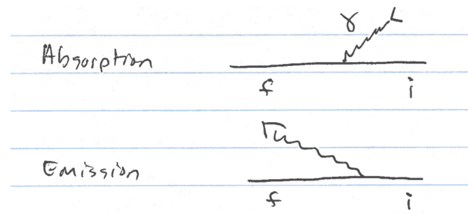

Figure 1: Absorption has a photon absorbed by the initial state and transforms to the final state. Emission emits a photon from the initial state and ends in the final state.

Recall Fermi's golden rule says that the rate of change of probability Γ per solid angle of photon Ω_γ is given by the density of states from converting k integral to energy integral $\rho_\gamma(k)$ and the matrix element $|V_{fi}(k)|^2$:

$$\frac{d\Gamma}{d\Omega_\gamma} = \int dE\, \frac{2\pi}{\hbar} \rho_\gamma(k) |M^{E1} 9k)|^2 \delta(E_f - E_i)$$

The density of states is given by:

$$\rho_\gamma(k) = \frac{1}{(2\pi)^3} k^2 \left(\frac{dE}{dk}\right)^{-1}.$$

Now use the dispersion relations of the photons $E = \hbar\omega_k = \hbar c k$ to get:

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

For spontaneous emission with $n = 0$, we have $\frac{\omega}{c}\mathbf{A}_0 = \sqrt{2\pi\omega\hbar}\boldsymbol{\epsilon}$ and $M^{E1}(k) = \langle f|\mathbf{D}|i\rangle$. As a result, we get the differential emission rate to be $\frac{d\Gamma^{E1}}{d\Omega_\gamma}$:

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

where we have the energy of the final atomic state $\langle f|$ plus $\hbar\omega$ equal the energy of the initial atomic state $|i\rangle$ from the delta function in the integral over energy. Hence, $\omega = \omega_k = \omega_{nm} = \omega_{if}$. The total rate is found by integrating over the solid angle:

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

In the dipole approximation, we have:

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

Note that the polarization vectors satisfy $\boldsymbol{\epsilon}_\alpha \cdot \mathbf{k} = 0$ in the Coulomb gauge and completeness gives us:

$$\sum_\alpha \epsilon_i(\mathbf{k},\alpha)\epsilon_j(\mathbf{k},\alpha) + \frac{k_i k_j}{|\mathbf{k}|^2} = \delta_{ij} \Rightarrow \sum_\alpha \epsilon_i(\mathbf{k},\alpha)\epsilon_j(\mathbf{k},\alpha) = \delta_{ij} - \frac{k_i k_j}{|\mathbf{k}|^2}.$$

Using these expressions, we get:

$$\begin{aligned}\Gamma_{f\leftarrow i} &= \frac{\omega^3 e^2}{2\pi\hbar c^3}\sum_{ij}\int d\Omega\left(\delta_{ij} - \frac{k_i k_j}{|\mathbf{k}|^2}\right)\langle f|r_i|i\rangle\langle i|r_j|f\rangle \\ &= \frac{\omega^3 e^2}{2\pi\hbar c^3}\sum_{ij}\left(\delta_{ij}\cdot 4\pi - \frac{k^2\delta_{ij}}{|\mathbf{k}|^2}\cdot 4\pi\cdot\frac{1}{3}\right)\langle f|r_i|i\rangle\langle i|r_j|f\rangle.\end{aligned}$$

Giving us the final result:

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

5 Lifetime

If we assume the form $\dot{p} = cp$ for the Fermi golden rule, then:

$$P_{\text{any}\leftarrow i} = e^{-\sum_{\text{any}}\Gamma_{\text{any}\leftarrow i}t} = e^{-\frac{t}{\tau_i}}$$

where

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

and

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

6 Orders of magnitude

Typical atomic frequency is $\omega \sim \frac{e^2}{a_0 c}$, so $ka_0 = \frac{\omega}{c}a_0 \sim \frac{e^2}{\hbar c} = \alpha$ where α is the fine structure constant which is approximately $1/137 \ll 1$. Hence, to get an order of magnitude approximation, we can get:

$$\Gamma^{E1} \sim \frac{w^3 e^2}{hc^3}a_0^2 \sim \frac{e^8}{a_0\hbar^4 c^3} \sim \alpha^4\frac{c}{a_0} \sim \frac{10^{-8}}{4}\frac{3\times 10^8\text{ m/s}}{0.5\times 10^{-10}\text{ m}} \sim 1.5\times 10^9\text{ sec}^{-1}$$

which implies

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

Forbidden rates are typically smaller by $(ka)^2 \sim t^2$, so we expect $\tau_{\text{M1}}, \tau_{\text{E2}} \sim 10^{-5}$ to 10^{-6} sec.