

Week ⑥

PHY 402 Atomic and Molecular Physics

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3 Interaction of Atoms with Electromagnetic Radiation

So far we had looked at what is called atomic structure, i.e. their energy levels and electron states, without any time dependence. Now we will begin to look at dynamics, in particular how to get from one energy level to another.

3.1 Atomic Transitions

3.1.1 Electromagnetic fields and charged particles

Unlike section 2.2 on static fields, we now want to simultaneously consider time-dependent E and B fields such as they occur within an electromagnetic wave.

It is often convenient to,

Express fields via potentials

$$\begin{aligned} \mathbf{E}(\mathbf{r}, t) &= -\nabla\varphi(\mathbf{r}, t) - \frac{\partial}{\partial t}\mathbf{A}(\mathbf{r}, t) & \varphi &= \text{Scalar Potential} & (3.1) \\ \mathbf{B}(\mathbf{r}, t) &= \nabla \times \mathbf{A}(\mathbf{r}, t) & \mathbf{A} &= \text{Vector Potential} \end{aligned}$$

Warning: Make sure in the following not to confuse \mathbf{E} with an energy or φ with a wave function, it should be obvious from context what they are!

Potentials are not unique, they can be changed via a

Gauge Transformation

$$\mathbf{A} \rightarrow \mathbf{A} + \nabla\chi(\mathbf{r}, t) \quad \varphi \rightarrow \varphi - \frac{\partial}{\partial t}\chi(\mathbf{r}, t) \quad (3.2)$$

where, $\chi(\mathbf{r}, t) \in \mathbb{R}$ is any differentiable function

We now use this freedom to choose the

Coulomb Gauge

$$\nabla \cdot \mathbf{A} = 0 \text{ and } \varphi = 0. \quad (3.3)$$

We can show from Maxwell's equations the

Wave equation

$$\nabla^2 \mathbf{A} - \frac{1}{c^2} \frac{\partial^2 \mathbf{A}}{\partial t^2} = 0, \quad (3.4)$$

with the following solution which represents an electro-magnetic wave-packet

$$\mathbf{A}(\mathbf{r}, t) = \int_0^\infty A_0(\omega) \boldsymbol{\epsilon} \cos(\mathbf{k} \cdot \mathbf{r} - \omega t + \delta_\omega) d\omega. \quad (3.5)$$

here $A_0(\omega)$ is the spectral Amplitude, $\boldsymbol{\epsilon} \in \mathbb{C}^3$ is the polarisation vector, $\omega = |\mathbf{k}|c$ as usual and δ_ω is the phase of frequency component ω .

- For a laser we would have $\delta_\omega = \text{fixed } \forall \omega$, e.g.=0
- For incoherent radiation: δ_ω is random for all ω .
- For a simple spectral distribution, imagine a narrow Gaussian centered on a central frequency ω_0 such as $A_0(\omega) = \bar{A} \exp[-(\omega - \omega_0)^2/\sigma_\omega^2]$.

Hamiltonian for charged electron in radiation field

$$\hat{H} = \frac{1}{2m}(\hat{p} + e\mathbf{A})^2 - \frac{Ze^2}{(4\pi\epsilon)r} \quad (3.6)$$

Insert $\hat{p} = -i\hbar\nabla$ and using $\nabla \cdot (\mathbf{A} \cdot \dots) = \mathbf{A} \cdot (\nabla \cdot \dots) + \underbrace{(\nabla \cdot \mathbf{A})}_{=0} \dots$ we get the

Atom-Radiation Hamiltonian

$$\hat{H}(t) = \underbrace{-\frac{\hbar^2}{2m}\nabla^2 - \frac{Ze^2}{(4\pi\epsilon)r}}_{=\hat{H}_0} - \underbrace{i\hbar\frac{e}{m}\mathbf{A}(\mathbf{r},t)\cdot\nabla + \frac{e^2}{2m}(\mathbf{A}(\mathbf{r},t))^2}_{=\hat{H}'(t)} \quad (3.7)$$

- This is written in the form (1.53) for time dependent perturbation theory
- it seems to depend on the gauge, but gauges just change inconsequential spatial phase of wavefunction, so any dependence cancels (see book)
- can neglect \mathbf{A}^2 term (and will do from now) except in very strong fields

3.1.2 Transition Rates

Assume we start in the specific atomic state $|\phi_a\rangle = |\phi_{n_a l_a m_a}\rangle$. (a is thus a short-hand index for all quantum numbers n_a, l_a, m_a).

Solving the TDSE $i\hbar\partial|\psi(t)\rangle/\partial t = \hat{H}(t)|\psi(t)\rangle$ for state vector $|\psi(t)\rangle = \sum_k c_k(t)|k\rangle$ is in general too hard. Hence, we use TDPT (see section 1.2.5) in order to find the amplitude for transition from state a to another state b : $|\phi_a\rangle \rightarrow |\phi_b\rangle$.

$$c_b^{(1)}(t) = (i\hbar)^{-1} \int_0^t H'_{ba}(t') \exp(i\omega_{ba}t') dt' \quad \text{where,} \quad (3.8)$$

$$\omega_{ba} = \frac{(E_b - E_a)}{\hbar} \quad (3.9)$$

We thus need the matrix-element

$$H'_{ba}(t') = \langle\phi_b|H'(t)|\phi_a\rangle \quad (3.10)$$

$$= -i\hbar\frac{e}{m} \int_0^\infty d\omega A_0(\omega) \boldsymbol{\epsilon} \cdot \langle\phi_b|\frac{1}{2}(e^{i\mathbf{k}\cdot\mathbf{r}-i\omega t+i\delta_\omega} + e^{-i\mathbf{k}\cdot\mathbf{r}+i\omega t-i\delta_\omega})\nabla|\phi_a\rangle \quad (3.11)$$

Insert Eq. (3.11) into Eq. (3.8):

$$c_b^{(1)}(t) = -\frac{e}{2m} \int_0^\infty d\omega A_0(\omega) \left[e^{i\delta_\omega} \langle\phi_b|e^{i\mathbf{k}\cdot\mathbf{r}}\boldsymbol{\epsilon}\cdot\nabla|\phi_a\rangle \int_0^t dt' e^{i(\omega_{ba}-\omega)t'} \right. \\ \left. + e^{-i\delta_\omega} \langle\phi_b|e^{-i\mathbf{k}\cdot\mathbf{r}}\boldsymbol{\epsilon}\cdot\nabla|\phi_a\rangle \int_0^t dt' e^{i(\omega_{ba}+\omega)t'} \right] \quad (3.12)$$

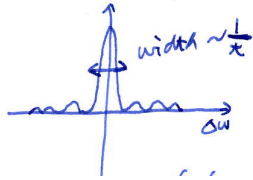
We can explicitly solve the time-integrals,

$$I \equiv \int_0^t dt' e^{i(\omega_{ba}\pm\omega)t'} = \frac{e^{i(\overbrace{\omega_{ba}\pm\omega}^{\equiv\Delta\omega})t} - 1}{i(\omega_{ba}\pm\omega)} \quad (3.13)$$

We see,

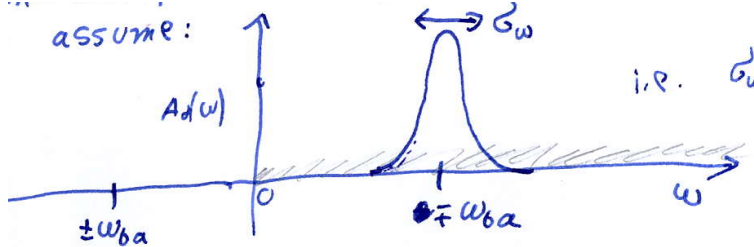
$$|I|^2 = \left| \frac{e^{i(\Delta\omega t')} - 1}{i\Delta\omega} \right|^2 = \left| e^{\frac{i(\Delta\omega t')}{2}} \frac{\left(e^{\frac{i(\Delta\omega t')}{2}} - e^{-\frac{i(\Delta\omega t')}{2}} \right)}{i\Delta\omega} \right|^2 = 2 \frac{\sin^2\left(\frac{\Delta\omega t}{2}\right)}{\Delta\omega^2} = F(\Delta\omega), \quad (3.14)$$

where the function F was defined in section 1.2.5.



left: Plot of $F(\Delta\omega)$

We see that the r.h.s. of 3.12 is only significant for $\Delta\omega = \omega_{ba} \pm \omega = 0 \Rightarrow \omega = -\omega_{ba}$ or $\omega = +\omega_{ba}$. Now our electromagnetic wave-packet (3.4) contains many different frequencies ω .



left: For simplicity we assume a wavepacket as on the left, i.e. with $\sigma_\omega \ll |\omega_{ba}|$ and $\omega_0 > 0$.

We can then have two cases:

- $E_b > E_a \Rightarrow \omega_{ba} > 0 \Rightarrow \omega_{ba} - \omega$ term in Eq. (3.12) will contribute
- $E_b < E_a \Rightarrow \omega_{ba} < 0 \Rightarrow \omega_{ba} + \omega$ term in Eq. (3.12) will contribute

These two cases give rise to:

Absorption $E_b > E_a$:

Neglect second term in Eq. (3.12) and write,

$$|c_b^{(1)}(t)| = \frac{1}{2} \left(\frac{e}{2m} \right)^2 \left| \int_0^\infty d\omega A_0(\omega) M_{ba} F(t, \omega - \omega_{ba}) e^{i\delta\omega} \right|^2 \quad (3.15)$$

with,

Matrix Element

$$M_{ba}(\omega) = \langle \phi_b | \exp(i\mathbf{k} \cdot \mathbf{r}) \boldsymbol{\epsilon} \cdot \nabla | \phi_a \rangle. \quad (3.16)$$

- Note, some other definitions might include the electric charge e into the matrix element.

- We write $M_{ba}(\omega)$ since the ME depends on ω through $\omega = \mathbf{k}c$.
- To obtain $|c_b^{(1)}(t)|$ we have to evaluate $|\int_0^\infty d\omega z(\omega)|^2 = \int_0^\infty d\omega \int_0^\infty d\omega' z^*(\omega)z(\omega')$, in which $z^*(\omega)z(\omega')$ contains a term $e^{-i(\delta_\omega - \delta_{\omega'})}$.
- Since we assume random $\delta_\omega, \delta_{\omega'}$ for (incoherent light) this part is on average zero unless $\omega = \omega'$.
- Using this we can simplify:

$$|c_b^{(1)}(t)|^2 = \frac{1}{2} \left(\frac{e}{2m}\right)^2 \int_0^\infty d\omega \underbrace{|A_0(\omega)|^2}_{\text{approx } |A_0(\omega)|^2 = |A_0(\omega_{ba})|^2} |M_{ba}(\omega)|^2 \underbrace{F^2(t, \omega - \omega_{ba})}_{\text{sharply peaked around } \omega = \omega_{ba}}$$
(3.17)

$$|c_b^{(1)}(t)|^2 = \frac{1}{2} \left(\frac{e}{2m}\right)^2 A_0^2(\omega_{ba}) |M_{ba}(\omega_{ba})|^2 \underbrace{\int_{\substack{-\infty \\ \omega_0^\infty \Rightarrow \omega_{-\infty}^\infty}}^{\infty} F(t, \Delta\omega) d\omega}_{=\pi t}$$
(3.18)

So Probability $P_b = |c_b^{(1)}(t)|^2$ to be in state b increases linearly in time, $P_b = W_{ba}t$, with

Transition rate for absorption (integrated over ω)

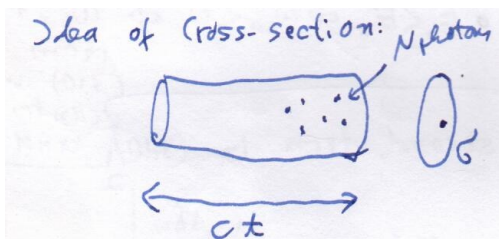
$$W_{ba} = \frac{\pi e^2}{2m} A_0^2(\omega_{ba}) |M_{ba}(\omega_{ba})|^2$$

$$= \frac{4\pi^2}{m^2 c^2} \frac{e^2}{(4\pi\epsilon_0)} \frac{I(\omega_{ba})}{\omega_{ba}^2} |M_{ba}(\omega_{ba})|^2$$
(3.19)

- second line uses intensity at ω

$$I(\omega) = \frac{1}{2} \epsilon_0 c \omega^2 A_0^2(\omega)$$
(3.20)

- so, most importantly, the rate is proportional to light intensity and matrix element $|M_{ba}(\omega_{ba})|^2$
- We can remove the intensity dependence of the absorption process by defining the



left:

Absorption cross section:

$$\sigma_{ab} = \hbar\omega W_{ba}/I(\omega_{ba})$$
(3.21)

The intensity is $I = \hbar\omega N_{\text{photons}}c$

Stimulated Emission $E_a > E_b$:

Through the same steps as above, we obtain the same expression for the transition rate (see book).

- If we have a thermal distribution of atoms at temperature T , the number of atoms in state a or b is given by $N_{a,b} \sim \exp\left(-\frac{E_{a,b}}{k_b T}\right)$ respectively, so there are more atoms in the lower energy state and it is thus more likely to absorb light (despite the same rates for absorption and emission)
- The principle of a Laser relies on population inversion, which means $N_b > N_a$ even though $E_b > E_a$. In that case stimulated emission can become more likely than absorption.

Spontaneous Emission:

In QED, the vector potential for absorption (**emission**) of a single photon from an N photon state, has the form:

$$\mathbf{A} = \boldsymbol{\epsilon} \left[\frac{2[N(\omega) + 1]\hbar}{V\epsilon_0\omega} \right]^{\frac{1}{2}} \frac{1}{2} \exp[i(\mathbf{k} \cdot \mathbf{r} - \omega t + \delta_\omega)]. \quad (3.22)$$

- Importantly the **+1** is only there for emission, not for absorption. V is the quantisation volume.
- One can see that absorption gives the same result as (3.19) [N and V go into the factor $I(\omega)$].
- However emission would be the same only if we replace $N(\omega) + 1 \rightarrow N(\omega)$.
- The piece **+1** is related to spontaneous emission, it takes place even without any external field (light), due to vacuum fluctuations of the electro-magnetic field.

3.2 Selection Rules

Rates depend most critically on matrix-element

$$M_{ba}(\omega) = \langle \phi_b | \exp(i\mathbf{k} \cdot \mathbf{r}) \boldsymbol{\epsilon} \cdot \nabla | \phi_a \rangle \quad \text{where,} \quad (3.23)$$

$$\exp(i\mathbf{k} \cdot \mathbf{r}) = 1 + (i\mathbf{k} \cdot \mathbf{r}) + \frac{1}{2!} (i\mathbf{k} \cdot \mathbf{r})^2 + \dots \quad (3.24)$$

For wavelength much larger than atomic size (r_0), we have that $|\mathbf{k} \cdot \mathbf{r}| \lesssim 2\pi \frac{r_0}{\lambda} \ll 1$ at all locations \mathbf{r} with non-vanishing electron density, i.e. $\phi_{a/b}(\mathbf{r}) \neq 0$. Thus we can replace the exp by 1. This is called the dipole approximation. Then we define the

Matrix-element in the dipole approximation

$$M_{ba}^D = \boldsymbol{\epsilon} \cdot \langle \phi_b | \nabla | \phi_a \rangle \quad (3.25)$$

To see more clearly why we use the name “dipole-approximation”, let us utilize:

$$\hat{\mathbf{p}} = m \frac{m}{\hbar} [\hat{H}_0, \hat{\mathbf{r}}], \text{ with } \quad \hat{\mathbf{p}} = -i\hbar \nabla \text{ and } \quad \nabla = -\frac{m}{\hbar^2} [\hat{H}_0, \mathbf{r}] \quad (3.26)$$

↓

$$\begin{aligned} M_{ba}^D &= \boldsymbol{\epsilon} \cdot \frac{-m}{\hbar^2} \langle \phi_b | (\hat{H}_0 \hat{\mathbf{r}} - \hat{\mathbf{r}} \hat{H}_0) | \phi_a \rangle \\ &= -\frac{\omega_{ba} m}{\hbar} \boldsymbol{\epsilon} \cdot \langle \phi_b | \mathbf{r} | \phi_a \rangle \end{aligned}$$

To reach this we had to also remember $\hat{H}_0 = \hat{\mathbf{p}}/2m + V(\hat{\mathbf{r}})$ and $[\hat{r}_i, \hat{p}_j] = i\hbar \delta_{ij}$. We call the result

Matrix-Element in length form

$$M_{ba}^D = \frac{m\omega_{ba}}{\hbar e} \boldsymbol{\epsilon} \cdot \mathbf{D}_{ba} \quad \text{where} \quad \mathbf{D}_{ba} = \langle \phi_b | (-e\hat{\mathbf{r}}) | \phi_a \rangle \quad (3.27)$$

with transition dipole moment vector operator \mathbf{D}_{ba} .

“Dipole-approximation” thus implies that only the dipole-moment of the electronic charge distribution is taken into account for interactions with the light.

If \mathbf{D}_{ba} does not vanish between two states $|\phi_a\rangle$ and $|\phi_b\rangle$, the transition between these states is called electric dipole allowed (E_1). Even if \mathbf{D}_{ba} vanishes, M_{ba} might not vanish due to higher order terms in $\exp(i\mathbf{k} \cdot \mathbf{r})$, e.g. $i(\mathbf{k} \cdot \mathbf{r})$ which gives rise to magnetic dipole (M_1) and electric quadrupole (E_2) transitions. These M_{ba} are however much smaller than non-vanishing \mathbf{D}_{ba} .

Let us thus now consider when M_{ba} can be nonzero, which depends on the transition dipole moment \mathbf{D}_{ba} and the polarisation vector $\boldsymbol{\epsilon}$. Let us first look at \mathbf{D}_{ba} in detail:

Elementary symmetry considerations:

$$|\phi_a\rangle = |\phi_{n_a l_a m_a}\rangle \implies R_{n_a l_a}(r) Y_{l_a m_a}(\theta, \varphi) \quad (3.28)$$

From Eq. (1.35) we can obtain the transformation law of the wavefunction for $\mathbf{r} \rightarrow \mathbf{r}' = -\mathbf{r}$. In polar co-ordinates $(r, \theta, \varphi \rightarrow r, \theta \rightarrow \pi - \theta, \varphi \rightarrow \varphi + \pi)$, hence we deduce $\phi(\mathbf{r}) \rightarrow (-1)^{l_a} \phi(\mathbf{r})$ where the

Factor under space inversion $(-1)^{l_a}$ is called parity of the state $|\phi_a\rangle$.

Thus $\mathbf{D}_{ba} = -e \int d^3\mathbf{r} \phi_b^*(\mathbf{r}) \mathbf{r} \phi_a(\mathbf{r})$ transforms like

$$\mathbf{D}_{ba} \rightarrow \mathbf{D}_{ba} (-1)^{l_a + l_b + 1}. \quad (3.29)$$

where we have used $\int d^3\mathbf{r} = \int d^3(-\mathbf{r})$. \implies We need $l_a + l_b + 1 = \text{even}$, otherwise \mathbf{D}_{ba} has to vanish. \implies dipole ME connects only states of opposite parity, independent of $\boldsymbol{\epsilon}$.

Full Calculation

We can write $\boldsymbol{\epsilon} \cdot \mathbf{D}_{\mathbf{b}\mathbf{a}} = (-e)\langle\phi_b|\boldsymbol{\epsilon} \cdot \mathbf{r}|\phi_a\rangle$ and,

$$\boldsymbol{\epsilon} \cdot \mathbf{r} = \begin{pmatrix} \epsilon_x \\ \epsilon_y \\ \epsilon_z \end{pmatrix} \begin{pmatrix} r \sin \theta \cos \phi \\ r \sin \theta \sin \phi \\ r \cos \theta \end{pmatrix} = -\frac{1}{\sqrt{2}} \underbrace{(\epsilon_x + i\epsilon_y)}_{\epsilon_1} \underbrace{\left[\frac{r \sin \theta e^{i\phi}}{\sqrt{2}} \right]}_{\equiv r_1} + \frac{1}{\sqrt{2}} \underbrace{(\epsilon_x - i\epsilon_y)}_{\epsilon_{-1}} \underbrace{\left[\frac{r \sin \theta e^{-i\phi}}{\sqrt{2}} \right]}_{\equiv r_{-1}} + \underbrace{\epsilon_z}_{\epsilon_0} \underbrace{r \cos \theta}_{r_0}, \quad (3.30)$$

where we have used so called ‘‘spherical components’’ r_q $q \in \{1, 0, -1\}$ of the vector \mathbf{r} .

Then an explicit integration gives:

$$\langle\phi_b|r_1|\phi_a\rangle \neq 0 \quad \text{if} \quad l_b = l_a \pm 1 \quad m_b = m_a + 1 \quad (3.31)$$

$$\langle\phi_b|r_{-1}|\phi_a\rangle \neq 0 \quad l_b = l_a \pm 1 \quad m_b = m_a - 1 \quad (3.32)$$

$$\langle\phi_b|r_0|\phi_a\rangle \neq 0 \quad l_b = l_a \pm 1 \quad m_b = m_a \quad (3.33)$$

Now if only some polarisation components $\epsilon_{-1,0,1}$ are non zero, we can select specific cases, and obtain:

Dipole Selection rules for absorption: Assuming light propagates along the \hat{k} direction (quantisation axis).

linearly polarized light (π transition)	$l_b = l_a \pm 1$	
only $\epsilon_0 \neq 0$	$m_b = m_a$	(3.34)

left handed circularly polarized light ($\sigma+$ transition),	$l_b = l_a \pm 1$	
only $\epsilon_1 \neq 0$	$m_b = m_a + 1$	(3.35)

right handed circularly polarized light ($\sigma-$ transition),	$l_b = l_a \pm 1$	
only $\epsilon_{-1} \neq 0$	$m_b = m_a - 1$	(3.36)

unpolarized or any other polarization direction	$l_b = l_a \pm 1$	
random mixture of $\boldsymbol{\epsilon}$ or all $\epsilon_k \neq 0$	$m_b = m_a, m_a \pm 1$	(3.37)

- $\sigma+$ means photon spin || quantisation axis, $\sigma-$ opposite.
- Rules for emission have swapped signs for $m_b = m_a \pm 1$.
- If the light is propagating in the $-\hat{k}$ direction, the allocation between σ_{\pm} and left- / right- is swapped.

3.2.1 More on Spontaneous Emission

Using the QED vector potential \mathbf{A} (3.22) we can derive a rate ,

$$W_{ba}^S = \frac{4\pi^2}{m^2} \left(\frac{e^2}{4\pi\epsilon_0} \right) \frac{\hbar}{V\omega_{ba}} |M_{ba}|^2 \delta(\omega - \omega_{ba}) \quad (3.38)$$

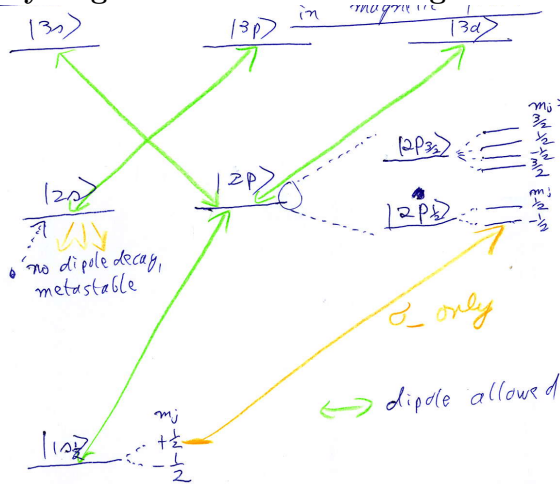
for the emission of a given photon with energy ω . To find the total spontaneous emission rate, we integrate over all possible photon states (momenta/ wave-vectors \mathbf{k})

Total spontaneous emission rate

$$W_{ba}^{S,TOT} = \frac{4\alpha}{3c^2} \omega_{ba}^3 |\langle \phi_b | \mathbf{r} | \phi_a \rangle|^2 \quad (3.39)$$

- we have used the dipole-approximation
- Important is the ω_{ba}^3 dependence: decay will always be dominantly to the state of the lowest energy that is accessible via dipole selection rules.
- The same selection rules apply for absorption, emission, and stimulated emission. \implies states that cannot decay via dipole-allowed transitions have comparatively longer lifetimes. These are called metastable.

Hydrogen transitions in a magnetic field:



left: Hydrogen level diagram

- Dipole radiation does not couple to spin, \implies all selection rules can be translated to j-basis (e.g. $\Delta m = 0 \implies \Delta m_j = 0$). It is a bit more tricky for the j quantum number (Even though Δl is not possible, $\Delta j = 0$ is possible, since e.g. $(l = 1, s = \frac{1}{2})$ and $(l = 2, s = \frac{1}{2})$ both have $j = \frac{3}{2}$).
- Hydrogen $|2s\rangle$ state metastable.
- Transition $|1s\rangle \rightarrow |3s\rangle$ can only happen via E_2 , M_1 or via a two-step process such as $|1s\rangle \rightarrow |2p\rangle \rightarrow |3s\rangle$ (e.g. using two lasers).