Recap:

Each EM mode behaves like a harmonic oscillator, where we know how to quantize each mode. Specifically,

$$\vec{A}(\vec{r},t) = \frac{1}{L^{3/2}}\left(\sum_{\vec{k},\alpha}\frac{2\pi\hbar c^2}{\omega_k}\right)^2 [a^\dagger_{\vec{k},\alpha}e^{-i\vec{k}\cdot\vec{r}+i\omega_k t} + a_{\vec{k},\alpha}e^{i\vec{k}\cdot\vec{r}-i\omega_{kt}}]\hat{e}_{\vec{k},\alpha}$$

with the algebra of the operator $a^\dagger, a$ as:

$$\begin{aligned}
[a^\dagger_{k,\alpha}, a^\dagger_{k',\alpha'}] &= 0 \\
[a_{k,\alpha}, a_{k',\alpha'}] &= 0 \\
[a_{k,\alpha}, a^\dagger_{k',\alpha'}] &= \delta_{\vec{k},\vec{k}'}\delta_{\alpha,\alpha'}
\end{aligned}$$

with equation of $\vec{E}, \vec{B}$ as:

$$\begin{aligned}
\vec{E}(\vec{r},t) &= -\frac{1}{c}\frac{\partial\vec{A}}{\partial t} \\
\vec{B}(\vec{r},t) &= \vec{\nabla}\times\vec{A}
\end{aligned}$$

Where, after doing some algebra, we get

$$\mathcal{H} = \sum_{\vec{k},\alpha}\hbar\omega_k\left[a^\dagger_{\vec{k},\alpha}a_{\vec{k},\alpha} + \frac{1}{2}\right] \tag{1}$$

the free space Hamiltonian. Note that this come from the classical result:

$$\mathbf{E} = \frac{1}{8\pi}\int[|\vec{E}|^2 + |\vec{B}|^2]\,d^3r$$

For the QM case, we can interpret our operators as:

- $a^\dagger_{\vec{k},\alpha}$: creation of a photon of energy $\hbar\omega_k$ with mode $\vec{k},\alpha$
- $a_{\vec{k},\alpha}$: destruction of a photon with energy ...
- $a^\dagger_{\vec{k},\alpha}a_{\vec{k},\alpha}$: the number of photons in mode $\vec{k},\alpha$.
  Which is just like the harmonic oscillator case!

Note that because (1) is true, we have a infinite amount of modes, and there exist a lowest energy state $\frac{1}{2}\hbar\omega_k$, this implies that the sum of $(1)\to\infty$, which implies a infinite vacuum energy.

While this is fine for many problems, as the zero point energy is trivial in many questions- especially experimentally as we always measure $\Delta\mathbf{E}$, but there is one very important physical interaction that cares about the ground state energy- gravity.

Now, the good news(not for the gravity case) is that sometimes we can use analytical extension to make $\mathcal{H}$ converge (e.g. $\Gamma(-1) = -\frac{1}{12}$)

Trivial Exercise:

Integrate gravity into quantum mechanics.

We must note that a photon is a boson. In fact, the operator relation is the defining feature of the boson. as the commutation relation is symmetric. Specifically:

$$\begin{aligned}
a^\dagger_{k,\alpha}a^\dagger_{k',\alpha'}|0\rangle &= |\vec{k}\alpha,\vec{k}'\alpha'\rangle \\
a^\dagger_{k',\alpha'}a^\dagger_{k,\alpha}|0\rangle &= |\vec{k}'\alpha',\vec{k}\alpha\rangle
\end{aligned}$$

Which indicates that the photon is a boson.

Spontaneous Emission:

Spontaneous emission means we start from an excited state $|i\rangle$, and the particle spontaneously goes to the final state $|f\rangle$ (ground state) and emit a photon.

This means that there is no EM emission to begin with, but we get a photon in the final state.

For a hydrogen atom transitioning from $|2,l,m\rangle \to |1,0,0\rangle$, we can write down the unperturbed Hamiltonian

$$\begin{aligned}\mathcal{H} &= \mathcal{H}_0 + \mathcal{H}_1 \\ &= \frac{p^2}{2m} - \frac{e^2}{r} + \sum_{\vec{k},\alpha} \hbar\omega_k (a^\dagger_{k,\alpha} a_{k,\alpha}) + \mathcal{H}_1\end{aligned}$$

with:
$|i\rangle = |2,l,m\rangle \otimes |0\rangle$ where the second ket is the ket of the EM ground state,
$|f\rangle = |1,0,0\rangle \otimes |1\rangle_{\vec{k}\alpha}$ in some mode.
$\implies E_f - E_i = (E_{100} + \hbar\omega_k) - E_{2lm}$

We can use **Fermi's Golden Rule**:

$$\Gamma_{i\to f} = \frac{2\pi}{\hbar} |\langle f|H_1|i\rangle|^2 \delta(E_f - E_i)$$

Where H_1 is how the hydrogen atom couples with the EM field:

$$H_1 = \frac{e}{mc}\vec{A}\cdot\vec{p}$$

(go back and check the dipole interaction Hamiltonian! Please check the commutation relation!)

Note that the algebra between $\hat{p}$ and $a^\dagger, a$ is an abelian one, as $a^\dagger, a$ is in the subspace of the photon- **not** the hydrogen wave function.

Matrix Element:

$$\langle f|H_1|i\rangle = \langle 100|\langle \vec{k},\alpha|\vec{A}\cdot\vec{p}|0\rangle|2lm\rangle$$

We focus on the matrix element of the photon space

$$\langle \vec{k}\alpha|\vec{A}|0\rangle$$

Note that we can write $\vec{A}$ to the sum of modes, and because $|0\rangle$ is on the right, only the creation operator $a^\dagger$ part of $\vec{A}$ will contribute. It is then easy to see that:

$$\langle \vec{k}\alpha|\vec{A}|0\rangle = \frac{1}{L^{3/2}}\left(\frac{2\pi\hbar c^2}{\omega_k}\right)^{1/2} e^{-i\vec{k}\cdot\vec{r}}\hat{e}_{\vec{k},\alpha}$$

in which we can make the dipole approximation such that $e^{-i\vec{k}\cdot\vec{r}} \sim 1$ because $\lambda = \frac{2\pi}{k} \gg a_0$.

We still have to compute $\vec{p}$ part of the matrix $\langle 100|\vec{p}|2lm\rangle \cdot \vec{e}_{\vec{k},\alpha}$
We learned earlier by looking in $[\vec{R}, H_0]$ that:

$$\langle f_0|\vec{p}|i_0\rangle = \frac{m}{i\hbar}(E^0_i - E^0_f)\langle f_0|\vec{R}|i_0\rangle$$

where $E^0_i - E^0_f = \hbar\omega$. This gives:

$$\begin{aligned}&\langle 100|\vec{p}|2lm\rangle \cdot \vec{e}_{\vec{k},\alpha} \\ &= im\omega\vec{e}\cdot\langle 100|\vec{R}|2lm\rangle \\ &= im\omega\vec{e}\cdot\int \psi_{100}(\vec{r})\vec{r}\psi_{2lm}(\vec{r})\, d^3r\end{aligned}$$

where we can use dipole selection rule and get:

$$l = 0$$
$$m = 0, \pm 1$$