\( \omega_0 = |E_A - E_B|/\hbar \)

\[ R_{a\rightarrow b} = R_{b\rightarrow a} = \rho(\omega_0) B \quad (6.106) \]

where \( B \) is some number. Thus

\[
\frac{dN_b}{dt} = -N_b B \rho(\omega_0) + N_a B \rho(\omega_0) - N_b A
\]

(6.107)

The coefficients \( A \) and \( B \) here are known as the Einstein’s A and B coefficients. According to the perturbation theory,

\[
B = \frac{1}{3} \frac{\pi |P^2|}{\epsilon_0 \hbar^2}
\]

(6.108)

and \( A = 0 \). However, as will be shown below, \( A \) is NOT zero.

**NOTE:** in our calculation above, we assume the E&M have a specific polarization and a unique wavevector. In reality, light (at a fixed frequency) can have wavevectors oriented in different directions and the polarization can be in different directions too. After averaging out these different directions, a factor 1/3 is obtained. This is where the extra 1/3 factor comes from.

In thermal equilibrium, \( N_a \) should not change with time and thus \( N_b = 0 \)

\[
\frac{dN_b}{dt} = -N_b B \rho(\omega_0) + N_a B \rho(\omega_0) - N_b A = 0
\]

(6.109)

Thus

\[
\rho(\omega_0) = \frac{N_a A}{N_a B - N_b B} = \frac{A/B}{\frac{N_a}{N_b} - 1}
\]

(6.110)

In thermal equilibrium, statistical physics tells us that

\[
\frac{N_a}{N_b} = \frac{\exp\left(\frac{E_a}{k_B T}\right)}{\exp\left(-\frac{E_a}{k_B T}\right)} = \exp\left(\frac{E_b - E_a}{k_B T}\right) = \exp\left(\frac{\hbar \omega_0}{k_B T}\right)
\]

(6.111)

So

\[
\rho(\omega_0) = \frac{A/B}{\exp\left(\frac{\hbar \omega_0}{k_B T}\right) - 1}
\]

(6.112)

In the study about black body radiation, we learned that the energy density of E&M waves satisfies the Planck distribution

\[
\rho(\omega_0) = \frac{1}{\pi^2 c^3} \frac{\hbar \omega_0^3}{\exp\left(\frac{\hbar \omega_0}{k_B T}\right) - 1}
\]

(6.113)

Thus, we find that

\[
\frac{A}{B} = \frac{\hbar \omega_0^3}{\pi^2 c^3}
\]

(6.114)

So

\[
A = \frac{\hbar \omega_0^3 B}{\pi^2 c^3} = \frac{\hbar \omega_0^3}{\pi^2 c^3} \frac{\pi |P^2|}{3 \epsilon_0 \hbar^2} = \frac{\pi |P^2| \omega_0^2}{3 \pi \epsilon_0 \hbar c^3}
\]

(6.115)

This is the rate of spontaneous emission (from \( b \) to \( a \)). This calculation tells us that in reality, even if we don’t perturb the system, a high energy state will still have finite probability to go to a lower energy state, by emitting a photon. In other words, if we prepare an atom in a high energy eigen-state, even if we don’t do anything, it will emit some light and go down to a lower energy state.

**This means that any excited state have a finite life time!**

In the absence of external perturbations, \( \rho(\omega) = 0 \)
\[
\frac{dN_b}{dt} = -N_b R_{b\rightarrow a} + N_a R_{a\rightarrow b} - N_b A = -N_b A
\] (6.116)

Thus,
\[
\frac{dN_b}{dt} = -N_b A
\] (6.117)

The solution of this differential equation is
\[
N_b(t) = N_b(0) e^{-At}
\] (6.118)

In other words, the number of particle on this high energy state is reducing exponentially as we increase \(t\). We can define a time scale \(\tau = 1/A\)
\[
N_b(t) = N_b(0) e^{-t/\tau}
\] (6.119)

This \(\tau\) is known as the lifetime of this state.

Of course, in reality, a high energy state \(\psi_b\) can go to multiple lower energy states, \(\psi_{a1}, \psi_{a2}, \ldots\), if \(H_0\) multiple eigenstates whose energies are lower than \(E_b\). Each of this procedure will have a spontaneous emission rate \(A_i, i = 1, 2, 3 \ldots\)
\[
\frac{dN_b}{dt} = -N_b A_1 - N_b A_2 - N_b A_3 - \ldots
\] (6.120)

Therefore,
\[
\frac{dN_b}{dt} = -(A_1 + A_2 + A_3 + \ldots) N_b
\] (6.121)

We can define total decay rate \(A\) as
\[
A = A_1 + A_2 + A_3 + \ldots
\] (6.122)

Thus the lifetime is
\[
\tau = 1/A = \frac{1}{A_1 + A_2 + A_3 + \ldots}
\] (6.123)

6.8.2. The origin of spontaneous emission

Q1: Where does this spontaneous emission come from? (Why \(A\) is NOT zero as the perturbation theory tells us?)

Q2: Why are \(A\) and \(B\) coefficients directly related?

A: This is because one assumption that we used above is wrong: \(R_{b\rightarrow a} = R_{a\rightarrow b}\)

Due to the time-reversal symmetry (physics laws remains the same as we reverse the arrow of time), the transition rate for a procedure must be identical to the inverse procedure. This is why we concluded that
\[
R_{b\rightarrow a} = R_{a\rightarrow b}
\] (6.124)

Q: How can this be wrong?

A: \(b \rightarrow a\) and \(a \rightarrow b\) are NOT inverse procedure of each other

If we only look at the atom, and forget about the E&M waves, \(b \rightarrow a\) and \(a \rightarrow b\) are indeed inverse procedure of each other. However, if we taken into account the E&M waves, they are NOT inverse of each other.

The origin of this error comes from the fact that in quantum mechanics, we treat particles and waves differently (they should be treated the same way due to the particle-wave duality). We treated particles as quantum particles (i.e. we use quantum theory treat particles, and particles follow totally different equations in QM, in comparison with classical physics). However, for E&M waves, we treat them same as classical waves (they follow the same Maxwell equations. There is nothing new beyond classical E&M).

Key: in QM, we couple classical waves with quantum particles. This is NOT a complete quantum theory, in which everything needs to be treated as a quantum object (particles as well as waves).

The correct way to quantize E&M waves will be discussed in quantum field theory, although other courses, like advanced mechanics, may
touch some aspect of the problem. After we quantize the E&M waves, we will find that $R_{b\rightarrow a}$ and $R_{a\rightarrow b}$ are slightly different

$$R_{b\rightarrow a} \neq R_{a\rightarrow b}$$ (6.125)

**Q: Why are $R_{b\rightarrow a}$ and $R_{a\rightarrow b}$ different?**

For absorption, an atom takes a photon and goes from a low energy state ($a$) to a high energy state ($b$). In addition to the transition $a\rightarrow b$ for the atom, the number of photon is reduced by 1. As a result, if we start from a system with $N$ photons, the final state has $N-1$ photons. We can write down the initial and final quantum states (including both the atom and photons) as:

$$|\psi_a;N\rangle \rightarrow |\psi_b, N-1\rangle$$ (6.126)

Here, to emphasize the photons, we write the absorption rate as: $R_{a\rightarrow b}$, $N$ The number $N$ in the subscript emphasizes that our system has $N$ photons when we start our experiment.

The inverse of this absorption is

$$|\psi_b; N-1\rangle \rightarrow |\psi_a, N\rangle$$ (6.127)

For emission, the quantum state of the atom changes from $\psi_b$ to $\psi_a$, and in the same time, the atom emits a photon and thus the photon number increases by 1. If we start with the same number of photons, which is $N$, the final state will have $N+1$ photons

$$|\psi_b; N\rangle \rightarrow |\psi_a, N+1\rangle$$ (6.128)

Here, to emphasize the photons, we write the emission rate as: $R_{b\rightarrow a}$, $N$ The number $N$ in the subscript emphasizes that our system has $N$ photons when we start our experiment.

If we compare the absorption and emission procedures, they are obviously NOT inverse to each other. Their photon numbers differ by 1. As a result, the transition rate also differ a little bit, and this is the origin of spontaneous emission. In fact, the inverse of emission (with $N$ photons in the initial state) is absorption with $N+1$ photons in the initial state. So we should have

$$R_{b\rightarrow a,N} = R_{a\rightarrow b,N+1} \neq R_{a\rightarrow b,N}$$ (6.129)

For absorption, we can use the same results that we obtained above:

$$R_{a\rightarrow b} = \frac{\pi}{3 \epsilon_0} \frac{P^2}{\hbar^2} \rho(\omega_0)$$ (6.130)

Because E&M waves are photons, the total energy carried by E&M waves are

$$u = 2 \int \frac{d\hat{k}}{(2\pi)^3} \hbar c \left| \hat{k} \right| n(\hat{k})$$ (6.131)

Here, $n(\hat{k})$ are number (density) of photons with wavevector $\hat{k}$, $\hbar c k = \hbar \omega$ is the energy of a photon. Here we sum over all wavevectors to compute the total energy. The over all factor “2” is because there are two polarizations for light.

$$u = 2 \int \frac{4\pi \hbar^2 d\hat{k}}{(2\pi)^3} \hbar c k n(k) = \int d\hat{k} \frac{\hbar c}{\pi^2} k^3 n(k)$$ (6.132)

Notice that $c k = \omega$, so we can change our integral parameter from $k$ to $\omega$.

$$u = \int d\hat{k} \frac{\hbar c}{\pi^2} k^3 n(k) = \int d\omega \frac{\hbar \omega^3}{\pi^2 c^3} n(\omega)$$ (6.133)

Compare with the definition for $\rho(\omega)$

$$u = \int d\omega \rho(\omega)$$ (6.134)

we find that

$$\rho(\omega) = \frac{\hbar}{\pi^2 c^3} \omega^3 n(\omega)$$ (6.135)

And thus
\[
R_{a\rightarrow b,N} = \frac{\pi}{3} \frac{|P|^2}{\epsilon_0 h^2} n(\omega_0) = \frac{\pi}{3} \frac{|P|^2}{\epsilon_0 h^2} \frac{\hbar}{\pi^2 c^3} n(\omega_0) \tag{6.136}
\]

However, for emission, (an atom gives out a photon and goes from a high energy state to a low energy state), as shown above, it should be the same as absorption with photon number increased by 1, so it is
\[
R_{b \rightarrow a,N + 1} = \frac{\pi}{3} \frac{|P|^2}{\epsilon_0 h^2} \frac{\hbar}{\pi^2 c^3} [n(\omega_0) + 1] \tag{6.137}
\]

Thus we find
\[
R_{b \rightarrow a,N} = \frac{\pi}{3} \frac{|P|^2}{\epsilon_0 h^2} \frac{\hbar}{\pi^2 c^3} n(\omega_0) + \frac{\pi}{3} \frac{|P|^2}{\epsilon_0 h^2} \frac{\hbar}{\pi^2 c^3} = R_{a \rightarrow b} + \frac{\pi}{3} \frac{|P|^2}{\epsilon_0 h^2} \frac{\hbar}{\pi^2 c^3} = R_{a \rightarrow b,N} + A \tag{6.138}
\]

The difference between \(R_{a \rightarrow b}\) and \(R_{b \rightarrow a}\) is precisely the \(A\) coefficient assumed by Einstein. In this fully quantum theory, we don't need to assume an \(A\) coefficient,
\[
\frac{dN_b}{dt} = -N_b R_{a \rightarrow b,N} + N_a R_{a \rightarrow b,N} \tag{6.139}
\]

Because the quantization of E&M waves tells us that \(R_{a \rightarrow b} = R_{a \rightarrow b} + A\), we get
\[
\frac{dN_b}{dt} = -N_b (R_{a \rightarrow b,N} + A) + N_a R_{a \rightarrow b,N} = -N_b A = -N_b B + N_a B - N_b A \tag{6.140}
\]

The spontaneous emission term, assumed by Einstein naturally arises

### 6.8.3. Selection rule

The transition rate is proportional to \(|P|^2\)
\[
R_{a \rightarrow b} = \frac{\pi}{\epsilon_0 h^2} p(\omega_0) \tag{6.141}
\]

If \(|P|^2\) is zero, then this transition rate becomes zero. For E&M waves with polarization along \(z\), we have shown that
\[
P = q \left( \langle \psi_b | z | \psi_a \rangle = q \int d^3 \vec{r} \psi_b^*(\vec{r}) z \psi_a(\vec{r}) \right) \tag{6.142}
\]

If we are considering eigenwavefunctions of a hydrogen atom, (assuming the \(a\) state has quantum numbers \(n, l, m\) and the \(b\) state has quantum numbers \(n', l'\) and \(m')\)
\[
P = q \int d^3 \vec{r} \psi_{n'l'm'}^*(\vec{r}) z \psi_{n'l'm}(\vec{r}) \tag{6.143}
\]

It turns out that one can prove that most of the time \(P = 0\), i.e. the transition rate is zero. To get a non-zero \(P\), the following two condition must be satisfied
\[
l' = l \pm 1 \tag{6.144}
\]
and
\[
m' - m = \pm 1 \text{ or } 0 \tag{6.145}
\]

These relations are called selection rules. They tells us that which transition is possible (and which is not). If we satisfy the selection rule, a transition rate is finite. Otherwise, the transition rate is zero even if we make the frequency matches \(|E_a - E_b|/\hbar\).

**Comment:** These selection rules come from angular momentum conservation. We can prove them purely based on angular momentum and their commutators (see our textbook for the proof).

**Question:** Is this transition rate absolutely zero when the selection rules are not satisfied?

**Answer:** Not really. The rate is usually much smaller, but will not be exactly zero for two reasons

(1) The conclusion above is based on the first order perturbation theory. If one consider higher order perturbations, even if \(P\), there is still some
transition rate (from higher order terms). Because they are from higher order terms, the rate is small. But it is not zero.

(2) The conclusions above only considers E&M waves. There are other channels to make the transition happen. For example, the collision between two atoms. In a gas of atoms, occasionally, two atoms collide with each other. Here, the two atom could exchange some energy, as a result, one of the atom may turn from state \( a \) to \( b \). Here, because it is NOT driving by E&M waves, the above calculation doesn’t applied and thus the selection rule become irrelevant.