Notes for Lecture 15

Photon absorption, emission

In previous couple of lectures, we prepared ourselves very well for dealing with the time dependent perturbation problem and the problem of the interaction between light and matter. Now, we are ready to collect some key results!

15.1 Master formulae

Our goal is to provide quantum mechanical formulae for photon absorption, photon emission (stimulated and spontaneous), and the photoelectric effect. All the required ingredients are well prepared for our use, from the last two lectures. **Key equations to use are Eqs. 13.30, 13.31, 14.35, and 14.36 (with QED corrections 14.39, 14.40, 14.41 for the last two), which are reproduced here for convenience. A new equation, Eq. 15.1, summarizes Eqs. 14.39 through 14.41, in an even more useful form.**

Time-dependent perturbation: $\hat{H}_1 = \hat{V}\, e^{-i\omega t} + \hat{V}^\dagger e^{i\omega t}$

$$R_{i\to f} = \frac{2\pi |V_{i\leftrightarrow f}|^2}{\hbar^2} \cdot \delta\big(\omega - |\omega_{f,i}|\big) \qquad \text{transition rate, Fermi's golden rule} \tag{13.31}$$

$$V_{i\leftrightarrow f} = \begin{cases} \left\langle f \left| \hat{V} \right| i \right\rangle & \text{for absorption } (\omega_f > \omega_i) \\ \left\langle f \left| \hat{V}^\dagger \right| i \right\rangle = \left\langle i \left| \hat{V} \right| f \right\rangle^* & \text{for emission } (\omega_f < \omega_i) \end{cases} \tag{13.30}$$

These results remain valid even when $\omega = 0$, with $\hat{V} \equiv \hat{H}_1$ in that case.

Interaction of light and electron: $\hat{H}_1 = \hat{V}\, e^{-i\omega t} + \hat{V}^{\dagger} e^{i\omega t}$

$$\hat{V} = \frac{e}{m_e}\sqrt{\frac{N_{>}\hbar}{2\epsilon_0\omega\mathcal{V}}}\, e^{i\vec{k}\cdot\hat{\vec{r}}}\,\vec{\varepsilon}\cdot\hat{\vec{p}} \qquad \mathcal{V} \text{ is volume; from Eqs. 14.36,39–41} \tag{15.1}$$

$$N_{>} \equiv \begin{cases} N & \text{absorption: } N \to N-1 \text{ photons} \\ N+1 & \text{emission: } N \to N+1 \text{ photons} \end{cases}$$

The above formulae are calculated for the most basic case, which involves a unique initial state, a unique photon state $(\vec{k}, \vec{\varepsilon})$, and a unique final state. For *incoherent* mixture of states, the prescription of Section 14.4 is applicable. In this case, each variable ω, ω_i, or ω_f must be integrated over its respective density of states. For more discussion, see Section 15.5.

Discussion on Fermi's golden rule

Note that the key part of the master formulae is Fermi's golden rule. Let us have some discussion on this important result of the time-dependent perturbation theory.

1. The Fermi's golden rule comes from the perturbation theory.
2. It imbues meaning to the off-diagonal element of the Hamiltonian. As the transition rate is proportional to $|V_{i\leftrightarrow f}|^2$ we can say that the off-diagonal element represents a transition amplitude up to a factor (please revisit LN 5 armed with this knowledge; page 5 of LN 5 in particular). Of course, this association is more fundamental than the Fermi's golden rule. It is embedded in the perturbation theory from the beginning: read page 4 of LN 13 (*advanced topic*).
3. It results from taking time t to a large value, compared to $2\pi/|\omega_{f,i}|$, i.e. the natural period of the system under investigation (page 10 of LN 13). This long time approximation results in the delta function $\delta(\omega - |\omega_{f,i}|)$, which is the statement of **the energy conservation**. That this energy conservation principle arises only in the long time limit is naturally explained by the energy time uncertainty principle. If the event is observed during a finite time interval Δt, then the energy uncertainty $\Delta E \gtrsim \hbar/\Delta t$. So, only in the limit of large time, $\Delta E \ll \hbar|\omega_{f,i}|$ can be achieved, which leads to the exact energy principle: $\hbar\omega + \hbar\omega_i = \hbar\omega_f$ (absorption) and $\hbar\omega_i = \hbar\omega_f + \hbar\omega$ (emission).
4. Last but not least, the front factor $2\pi/\hbar^2$ is dimensionally correct to give the dimension of frequency for $R_{i\to f}$.

15.2 Dipole approximation

The above formulae are left, purposefully, in a very general and elementary form. However, an important case occurs when the so-called **dipole approximation** is valid. We will discuss this approximation here, and will assume it for the rest of this lecture.

15.2.1 Length scales

Let us recall that the perturbation term due to interaction of light and electron carries the exponential term $\exp(i\vec{k}\cdot\vec{r})$ due to the travelling wave nature of light.

However, often, the following approximation is valid

$$\exp(i\vec{k}\cdot\vec{r}) \approx 1 \qquad \text{dipole approximation} \tag{15.2}$$

When would such an approximation make sense? Clearly, it is when $\vec{k}\cdot\vec{r} \ll 1$. Note that for light interacting with an electron that is bound to an atom, the average magnitude of $\vec{r}$ is given by $\sim a_B/Z$ (Eq. 7.6 or 7.8). Since a_B is 0.5 Å, we see that $\vec{r}$ is of the order of an Å at the most. On the other hand, the magnitude of $\vec{k}$ is given by $k = 2\pi/\lambda$, where λ is the wavelength of the photon. Therefore, we get $\vec{k}\cdot\vec{r} \sim 2\pi a_B/(\lambda Z)$. Given that

$$\lambda\,(\text{Å}) = \frac{12398}{E\,(\text{eV})} \qquad \text{for photon } (\because \hbar c = 1973 \text{ eVÅ}) \tag{15.3}$$

we see that for visible light (2-3 eV) or near-UV light ($\sim$ 10 eV) the dipole approximation is very good, since λ is on the order of 1000 or 100 Å.

A more sophisticated argument for the dipole approximation for a single atom can be made if one notes that $\vec{k}\cdot\vec{r} \sim \hbar\omega a_B/(Z\hbar c) \sim RZ^2 a_B/(Z\hbar c)$, where in the second step the near resonance condition $\hbar\omega \sim RZ^2$ (Eq. 7.10) is used. Using $R = e^2/(8\pi\epsilon_0 a_B)$ (Eq. 7.10), we get $\vec{k}\cdot\vec{r} \sim \alpha Z/2$, were α is the fine structure constant (Eq. 6.20). So, for deep core levels (i.e., those atomic orbitals with high binding energy) in moderately heavy atoms (Z on the order of 10), the dipole approximation remains valid since $Z\alpha \ll 1$. Note that $Z = 137$ would correspond to $RZ^2 = 255$ keV (γ ray).

[*Optional reading*] However, the argument in the previous paragraph needs to be augmented by additional consideration if a crystal of atoms, not a single atom, is involved. In this case, ka, where a is the lattice constant (typically a few Å) must be small, also. This means light energy less than that (10s of keV) of hard X-ray, for which the dipole approximation breaks down; the space-dependent phase factor $\exp(i\vec{k}\cdot\vec{r})$ is the origin of the diffraction phenomenon that occurs when hard X-ray impinges on a crystal.

15.2.2 Dipole moment

Why does Eq. 15.2 imply a dipole approximation? (And, why would omitted terms of the Taylor expansion give rise to higher multi-poles?) Answers to these questions will become clear from the following discussion.

With Eq. 15.2 assumed, the only operator in Eq. 15.1 is $\hat{\vec{p}}$. Thus, for $V_{1,0}$ we need to evaluate the matrix element

$$_1\left\langle\hat{\vec{p}}\right\rangle_0 \equiv \left\langle 1 \left|\hat{\vec{p}}\right| 0\right\rangle$$

where the short-hand notation for the matrix element is as we have been using since Lecture 13. It is left for your work (homework) to show that

$$_1\left\langle\hat{\vec{p}}\right\rangle_0 = i m_e \omega_{1,0}\, {}_1\left\langle\hat{\vec{r}}\right\rangle_0 \tag{15.4}$$

which is derived in a straightforward fashion, once it is seen that

$$\left[\hat{\vec{r}}, \hat{H}_0\right] = \frac{i\hbar\hat{\vec{p}}}{m_e} \tag{15.5}$$

where $\hat{H}_0$ is as defined in Eq. 14.18. Eq. 15.4 makes it clear why the approximation of Eq. 15.2 is named the (electric) dipole approximation. Indeed, for the current problem,

$$\hat{\vec{\mathbb{p}}} \equiv -e\hat{\vec{r}} \qquad \text{electric dipole moment operator} \tag{15.6}$$

Why is this? Note that the dipole moment is defined generally as $\sum_i q_i\vec{r}_i$. In the current case, the only other charge than the electric charge is due to the nucleus, which gives a vanishing contribution to the dipole moment due to it being located at the origin of the coordinate system. Therefore, finally we have

$$_1\left\langle\hat{\vec{p}}\right\rangle_0 = -\frac{i m_e \omega_{1,0}}{e}\, {}_1\left\langle\hat{\vec{\mathbb{p}}}\right\rangle_0 \tag{15.7}$$

15.3 Absorption

Let us assume that there are N photons of with frequency ω initially[1], with $\omega \approx \omega_{1,0}$. What is the rate at which the photon gets absorbed by our two-level system? That is, what is the rate at which the electronic state transitions from 0 to 1?

The answer follows if we just combine Eqs. 13.31,13.30,15.1,15.7.

$$R_{0\to1,\,N\to N-1} = \frac{\pi N\omega}{\hbar\epsilon_0\mathcal{V}}\left|\vec{\varepsilon}\cdot {}_1\!\left\langle\hat{\vec{\mathbb{p}}}\right\rangle_0\right|^2 \delta(\omega-\omega_{1,0}) \tag{15.8}$$

In deriving this, use is made of the fact $\omega_{1,0} = \omega$, by virtue of the delta function. Also, note that the subscript of R is now expanded to include the second part, which stands for the change of the number of photons as the result of the process in question.

15.4 Emission

For the absorption, we get the same expression! One thing to be keenly aware of is the factor $N_>$ in Eq. 15.1. We get

$$R_{1\to0,\,N\to N+1} = \frac{\pi(N+1)\omega}{\hbar\epsilon_0\mathcal{V}}\left|\vec{\varepsilon}\cdot {}_1\!\left\langle\hat{\vec{\mathbb{p}}}\right\rangle_0\right|^2 \delta(\omega-\omega_{1,0}) = R_{0\to1,\,N+1\to N} \tag{15.9}$$

That $R_{1\to0,\,N\to N+1} = R_{0\to1,\,N+1\to N}$ (**the principle of detailed balance**) is a clear manifestation of the underlying **time reversal symmetry**.

15.4.1 Stimulated emission

As you can see above, there is only one formula for emission. For historical reason, however, the above expression with $N+1$ replaced by N, justified in the classical optics limit, is called the **stimulated emission**. Namely, the stimulated emission is the emission predicted by theory prior to Sec. 14.4, i.e. using Eq. 14.36, without realizing the correct value to use ($N_>$) as explained in Sec. 14.4 and summarized in Eq. 15.1. In other words, if we assume that $N \gg 1$, appropriate for the classical optics

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[1] This is not the only possible state, as you can imagine, but it is a convenient and basic one to consider. A general state of photons (or for any other particles, for that matter) is a pure state, a linear combination of states with different numbers of photons, or an incoherent mixture of such pure states. Read discussion in Section 15.5.

regime,

$$\begin{aligned} R_{1\to 0,\,SEA} &\approx R_{1\to 0,\,N-1\to N} \text{ for } R_{1\to 0,\,N\to N+1} && \text{stimulated emission approx.} \quad (15.10)\\ R_{1\to 0,\,SEA} &= R_{0\to 1,\,N\to N-1} && \text{detailed balance for SEA} \quad (15.11)\end{aligned}$$

where the first equation follows by noting that $R_{1\to 0,\,N\to N+1} = \frac{N+1}{N} R_{1\to 0,\,N-1\to N}$, from Eq. 15.9, and taking $N \to \infty$.

In short, the notion of stimulated emission and the principle of detailed balance associated with it are the approximations valid only in the classical optics regime, i.e., when light is bright. Note the more correct, fully quantum, equation (Eq. 15.9) and the more precise nature of the detailed balance expressed in that equation.

The stimulated emission is the principle that makes the laser work. In fact, as you may well know, the "se" part of the word laser stands for stimulated emission! The key physics is that the photon in the initial state and the photon in the final state are "coherent" (cf. Section 15.5). So, in a stimulated emission, you get exactly the same light state as you put in, except that the number of photons has increased by one – this process is repeated in a laser for light amplification.

15.4.2 Spontaneous emission

Eq. 15.9 with $N = 0$ corresponds to the **spontaneous emission**.

$$R_{1\to 0,\,SE} = \frac{\pi\omega}{\hbar\epsilon_0\mathcal{V}} \left| \vec{\varepsilon}\cdot {}_1\!\left\langle \hat{\vec{\mathbb{p}}} \right\rangle_0 \right|^2 \delta(\omega-\omega_{1,0})$$

While both the spontaneous emission and the stimulated emission are derived from a single common formula (Eq. 15.9), a key physical difference is worth noting. The spontaneous emission occurs no matter what, and it is beyond our control! This is because the vacuum includes already the zero point motion of photons at all frequencies and all polarizations. The stimulated emission process *is* under our control, to the extent that we can trigger it, or control its likelihood, by preparing the initial state of photons.

Let us now consider an important experiment in which we do not measure the final state of the photon. Then, we need to sum over all possible polarizations and all possible $\vec{k}$ values for the given frequency $\omega = \omega_{1,0}$. Taking the average over random polarizations, we get (cf. Section 15.6): $\left| \vec{\varepsilon}\cdot {}_1\!\left\langle \hat{\vec{\mathbb{p}}} \right\rangle_0 \right|^2_{ave} = \frac{1}{3} \left| {}_1\!\left\langle \hat{\vec{\mathbb{p}}} \right\rangle_0 \right|^2$. The delta function expression above must be changed to the photon density of states $\rho(\omega_{1,0})$, the result of applying the integration operator $\int_0^\infty d\omega\, \rho(\omega)$ to the above formula. Now, we must calculate the **density of states** $\rho(\omega)$, by considering the number of possible photon modes (N_m) in a box of volume $\mathcal{V}$. Let us do it. $dN_m = \rho(\omega)d\omega$ corresponds to the number of allowed photon modes (i.e. the number of $\vec{k}$ values allowed times the number of polarizations allowed) with momentum values contained in a thin spherical shell in the $\vec{k}$ space. We need to divide the volume of this thin shell by "volume per $\vec{k}$" (again, this is the $\vec{k}$ space volume) in order to compute the number of allowed $\vec{k}$ values in that volume. This "volume per $\vec{k}$" is most easily calculated using the periodic boundary condition. For a free particle (including photon!) the spatial wave function $\propto \exp(i\vec{k}\cdot\vec{r}) = \exp(ik_x x)\exp(ik_y y)\exp(ik_z z)$. Imagine that the volume is a cube with side lengths L. For the wave function to be periodic ($\psi(x+L) = \psi(x)$ and similarly for y, z), we must impose the condition that $k_x L = 2\pi n_x$ (n_x = integer, and similarly for k_y and k_z. Thus, the volume per $\vec{k}$ is given by $\frac{2\pi}{L} \times \frac{2\pi}{L} \times \frac{2\pi}{L} = \frac{8\pi^2}{\mathcal{V}}$.

$$dN_m \equiv \rho(\omega)d\omega = \overbrace{2}^{\text{two polarizations}} \cdot \frac{\overbrace{4\pi k^2 dk}^{\vec{k}\text{ shell volume}}}{\underbrace{(2\pi)^3/\mathcal{V}}_{\text{volume per }\vec{k}}} \tag{15.12}$$

$$= \frac{\mathcal{V}\omega^2}{\pi^2 c^3} d\omega \qquad \text{using } \omega = ck$$

$$\rho(\omega) = \frac{\mathcal{V}\omega^2}{\pi^2 c^3} \tag{15.13}$$

Therefore, we get this very important result, which is expressed using the famous Einstein symbol A, anticipating later discussion of this lecture (cf. Section 15.6).

$$A \equiv R_{1\to 0,\,SE} = \frac{\pi\omega_{1,0}}{3\hbar\epsilon_0\mathcal{V}} \left| {}_1\langle \hat{\vec{\mathbb{P}}} \rangle_0 \right|^2 \rho(\omega_{1,0}) \tag{15.14}$$

$$= \frac{\omega_{1,0}^3}{3\pi\hbar\epsilon_0 c^3} \left| {}_1\langle \hat{\vec{\mathbb{P}}} \rangle_0 \right|^2 \tag{15.15}$$

The spontaneous emission is strictly a quantum phenomenon, as it is driven by the zero point motion associated with the zero photon state, i.e. quantum fluctuations of light that exist even when "there is no photon." Also, note that the spontaneous emission (SE) formula is an exact quantum result, in contrast to the preceding formula for stimulated emission approximation (SEA).

If photon is the manifestation of a simple harmonic oscillation of *something*, then we know from our knowledge of the simple harmonic oscillator physics that even in the ground state (zero photon state) the oscillation of that something still exists (zero point motion). That oscillation is what is often referred to as the **quantum fluctuation**[2], which can be thought to arise from the Heisenberg uncertainty principle. The existence of the spontaneous emission in nature is therefore evidence that our view of photon as due to a simple harmonic oscillator of some underlying thing is correct.

The expression "spontaneous emission" or "zero photon state" may ultimately be a misnomer. As the ground state energy with "zero photon" *is* significant, $\hbar\omega/2$, one can simply say that *you cannot turn off (quantum) light completely* and therefore any emission can in fact viewed as a stimulated emission, in the sense that there *is always* light field that couples to the electronic system (our two level system) in the initial state. As we are on this topic, let us note, in more general terms, that the concept of "zero" or "nothingness," which seems so natural to us classical beings, is totally unsuitable for describing quantum phenomena[3].

15.5 General comments, coherence/incoherence

The theory that we have developed so far is an extremely simple one, in the end, but it is also an very powerful one, for dealing with the interaction of light and electron.

It is a simple one, since, essentially, the only mathematically formula to look up for the final result, assuming that the dipole approximation is valid, is Eq. 15.8. The emission part is identical with it by the exact principle of detailed balance.

It is also a powerful one, since it can be easily made suitable for any "configurations" for the initial state or the final state, whether we are concerned with the distribution of electronic states or photon states, as long as a configuration involves an incoherent mixture of states. Now, we must have some discussion about "coherence/incoherence."

One thing that we did not allow in this formalism (as had been mentioned in some footnotes) is the possibility that the electronic state or the photon state is a linear combination of respective energy eigenstates ($\hat{H}_0$ eigenstates, in the case of electron; states with definite photon numbers, in the case of photon). Such a linear combination state is often referred to as a "coherent mixture" of states corresponding to different terms in the linear combination[4]. This terminology adheres to the general notion

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[2] As opposed to thermal fluctuation, or "classical fluctuation," driven by finite temperature.

[3] So, the description "zero photon state" may be viewed as a human centered one, and, eventually, a misleading one.

[4] There is also a special state of photons called *the coherent state*. Here we are *not* discussing *that* particular coherent state. Instead, we are discussing coherence, in more general terms.

of "coherence," i.e. that two or more waves are characterized by precisely defined relative phases. How would our formulae change if the initial state for photon or electron is a coherent mixture of respective energy eigenstates? The formalism will get complicated. While the mathematics complication will not be unbearable[5], new physics must be recognized. Even at first order, there might be multiple channels by which the final state is reached, and, if this is the case, then the transition rate will no longer be proportional to a single matrix element squared $|V_{i\leftrightarrow f}|^2$, but it will involve an "amplitude sum" of two or more matrix elements $V_{i,j}$, characterized by the *interference* between different transition channels[6]. These effects are outside the scope of this course.

Here, we consider an *incoherent* mixture of states. We have in fact dealt with such cases already in Sec. 14.4. In case when the initial state is an incoherent mixture of states, then we can calculate the transition probabilities/rates for each state, and simply add them up, since there cannot be any interference between processes starting from incoherent initial states. What kind of states correspond to an incoherent mixture of states? For instance, a thermal ensemble (or electronic states or photon states) is such an example: different energy eigenstates are occupied with probabilities proportional to the Boltzmann factor $\exp(-\beta E_n)$, while the relative phases of different energy eigenstates are completely random. In the case of the photon state, we can also recognize the importance of the photon source: if the photon source is a laser source, then the photon state will be a coherent mixture of states, while if the photon source is a "conventional source" (like Hg lamp) then it will be an incoherent mixture of states.

In any case, let us keep in mind from Sec. 14.4 that the sum over an incoherent mixture of states can be often expressed as an integral over the density of states $\rho(\omega)$, $\rho_i(\omega_i)$ or $\rho_f(\omega_f)$, corresponding to the photon state, the electronic initial state, or the electronic final state, or, in a more general case, the joint density states. Below, we will deal with the particular case when the photon density of states $\rho(\omega)$ is important[7].

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[5] I dare say that a well-motivated student has a very high chance to successfully retrace the formalism that we have developed here to establish more general formulae that are applicable to coherent mixture(s) of states without too much difficulty.

[6] These interference terms arise naturally at higher orders of perturbations, even if the initial state and the final state are unique energy eigenstates.

[7] In the textbook, the symbol $\rho(\omega)$ is used for the energy density distribution function, with $\rho(\omega)d\omega$ giving the energy density. However, in this lecture note, $\rho(\omega)$ is used for the density of states (including, or per, polarization), as this is a more established modern convention. So, $\rho(\omega)d\omega$ is the number of photon modes (including, or per, polarization). To get the energy density distribution function, for which we use symbol $u(\omega)$, from the density of states, $\rho(\omega)$, multiply it by $N\hbar\omega/\mathcal{V}$.

15.6 Einstein coefficients

Famously, Einstein used his typical mix of (1) simple but enormously powerful physical arguments and (2) deep appreciation of known experimental results, to establish a phenomenological theory of the interaction of light and matter, well before quantum mechanics, not to mention quantum optics (i.e. quantum electrodynamics), has been established, foreboding essential quantum features well in advance.

The essence of his phenomenological theory is contained in his A and B coefficients. In his paper, he used the Wien displacement law, known at that time as

$$u(\omega, T) = \omega^3 f(\omega/T) \tag{15.16}$$

where u is the energy density distribution function (see footnote 7), f was an yet-unknown function, $\propto \exp(-\hbar\omega/(k_B T))$ at high temperature. The rate at which the energy level 1 is populated was assumed to be

$$N_0 u(\omega, T) B_{0\to 1} \tag{15.17}$$

where N_0 is the number of atoms in state 0, while the rate at which the energy level 1 is de-populated was assumed to be

$$N_1 \left[u(\omega, T) B_{1\to 0} + A \right] \tag{15.18}$$

where N_1 is the number of atoms in state 1. In his theory, he thus conjectured spontaneous emission (A), stimulated emission ($B_{1\to 0}$), and absorption ($B_{0\to 1}$). One can only imagine what courage and conviction[8] it would have taken for Einstein to conjecture "spontaneous emission" in 1917, eight years before the Schrödinger equation or the Heisenberg matrix mechanics was discovered! In any case, these two rates must be exactly the same in an equilibrium, where N_1 must be constant (and so must N_0). This means

$$u(\omega, T) = \frac{N_1 A}{N_0 B_{0\to 1} - N_1 B_{1\to 0}} \tag{15.19}$$

$$= \frac{A}{\frac{N_0}{N_1} B_{0\to 1} - B_{1\to 0}} \tag{15.20}$$

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[8] However, to help understand what facts must have bolstered such courage and conviction, one should note the following. (1) Stimulated emission and stimulated absorption can be considered as plausible within the classical picture – so they must be included. (2) However, they alone cannot explain the then-well-known Planck's radiation law (proof of this based on the rate consideration above is left for your exercise). (3) So, one may conjecture some "mysterious processes" such as "spontaneous emission" or "spontaneous absorption." (4) Then, the theory is consistent with the Planck's radiation law, only if the spontaneous emission, but *not* the "spontaneous absorption," is included (proof of this using the rate argument is also left for your exercise).

Using Boltzmann factors, $N_0/N_1 = \exp\left(\frac{\hbar\omega_{1,0}}{k_B T}\right)$, and so

$$u(\omega,T) = \frac{A}{\exp\left(\frac{\hbar\omega_{1,0}}{k_B T}\right) B_{0\to1} - B_{1\to0}} \tag{15.21}$$

By putting $\omega_{1,0} = \omega$ (Bohr condition), $B_{0\to1} = B_{1\to0} \equiv B$ (detailed balance by Boltzmann), Einstein was able to deduce that

$$u(\omega,T) = \frac{A}{B\left[\exp\left(\frac{\hbar\omega}{k_B T}\right) - 1\right]} \tag{15.22}$$

Comparing this with Planck's law, he could then deduce that

$$\frac{A}{B} = \frac{\hbar\omega^3}{\pi^2 c^3} \tag{15.23}$$

That his results using these simple arguments have stood the test of time and forebode what were to come years and decades later is simply remarkable, to say the least.

How would *we* derive A and B, based on the theory that we have developed so far? The answer is "very well," of course. In Einstein's treatment, the transition rate per atom is defined as A (spontaneous emission) and $Bu(\omega,T)$ (absorption and stimulated absorption). These are precisely what we have been considering prior to this section.

In fact, we have already calculated A for unpolarized light (Eq. 15.15). How about B? Integrating Eq. 15.8 over the density of states $\rho(\omega)$, identifying the result as $Bu(\omega,T)$, and using the conversion between $u(\omega,T)$ and $\rho(\omega)$, as noted in footnote 7, we get

$$B = \frac{\pi}{\hbar^2\epsilon_0}\left|\vec{\varepsilon}\cdot {}_1\!\left\langle\hat{\vec{\mathbb{P}}}\right\rangle_0\right|^2 \qquad \text{polarized light} \tag{15.24}$$

$$B = \frac{\pi}{3\hbar^2\epsilon_0}\left|{}_1\!\left\langle\hat{\vec{\mathbb{P}}}\right\rangle_0\right|^2 \qquad \text{unpolarized light} \tag{15.25}$$

Combining this last result with that of Eq. 15.15, we reproduce Eq. 15.23 exactly, from our fully quantum mechanical formalism! Now, since within our theory, $A = u(\omega,T)B/N$ (i.e. the spontaneous emission is simply the stimulated emission "with $N = 1$"), we must have

$$u(\omega,T) = \frac{\hbar\omega^3}{\pi^2 c^3} N \tag{15.26}$$

Comparing this with Plank's radiation law, we conclude that

$$N = \frac{1}{\exp\left(\frac{\hbar\omega}{k_B T}\right) - 1} \tag{15.27}$$

which is, as we have defined it, the number of photons per photon mode $(\vec{k}, \vec{\varepsilon})$. This is what is known as the **Planck distribution function** or the **Bose-Einstein distribution function with zero chemical potential**, well-known in quantum statistical mechanics.

15.7 Spontaneous emission and lifetime

Let us continue to consider the two level system. Let us assume that the system is *in complete vacuum*, completely isolated from all other things in the Universe. Nevertheless, it cannot escape the zero point fluctuations of the photon field, as we discussed so far. If the two level system is in the ground state ($|0\rangle$), then it will be in that state forever. However, what if the system is in the excited state, $|1\rangle$? The decay by spontaneous emission defines the **lifetime** of the excited state!

$$\tau \equiv \frac{1}{A} \qquad \textbf{lifetime of the excited state} \qquad (15.28)$$

This is the so-called $1/e$ lifetime, and it means that the **survival probability** $P_{1\to1}(t)$ is given as

$$P_{1\to1}(t) = \exp\left(-\frac{t}{\tau}\right) = \exp\left(-At\right) \qquad \text{for } \textit{any } t \geq 0, \text{ if } |\psi\rangle_{t=0} = |1\rangle \qquad (15.29)$$

This result may surprise you. After all, we mentioned clearly that the perturbation theory is valid only if $|V_{1,0}|t/\hbar$ is small (Section 13.2). Clearly, then, our theory cannot be taken to be valid for any $t > 0$ as claimed here?! However, the above result may also appeal to you, since it is the famous **Rutherford decay law**[9]. This result is indeed correct, as we will show now.

As we can reason from Eq. 13.29, we have $P_{1\to0}(t) = At$ by spontaneous emission, if t is small enough for the perturbation theory to be valid ($t \ll \hbar/|V_{1,0}|$, or, equivalently for this problem, $At \ll 1$), but large compared to the natural period of the system ($t \gg 2\pi/\omega_{1,0}$). By probability sum rule, we then get

$$P_{1\to1}(t) = 1 - At \qquad \frac{2\pi}{\omega_{1,0}} \ll t \ll \tau = \frac{1}{A} \qquad (15.30)$$

Note that the condition for t requires that $\tau \gg \frac{2\pi}{\omega_{1,0}}$, which is a reasonable condition for the two energy levels to be sufficiently distinguishable, as it implies $E_1 - E_0 \gg 2\pi\Delta E_1$ where $\Delta E_1 \sim \hbar/\tau$ is the energy uncertainty of the state $|1\rangle$ due to τ, via the

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[9] The Rutherford decay law was formulated only for the radioactive decay, originally. However, it is valid for any quantum particle decaying with a constant transition rate, as we show here.

spontaneous emission. Now, to compute the total survival probability, we can divide any finite time interval t, into $M = t/\Delta t$ segments, with $\frac{2\pi}{\omega_{1,0}} \ll \Delta t \ll \frac{1}{A}$. For the excited state to survive the whole time, it is clearly required that it is found to be in the original state $|1\rangle$ at the beginning of *each* segment. Therefore, we can apply Eq. 15.30 to *each* segment. By the rule of probability, we then get

$$\begin{aligned} P_{1\to 1}(t) &= (P_{1\to 1}(\Delta t))^M = (1 - A\Delta t)^M && \text{from the previous equation} \quad (15.31) \\ &= \left[(1 - A\Delta t)^{-1/(A\Delta t)}\right]^{-MA\Delta t} && A\Delta t \ll 1 \quad (15.32) \\ &\approx e^{-At} && \lim_{\delta\to 0}(1+\delta)^{1/\delta} = e, \quad M\Delta t = t \quad (15.33) \end{aligned}$$

proving the Rutherford decay law, Eq. 15.30, for *any* $t \geq 0$.

So far, we considered only one atom. In a real experiment, there will be a large number of atoms to be involved. So the Rutherford decay law can be, and is usually, written in terms of the number of particles, $N(t)$ (in the excited state, in the current example).

$$N(t) = N(0) \exp\left(-\frac{t}{\tau}\right) \qquad (15.34)$$

Note that if an atomic level can decay into multiple different energy levels, then its transition rate will add up. In that case,

$$\frac{1}{\tau} = A_1 + A_2 + A_3 + \ldots \qquad (15.35)$$

where A_i is the spontaneous emission rate for each final state involved.

15.8 Dipole selection rules

We shall refer to the condition for the non-vanishing matrix element ${}_1\langle \hat{\vec{\mathbb{p}}} \rangle_0 \propto {}_1\langle \hat{\vec{r}} \rangle_0$ as the **dipole selection rule**.

Here is the summary of all the rules.

$$\begin{aligned} \Delta m_l &= 0, \pm 1 && (15.36) \\ \Delta l &= \pm 1 && (15.37) \\ \Delta j &= 0, \pm 1 \qquad j = 0 \text{ to } j = 0 \text{ transition is forbidden} && (15.38) \end{aligned}$$

Additionally, the parity along the light polarization $\vec{\varepsilon}$ must flip.

Here, Δ means "1" minus "0." I.e., the value of state 1 minus the value of state 0.

Let me say a few words about the origin of these rules. Note that we are considering the matrix elements ${}_1\langle\hat{x}\rangle_0$, ${}_1\langle\hat{y}\rangle_0$, and ${}_1\langle\hat{z}\rangle_0$. The basic thing is that the three functions, x, y, z, correspond to the three states $|p_x\rangle$, $|p_y\rangle$, and $|p_z\rangle$, up to the factor $\sqrt{\frac{3}{4\pi}}\frac{1}{r}$, as we saw in Eq. 6.23. More explicitly, one can re-write Eq. 6.23 as

$$\begin{aligned}
x &= r\sqrt{\frac{2\pi}{3}}\left(Y_{1,-1} - Y_{1,1}\right) \\
y &= r\sqrt{\frac{2\pi}{3}}\, i\left(Y_{1,1} + Y_{1,-1}\right) \qquad (15.39) \\
z &= r\sqrt{\frac{4\pi}{3}}\, Y_{1,0}
\end{aligned}$$

Or, these can be thought of as coming directly from

$$Y_{10} = \sqrt{\frac{3}{4\pi}}\frac{z}{r} \qquad (15.40)$$

$$Y_{1,\pm 1} = \mp\sqrt{\frac{3}{4\pi}}\,\frac{1}{\sqrt{2}}\,\frac{x \pm iy}{r} \qquad (15.41)$$

Having expressed x, y, z in terms of $Y_{1,m}$'s in Eq. 15.39, the dipole selection rules above follow from the various aspects of the angular momentum addition. Recall that multiplying two angular momentum eigenfunctions correspond to adding the two angular momenta (cf. Eq. T4.186). Therefore, ${}_1\left\langle\hat{\vec{r}}\right\rangle_0$ can be thought of as "adding angular momentum of $\vec{r}$ to $|0\rangle$ and taking the inner product with $|1\rangle$."

$$\left\langle 1 \left| \hat{\vec{r}} \right| 0 \right\rangle = \underbrace{\langle n_1, l_1, m_{l,1}|}_{\text{must have } l_1 = l_t,\ m_{l,1} = m_t} \overbrace{\overbrace{\hat{\vec{r}}}^{l=1, m_l}\ \overbrace{|n_0, l_0, m_{l,0}\rangle}^{l_0, m_{l,0}}}^{\text{ang. mom. addition } = l_t, m_t} \qquad (15.42)$$

$$= \underbrace{\langle n_1, j_1, m_{j,1}|}_{\text{must have } j_1 = j_t,\ m_{j,1} = m_t} \overbrace{\overbrace{\hat{\vec{r}}}^{j=1, m_j}\ \overbrace{|n_0, j_0, m_{j,0}\rangle}^{j_0, m_{j,0}}}^{\text{ang. mom. addition } = j_t, m_t} \qquad (15.43)$$

where n_0 and n_1 represent non-angular-momentum quantum numbers, which are unimportant in the current discussion.

1. The rule $\Delta m_l = 0, \pm 1$ follows from the fact that m_l either goes up or down by one (for x or y) or stays the same (for z).
2. The rule $\Delta l = \pm 1$ follows from the fact that in adding two orbital angular momenta, l_0 and 1 (since x, y, z correspond to $l = 1$ as shown above), we get $l_t = l_0 + 1$, l_0, or $|l_0 - 1|$. So, we explain why $\Delta l = \pm 1$ is allowed. But, why is $\Delta l = 0$ (i.e., $l_1 = l_t = l_0$) not allowed? This is a bit complicated, and is explained below.
3. The rule $\Delta j = 0, \pm 1$ comes from the fact that x, y, z correspond to the *total* angular momentum 1 (as there is no spin component in x, y, z, when we view them in terms of the total angular momentum, they correspond to $j = l = 1$). However, $j_0 = 0$ to $j_1 = 0$ transition is disallowed, since it is impossible to add $j = 1$ to $j_0 = 0$ to get $j_t = 0$ (remember that $j_t = |j - j_0|, ..., j + j_0$).

Now, we discuss why the $\Delta l = 0$ transition is not allowed. This is due to the fact that $Y_{lm} r^l$ is a linear combination of the "l-th power of x, y, z," defined as $x^p y^q z^r$ with non-negative integer indices p, q, r satisfying $p + q + r = l$. This fact can be proven by induction, using the orthogonality of Y_{lm}'s. (If you prove it, please post your solution on line – bonus will be waiting for you!) Note that with this fact in hand, the fact that $\Delta l = 0$ is not allowed is easily proved: $\Delta l = 0$ involves the integral of a linear combination of odd powers of x, y, z each of which gives zero, when integrated, due to parity.

For alternative proofs of the first two selection rules, read Section T9.3.3. For an alternative proof of the third selection rule, read, e.g., page 240 by Sakurai, *Modern Quantum Mechanics*.

Note the following (from Eq. 15.39).

$$ {}_1\langle x \rangle_0 = i \, {}_1\langle y \rangle_0 \qquad \Delta m = 1 \tag{15.44} $$

$$ {}_1\langle x \rangle_0 = -i \, {}_1\langle y \rangle_0 \qquad \Delta m = -1 \tag{15.45} $$

So, it is not necessary to calculate ${}_1\langle y \rangle_0$ once ${}_1\langle x \rangle_0$ has been calculated.

What is the "rule" (as opposed to principle or law) nature of these conditions? They can be broken if higher order perturbations or higher multi-pole expansions are considered. So, if an excited state has an infinite lifetime ("forbidden transition") within the dipole approximation, in the sense as we developed it so far, it does not mean that the lifetime is really infinite. What it means is that lifetime will be long. Such a state is generally referred to as a **meta-stable state**.