Quantum theory of light-matter interaction: Fundamentals

Lecture 7

Atom in electromagnetic field

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BEFEKTETÉS A JÖVŐBE

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Introduction

In this lecture we will apply time-dependent perturbation theory introduced in the previous lecture to study atomic dynamics in an external time-periodic electromagnetic field.

We apply the dipole approximation, which means that the spatial dependence of the field can be neglected and the field strength is taken to be

$$\mathbf{E}(z,t) = \mathbf{E}_0 \cos \omega t.$$

Here, $\mathbf{E}_0$ is the field amplitude, which is assumed to be a constant in this lecture.
We have also learnt that the relevant interaction Hamiltonian in this case can be taken in the form

$$K_S = -\mathbf{D}\mathbf{E} = -\mathbf{D}\mathbf{E}_0 \cos \omega t.$$

Introduction

The equation to be solved is now the following time-dependent Schrödinger equation:

$$i\hbar\frac{\partial\left|\Psi(t)\right\rangle}{\partial t} = \left(H_0 + K(t)\right)\left|\Psi(t)\right\rangle = \left(H_0 - \mathbf{D}\mathbf{E}_0\cos\omega t\right)\left|\Psi(t)\right\rangle . \qquad \text{(SchE)}$$

We look for the amplitudes $C_k(t)$ in the expansion:

$$\left|\Psi(t)\right\rangle = \sum C_k(t)e^{-i\varepsilon_k t/\hbar}\left|k\right\rangle ,$$

where $\left|k\right\rangle$ is the eigenstate of H_0 with eigenvalue ε_k.
In Lecture 6, we derived the following equation for $C_k(t)$ in the first-order approximation

$$\frac{dC_k^{(1)}(t)}{dt} = -\frac{i}{\hbar}K_{ki}e^{i\omega_{ki}t}, \qquad \text{with the assumption } C_k^{(1)}(0) = \delta_{ik}.$$

The assumption means that the atom is *initially* in the stationary state $\left|i\right\rangle$.

Interaction with the atomic dipole

The matrix element K_{ki} is given by

$$K_{ki} = -\langle k|\,\mathbf{D}\,|i\rangle\,\mathbf{E}_0\cos\omega t = -\mathbf{d}_{ki}\mathbf{E}_0\cos\omega t,$$

where $\langle k|\,\mathbf{D}\,|i\rangle =: \mathbf{d}_{ki}$, as it is the dipole moment $\mathbf{D}$ that represents an atomic operator, while $\mathbf{E}_0\cos\omega t$ is an ordinary c number.
We shall not go beyond the first-order approximation in this lecture, so we omit the superscript (1) from now on, and write $C_k(t)$ for $C_k^{(1)}(t)$.

$$\frac{dC_k(t)}{dt} = -\frac{i}{\hbar}K_{ki}e^{i\omega_{ki}t} = \frac{i}{\hbar}\mathbf{d}_{ki}(\mathbf{E}_0\cos\omega t)e^{i\omega_{ki}t}$$

Solution for the final state amplitude

The differential equation

$$\frac{dC_k(t)}{dt} = -\frac{i}{\hbar} K_{ki} e^{i\omega_{ki} t} = \frac{i}{\hbar} \mathbf{d}_{ki} (\mathbf{E}_0 \cos \omega t) e^{i\omega_{ki} t}$$

is easily integrated:

$$C_k(t) = -\frac{i}{\hbar} \int_0^t K_{ki} e^{i\omega_{ki} t_1} dt_1 = \frac{i}{\hbar} \int_0^t \mathbf{d}_{ki} (\mathbf{E}_0 \cos \omega t) e^{i\omega_{ki} t'} dt' \qquad \text{for } k \neq i.$$

We are interested in a specific *final* state amplitude $C_f(t)$ i.e., $k = f \neq i$. As $\cos \omega t = (e^{i\omega t} + e^{-i\omega t})/2$, we can perform the integration:

$$C_f(t) = \frac{1}{\hbar} \frac{\mathbf{d}_{fi} \mathbf{E}_0}{2} \left(\frac{e^{i(\omega_{fi} + \omega)t} - 1}{\omega + \omega_{fi}} + \frac{e^{i(\omega_{fi} - \omega)t} - 1}{\omega_{fi} - \omega} \right).$$

Transition dipole moment

The *matrix element of the dipole moment operator*, $\mathbf{d}_{fi}$ sometimes called as the *transition dipole moment*, is a very important notion in atomic physics and spectroscopy. This is the atomic parameter that determines the probability of a transition, and in case of emission, the intensity of the emitted radiation.

$\mathbf{d}_{fi}$ is a vector, as the dipole moment operator is a vector itself. The $C_f(t)$ amplitude of the final state, and therefore the transition probability is nonzero only if $\mathbf{d}_{fi} \neq 0$.

This leads us to dipole selection rules, to be discussed a little later.

Absorbtion and stimulated emission I

We see in the solution

$$C_f(t) = \frac{1}{\hbar}\frac{\mathbf{d}_{fi}\mathbf{E}_0}{2}\left(\frac{e^{i(\omega_{fi}+\omega)t}-1}{\omega+\omega_{fi}}+\frac{e^{i(\omega_{fi}-\omega)t}-1}{\omega_{fi}-\omega}\right)$$

two terms that differ in their denominators.

(St) The first term is large and dominates if $\omega_{fi}+\omega \approx 0$, then $|\omega_{fi}-\omega| \approx 2\omega \gg 0$

(Ab) The second is large and dominates if $\omega_{fi}-\omega \approx 0$, then $|\omega_{fi}+\omega| \approx 2\omega \gg 0$

Note that for optical fields $\omega \simeq 10^{15}\ 1/s$.
In addition, the nominator of the dominant term varies slowly in time with frequency close to zero, in contrast to the other term where the nominator varies rapidly and has a small average over a time interval longer than $2\pi/\omega$.

Absorbtion and stimulated emission II

(St) case: we omit the second term and have

$$\omega_{fi} + \omega \approx 0, \qquad \varepsilon_f = \varepsilon_i - \hbar\omega. \tag{St}$$

The final state has lower energy than the initial one, this process corresponds to *stimulated (or induced) emission* driven by the external field. The atom emits a "photon" of energy $\hbar\omega$ and its energy decreases.

(Ab) case: we omit the first term and have

$$\omega_{fi} - \omega \approx 0, \qquad \varepsilon_f = \varepsilon_i + \hbar\omega. \tag{Ab}$$

The final state has higher energy than the initial one, this process corresponds to *absorbtion* driven by the external field. The atom absorbs a "photon" of energy $\hbar\omega$ and its energy increases.

Quote marks refer to the situation: *no quantized field=no photon.* The concept of the photon makes no sense actually in this approach. Still allowed to speak of it, as QED leads essentially to the same result.

Absorbtion and stimulated emission III

The description of the two processes are very similar, and we can write both as a single equation for C_f, where the upper sign refers to (St), the lower to (Ab)

$$C_f(t) = \frac{1}{\hbar}\frac{\mathbf{d}_{fi}\mathbf{E}_0}{2}\left(\frac{e^{i(\omega_{fi}\pm\omega)t/2} - e^{-i(\omega_{fi}\pm\omega)t/2}}{\omega_{fi}\pm\omega}\right)e^{i(\omega_{fi}\pm\omega)t/2},$$

where we picked out a factor $e^{i(\omega_{fi}\pm\omega)t/2}$, for later convenience. For the probability of finding the system in the state f we take the square of the absolute value of the probability amplitude,

$$\left|C_f(t)\right|^2 = \left(\frac{\mathbf{d}_{fi}\mathbf{E}_0}{2\hbar}\right)^2 \frac{\sin^2\left[(\omega_{fi}\pm\omega)t/2\right]}{\left[(\omega_{fi}\pm\omega)/2\right]^2} = \left(\frac{\mathbf{d}_{fi}\mathbf{E}_0}{2\hbar}\right)^2 4\frac{\sin^2\frac{\Delta t}{2}}{\Delta^2},$$

where $\Delta := \omega_{fi}\pm\omega$. The expression above is signficant when $(\varepsilon_f - \varepsilon_i)/\hbar = \omega$ (absorbtion: upper sign), or when $(\varepsilon_f - \varepsilon_i)/\hbar = -\omega$, (stimulated emission: lower sign).

Transition probability

Take for a moment $\mathbf{d}_{fi}\mathbf{E}_0 = d_{fi}E_0$ (we will correct this below).

$$P_f(t) = \left|C_f(t)\right|^2 = \left(\frac{d_{fi}E_0}{2\hbar}\right)^2 t^2 \frac{\sin^2\frac{\Delta t}{2}}{(\Delta t/2)^2}$$

For $\Delta = 0$, the factor $\frac{\sin^2\frac{\Delta t}{2}}{(\Delta t/2)^2} = 1,$ the probability of finding the system in $|f\rangle$

$$P_f(t, \Delta = 0) = \left(\frac{d_{fi}E_0}{2\hbar}\right)^2 t^2$$

grows as t^2, which cannot be the case for long times, because normalization requires $\sum_k |C_k(t)|^2 = 1$.

Perturbation theory fails. The effect of a monochromatic field in exact resonance with the atomic transition cannot be calculated in this way.

Interaction with a field with a wide-band spectrum

Still the previous result can be used when the atom is placed in the field which has a *wide-band spectrum*, like black-body radiation.

Then the divergence in the formula for $\left|C_f(t)\right|^2$ above is compensated by the effect, that the interaction is effective only with an infinitesimal part of the spectrum where the atom emits or absorbs.

In order to see this, we use first the limiting form of the function $g(t,\Delta) = \frac{\sin^2[\Delta t/2]}{t(\Delta/2)^2} = t\frac{\sin^2[\Delta t/2]}{t^2(\Delta/2)^2}$. Then $g(t,0) = t$, and $g(t,\Delta) < 1/(t(\Delta/2)^2)$ for $\Delta t > 2\pi$. For any smooth function, $f(\Delta)$:

$$\lim_{t\to\infty}\int f(\Delta)\frac{\sin^2\left[\Delta t/2\right]}{t(\Delta/2)^2}d\Delta = 2\pi f(0)$$

$$\text{thus} \qquad \lim(t\to\infty)\frac{\sin^2\left[\Delta t/2\right]}{(\Delta/2)^2} = 2\pi t\delta(\Delta)$$

where $\delta(\Delta)$ is the Dirac delta.

Golden rule

$$\lim(t \to \infty) \left|C_f(t)\right|^2 = 2\pi t \frac{(d_{fi}E_0)^2}{4\hbar^2} \delta(\omega_{fi} \pm \omega)$$

The transition probability per unit time is given by for the (Ab) case:

$$w_{fi} = \frac{1}{t} \left|C_f(t)\right|^2 = \frac{(d_{fi}E_0)^2}{2\hbar^2} \pi \delta(\omega_{fi} - \omega).$$

This is a specific case of a more general rule called *Fermi's golden rule*, describing an energy conserving transition from or to a discrete level or level pairs to continuum. Here the role of the continuum is played by all the possible photon energies $\hbar\omega$. The derivation is due to Dirac, who did this earlier than Fermi.

Transition rate =Transition probability/unit time

Now if the field is polychromatic E_0^2 is to be replaced by $E^2(\omega)d\omega$, where $E(\omega)$ is the Fourier amplitude (spectrum) of the field at the angular frequency ω, and the transition probability per unit time is obtained after integration with respect to ω :

$$w_{fi} = \pi \int \frac{(d_{fi})^2}{2\hbar^2} E^2(\omega)\delta(\omega_{fi} - \omega)d\omega = \pi \frac{d_{ki}^2}{2\hbar^2} E_0^2(\omega_{fi}).$$

The square of the field amplitude is proportional to the field energy density, and it will be useful to make use of :

$$\overline{u(\omega)} = \frac{1}{2}\varepsilon_0 \overline{E^2(\omega)} + \frac{1}{2\mu_0}\overline{B^2(\omega)} = \varepsilon_0 \overline{E^2(\omega)} = \frac{1}{2}\varepsilon_0 E_0^2(\omega),$$

which is valid for plane waves. Time average of the $\cos^2\omega t$ introduces the factor 1/2. Then $E_0^2(\omega) = 2\overline{u(\omega)}/\varepsilon_0$ and the transition probability/unit time

$$w_{fi} = \pi \frac{d_{fi}^2}{\varepsilon_0 \hbar^2} u(\omega_{fi}).$$

Random direction correction

We have taken so far $\mathbf{d}_{fi}\mathbf{E} = d_{fi}E$, while in reality the relative direction of $\mathbf{d}_{fi}$ and $\mathbf{E}$ is a random angle ϑ.
Thus $\mathbf{d}_{fi}\mathbf{E} = d_{fi}E\cos\vartheta$, and spatial averaging of the square containing $\cos^2\vartheta$ over all directions yields $1/3$.
So the the final result for absorbtion is

$$\text{transition probability/unit time=transition rate=} \; w_{fi} = \frac{\pi d_{fi}^2}{3\varepsilon_0\hbar^2} u(\omega_{fi})$$

The result is the same for the (Ab) and the (St) case, so
w_{fi} *is proportional to the energy density of the field,* $u(\omega)$ *in both cases* with the same constant of proportionality. (This is to be refined when level degeneracy is taken into account).

B coefficient

Long before this quantum theoretical calculation, done first by Dirac in 1927, in 1916 Einstein simply postulated the existence of absorbtion and stimulated emission, when he introduced phenomenologically the notion of *transition probability and transition rate* into atomic physics. (Ironically, later on, he became the main opponent of the sole probabilistic interpretation of quantum physics.)

Einstein denoted the coefficient multiplying $u(\omega_{fi})$ by B_{if}, so

$$B_{if} = \frac{\pi d_{fi}^2}{3\varepsilon_0 \hbar^2}. \tag{Bcoeff}$$

Lacking genuine quantum mechanics in 1916, Einstein could not calculate the explicit value from the atomic data, seen to be contained in the matrix element d_{fi}. (Note the order of the indices in B_{if} is the opposite to the one used in quantum mechanics.)

A coefficient

Besides (Ab) and (St) Einstein did also consider spontaneous emission (Sp) and postulated the transition from an upper to a lower level even without the presence of the field, and denoted the transition rate from level 2 to level 1 by A_{21}.

Note that quantum electrodynamics puts this process into a different perspective, explaining spontaneous emission by the effect of fluctuations of the vacuum field.

By a simple consideration of the transition rates for a gas of atoms, which is assumed to be in thermal equilibrium with a cavity filled with black body radiation, Einstein derived a simple relation between the B and A coefficients.

Einstein's argument

Einstein's argument
Denote here the lower and upper levels by indices 1 and 2, and the number of atoms in the corresponding levels by N_1 and N_2, respectively.

According to the three possible processes considered by Einstein, the rate equations are obviously

$$\dot{N}_1 = (B_{21}N_2 - B_{12}N_1)u(\omega_0) + A_{21}N_2, \quad \dot{N}_2 = -\dot{N}_1 \tag{Einstein}$$

with $\omega_0 = \omega_{fi} = (\varepsilon_2 - \varepsilon_1)/\hbar$.
In *thermal equilirium*, when the time derivatives vanish and according to Boltzmann we must have $N_2/N_1 = e^{-\hbar\omega_0/kT}$, we obtain

$$u(\omega_0) = \frac{A_{21}}{B_{21}} \frac{1}{\frac{B_{12}}{B_{21}}\frac{N_1}{N_2} - 1} = \frac{A_{21}}{B_{21}} \frac{1}{\frac{B_{12}}{B_{21}} e^{\hbar\omega_0/kT} - 1}.$$

Einstein's A coefficient, and spontaneous lifetime

Compare this with Planck's formula for $u_P(\omega_0)$ of black body radiation

$$u(\omega_0) = \frac{A_{21}}{B_{21}} \frac{1}{\frac{B_{21}}{B_{12}} e^{\hbar\omega_0/kT} - 1} \quad \text{compare} \quad u(\omega_0) = \frac{\hbar\omega_0^3}{\pi^2 c^3} \frac{1}{e^{\hbar\omega_0/kT} - 1}$$

(Planck)

yielding:

$$A_{21} = B_{21} \frac{\hbar\omega_0^3}{\pi^2 c^3} \qquad B_{21} = B_{12}.$$

Note that this is to be modified if level degeneracy is taken into account. This is left to a problem.

An interpretation of the factor: $\frac{\hbar\omega_0^3}{\pi^2 c^3}$. The product of $\hbar\omega_0$ (single photon energy) times the volume mode density at ω_0: $\frac{\omega_0^2}{\pi^2 c^3}$.

Problem:

In case of degenerate levels, i.e., multiple quantum states with the same energies this is to be modified. Repeat the above derivation with level degeneracies g_i, and show that $g_1 B_{12} = g_2 B_{21}$.

A coefficient and spontaneous lifetime

In case of nondegenerate levels then

$$A_{21} = \frac{\pi d_{21}^2}{3\varepsilon_0 \hbar^2} \frac{\hbar\omega_0^3}{\pi^2 c^3} = \frac{1}{4\pi\varepsilon_0} \frac{4}{3} \frac{d_{ki}^2 \omega_0^3}{\hbar c^3} = \gamma_0$$

Important notes:

1. The inverse of the spontaneous transition rate

$$1/\gamma_0 = \tau_0$$

   is the natural life time of the level if there is only one lower state where to decay.

2. According to the rate equation in the absence of external fields this decay is exponential.

Problem:

Show that exponential decay results in Lorentzian line shape with a line width γ_0, this is called the natural line width.

On spontaneous lifetime

3. The life time is inversely proportional to ω_0^3, so the lifetimes of levels are much smaller in the visible than, say, in the infrared.

Problems:

Estimate the lifetime of an atomic transition in the visible domain around $\lambda_0 = 500$ nm , by assuming as an order of magnitude $d = q_0 a_0$, where q_0 is the charge of the electron and a_0 is the Bohr radius.

Calculate the life time more precisely corresponding to the Lyman α line ($2p \to 1s$) of the H atom.

Role of the dipole matrix element

The dipole transition matrix elements $\mathbf{d}_{fi} = \langle f | \, \mathbf{D} \, | i \rangle$ must be nonzero in order to have a transition in the dipole approximation.

We derive now certain selection rules that determine when these matrix elements are nonzero.

In atoms the single active electron we consider is in the field of the other electrons which can be approximated by a central potential $V(r)$. This is exact in the case of Hydrogen like atoms where the potential of the unperturbed electron is the Coulomb field originating from the nucleus.

Parity of a quantum state

In a central potential the square of the orbital angular momentum is a constant of motion, as well as any of its components as the commutators $[H_0, L^2] = [H_0, L_i] = 0$ for $i = x, y, z$.

This is the reason why in the case of atoms the orbital angular momentum quantum number ℓ as well as the magnetic quantum number m are good quantum numbers, they can be used to label the eigenstates of H_0.

An important point also is that the angular momentum eigenstates have definite parity, i. e. on reflection with respect to the origin they are are either even or odd depending on ℓ .
In the abstract notation with the parity operator or in coordinate representation this means

$$\Pi \left|u_{n,\ell,m}\right\rangle = (-1)^{\ell} \left|u_{n,\ell,m}\right\rangle ,$$

$$\Pi u_{n,\ell,m}(\mathbf{r}) = u_{n,\ell,m}(-\mathbf{r}) = (-1)^{\ell} u_{n,\ell,m}(\mathbf{r}).$$

Parity and dipole moment anticommute

Laporte rule:

Dipole transition is possible only between states of different parity.

Proof: The dipole moment operator for a single electron is $\mathbf{D} = q_0\mathbf{R}$, here q_0 is the charge of the electron, $q_0 < 0$, and $\mathbf{R}$ points from the nucleus to the electron.

The parity operator anticommutes with $\mathbf{R}$, as the latter is a polar vector, i.e., it changes sign if mirroring with respect to the origin. This means that $\Pi\mathbf{R} = -\mathbf{R}\Pi = 0$, or $\Pi\mathbf{R} + \mathbf{R}\Pi = 0$.

To see this take any function $\psi(\mathbf{r})$, and calculate

$$\Pi(\mathbf{R}\psi(\mathbf{r})) = \Pi(\mathbf{r}\psi(\mathbf{r})) = -\mathbf{r}\psi(-\mathbf{r}).$$

On the other hand, $\mathbf{R}(\Pi\psi(\mathbf{r})) = \mathbf{r}\psi(-\mathbf{r})$, which proves the anticommutation.

Proof of Laporte rule

We use that parity is a selfadjoint operator and calculate

$$0 = \langle u_{n',\ell',m'}|\Pi\mathbf{R} + \mathbf{R}\Pi|u_{n,\ell,m}\rangle = \tag{1}$$

$$(-1)^{\ell'}\langle u_{n',\ell',m'}|\mathbf{R}|u_{n,\ell,m}\rangle + (-1)^{\ell}\langle u_{n',\ell',m'}|\mathbf{R}|u_{n,\ell,m}\rangle = \tag{2}$$

$$((-1)^{\ell'} + (-1)^{\ell})\langle u_{n',\ell',m'}|\mathbf{R}|u_{n,\ell,m}\rangle. \tag{3}$$

Because $(-1)^{\ell'} + (-1)^{\ell} = \pm 2$ whenever ℓ' and ℓ are of the same parity, the other factor must then be zero

$$\langle u_{n',\ell',m'}|\mathbf{R}|u_{n,\ell,m}\rangle = 0, \quad \text{if } \ell^{'} \text{ and } \ell \text{ are of the same parity.}$$

This proves Laporte rule.

Problem: Prove the same result by using the coordinate representation form of the above matrix element.

The selection rule for angular momentum quantum number

A special case of the Laporte rule is that the diagonal matrix elements of **R** and **D** do vanish, as then the two eigenstates have obviously the same parity.

The same result holds whenever the difference of ℓ and ℓ' is even.

In reality the selection rules for dipole transitions are more stringent. The matrix elements of **R** vanish unless $\Delta\ell = \pm 1$.

This selection rule is also connected with a symmetry, it follows from the rotational properties of **R** and $|u_{n,\ell,m}\rangle$. It will not be proven here, neither the more complicated selection rules between levels depending on the spin, etc.
See the specialized literature in atomic physics.

Questions

1. What is the operator the matrix elements of which play the most important role in describing an atom in electromagnetic radiation?
2. What physical processes were we able to identify using a perturbative approach?
3. Why first order perturbation calculations are valid only on a short time scale?
4. What is the usual name for the "one to many" (from a discrete level to continuum) transition rate?
5. What physical quantity of the broadband radiation determines the transition rate w_{fi}?
6. What physical process is described by Einstein's B coefficient?

Questions (continued)

7. What physical process is described by Einstein's A coefficient?
8. Without degeneracy, what is the relation between Einstein's A and B coefficients?
9. Show that exponential decay results in Lorentzian line shape with a line witdth γ_0, this is called the natural line width.
10. Estimate the life time of an atomic transition in the visible domain around $\lambda_0 = 500$ nm , by assuming as an order of magnitude $d = q_0 a_0$, where q_0 is the charge of the electron and a_0 is the Bohr radius.
11. Calculate the life time more precisely corresponding to the Lyman α line ($2p \to 1s$) of the H atom.
12. What is Laporte rule?
13. Prove Laporte rule by using the coordinate representation form of the matrix elements.

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