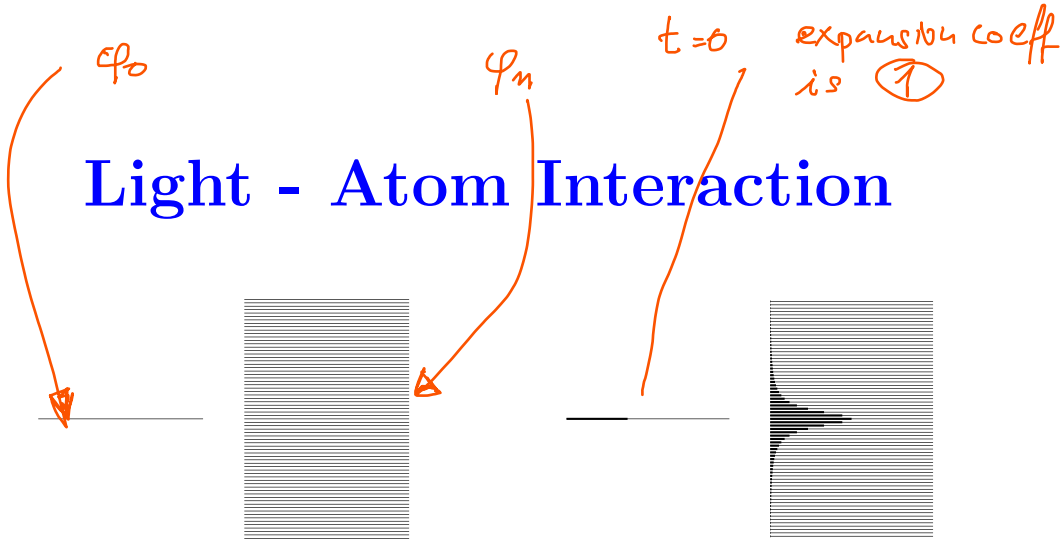


# Light - Atom Interaction



PHYS261 autumn 2013

Version 04.12.2013

[Go to list of topics](#)

2 level state



Overview Discussion

**Time dep. QM- two-well problem**

**One level in continuum**

→ Time-Dependent Schrödinger Equation

**Perturbation theory for TDSE**

→ Dirac delta-function ✓

→ Fermi Golden Rule ✓ *time independ*

→ **Constant rate and exponent. decay** ✓

→ **Line width from exponential decay** ✓

Emission of Radiation by Excited Atom

**The matrix element reduction**

Dipole Approximation

Detailed Evaluation of Emission rate

**Final  $W = 1/\tau$  result**

Stimulated emission

~~Eigenmodes for coupled vibrations.~~ ✓

Algebraic Method for Harm. Osc.

Quant. th. of extended systems - fields

Electromagnetic fields

**The Quant Th. of Elmag. Field**

Density of States →

Charged Particles In an Elmag. Field

The Hamiltonian of Interaction

Golden Rule Simulator part

T.-Dep. Schrödinger Eq. in Simulator

Atomic Units

[Go to list of topics](#)

## Overview

1. Time dependent quantum mechanics:  
two isolated states, contrasted to  
one isolated level  
energetically embedded in (quasi-) continuum of states
2. derivation and understanding of the transition rate (probability change per time unit)
3. Time dependent perturbation theory
4. Fermi Golden rule derivation
5. The delta function (often mentioned as energy conservation; that is not precise).

6. In contrast to the delta function, the Lorentzian shape; finite line width (also known as Breit-Wigner formula or shape)
7. Electromagnetic field is an extended (actually continuous) system, therefore we must learn how to understand eigenmodes of large system. Coupled oscillators transformed to a system of independent, de-coupled eigenmodes.
8. Any harmonic oscillator can be described by so called creation and annihilation operators. Harmonic oscillator via the algebraic method.
9. Follows quantization of the radiation field; **photons**
10. Evaluation of the transmission rate for the emission process
11. Spontaneous and Stimulated Emission

[Go to list of topics](#)

# 1 Time dependent Q.M. - Two-well problem

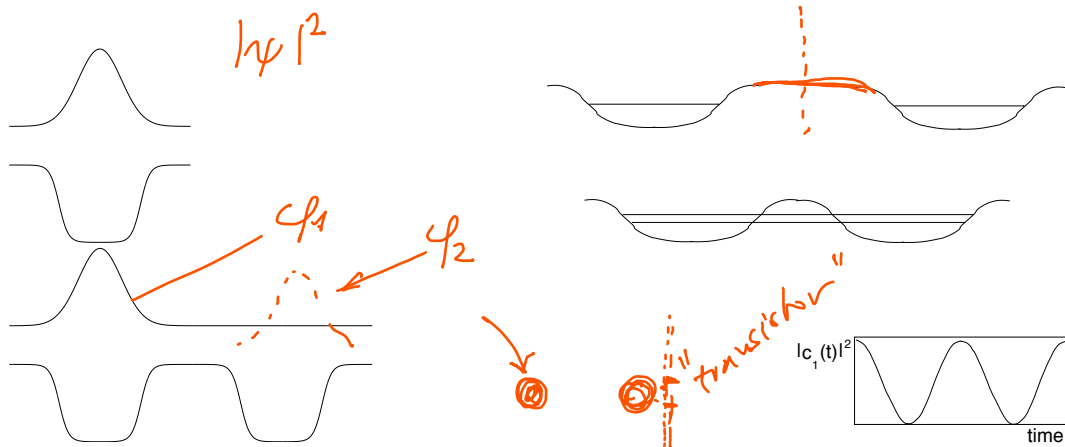


Figure 1: Top left: Well with 1 bound state; Bottom left: Two wells. System (particle) placed in a state which is not an eigenstate Right column: Eigenstates and time oscillations of population

[Go to list of topics](#)

Quantum "dot"  $\equiv$  artificial atoms  
 2 dots place electron in 1 dot

The two eigenstates in each of the isolated wells are  $\varphi_1$  and  $\varphi_2$ .

The static eigenstates of the particle confined to both of the wells are approximated by

$$\psi_+ = \frac{1}{\sqrt{2}} (\varphi_1 + \varphi_2)$$

$$\psi_- = \frac{1}{\sqrt{2}} (\varphi_1 - \varphi_2)$$

$$(T + V_1) \varphi_1 = \varepsilon \varphi_1$$

Clearly,

$$(T + V_2) \varphi_2 = \varepsilon \varphi_2$$

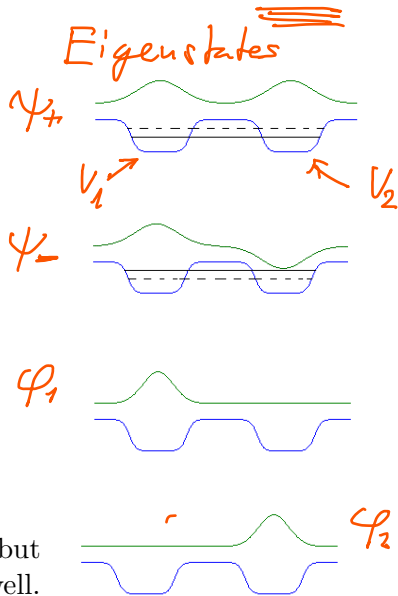
$$\varphi_1 = \frac{1}{\sqrt{2}} (\psi_+ + \psi_-)$$

$$\varphi_2 = \frac{1}{\sqrt{2}} (\psi_+ - \psi_-)$$

The states  $\psi_+, \psi_-$  are eigenstates of the Hamiltonian, but  $\varphi_1, \varphi_2$  are not, they are eigenstates for each isolated well.

Go to list of topics

$$H = T + V_1 + V_2$$



$$i\hbar \frac{\partial}{\partial t} \Psi = E \Psi \quad e^{i\omega_+ t} \psi_+ + e^{i\omega_- t} \psi_- \quad |\Psi(t)|^2$$

If at  $t = 0$  the system is brought into the state  $\varphi_1$ ,

$$\Psi(t = 0) = \varphi_1 = \frac{1}{\sqrt{2}} (\psi_+ + \psi_-)$$

then at any other later time

$$\Psi(t) = \frac{1}{\sqrt{2}} (\psi_+ e^{-iE_+ t/\hbar} + \psi_- e^{-iE_- t/\hbar})$$

This can be rewritten schematically as

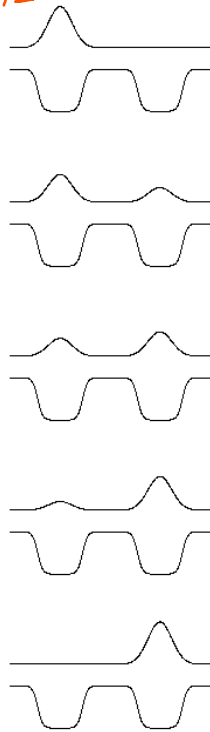
$$C(t) = e^{-i\omega_+ t} \quad \Psi(t) = C(t) (\psi_+ + \psi_- e^{i\omega t})$$

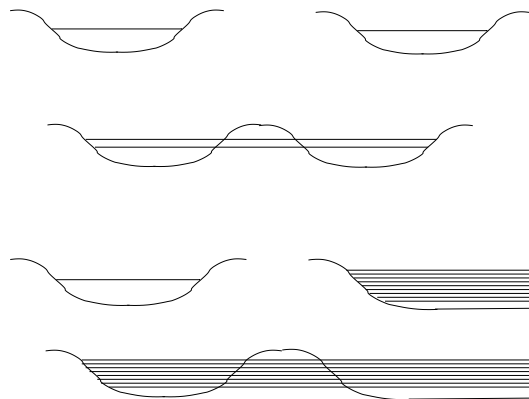
so that we can see immediately that for

$$t_n = n \frac{\pi}{\omega}$$

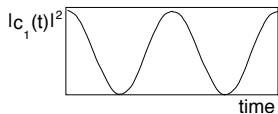
the  $\Psi(t_n)$  will be a multiple of  $\varphi_1$ , i.e. concentrated to the left, for even  $n$ , and a multiple of  $\varphi_2$ , i.e. to the right, for odd  $n$ . At other times there would be a changing distribution between the two regions.

List of topics





oscillation  
2 states



decay

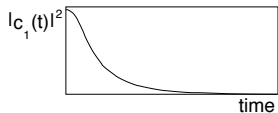
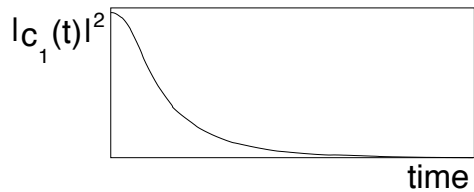
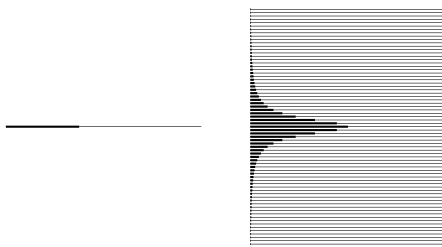


Figure 2: Above: 2 isolated states in two equal potential wells ; starting in left well - oscillations. Below: Many states in two potential wells; starting in left well - decay [Go to list of topics](#)







[Go to list of topics](#)

## 2 Time-Dependent Schrödinger Equation

Go to list of topics

The time-dependent Schrödinger equation

$$\langle \phi_j | \quad i \hbar \frac{\partial}{\partial t} | \psi(t) \rangle = H(t) | \psi(t) \rangle \quad (3)$$

is very often solved via a transformation to the matrix formulation. The matrix formulation arises from expansion of the unknown wavefunction  $|\psi(t)\rangle$  in a set of basis functions  $|\phi_i\rangle$ , much in analogy with Fourier series or expansions using orthogonal polynomials

$$|\psi(t)\rangle = \sum \alpha_i(t) |\phi_i\rangle \quad \text{Expansion} \quad (4)$$

The unknown quantities to be found are the expansion coefficients, which form a vector. In this formulation, the time-dependent Schrödinger equation (eq. (3) above) is replaced by a set of coupled differential equations.

(we shall use the same technique for time-independent)

$|\psi(t)\rangle = \sum_i \alpha_i(t) |\phi_i\rangle$   $\langle \beta |$   
 The system of coupled equations is conveniently expressed by matrix notation

2.

$$i \hbar \frac{d}{dt} \begin{bmatrix} \alpha_1 \\ \alpha_2 \\ \vdots \\ \alpha_n \end{bmatrix} = \begin{bmatrix} H_{11}(t) & H_{12}(t) & \dots & H_{1n}(t) \\ H_{21}(t) & H_{22}(t) & \dots & H_{2n}(t) \\ \dots & \dots & \dots & \dots \\ H_{n1}(t) & H_{n2}(t) & \dots & H_{nn}(t) \end{bmatrix} \begin{bmatrix} \alpha_1 \\ \alpha_2 \\ \vdots \\ \alpha_n \end{bmatrix}$$

where

$$H_{ij}(t) = \langle \phi_i | H(t) | \phi_j \rangle$$

This can also be written as

3.

$$i \hbar \begin{bmatrix} \dot{\alpha}_1 \\ \dot{\alpha}_2 \\ \vdots \\ \dot{\alpha}_n \end{bmatrix} = \begin{bmatrix} H_{11}(t) & H_{12}(t) & \dots & H_{1n}(t) \\ H_{21}(t) & H_{22}(t) & \dots & H_{2n}(t) \\ \dots & \dots & \dots & \dots \\ H_{n1}(t) & H_{n2}(t) & \dots & H_{nn}(t) \end{bmatrix} \begin{bmatrix} \alpha_1 \\ \alpha_2 \\ \vdots \\ \alpha_n \end{bmatrix}$$

which is a short-hand notation for

1.

$$i \hbar \dot{\alpha}_k = \sum_i H_{ki}(t) \alpha_i$$


Eq. for  
the  
expansion  
coefficients

[Go to list of topics](#)

### 3 Perturbation theory for the Time-dependent Schrödinger Equation

Go to list of topics

To apply the perturbation theory, we must identify the small perturbation term. Usually the Hamiltonian  $H(t)$ , differs only slightly from well known Hamiltonian  $H^0$  so that the perturbation  $H'(t)$

 constant  $H$



$$H(t) = H^0 + H'(t) \quad \text{small!} \quad (5)$$

*Handwritten notes: TDPT, TDS E,  $H^0 + V(t)$*

If the perturbation  $H'(t)$  were not present, and choosing then as  $|\phi_k\rangle$  the eigensolutions of

$$H^0 |\phi_k\rangle = E_k |\phi_k\rangle \quad (6)$$

the matrix for  $H(t) \rightarrow H^0$  would be diagonal with the eigenenergies  $E_k$  on the diagonal. The solutions for the the  $\alpha_k(t)$  would be then very simply

$$\alpha_k(t) = e^{-iE_k t/\hbar} \quad (7)$$

and for usual stationary states only one of the  $\alpha_k(t)$  would be different from

zero. Since the probability  $\underline{P_a}$  of the system being in a state  $\underline{a}$  is

$$P_a(t) = |\alpha_a(t)|^2$$

it means that the system with probability 1 is in that state  $a$ , and with 0 in any other state, i.e.

$$|\alpha_k(t=0)| = \underline{\delta_{ka}} \quad (8)$$

If the perturbation really is small, the  $|\alpha_a(t)|$  remains  $\approx 1$  for all times  $t$ , while all others remain close to zero.

We will thus use the so called perturbation theory, an approximate method to solve the system of equations

$$i \hbar \dot{\alpha}_k = \sum_i H_{ki}(t) \alpha_i$$

while keeping

$$|\alpha_a(t)| \approx 1 \quad \longrightarrow \quad \underline{\alpha_a(t) = 1}$$

and "preserving"

[Go to list of topics](#)

$$|\alpha_k(t=0)| = \delta_{ka} \quad \longrightarrow \quad |\alpha_k(t > 0)| \approx 0 \quad \text{for } k \neq a$$

To simplify the notation we make a substitution  $\alpha_k(t) \rightarrow c_k(t) \exp(-i\frac{E_k}{\hbar}t)$ .  
 Inserting this into the last equation

$$i \hbar \dot{\alpha}_k = \sum_i H_{ki}(t) \alpha_i \quad \alpha \rightarrow c$$

we get (using  $d/dt(c \exp(-iEt)) = \dot{c} \exp(-iEt) + -iE c \exp(-iEt)$ )

$$(i \hbar \dot{c}_k + E_k c_k) \exp(-i\frac{E_k}{\hbar}t) = \sum_i H_{ki}^0 c_i \exp(-i\frac{E_i}{\hbar}t) + \sum_i H_{ki}(t) c_i \exp(-i\frac{E_i}{\hbar}t)$$

With  $H_{ki}^0 = E_k \delta_{ki}$   $\omega_{ka} = \frac{E_k - E_a}{\hbar}$  (9)

$$i \hbar \dot{c}_k + E_k c_k = E_k c_k + \sum_i H'_{ki}(t) c_i \exp(i\frac{E_k - E_i}{\hbar}t)$$

$$i \hbar \begin{bmatrix} \dot{c}_1 \\ \dot{c}_2 \\ \vdots \\ \dot{c}_n \end{bmatrix} = \begin{bmatrix} H'_{11}(t) & H'_{12}(t)e^{i\omega_{12}t} & \dots & H'_{1n}(t)e^{i\omega_{1n}t} \\ H'_{21}(t)e^{i\omega_{21}t} & H'_{22}(t) & \dots & H'_{2n}(t)e^{i\omega_{2n}t} \\ \dots & \dots & \dots & \dots \\ H'_{n1}(t)e^{i\omega_{n1}t} & H'_{n2}(t)e^{i\omega_{n2}t} & \dots & H'_{nn}(t) \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \\ \vdots \\ c_n \end{bmatrix} \quad \begin{matrix} 1 \\ 0 \\ 0 \\ 0 \end{matrix}$$

[Go to list of topics](#)

Taking the perturbation theory assumptions

$$|\alpha_a(t)| \approx 1 \quad |\alpha_{k \neq a}(t > 0)| \approx 0 \quad \longrightarrow \quad |\alpha_k(t = 0)| = \delta_{ka}$$

the above matrix system of coupled equations decouple - we get independent equations for each  $c_k(t)$

$$i \hbar \frac{d}{dt} c_k(t) = H_{ka}(t) e^{i\omega_{ka}t} \quad (10)$$

where we made a substitution  $\alpha_k(t) \rightarrow c_k(t) \exp(-i\frac{E_k}{\hbar}t)$ .

We say that the original assumption about the coefficients is a 'zero-th order approximation, thus the superscript (0), :

$$c_k^{(0)} = \delta_{ka} \quad (\delta_{(k-a)}) \quad (11)$$

while the above equation is the first order, thus we rewrite it

$$\dot{c}_b^{(1)} = \frac{1}{i\hbar} H' e^{(i\omega_{ba}t)} \quad H \text{ time index} \quad (12)$$

A detailed description of perturbation theory pictures it as an iterative process. Each order is obtained by applying the preceding order of the approximation.

[Go to list of topics](#)

Equation of the form  $\dot{c} = f(t)$  is easily solved by integration  $\Rightarrow c = \int f(t) dt$  time-independent case

$$c_b^{(1)}(t) = \frac{1}{i\hbar} \int_{t_b}^t H' e^{i\omega_{ba}t'} dt' \quad \underline{H'(t) \equiv H'} \quad (13)$$

So the transition probability for going from a state 'a' to a state 'b' is defined like [Go to list of topics](#)

Apply the same to Time-indep.

$$P_{ba}(t) = |c_b^{(1)}(t)|^2 \quad (14)$$

Now we evaluate the integral in eq.(13), which is elementary for a constant potential: [Go to list of topics](#)

constant of time

$$\int e^{iat} dt = \frac{1}{ia} e^{iat}$$

$$c_b^{(1)}(t) = H'_{ba} \frac{1}{i\hbar} \int_{t_0}^t e^{i\omega_{ba}t} dt \quad ; \quad \underline{t_0 = 0}$$

$$= H'_{ba} \frac{1}{i\hbar} \frac{1}{i\omega_{ba}} (e^{i\omega_{ba}t} - 1)$$

$$= -\frac{H'_{ba}}{\hbar\omega_{ba}} (e^{i\omega_{ba}t} - 1)$$

solution approx.

(15)



and rearrange  $(e^{i\omega t} - 1)$  (in the following:  $\omega_{ba} \rightarrow \omega$ )

$$\begin{aligned} e^{i\omega t} - 1 &= e^{i\frac{\omega t}{2}} \left[ e^{i\frac{\omega t}{2}} - e^{-i\frac{\omega t}{2}} \right] \\ &= 2ie^{i\frac{\omega t}{2}} \sin \frac{\omega t}{2} \end{aligned}$$

$$\begin{aligned} e^a - 1 &= e^{a/2} (e^{a/2} - e^{-a/2}) \\ \frac{e^{ia} - e^{-ia}}{2i} &\equiv \sin a \end{aligned}$$

Inserting this back into eq.(13)

$$c_b^{(1)}(t) = \frac{1}{i\hbar} \int_{t_0}^t H' e^{i\omega t'} dt' \quad (16)$$

$$|c_b^{(1)}(t)|^2 = \frac{1}{\hbar^2} |H'_{ba}|^2 F(t, \omega) \quad F(t, \omega) = 4 \cdot \frac{\sin^2 \frac{\omega t}{2}}{\omega^2} \quad (17)$$

where the phase factor reduces to its absolute value one.

[Go to list of topics](#)

## 4 Dirac delta-function

[Go to list of topics](#)

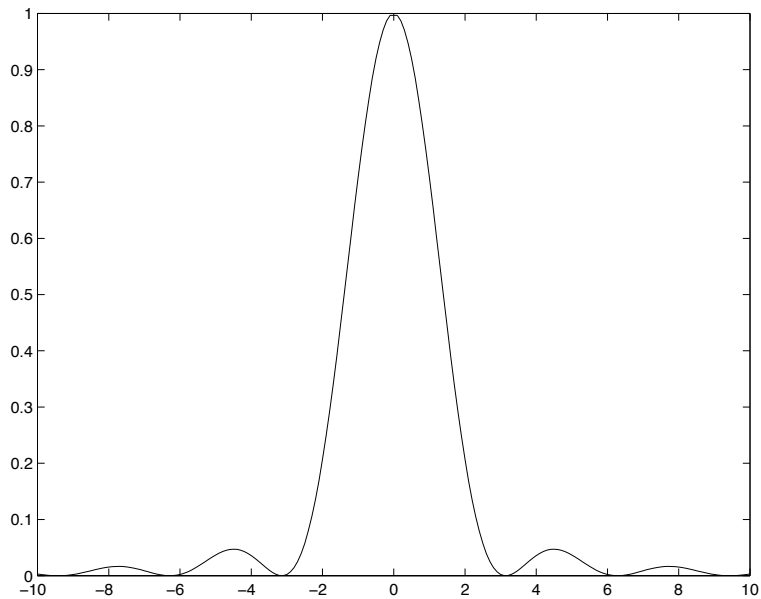
It is easy to find that the 'F' is a function of  $t$  and  $\omega$ , and for each time 't' it is equal to

$$\begin{aligned} F(t, \omega) &= 4 \cdot \frac{\sin^2 \frac{\omega t}{2}}{\omega^2} \\ &= 4 \cdot \frac{t^2}{4} \cdot \frac{\sin^2 \frac{\omega t}{2}}{\frac{\omega^2 t^2}{4}} \\ &= t^2 \cdot \frac{\sin^2 x}{x^2} \quad ; \quad \left( x = \frac{\omega t}{2} \right) \end{aligned}$$

$\omega, t$   
 $x, \omega$   
 $x, t$

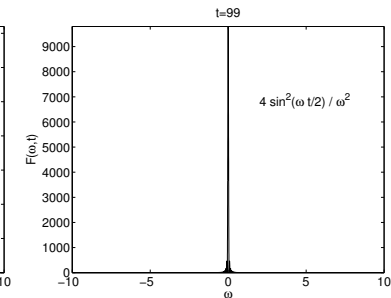
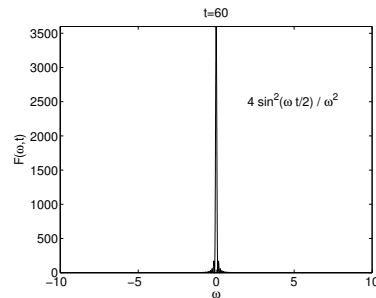
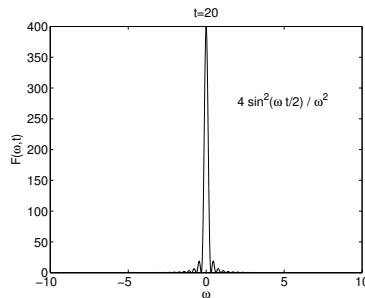
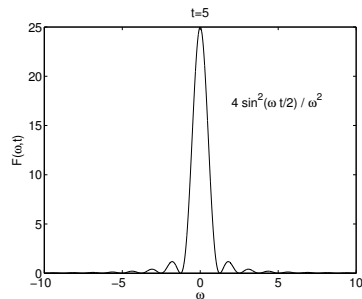
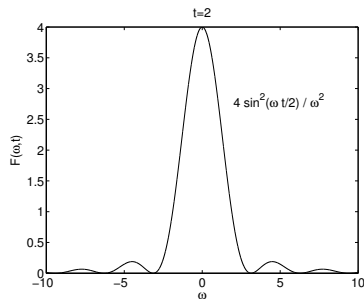
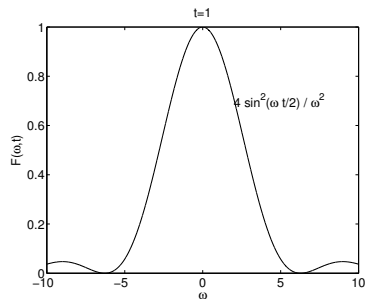
(18)

It can be seen that the function  $F(\omega, t)$  for larger and larger  $t$  approaches the shape of the Dirac delta-function, (see the drawing). (Animated on the [www](#))



Plot of the function

$$\frac{\sin^2 x}{x^2}$$



Approaching the  $\delta$ -function with increasing  $t$ :

[Go to list of topics](#)

$$F(\omega, t) = 4 \cdot \frac{\sin^2 \frac{\omega t}{2}}{\omega^2}$$

# Why integrate over $\omega$ ??

Trying to integrate the function 'F' over  $\omega$  shows this

$\hbar^2$



$$\begin{aligned} t^2 \int_{-\infty}^{\infty} \frac{\sin^2 x}{x^2} d\omega &= 2t \int_{-\infty}^{\infty} \frac{\sin^2 x}{x^2} \cdot d\left(\frac{\omega t}{2}\right) \\ &= 2t \int_{-\infty}^{\infty} \frac{\sin^2 x}{x^2} dx \\ &= 2\pi t \end{aligned}$$

$\omega$  is energy DIFFERENCE

$$x = \frac{\omega t}{2}$$

well known that

$$\int_0^{\infty} \frac{\sin^2 x}{x^2} dx = \frac{\pi}{2} \quad (19)$$

that for large  $t$  it really behaves as

behaves as

$$F(t, \omega) = \frac{\sin^2 \frac{\omega t}{2}}{\left(\frac{\omega}{2}\right)^2} \rightarrow \underline{2\pi t \delta(\omega)} \quad (20)$$

when  $t \rightarrow \infty$

The summation over all the states used for the expansion can be assumed to be replaced by the integration over  $\omega$  or the energy  $E = \hbar\omega$ . This however needs to determine the factor  $\rho(E)$  which accounts for the density of states. Since the 'F' approaches delta-function, we only need the density of states close to the final state  $b$ :

$$P = \frac{1}{\hbar^2} \sum_i P$$

$$\bar{P}_{ba}(t) = \frac{1}{\hbar^2} \int_{E_b-\eta}^{E_b+\eta} |H'_{ba}|^2 F(t, \omega) \rho(E) dE \quad (21)$$

$\sum_i \rightarrow \int dE$

and also integration over  $d\omega$  gives

$$\int \delta(\omega) d\omega = \int \delta(E) dE$$

$$\delta(\omega) = \delta(E) \cdot \frac{dE}{d\omega}$$

$$= \hbar \delta(E - E_b)$$

Derivation of density of states (22)

usually built on  
density of states  
in  $\vec{k}$ -wave number  
(which is constant)

[Go to list of topics](#)

# 5 Fermi Golden Rule

[Go to list of topics](#)

The final result for the probability of populating the group of states close to the final state  $|b\rangle$  is

$$\begin{aligned}
 P_{ba}(t) &= \frac{1}{\hbar} \int_{E_b-\eta}^{E_b+\eta} 2\pi t |H'_{ba}|^2 \delta(E - E_b) \rho(E) dE \\
 &= \frac{2\pi}{\hbar} t |\langle b|H'|a\rangle|^2 \rho(E_b) \quad \text{for } t \rightarrow \infty
 \end{aligned}
 \tag{23}$$

$F(\omega, t)$  ← dimension by integration factor  
 for  $t \rightarrow \infty$

The derivation of the above formula has been based on the assumption of a small perturbation. It shows that the probability of transition to the state  $b$  or states close to  $b$  increases linearly with time. Thus the rate of probability change per time is given by

$$\frac{dP_{ba}}{dt} = W_{ba} = \frac{2\pi}{\hbar} |\langle b|H'|a\rangle|^2 \rho(E_b)
 \tag{24}$$

This result is known as *Golden Rule* formula or *Fermi Golden Rule*.

line →  
spectra

$\delta$ -function



## 6 Constant rate and exponential decay

[Go to list of topics](#)

Fermi golden rule gives a constant rate

to populate  $f$ -states

$$\frac{dP_f}{dt} = w \quad (25)$$

or if we consider the probability decrease to find the system in the original state,

~~$$\frac{dP_i}{dt} = -w \quad (26)$$~~

If this, instead of a definition, is taken as a differential equation

~~$$P_i = P_0 - wt \quad (27)$$~~

can quickly become negative. However, one can quite easily realize that the correct differential equation must be

$$\frac{dP_i}{dt} = -wP_i \quad (28)$$



since the loss of probability must be proportional to 'how much is left', i.e. the  $P_i$  itself. It can also be guessed from the differential equations of Q.M. (leading to the  $\frac{dP_f}{dt}$ ), since they contained the amplitude, which we replaced by 1.

The last differential equation leads to the well known exponential decay, since its solution is

$$P_i = e^{-\omega t} \quad (29)$$

since  $P_i(t=0) = \underline{\underline{1}}$

$$\frac{dP}{dt} = -\omega P$$

$$\frac{dP}{P} = -\omega dt$$
$$\log P = -\omega t + \log P_0$$
$$P_0 e^{-\omega t}$$

[Go to list of topics](#)

## 7 Line width from exponential decay

[Go to list of topics](#)

In the equation (10) the expansion coefficient of the initial state  $\alpha_0(t) \rightarrow 1$  for all times leads to the delta function for energy (frequency). In order to take into account the flow of probability from the initial state 0, the relation

$$\alpha_k(t) = \delta_{ka}$$

when working with the time dependent problem must be changed to

$$|\alpha_k(t)| = \delta_{ka} \exp\left(-\frac{w}{2}t\right)$$

where  $w$  is the constant rate factor obtained in the perturbation theory.

If we take into account the result of previous section 6, we have  $|c_0(t)| \rightarrow \exp(-wt/2)$ . Inserting this into equation (10), the integrals can still be performed, but the expressions which were found to converge to the  $\delta$ -function in frequency (energy) for time going to infinity are not obtained. The term

$$\int V_{ba} e^{i\omega_{ba}t} dt$$

leading to

$$-V_{ba} \frac{1}{\omega_{ba}} (e^{i\omega_{ba}t} - 1)$$

which has been shown to lead to  $\delta$ -function like behaviour when integrated over  $\omega$  is now replaced by

$$\frac{e^{i(\omega - \omega_{ba})t} e^{-wt/2} - 1}{i(\omega - \omega_{ba}) - \frac{w}{2}}$$

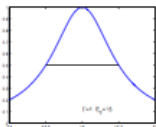
at large times  $t$  the factor  $e^{-wt/2} \rightarrow 0$  and this leads to

$$\left| \frac{1}{i(\omega - \omega_{ba}) - \frac{w}{2}} \right|^2 = \frac{1}{(\omega - \omega_{ba})^2 + \frac{1}{4}w^2}$$

The rate, which has the dimension of frequency becomes the energy width

$$\Gamma = \hbar w$$

when multiplied by  $\hbar$ . the so called Lorentz shape of the line,

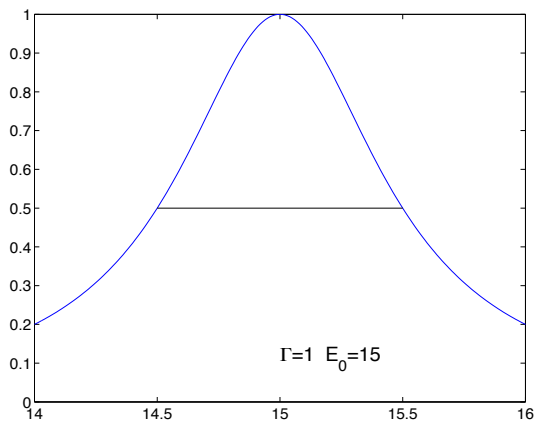
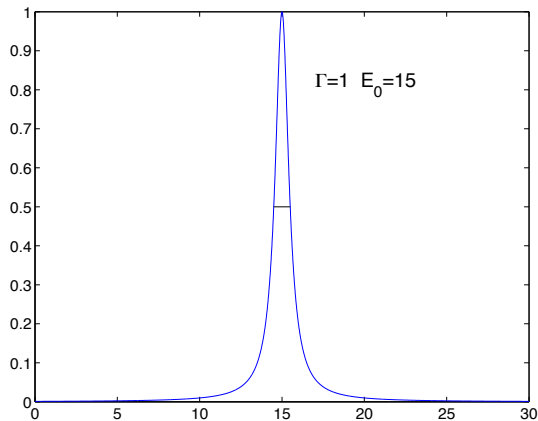


$$I(E) \approx I_0 \frac{\left(\frac{\Gamma}{2}\right)^2}{(E - E_0)^2 + \left(\frac{\Gamma}{2}\right)^2} \quad (30)$$

Fermi rule  $\rightarrow$   $w$   $\xrightarrow{\text{large time}}$  Lorentz

Thus a more realistic treatment than the perturbation theory with constant decay rate leads to the natural width of the energy spectrum of the ejected photons as observed. This behaviour has been illustrated in our Golden Rule Simulator program

[Go to list of topics](#)



instead of  
 $\delta$ -function

$$I(E) \approx I_0 \frac{\left(\frac{\Gamma}{2}\right)^2}{(E - E_0)^2 + \left(\frac{\Gamma}{2}\right)^2}$$

$w$

## 8 Generally on quantum treatment of extended systems - fields.

[Go to list of topics](#)

The system to be considered consists of an atom and the electromagnetic field.

The field has in principle infinitely many degrees of freedom, i.e. the values of field variables in each point of space.

The electromagnetic field can be treated by wave equations, it is thus a sort of a **harmonic system**. The energy of a *finite* harmonic system can always be transformed to a sum of independent harmonic oscillators, each of them is in fact an eigenmode.

Each harmonic oscillator can be then described using the equations for harmonic oscillator, with the algebraic method and number of quanta states - The creation and annihilation operators - click [10](#).

The normal modes or eigenmodes for a general harmonic system are discussed in the section [9](#).

The prescription

1. identify the eigenmodes
2. quantize each of the modes as independent harmonic oscillator
3. use quanta of eigenmodes
4. express the general coordinates of the system using the eigenmode coordinates (inverse transformations to those discussed in section 9. Each coordinate  $\chi_i$  will then be replaced by its combination of the creation and annihilation operators as discussed in section 10.

[Go to list of topics](#)

## 9 Normal Coordinates for coupled harmonic vibrations.

[Go to list of topics](#)



Transformation to normal coordinates can be described as follows:

Take the total energy,  $\mathbf{x}$  represents the vector of all coordinates,  $\mathbf{x}^T$  represents the transposed vector,  $\mathbf{M}$  is the mass matrix,  $\mathbf{V}$  is the matrix which gives the potential energy, including the couplings.

Note that the mass matrix is written in a very general form, most often this matrix would be diagonal.

$$E = \frac{1}{2} \dot{\mathbf{x}}^T \mathbf{M} \dot{\mathbf{x}} + \frac{1}{2} \mathbf{x}^T \mathbf{V} \mathbf{x}$$

2 modes

First we transform the kinetic energy to a "spherical" form



2 modes

$$\begin{pmatrix} m_1 & 0 \\ 0 & m_2 \end{pmatrix}$$

$m_1 - m_2$

together

$$u_1 + u_2$$

$$\frac{1}{2}\dot{\mathbf{x}}^T \mathbf{M} \dot{\mathbf{x}} = \frac{1}{2}\dot{\eta}^T \mathbf{S}^T \mathbf{M} \mathbf{S} \dot{\eta} = \frac{1}{2}\dot{\eta}^T \dot{\eta}$$

This transformation does not conserve the lengths. The N-dimensional ellipsoid is transformed to an N-dim. sphere.

$$\mathbf{S}^T \mathbf{M} \mathbf{S} = \mathbf{1}$$

If  $\mathbf{M}_{ij} = m_j \delta_{ij}$ , it is quite easy to find  $\mathbf{S}_{ij} = m_j^{-1/2} \delta_{ij}$ , Transformation  $\mathbf{S}$  simplifies the kinetic energy, but the potential remains complicated. Therefore we use one more, from  $\eta$  to  $\chi$ ,

$$\frac{1}{2}\mathbf{x}^T \mathbf{V} \mathbf{x} = \frac{1}{2}\eta^T \mathbf{S}^T \mathbf{V} \mathbf{S} \eta = \frac{1}{2}\chi^T \mathbf{U}^{-1} \mathbf{S}^T \mathbf{V} \mathbf{S} \mathbf{U} \chi$$

Transformation  $\eta = \mathbf{U} \chi$  is a simple rotation obtained by diagonalizing the matrix of potential energy: [Go to list of topics](#)

$$\left( \mathbf{U}^{-1} \mathbf{S}^T \mathbf{V} \mathbf{S} \mathbf{U} \right)_{ij} = \Omega_j^2 \delta_{ij} = \mathbf{W}_{ij}$$



Therefore we took  $\mathbf{U}^{-1} = \mathbf{U}^T$ . We can see that the "length" is conserved.

$$\frac{1}{2}\dot{\eta}^T \dot{\eta} = \frac{1}{2}\dot{\chi}^T \mathbf{U}^{-1} \mathbf{U} \dot{\chi} = \frac{1}{2}\dot{\chi}^T \dot{\chi}$$

$$E = \frac{1}{2}\dot{\mathbf{x}}^T \mathbf{M} \dot{\mathbf{x}} + \frac{1}{2}\mathbf{x}^T \mathbf{V} \mathbf{x} = \frac{1}{2}\dot{\chi}^T \dot{\chi} + \frac{1}{2}\chi^T \mathbf{W} \chi$$

This expression however is a sum over the new mutually independent degrees of freedom, since  $\mathbf{W}$  is diagonal.

$$\frac{1}{2}\dot{\chi}^T \dot{\chi} + \frac{1}{2}\chi^T \mathbf{W} \chi = \sum_{i=1}^N \left( \frac{1}{2}\dot{\chi}_i^2 + \frac{1}{2}\Omega_i^2 \chi_i^2 \right)$$

quadratic forms

**Summary:** for any type of coupled oscillations **normal modes** or *eigenmodes* can be found by linear transformations (diagonalization)

$$\sum_{i=1}^N \frac{1}{2} m_i \dot{x}_i^2 + \frac{1}{2} \sum_{i,j=1}^N V_{ij} x_i x_j \quad \longrightarrow \quad \sum_{i=1}^N \left( \frac{1}{2} \dot{\chi}_i^2 + \frac{1}{2} \Omega_i^2 \chi_i^2 \right)$$

[Go to list of topics](#)

## Example

[Go to list of topics](#)

A string of balls of mass  $m$  connected by springs of equal spring constant is described by displacements  $u_i$ . We can label the displacements  $u_i = u(x_i)$  where  $x_i$  is the equilibrium position of the  $i$ -th ball. In the limit of infinitesimal small balls and short springs this would then lead to a "wave equations" for a continuous elastic string, with continuously observed displacement  $u(x)$ .

The total energy is:

$$\frac{1}{2} \sum_i m (\dot{u}(x_i))^2 + \frac{1}{2} k \sum_i (u(x_i) - u(x_{i+1}))^2 + \frac{1}{2} k u(x_1)^2 + \frac{1}{2} k u(x_N)^2$$

The last two terms represent the fixed end springs. The matrix  $M$  is simply a diagonal matrix with  $m$  as all diagonal elements. The matrix  $V$  is a band matrix (below).

The transformation from  $u(x_i)$  to  $\chi_i$  can also be reversed. The reversed transformation in this case simply consists of eigenvectors of the matrix  $V$ , so that each of the eigenmodes is simply given by a function of time

$$\chi_k(t) = \chi_{k0} e^{i\Omega_k t}$$

where  $\chi_{k0}$  is the amplitude, and the actual displacements for the k-th mode can be written as

$$u_k(x_i) = S_i^k \chi_k(t) = S_i^k \chi_{k0} e^{i\Omega_k t}$$

where  $S_i^k$  is the i-th component of the k-th eigenmode with the frequency  $\Omega_k$

The matrix  $V$  has the form

$$\begin{bmatrix} +\mathbf{2} & -\mathbf{1} & 0 & 0 & 0 & \dots & 0 \\ -\mathbf{1} & +\mathbf{2} & -\mathbf{1} & 0 & 0 & \dots & 0 \\ 0 & -\mathbf{1} & +\mathbf{2} & -\mathbf{1} & 0 & \dots & 0 \\ 0 & 0 & -\mathbf{1} & +\mathbf{2} & -\mathbf{1} & \dots & 0 \\ 0 & \dots & \dots & \dots & \dots & \dots & \dots \\ 0 & \dots & \dots & \dots & +\mathbf{2} & -\mathbf{1} & 0 \\ 0 & \dots & \dots & \dots & -\mathbf{1} & +\mathbf{2} & -\mathbf{1} \\ 0 & \dots & \dots & \dots & 0 & -\mathbf{1} & +\mathbf{2} \end{bmatrix}$$

The eigenvectors - giving the eigenmodes - are eigenvectors of this band matrix. The modes are "standing waves", in the string limit. For infinite system - traveling waves. **leads to Fourier expansions for fields** ) see (link) [A\(r\) expressed in eigenmodes](#) [Go to list of topics](#)

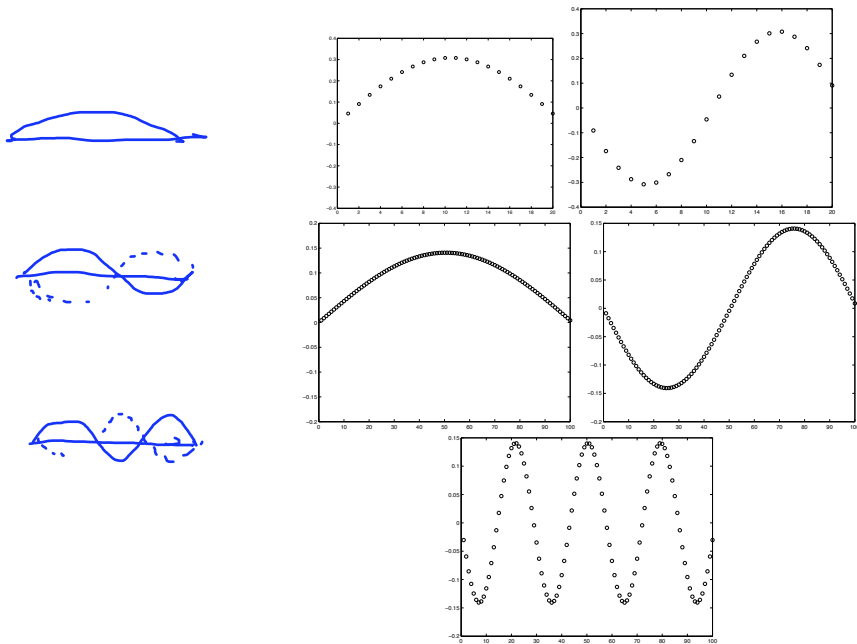


Figure 3: Components of eigenmodes at positions  $x_i$ . For  $N = 20$  first and second node, for  $N = 100$  nodes 1, 2, and 6.

[Go to list of topics](#)

*independent + harmonic oscillators*

## 10 Algebraic Method for Harmonic Oscillator.

[Go to list of topics](#)

In this section we show how one can work with the harmonic oscillator introducing so called ladder operators which move from state to state, the states being separated by the same 'quantum of energy'.

The classical hamiltonian can be transformed:

$$\frac{1}{2m} p^2 + \frac{m\omega^2}{2} q^2 \quad \text{transforms to} \quad \frac{\hbar\omega}{2} (P^2 + Q^2)$$

$$P = \sqrt{\frac{1}{\hbar m \omega}} p \qquad Q = \sqrt{\frac{m\omega}{\hbar}} q$$

With this the commutator

$$[q, p] = i\hbar$$

becomes

$$[Q, P] = i$$

This simplifies the equation and brings it into a form where the energy is expressed in  $\hbar\omega$ .

The main transformation, however, is to go over to linear combinations of  $P$  and  $Q$

$$a = \frac{1}{\sqrt{2}}Q + \frac{i}{\sqrt{2}}P \quad \text{and} \quad a^+ = \frac{1}{\sqrt{2}}Q - \frac{i}{\sqrt{2}}P$$

By a very simple algebra we find that for their commutator

$$[a, a^+] = 1$$

and the energy is transferred to [Go to list of topics](#)

$$\frac{\hbar\omega}{2} (P^2 + Q^2) \quad \rightarrow \quad \frac{\hbar\omega}{2} (a a^+ + a^+ a)$$

Using the commutator  $a a^+ - a^+ a = 1$  we finally get

$$H = \hbar\omega a^+ a + \frac{\hbar\omega}{2} = \hbar\omega N + \frac{\hbar\omega}{2}$$

where we already include that

$$N = a^+ a$$

will be a *number* operator.

Why number? Let us play with  $[a, a^+] = 1$  or alternatively  $a a^+ - a^+ a = 1$  and the operator  $N$ . We quickly derive that

$$[N, a^+] = a^+ \quad \text{and} \quad [N, a] = -a$$

This is done simply by writing out [Go to list of topics](#)

$$[N, a^+] = N a^+ - a^+ N = (a^+ a) a^+ - a^+ (a^+ a) = a^+ (a a^+ - a^+ a) = a^+ [a, a^+] = a^+$$

Since  $H = \hbar\omega N + \frac{\hbar\omega}{2}$  we also have

$$[H, a^+] = \hbar\omega a^+ \quad \text{and} \quad [H, a] = -\hbar\omega a$$

These are the last equations which bring the physical interpretation.

If there is a Q.M. state  $\psi(q) \rightarrow |\psi\rangle$  such that

$$H |\psi\rangle = E |\psi\rangle$$

then

$$H(a|\psi\rangle) = aH|\psi\rangle - \hbar\omega a|\psi\rangle = aE|\psi\rangle - \hbar\omega a|\psi\rangle = (E - \hbar\omega)(a|\psi\rangle)$$

that means that  $(a|\psi\rangle)$  is also an eigenstate. It has energy lower by  $\hbar\omega$ . This we can continue again and again, getting eigenstates for

$$E - \hbar\omega, E - 2\hbar\omega, E - 3\hbar\omega, E - 4\hbar\omega, E - 5\hbar\omega \dots\dots$$

Since this cannot go on infinitely, we get finally a state such that

$$a|\psi_0\rangle = 0$$

We quickly verify that this state has [Go to list of topics](#)

$$E_0 = \frac{\hbar\omega}{2}$$

further that the same thing is possible with  $a^+$  only with opposite sign, so that we get energies

$$E_0, E_0 + \hbar\omega, E_0 + 2\hbar\omega, E_0 + 3\hbar\omega, E_0 + 4\hbar\omega, E_0 + 5\hbar\omega \dots\dots$$



Each of the eigenstates is an eigenstate of both  $H$  and  $N$  with obvious number of quanta. Therefore we call  $a^+$  and  $a$  *creation and annihilation* operators. They make states with one more or one less *quantum*  $\hbar\omega$

We can complete this treatment by a complete solution for the wavefunction:

$$a |\psi_0\rangle = 0 \quad a = \frac{1}{\sqrt{2}} (Q + iP) \quad P = -i \frac{\partial}{\partial Q}$$

Thus, writing  $|\psi_0\rangle \rightarrow \psi_0(Q)$

$$a |\psi_0\rangle = 0 \quad \longrightarrow \quad \left( Q + \frac{\partial}{\partial Q} \right) \psi_0(Q) = 0$$

The solution of 1. order differential eq. to the left is easy

$$\psi_0(Q) = C_0 e^{-Q^2/2}$$

and using the expression for  $a^+$  and the  $|\psi_n\rangle$  [Go to list of topics](#)

$$\psi_1(Q) = C_1 \left( Q - \frac{\partial}{\partial Q} \right) e^{-Q^2/2} \quad \psi_2(Q) = C_2 \left( Q - \frac{\partial}{\partial Q} \right) \left( Q - \frac{\partial}{\partial Q} \right) e^{-Q^2/2}$$

and  $n$  times for general  $|\psi_n\rangle$ . cf. recursion relations for Hermite polynomials.

# 11 Electromagnetic fields

[Go to list of topics](#)

In atomic physics we prefer to work in Gaussian units, where the strengths of the fields have the same physical dimension. In vacuum  $\mathbf{D} = \mathbf{E}$  and  $\mathbf{H} = \mathbf{B}$

The classical electromagnetic field is described by electric and magnetic field vectors  $\mathbf{E}$  and  $\mathbf{B}$ , which satisfy Maxwell's equations:

$$\nabla \cdot \mathbf{E} = 4\pi\rho \quad (31)$$

$$\nabla \cdot \mathbf{B} = 0 \quad (32)$$

$$\nabla \times \mathbf{E} = -\frac{1}{c} \frac{\partial \mathbf{B}}{\partial t} \quad (33)$$

$$\nabla \times \mathbf{B} = \frac{1}{c} \left( \frac{\partial \mathbf{E}}{\partial t} + 4\pi\mathbf{J} \right) \quad (34)$$

The electric field  $\mathbf{E}$  and magnetic field  $\mathbf{B}$  can be generated from scalar and vector potentials  $\phi$  and  $\mathbf{A}$  by

$$\mathbf{E}(\mathbf{r}, t) = -\nabla\phi(\mathbf{r}, t) - \frac{1}{c} \frac{\partial}{\partial t} \mathbf{A}(\mathbf{r}, t) \quad (35)$$

$$\mathbf{B}(\mathbf{r}, t) = \nabla \times \mathbf{A}(\mathbf{r}, t) \quad (36)$$

The potentials are not unique, observable field strengths  $\mathbf{E}(\mathbf{r}, t)$  and  $\mathbf{B}(\mathbf{r}, t)$  remain the same when the potentials are changed by

$$\mathbf{A}(\mathbf{r}, t) \rightarrow \mathbf{A}(\mathbf{r}, t) + \nabla\lambda(\mathbf{r}, t)$$

$$\phi(\mathbf{r}, t) \rightarrow \phi(\mathbf{r}, t) - \frac{\partial\lambda(\mathbf{r}, t)}{\partial t}$$

where  $\lambda(\mathbf{r}, t)$  is any scalar field. [Go to list of topics](#)

This property is called gauge invariance. It allows us to choose  $\mathbf{A}$  so that

$$\nabla \cdot \mathbf{A} = 0 \quad (37)$$

When  $\mathbf{A}$  satisfies this condition, we are using the "Coulomb Gauge". From Maxwell's equations (without sources) we can show that  $\mathbf{A}$  satisfies the wave equation

$$\nabla^2 \mathbf{A} - \frac{1}{c^2} \frac{\partial^2 \mathbf{A}}{\partial t^2} = 0 \quad (38)$$

Also  $\phi$ ,  $\mathbf{B}$  and  $\mathbf{E}$  satisfy wave equations, but for radiation problems in empty space (vacuum) we have the potential  $\phi = 0$  since there are no charges there.

The energy stored or contained in the electromagnetic field is given by the formula

$$H_{field} = \frac{1}{8\pi} \int d^3\mathbf{r} (\mathbf{E} \cdot \mathbf{E} + \mathbf{B} \cdot \mathbf{B}) \quad (39)$$

Eigenmode in an "infinite box" is a plane wave solution of equations (37) and (38) with angular frequency  $\omega$  (i.e. the frequency  $\nu = \omega/2\pi$ ) is given by the vector potential  $\mathbf{A}$  [Go to list of topics](#)

$$\begin{aligned} \mathbf{A}(\omega; \mathbf{r}, t) &= 2\mathbf{A}_0(\omega) \cos(\mathbf{k} \cdot \mathbf{r} - \omega t + \delta_\omega) \\ &= \mathbf{A}_0(\omega) [\exp[i(\mathbf{k} \cdot \mathbf{r} - \omega t + \delta_\omega)] + c.c.] \end{aligned} \quad (40)$$

# 12 The Quantum Theory of Electromagnetic Field

[Go to list of topics](#)

The energy stored or contained in the electromagnetic field is given by the formula

$$H_{field} = \frac{1}{8\pi} \int d^3\mathbf{r} (\mathbf{E} \cdot \mathbf{E} + \mathbf{B} \cdot \mathbf{B}) \quad (41)$$

Gaussian units, the electric and magnetic field strengths have the same physical dimension.

The energy of extended system can be written as a sum of energies in eigenmodes. The eigenmodes in "infinite box" are the plane waves.

The sum over plane waves gives the form of Fourier series - for the operator of the vector potential  $\mathbf{A}(\mathbf{r})$

$$\mathbf{A}(\mathbf{r}) = \sum_{\mathbf{k}\lambda} \sqrt{\frac{2\pi\hbar c^2}{V\omega_k}} \hat{\mathbf{e}}_{\mathbf{k}\lambda} \left( a_{\mathbf{k}\lambda} e^{i\mathbf{k}\cdot\mathbf{r}} + a_{\mathbf{k}\lambda}^+ e^{-i\mathbf{k}\cdot\mathbf{r}} \right) \quad (42)$$

The sum includes all the possible values of the propagation vector  $\mathbf{k}$  and also

the two possible polarizations  $\lambda = 1, 2$ . In a *finite box* the boundary conditions lead to quantization of wave vectors  $\mathbf{k}$  as discussed in "Density of states" section. Periodicity on the box walls gives allowed values  $(n_x, n_y, n_z) \frac{2\pi}{L}$  where  $n_i$  are integers.

The dimensional factor

$$\sqrt{\frac{2\pi\hbar c^2}{V\omega_k}}$$

is determined by the necessity that

[Go to list of topics](#)

$$\langle \Phi | H_{rad} | \Phi \rangle = \langle \Phi | \int_V \mathcal{H} dV | \Phi \rangle = \langle \Phi | \int_V \frac{(E^2 + B^2)}{8\pi} dV | \Phi \rangle \quad (43)$$

must give the total energy of the electromagnetic field inside the box, when written as sum over quantized eigenmodes

$$\langle \Phi | H_{rad} | \Phi \rangle = \langle \Phi | \sum_{\mathbf{k}\lambda} H_{\mathbf{k}\lambda} | \Phi \rangle = \langle \Phi | \sum_{\mathbf{k}\lambda} \hbar\omega_k a_{\mathbf{k}\lambda}^+ a_{\mathbf{k}\lambda} | \Phi \rangle \quad (44)$$

This is done using

$$\mathbf{B}(\mathbf{r}) = i \mathbf{k} \times \mathbf{A}(\mathbf{r}) \quad \mathbf{E}(\mathbf{r}) = i \frac{\omega_k}{c} \mathbf{A}(\mathbf{r}) \quad \omega_k = kc$$

The operators  $a_{\mathbf{k}\lambda}$ ,  $a_{\mathbf{k}\lambda}^+$  and  $N_{\mathbf{k}\lambda}$  are "annihilation", is called "creation" and number operators for photons in each eigenmode.

One ignores the term  $\frac{1}{2} \sum_{\mathbf{k}\lambda} \hbar\omega_k$  that refers to "zero point energy" (infinite number of modes - Casimir effect).

The state of the field can be written as a *direct product* of the vector states for each of the oscillators [Go to list of topics](#)

$$|\Phi\rangle \rightarrow |\cdots n_{\mathbf{k}\lambda} \cdots n_{\mathbf{k}'\lambda'} \cdots\rangle = |\cdots\rangle \cdots |n_{\mathbf{k}\lambda}\rangle \cdots |n_{\mathbf{k}'\lambda'}\rangle \cdots \quad (45)$$

For such state vectors:

$$a_{\mathbf{k}\lambda} |\cdots n_{\mathbf{k}\lambda} \cdots n_{\mathbf{k}'\lambda'} \cdots\rangle = \sqrt{n_{\mathbf{k}\lambda}} |\cdots n_{\mathbf{k}\lambda} - 1 \cdots n_{\mathbf{k}'\lambda'} \cdots\rangle \quad (46)$$

$$a_{\mathbf{k}\lambda}^+ |\cdots n_{\mathbf{k}\lambda} \cdots n_{\mathbf{k}'\lambda'} \cdots\rangle = \sqrt{n_{\mathbf{k}\lambda} + 1} |\cdots n_{\mathbf{k}\lambda} + 1 \cdots n_{\mathbf{k}'\lambda'} \cdots\rangle \quad (47)$$

$$N_{\mathbf{k}\lambda} |\cdots n_{\mathbf{k}\lambda} \cdots n_{\mathbf{k}'\lambda'} \cdots\rangle = n_{\mathbf{k}\lambda} |\cdots n_{\mathbf{k}\lambda} \cdots n_{\mathbf{k}'\lambda'} \cdots\rangle \quad (48)$$

$$H_{\mathbf{k}\lambda} |\cdots n_{\mathbf{k}\lambda} \cdots n_{\mathbf{k}'\lambda'} \cdots\rangle = \hbar\omega_k n_{\mathbf{k}\lambda} |\cdots n_{\mathbf{k}\lambda} \cdots n_{\mathbf{k}'\lambda'} \cdots\rangle \quad (49)$$

where

$$n_{\mathbf{k}\lambda} = 0, 1, 2, 3, \dots, \infty$$

## 13 Density of States

[Go to list of topics](#)

We consider the electromagnetic field enclosed in a box with volume  $V$ . For a finite volume there is a discrete number of modes satisfying the imposed boundary conditions. Therefore the sum over final states is an ordinary sum. As this volume approaches infinite size, the summation over  $\mathbf{k}$ , will be approaching an integral.

The density of states factor is found from performing such a limiting process, using following relations.

The summation will be replaced by an integral

$$\sum_{\mathbf{k}} \longrightarrow \int \rho(\mathbf{k}) d\mathbf{k} \quad \begin{array}{l} \text{wave number} \\ \mathbf{k} \end{array} \quad (50)$$

$\rho(\mathbf{k})$  is the density of states in the  $\mathbf{K}$ -space.

The allowed discrete values of  $\mathbf{k}$  are obtained by combinations of components

$$k_x^{(n_x)} = \frac{2\pi}{L} n_x \quad k_y^{(n_y)} = \frac{2\pi}{L} n_y \quad k_z^{(n_z)} = \frac{2\pi}{L} n_z \quad (51)$$



where the numbers  $n_x, n_y, n_z$  are positive and negative integers. It means that each of the allowed vectors  $\mathbf{k}$  occupies a small volume of the K-space

$$\Delta k_x \Delta k_y \Delta k_z = \left(\frac{2\pi}{L}\right)^3 = \frac{(2\pi)^3}{V} \quad (52)$$

The density of states in the K-space is thus a constant (i.e. one per the above small k-space volume), and the above relation can be written as

$$\sum_{\mathbf{k}} \longrightarrow \frac{V}{(2\pi)^3} \int d\mathbf{k} \quad (53)$$

Since the derivation of the golden rule assumes integration over frequencies, or energies, we shall transform this integral over momenta (i.e. wave numbers  $\mathbf{k}$ ) to integral over energy, [Go to list of topics](#)

$$\frac{V}{(2\pi)^3} \int d\mathbf{k} \longrightarrow \int \rho(E) dE$$

$$\frac{V}{(2\pi)^3} \int d\mathbf{k} = \frac{V}{(2\pi)^3} \int_{\Omega_k} d\Omega_k \int k^2 dk = \int_{\Omega_k} \int \left[ \frac{V}{(2\pi)^3} k^2 \frac{dk}{dE} d\Omega_k \right] dE \quad (54)$$

so that the  $\rho(E)$  can be identified as

$$\frac{V}{(2\pi)^3} k^2 \frac{dk}{dE} \int_{\Omega_k} d\Omega_k \quad (55)$$

If the processes depend on the direction of the wave vector, which is true in photon emission case, we must keep the angular information inside of the density of states, and perform the angular integration afterwards.

We must now evaluate the above density of states in terms of energy only, using

$$k = \frac{\omega}{c} \quad E = \hbar k c$$

Setting these relations of  $k$  and  $E$ , we obtain the expression for  $\rho(E)$

$$\rho(E) = \frac{V}{(2\pi)^3} \cdot \frac{E^2}{(\hbar c)^3} d\Omega_k = \frac{V}{(2\pi)^3} \cdot \frac{1}{\hbar} \cdot \frac{\omega^2}{c^3} d\Omega_k \quad (56)$$

[Go to list of topics](#)

## 14 Charged Particle In Electromagnetic Field

In classical mechanics Newton equations with the electromagnetic Lorentz force

$$m\ddot{\mathbf{r}} = q \left( -\nabla\Phi + -\frac{1}{c} \frac{\partial \mathbf{A}}{\partial t} + \frac{1}{c} \mathbf{v} \times [\nabla \times \mathbf{A}] \right)$$

can be derived from a surprisingly simple Lagrange function

$$L(\mathbf{r}, \dot{\mathbf{r}}, t) = \frac{1}{2} m \mathbf{v}^2 - q\Phi(\mathbf{r}, t) + \frac{q}{c} \mathbf{v} \cdot \mathbf{A}(\mathbf{r}, t)$$

From this Lagrange function follows the Hamiltonian for a particle of charge  $q$  and mass  $m$

$$H = \frac{1}{2m} (\mathbf{p} - \frac{q}{c} \mathbf{A})^2 + q\phi \quad (57)$$

where  $\mathbf{p}$  is the generalized momentum of the particle. For the electron in a hydrogenic atom  $q = -e$ . The electrostatic potential is  $\phi = -\frac{Ze^2}{r}$  between the electron and the nucleus. The radiation field which perturbs the atom is described in terms of a vector potential  $\mathbf{A}$  alone

The time dependent Schrödinger equation for a hydrogenic atom in an electromagnetic field then reads

$$i\hbar \frac{\partial}{\partial t} \psi(r, t) = \left[ \frac{1}{2m} (-i\hbar \nabla + \frac{e}{c} \mathbf{A})^2 - \frac{Ze^2}{r} \right] \psi(r, t) \quad (58)$$

where we have written  $\mathbf{p} = -i\hbar \nabla$ . Because of the gauge condition  $\nabla \cdot \mathbf{A} = 0$ , we have

$$\nabla \cdot (\mathbf{A}\psi) = \mathbf{A} \cdot (\nabla\psi) + \underbrace{(\nabla \cdot \mathbf{A})}_{0} \psi = \mathbf{A} \cdot (\nabla\psi) \quad (59)$$

so that  $\nabla$  and  $\mathbf{A}$  effectively commute. Then

$$i\hbar \frac{\partial}{\partial t} \psi(r, t) = \left[ -\frac{\hbar^2}{2m} \nabla^2 - \frac{Ze^2}{r} - \frac{i\hbar e}{mc} \mathbf{A} \cdot \nabla + \frac{e^2}{2mc^2} \mathbf{A}^2 \right] \psi(r, t) \quad (60)$$

In "weak field case" the term with  $\mathbf{A}^2$  is small compared with the linear term  $\mathbf{A}$ .

[Go to list of topics](#)

# 15 The Hamiltonian of Interaction

[Go to list of topics](#)

Now, we study the interaction between radiation and atomic system. In this case the total Hamiltonian of the system is written as

$$\begin{aligned} H &= H_{atom} + H_{rad} + H_I \\ &= H^0 + H_I \end{aligned} \quad (61)$$

$H_{atom}$  is the Hamiltonian of the atomic system and  $H_{rad}$  is the Hamiltonian of the free radiation field.  $H_I$  shows the Hamiltonian of the interaction effect between two previous systems. By replacing  $H_I$ , we replace  $\mathbf{p}$  by  $\mathbf{p} + e/c\mathbf{A}$  in  $H_{atom}$  we can construct  $H_I$  as

$$H_I = \frac{e}{mc}\mathbf{p} \cdot \mathbf{A} + \frac{e^2}{2mc^2}\mathbf{A}^2 \quad H_I \rightarrow \frac{e}{mc}\mathbf{p} \cdot \mathbf{A} \quad (62)$$

As we see the first term of the eq.(62), is proportional to  $\mathbf{A}$  that contributes in the transitions involving the emission or absorption of a single photon and the

next term that's proportional to  $\mathbf{A}^2$  contributes in the transitions involving the emission or absorption of two photons. We can also see that the first term;  $\mathbf{A}$ ; contains just one creation or annihilation operator, but  $\mathbf{A}^2$  contains the terms as :  $a_{\mathbf{k}\lambda}a_{\mathbf{k}\lambda}$  ,  $a_{\mathbf{k}\lambda}^+a_{\mathbf{k}\lambda}^+$  ,  $a_{\mathbf{k}\lambda}a_{\mathbf{k}\lambda}^+$  ,  $a_{\mathbf{k}\lambda}^+a_{\mathbf{k}\lambda}$  which correspond to absorption of two photons; emission of two photons. Here we study the first term. The probability for a transition involving two photons contains  $e^4$  while this probability for one photon is proportional to  $e^2$ . This extra power of  $e^2$  will lead to one more power of  $\alpha \simeq 1/137$ .

The eigenfunctions of the unperturbed Hamiltonian  $H_0$  are direct products of the atomic and radiation wave functions

$$\psi_{atom}\psi_{rad} = |\psi_a; n_1, n_2, \dots, n_i, \dots\rangle \quad (63)$$

where  $\psi_a$  is the wave function of the atomic Hamiltonian,  $n_i \equiv n_{\mathbf{k}_i\lambda_i}$  is the wave function describing the mode  $\mathbf{k}_i\lambda_i$  in the radiation field.

[Go to list of topics](#)

## 16 Emission of Radiation By an Excited Atom:

[Go to list of topics](#)

Here we study the emission of a single photon by an excited atom, and we use the time-dependent perturbation theory to find the transition probability for atom. If we consider  $|i\rangle$  as the initial state and  $|f\rangle$  as the final state, then the probability per unit time for a transition by the emission of a single photon from the initial to final state is given by

$$W_{i \rightarrow f}(\mathbf{k}, \lambda) = \frac{2\pi}{\hbar} |\langle f | H_I | i \rangle|^2 \rho(E_f) \quad (64)$$

where  $\hbar\mathbf{k}$  denotes the momentum and  $\lambda$  denotes the polarization, and  $H_I$  is the perturbing Hamiltonian. This equation is known as *Fermi's Golden Rule*.

The perturbing Hamiltonian for this process is

$$H_I = -\frac{e}{mc} \mathbf{p} \cdot \mathbf{A} \quad (65)$$

by referring to the eq.(42), we have

$$H_I = -\frac{e}{mc} \sum_{\mathbf{k}\lambda} \sqrt{\frac{2\pi\hbar c^2}{V\omega_k}} \mathbf{p} \cdot \hat{\mathbf{e}}_{\mathbf{k}\lambda} \left( a_{\mathbf{k}\lambda} e^{i\mathbf{k}\cdot\mathbf{r}} + a_{\mathbf{k}\lambda}^+ e^{-i\mathbf{k}\cdot\mathbf{r}} \right) \quad (66)$$

The initial and final states  $|i\rangle; |f\rangle$ ; i.e. the unperturbed wavefunctions before and after the emission of one photon is

$$|i\rangle = |a\rangle |\cdots n_{\mathbf{k}\lambda} \cdots\rangle \quad (67)$$

$$|f\rangle = |b\rangle |\cdots n_{\mathbf{k}\lambda} + 1 \cdots\rangle \quad (68)$$

The energy difference of these two states is

$$E_f - E_i = (E_b + n_{\mathbf{k}\lambda}\hbar\omega_k + \hbar\omega_k) - (E_a + n_{\mathbf{k}\lambda}\hbar\omega_k) = E_b - E_a + \hbar\omega_k \quad (69)$$

For spontaneous emission, no photon is present in the initial state:  $n_{\mathbf{k}} \rightarrow 0$  and  $(n_{\mathbf{k}} + 1) \rightarrow 1$

[Go to list of topics](#)



## 17 The matrix element reduction

[Go to list of topics](#)

Inserting the final and initial states and the Hamiltonian into the matrix element, we obtain

$$\langle f | H_I | i \rangle = -\frac{e}{mc} \sqrt{\frac{2\pi\hbar c^2}{V\omega_k}} \langle b | \mathbf{p} \cdot \hat{\mathbf{e}}_{\mathbf{k}\lambda} e^{-i\mathbf{k}\cdot\mathbf{r}} | a \rangle \sqrt{n_{\mathbf{k}\lambda} + 1} \quad (70)$$

For spontaneous emission, no photon is present in the initial state:  $n_{\mathbf{k}} \rightarrow 0$  and  $(n_{\mathbf{k}} + 1) \rightarrow 1$

By considering the eq.(70) we can transform the Golden Rule formula eq.(64) for spontaneous emission

$$W_{i \rightarrow f}(\mathbf{k}, \lambda) = \frac{2\pi}{\hbar} \left( \frac{e}{mc} \right)^2 \left( \frac{2\pi\hbar c^2}{V\omega_k} \right) \left| \langle b | \mathbf{p} \cdot \hat{\mathbf{e}}_{\mathbf{k}\lambda} e^{-i\mathbf{k}\cdot\mathbf{r}} | a \rangle \right|^2 \rho(E_f) \quad (71)$$

$$\langle \Psi_{fin} | H_I | \Psi_{init} \rangle$$

$$H_I \rightarrow \frac{e}{m c} \vec{p} \cdot \vec{A}$$

$$\langle \Psi_{fin} | \frac{e}{m c} \vec{p} \cdot \vec{A} | \Psi_{init} \rangle$$

$$| \Psi_{init} \rangle \rightarrow | 0_{photon} \rangle | \varphi_{EXC} \rangle$$

$$\langle \Psi_{fin} | \rightarrow \langle \varphi_{GS} | \langle \hbar \omega |$$

$$\langle \varphi_{GS} | \langle \hbar \omega | \frac{e}{m c} \vec{p} \cdot \vec{A} | 0_{photon} \rangle | \varphi_{EXC} \rangle$$

$$\vec{A} \rightarrow \sum_{\vec{\epsilon}_{kk}} \vec{\epsilon}_k \sqrt{\frac{2\pi\hbar c^2}{\omega_k V}} e^{i\vec{k} \cdot \vec{r}} a^\dagger \quad \vec{p} \cdot \vec{A} \rightarrow \sum \vec{p} \cdot \vec{\epsilon} \sqrt{\frac{2\pi\hbar c^2}{\omega V}} e^{i\vec{k} \cdot \vec{r}} a^\dagger$$

$$\langle \varphi_{GS} | \langle \hbar \omega | \frac{e}{m c} \sum \vec{p} \cdot \vec{\epsilon} \sqrt{\frac{2\pi\hbar c^2}{\omega V}} e^{i\vec{k} \cdot \vec{r}} a^\dagger | 0_{photon} \rangle | \varphi_{EXC} \rangle$$

$$\frac{e}{m c} \sqrt{\frac{2\pi\hbar c^2}{\omega V}} \langle \varphi_{GS} | \vec{p} \cdot \vec{\epsilon} e^{i\vec{k} \cdot \vec{r}} | \varphi_{EXC} \rangle \langle \hbar \omega | a^\dagger | 0_{photon} \rangle$$

# 18 Dipole Approximation

[Go to list of topics](#)

An important simplification is obtained by applying the so called dipole approximation, considering the case  $kr \ll 1$ . This means that the wavelength of the emitted photon is much larger than atomic dimension. The electric dipole approximation is obtained by replacing, to a good approximation,

$$e^{i\mathbf{k}\cdot\mathbf{r}} \approx 1$$

i.e.

$$\langle b | \mathbf{p} e^{-i\mathbf{k}\cdot\mathbf{r}} | a \rangle \rightarrow \langle b | \mathbf{p} | a \rangle$$

This approximation is limited by these requirements:

$$\lambda \gg 1\text{\AA} \quad \text{and} \quad \hbar\omega \ll 10 \text{ keV.}$$

Here we also derive the relation between matrix element of momentum and coordinate using the following commutation relations

$$[r, p^2] = p [r, p] + [r, p] p = 2i\hbar p \tag{72}$$

$$[\mathbf{r}, H_{atom}] = \frac{i\hbar}{m} \mathbf{p} \quad (73)$$

we change the matrix element of the momentum to a matrix element of the special coordinate of the atomic electron

$$\begin{aligned} \langle b | \mathbf{p} | a \rangle &= \frac{m}{i\hbar} \langle b | [\mathbf{r}, H_{atom}] | a \rangle \\ &= \frac{im}{\hbar} (E_a - E_b) \langle b | \mathbf{r} | a \rangle \\ &= i m \omega_{ab} \langle b | \mathbf{r} | a \rangle \end{aligned} \quad (74)$$

In summary,

$$\langle b | \mathbf{p} e^{-i\mathbf{k}\cdot\mathbf{r}} | a \rangle \longrightarrow i m \omega_{ab} \langle b | \mathbf{r} | a \rangle$$

[Go to list of topics](#)

## 19 Detailed Evaluation of Emission rate

[Go to list of topics](#)

For *spontaneous emission* that, we first perform the summation over the two possible polarizations by considering the following figure, fig.4. The figure shows that placing for a moment the z-axis in the direction of the wavevector  $\mathbf{k}$ , the directions of the polarization vectors  $\hat{\mathbf{e}}_{\mathbf{k}\lambda}$ , for  $\lambda = 1, 2$  can then define the x- and y-axes, so that

$$\begin{aligned} \sum_{\lambda=1,2} \left| \langle b | \mathbf{p} \cdot \hat{\mathbf{e}}_{\mathbf{k}\lambda} e^{-i\mathbf{k}\cdot\mathbf{r}} | a \rangle \right|^2 &= \left| \langle b | \mathbf{p} e^{-i\mathbf{k}\cdot\mathbf{r}} | a \rangle \right|^2 (\sin^2\theta \cos^2\phi + \sin^2\theta \sin^2\phi) \\ &= \left| \langle b | \mathbf{p} e^{-i\mathbf{k}\cdot\mathbf{r}} | a \rangle \right|^2 (\sin^2\theta) \end{aligned} \quad (75)$$

where the angle  $\theta$  is the angle between the wave number  $\mathbf{k}$  and the momentum vector of the electron (if it were classically defined). Conversely, after performing this reduction, we can think that our z-axis is always placed along the direction of  $\mathbf{p}$ , so that we can identify the angle  $\theta$  with the polar angle of the photon emission to be integrated over.

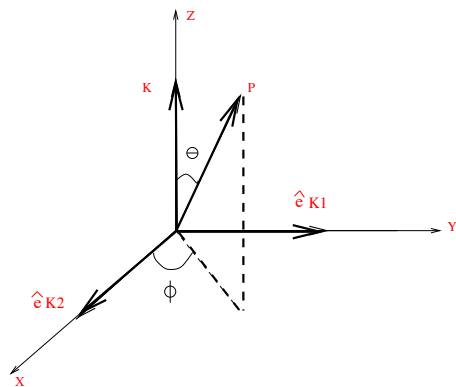


Figure 4: As the z-axis is for the moment in the direction of the wavevector  $\mathbf{k}$ , the directions of the polarization vectors  $\hat{\mathbf{e}}_{\mathbf{k}\lambda}$  (perpendicular to each other and to the vector  $\mathbf{k}$ , can then define the x- and y-axes. The angle  $\theta$  is the angle between the wave number  $\mathbf{k}$  and the momentum vector of the electron  $\mathbf{p}$ .

[Go to list of topics](#)

By using the eq.(55) and dipole approximation discussed above, we can evaluate the integral over all emission angles  $\Omega_k$ ,

$$\left(\frac{1}{\tau}\right)_{a \rightarrow b} = \frac{e^2}{2\pi m^2} \frac{\omega_k}{\hbar c^3} \int |\langle b | \mathbf{p} | a \rangle|^2 \sin^2 \theta d\Omega_k \quad (76)$$

where the integration angular variables are

$$d\Omega_k = \sin \theta d\theta d\phi \quad (77)$$

Note that in the above evaluations the volume  $V$  in  $\rho[E_f]$  cancels the volume in the field normalization factor

$$\sqrt{\frac{2\pi \hbar c^2}{V \omega_k}}$$

in equation (42).

The last equation eq.(76) then becomes

[Go to list of topics](#)

$$\left(\frac{1}{\tau}\right)_{a \rightarrow b} = \frac{e^2}{2\pi m^2} \frac{\omega_k}{\hbar c^3} |\langle b | \mathbf{p} | a \rangle|^2 \int d\phi \int \sin^2 \theta \sin \theta d\theta \quad (78)$$

The angular integration is easily seen to yield a factor  $8\pi/3$ , so that finally

$$\left(\frac{1}{\tau}\right)_{a \rightarrow b} = \frac{4\omega_{ab}e^2}{3\hbar m^2 c^3} |\langle b | \mathbf{p} | a \rangle|^2 \quad (79)$$

Further we use the relation between matrix element of momentum and coordinate eq. (74) in section 18  $\langle b | \mathbf{p} | a \rangle = im\omega_{ab} \langle b | \mathbf{r} | a \rangle$  and thus eq.(79) becomes

$$W_{sp. em.} = \left(\frac{1}{\tau}\right)_{a \rightarrow b} \quad (80)$$

$$= \frac{4e^2\omega_{ab}^3}{3\hbar c^3} |\langle b | \mathbf{r} | a \rangle|^2 \quad (81)$$

$$= \frac{4}{3} \left(\frac{\varepsilon_0}{\hbar}\right) \left(\frac{\hbar\omega_{ab}}{\varepsilon_0}\right)^3 \alpha^3 \left| \langle b | \frac{\mathbf{r}}{a_0} | a \rangle \right|^2 \quad (82)$$

$$a_0 = \hbar^2/me^2 \quad \varepsilon_0 = 2 Ryd = e^2/a_0 = 27.21 eV$$

$$\alpha = e^2/\hbar c = 1/137.04, \text{ the fine structure constant} \quad \hbar = 0.6582 \cdot 10^{-15} eV s$$

For one-electron hydrogenlike atoms (or ions), the life time of the transition of  $2p \rightarrow 1s$  of one photon is given by

$$\left(\frac{1}{\tau}\right)_{2p \rightarrow 1s} = 0.6 \times 10^9 Z^4 sec^{-1} \quad (83)$$

[Go to list of topics](#)



## 20 Stimulated emission

[Go to list of topics](#)

For the case of *stimulated emission*, that is dependent on the number of photons in the field (intensity), we must keep the  $\sqrt{n_{\mathbf{k}\lambda} + 1}$  term of the  $n_{\mathbf{k}\lambda}$  initial photon state and start from

$$W_{i \rightarrow f}(\mathbf{k}, \lambda) = \frac{2\pi}{\hbar} \left( \frac{e}{mc} \right)^2 \left( \frac{2\pi\hbar c^2}{V\omega_k} \right) (n_{\mathbf{k}\lambda} + 1) \left| \langle b | \mathbf{p} \cdot \hat{\mathbf{e}}_{\mathbf{k}\lambda} e^{-i\mathbf{k}\cdot\mathbf{r}} | a \rangle \right|^2 \rho(E_f) \quad (84)$$

The emission rate then becomes

$$W_{st. em.} = \left( \frac{1}{\tau} \right)_{a \rightarrow b} \quad (85)$$

$$= \frac{4}{3} \left( \frac{\varepsilon_o}{\hbar} \right) \left( \frac{\hbar\omega_{ab}}{\varepsilon_o} \right)^3 \alpha^3 (n_{\omega} + 1) \left| \langle b | \frac{\mathbf{r}}{a_o} | a \rangle \right|^2 \quad (86)$$

where  $n_{\omega}$  represents the number of photons in the field, with the energy of  $E_{\omega} = \hbar\omega$ .

The last equation can be considered as a sum of two terms; one is proportional to the number of photons in the field  $n_{\mathbf{k}\lambda}$ , so it's radiation field intensity-dependent, and describes the stimulated emission; the other one (expressed by number one in the paranthesis) is independent of the field intensity.

The term with is the said to account for the *spontaneous emission* contribution.

[Go to list of topics](#)

## 21 Fermi Golden Rule Simulation

————- [Go to list of topics](#) ————— [Time dependent wavefunction](#) —————  
[Model realization](#) ————— [The Hamiltonian of the model](#) —————

---

The physical problem: solve the time-dependent Schrödinger equation with hamiltonian as in the derivations of the Fermi Golden Rule.

*continuum* of textbook derivation  $\rightarrow$  *quasicontinuum* here, i.e. a set of many equidistantly closely spaced levels.

The idea is to demonstrate how the line width is proportional to the density of states and the strength of the coupling.

Only the couplings from the discrete states to continuum and back are nonzero, have a constant value.

## 22 Realization of the model

————— [Start of the simulator part](#) ————— [Go to list of topics](#) —————

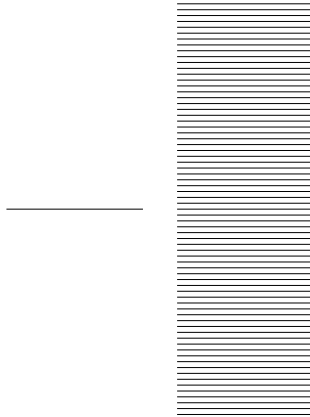


Figure 5: Schematic representation of the Energy levels

The figure 5 shows the energy levels: the single discrete level and the two quasicontinua. Note that each has a different density of levels.

The Hamilton operator matrix - see figure 7

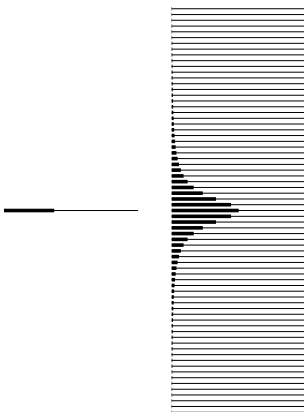


Figure 6: Schematic representation of the population probabilities, drawn at the energy levels

## 23 The time-dependent wavefunction

————— [Start of the simulator part](#) ————— [Go to list of topics](#) —————

The time-dependent wavefunction  $\Psi(t)$  is expanded in terms of the model states  $\varphi_i(t)$  as

$$\Psi(t) = \sum_i c_i(t) \varphi_i(t)$$

with the initial condition

$$c_1(0) = 1, c_2(0) = 0, c_3(0) = 0, \dots\dots$$

and inserted in the Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} \Psi(t) = H \Psi(t)$$

In the usual way this results in a set of coupled equations. The populations of the states, i.e. the absolute value squared of the expansion coefficients  $c_i(t)$  is shown in fig. 6.

$$\left[ \begin{array}{cccccccc}
 E_0 & V_1 & V_1 & V_1 & V_1 & V_1 & \dots & V_1 \\
 V_1 & E_{-n} & 0 & 0 & 0 & 0 & & 0 \\
 V_1 & 0 & E_{-n+1} & 0 & 0 & 0 & & 0 \\
 V_1 & 0 & 0 & E_{-n+2} & & 0 & & 0 \\
 V_1 & 0 & 0 & 0 & \cdot & & & \\
 V_1 & & & & & \cdot & & \\
 \vdots & & & & & & E_0 & \\
 \vdots & & & & & & & \cdot \\
 \vdots & & & & & & & \cdot \\
 V_1 & 0 & 0 & 0 & 0 & & 0 & E_n
 \end{array} \right]$$

Figure 7: Schematic representation of Hamiltonian Matrix

[Go to list of topics](#)

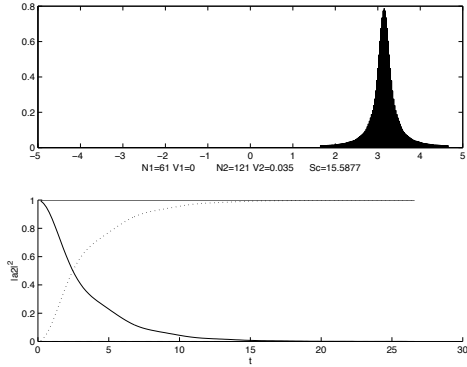


Figure 8: Decay in the simulator

— [Start of the simulator part](#) —

— [Go to list of topics](#) —



## 24 Atomic Units

Unit of length is the Bohr radius:

$$a_0 = \frac{\hbar^2}{m_e e^2} \left( = 4\pi\epsilon_0 \frac{\hbar^2}{m_e e^2} \right)$$

The first is in atomic units, second in SI-units. This quantity can be remembered by recalling the virial theorem, i.e. that in absolute value, half of the potential energy is equal to the kinetic energy. This gives us

$$\frac{1}{2} \frac{e^2}{a_0} = \frac{\hbar^2}{2m_e a_0^2}$$

and if we accept this relation, we have the above value of  $a_0$ .

The so called fine structure constant

$$\alpha = \frac{e^2}{\hbar c}$$

expresses in general the *weakness* of electromagnetic interaction.

[List of topics](#)

## Some Constants and Quantities

$v_0 = \alpha c = 2.18710^6 \text{ m s}^{-1}$	Bohr velocity
$a_0 = 0.529177 \cdot 10^{-10} \text{ m}$	Bohr radius
$\hbar = 0.6582 \cdot 10^{-15} \text{ eV s}$	Planck's constant
$k_B = 0.8625 \cdot 10^{-4} \text{ eV } ^\circ\text{K}^{-1}$	Boltzmann constant

$$R = N_A k_B$$

$N_A = 6.0222 \cdot 10^{23}$	Avogadro's number
------------------------------	-------------------

$\mu_B = 0.579 \cdot 10^{-4} \text{ eV (Tesla)}^{-1}$	Bohr magneton
---	---------------

## Plank's formula

$$\rho(\omega_{ba}) = \frac{\hbar \omega_{ba}^3}{\pi^2 c^3} \frac{1}{e^{\hbar \omega / kT} - 1}$$

List of topics

## Overview of the topics

Time dependent QM- two-well problem

Perturbation theory for TDSE

Fermi Golden Rule

Line width from exponential decay

Eigenmodes for coupled vibrations.

Electromagnetic fields

Density of States

The Hamiltonian of Interaction

The matrix element reduction

Detailed Evaluation of Emission rate

Golden Rule Simulator part

## One level in continuum

Final  $W = 1/\tau$  result

Time-Dependent Schrödinger Equation

Dirac delta-function

Constant rate and exponential decay

Quantum theory of extended systems - fields

Algebraic Method for Harmonic Oscillator.

The Quantum Theory of Electromag. Field

Charged Particles In an Electromag. Field

Emission of Radiation by an Excited Atom

Dipole Approximation

Stimulated emission

Time-Dependent Schrödinger

Equation in Simulator