Quantum Theory of Radiation

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Foreword

The beginning of quantum theory of light is the year 1900, when Max Planck explained the spectral distribution of thermal radiation (electromagnetic radiation generated by the thermal motion of charged particles, constituents of all matter) by introducing an *energy quantum $\hbar\omega$* of the harmonic oscillator. Albert Einstein was the first one who used this idea for the explanation of photoelectric effect in 1905. Two years later, Einstein used quanta of harmonic oscillations to explain the vanishing heat capacity of solids at low temperatures. In 1913 Niels Bohr realized that atomic structure can be understood from the quantum perspective only. In 1925 Erwin Schrödinger formulated the quantum theory, which allowed describing a hydrogen atom. These were only the first steps that showed the importance of quantization in modern physics. At present time quantum theory has evolved into universal theory, the base for the real world.

This course is devoted to the essentials of electromagnetic radiation and its interaction with atoms and classic gravitation field. Radiation is considered as a quantum phenomenon, being a collection of modes of the radiation field. Each mode corresponds to a quantized harmonic oscillator. Quantization of radiation produces zero-point oscillations of the electromagnetic field, which correspond to the zero-point energy. These vacuum fluctuations have no classical counterparts. Vacuum fluctuations can explain the Casimir effect, inter-atomic and inter-molecular van der Waals interactions, Unruh and black hole (Hawking) thermal radiation, and many other physical phenomena. Furthermore, there are reasons to assume that Universe itself was born from a quantum fluctuation (see E.P. Tryon, *Nature*, 1973).

In this short course, some general problems of quantum field theory are considered. Among them, the effects of the classical gravitational field on quantum excitations in the Planck limit and the structure of the Universe on the Planck scale are considered. In particular, the original quantum mechanism of the expansion of the Universe on the Planck scale is presented, which made it possible to express the temperature of 2.7 K of the relic radiation involved in this process through Hubble constants and universal ones. We also consider a number of problems of interaction of quantum radiation with atomic systems that are traditional for quantum theory courses, such as coherent, squeezed, mixed and entangled states, Rabi oscillations, self-induced transparency, Dicke superradiance. The course also includes the theory of resonant secondary radiation of optical centers in crystals, developed at the Institute of Physics of the Estonian Academy of Sciences fifty years ago. In this theory, based on the Heisenberg-Kramers formula, the optically excited (secondary) radiation of the center is represented as the sum of Rayleigh's and Raman scattering, ordinary and hot luminescence. The derivation of the Raman scattering transformation method developed in this theory, which allowed us to link the excitation profiles of Raman scattering with the absorption spectrum, is given.

This course of lectures, with minor changes, has been held at the Physical Department of the University of Tartu over the past few decades. It includes quantum effects of the elec-

tromagnetic field from cosmological to Planck scale. The course is translated from Estonian into English by V. Boltrushko.

CHAPTER 1

Basic equations

1.1 Quantization of the electromagnetic field

1.1.1 Mode expansion of field operators

In quantum theory physical quantities are set in correspondence with operators (see [24], [29]). Any physically measurable quantity has the corresponding *Hermitian operator* (a linear operator on a Hilbert space that equals its adjoint).

The relations between operators are the same as between quantities in classical physics. Therefore, we begin studying radiation with the classical electromagnetics. In this theory a source-free electromagnetic field is described by the wave equation:

$$\nabla^2 \vec{A} - \frac{1}{c^2} \frac{\partial^2}{\partial t^2} \vec{A} = 0 \tag{1.1}$$

where $\vec{A}$ is a vector potential (defined by the gauge condition). In a free space without sources of radiation, $\text{div} \vec{A} \equiv \nabla \cdot \vec{A} = 0$ (the Coulomb gauge).

In classical physics $\vec{A}$ is not an observable/measurable quantity, unlike the magnetic and the electric field strengths, defined by $\vec{A}$:

$$\mu_0 \vec{H} = \nabla \times \vec{A}, \vec{E} = -\nabla \phi - \frac{\partial \vec{A}}{\partial t} = -\frac{\partial \vec{A}}{\partial t}. \tag{1.2}$$

In quantum theory vector $\vec{A}$ is also observable, as demonstrated by the Josephson effect or the Aharonov-Bohm effect).

Field quantization by plane wave expansion

Consider a cubic cavity (edge length is L) with perfectly conducting walls (electric field vanishes on them). Applying periodic boundary conditions produces a space consisting of periodically placed cavities. Then vector $\vec{A}$ is periodic in three mutually perpendicular directions:

$$\vec{A}(x, y, z) = \vec{A}(x + nL, y + lL, z + mL),$$

where $n, l, m = 0, \pm 1, \pm 2, \ldots$ If we take L large enough, the field properties should not depend on the magnitude of L or boundary conditions.

Vector $\vec{A}$ can be expanded in series of harmonic waves (modes, i.e. the plane waves with a given polarization) having different propagation directions, frequencies and polarizations:

$$\vec{A} = \sum_{\vec{k}} \vec{A}_{\vec{k}} e^{i\vec{k}\vec{r} - i\omega t}. \tag{1.3}$$

Series expansion of $\vec{E}$ and $\vec{H}$ can be done in a similar way. Equation 1.3 is the solution of the initial Equation 1.1, by substitution one gets

$$\sum_{k} \left(-k^2 + \frac{\omega^2}{c^2} \right) e^{i\vec{k}\vec{r} - i\omega t} = 0,$$

from which it follows that $k = \omega / c$.

The parameters of modes k should be taken to satisfy boundary conditions. Only the following set of components is valid:

$$\left\{ k_x = \frac{2\pi}{L} \nu_x, \; k_y = \frac{2\pi}{L} \nu_y, \; k_z = \frac{2\pi}{L} \nu_z \right\},$$

where $\nu_{x,y,z} = 0, \pm 1, \pm 2, \ldots$ are positive and negative integers. Wave vectors define a cubic lattice with lattice constant $2\pi / L$.

> In case of periodic boundary conditions the radiation field is considered as a collection of modes, and each mode is a discrete object with a corresponding value of $\vec{k}$.

Equation 1.3 can be presented as a combination of harmonic functions $\sin(\vec{k}\vec{r})$ and $\cos(\vec{k}\vec{r})$, instead of $e^{i\vec{k}\vec{r}}$. One such solution

$$\begin{cases} E_x(\vec{r}, t) & = E_{0x}(t) \cos\left(\dfrac{2\pi x \nu_x}{L}\right) \sin\left(\dfrac{2\pi y \nu_y}{L}\right) \sin\left(\dfrac{2\pi z \nu_z}{L}\right) \\[2mm] E_y(\vec{r}, t) & = E_{0y}(t) \sin\left(\dfrac{2\pi x \nu_x}{L}\right) \cos\left(\dfrac{2\pi y \nu_y}{L}\right) \sin\left(\dfrac{2\pi z \nu_z}{L}\right) \\[2mm] E_z(\vec{r}, t) & = E_{0z}(t) \sin\left(\dfrac{2\pi x \nu_x}{L}\right) \sin\left(\dfrac{2\pi y \nu_y}{L}\right) \cos\left(\dfrac{2\pi x \nu_z}{L}\right) \end{cases} \tag{1.4}$$

satisfies both periodic boundary conditions (including the longitudinal components of the field on the *walls,* ($y, z = 0$; $z, x = 0, L$; $x, y = L, 0$) become zero) as well as field transversal condition $\nabla \cdot \vec{E} = 0$ in all points of space, when $\vec{k} \cdot \vec{E}_0 = 0$ if

$$k_x = 2\pi \nu_x / L, \quad k_y = 2\pi \nu_y / L, \quad k_z = 2\pi \nu_z / L.$$

Periodic boundary conditions mean that the solution does not change if we make a substitution $r \to r'$:

$$\begin{cases} r \in (x, y, z) \\ r' \in \left(x + 2nL, y + 2lL, z + 2mL\right), \quad n, l, m = 0, \pm 1, \pm 2, \dots \end{cases}$$

where $2nL$ is the displacement in x-direction.

If $k_x L = 2\pi v_x$, then we have a periodic function in the exponent. Consequently, periodic boundary conditions are indeed satisfied if

$$k_x = \frac{2\pi}{L} v_x \, k_y = \frac{2\pi}{L} v_y \, k_z = \frac{2\pi}{L} v_z$$

Wave vectors constitute the cubic lattice with lattice constant $2\pi/L$.

The condition $\nabla \cdot \vec{E} = 0$ gives us

$$\nabla \cdot \vec{E} = (\vec{E}_0 \cdot \vec{k}) \sin\left(\frac{2\pi x v_x}{L}\right) \sin\left(\frac{2\pi y v_y}{L}\right) \sin\left(\frac{2\pi z v_z}{L}\right) = 0. \tag{1.5}$$

This holds for all points in the space, if the field is transversal (vectors $\vec{E}$ and $\vec{k}$ are orthogonal), that is $\vec{E}_0 \cdot \vec{k} = 0$. Transversality of the field, i.e. $\nabla \cdot \vec{A} = 0$, $\vec{k} \cdot \vec{A} = 0$, results in two possible polarizations. In other words, for every $\vec{k}$ there are 2 modes with different polarizations.

Density of modes

In the k-space, let us find the number of modes in the range of $(k, k + dk)$, where dk is relatively small. For the large number of modes we assume that $2\pi/L < dk$. Corresponding volume of a spherical shell is $V_k = 4\pi k^2 dk$. One mode corresponds to a volume $(2\pi/L)^3$. Thus, the number of modes in the volume V_k equals

$$N_k = \frac{V_k}{(2\pi/L)^3} \times 2 = \frac{k^2}{\pi^2} L^3 dk$$

(the factor 2 takes into account two polarizations), which gives the number of modes in unit space (*density of modes in k-space*)

$$\rho_k dk = \frac{N_k}{L^3} = \frac{k^2}{\pi^2} dk \quad \Rightarrow \quad \rho_k = \frac{k^2}{\pi^2} \tag{1.6}$$

Transition to the frequency domain gives

$$\rho_k dk = \rho_\omega d\omega = \frac{\omega^2}{\pi^2 c^3} d\omega \quad \Rightarrow \quad \rho_\omega = \frac{\omega^2}{\pi^2 c^3} \tag{1.7}$$

Density $\rho_\omega \sim \omega^2$ grows rapidly with a frequency in the three-dimensional space. In two dimensions, the density is a linear function of frequency: $\rho_\omega = \omega/(\pi c^2)$, and in one dimension it is a constant: $\rho_\omega = 1/c$.

Summary

Electromagnetic field is defined by the mode expansion of the vector potential:

$$\vec{A} = \sum_{\vec{k}} (\vec{A}_{\vec{k}} e^{i\vec{k}\vec{r} - i\omega_k t} + \vec{A}_{\vec{k}}^* e^{-i\vec{k}\vec{r} + i\omega_k t}), \tag{1.8}$$

where $\vec{A}$ is real, $\vec{A}_{\vec{k}}$ is complex, and $\omega \equiv \omega_k = kc$. Electric field vector is

$$\vec{E} = -\frac{\partial \vec{A}}{\partial t} = i \sum_{\vec{k}} \omega_k (\vec{A}_{\vec{k}} e^{i\vec{k}\vec{r} - i\omega_k t} - \vec{A}_{\vec{k}}^* e^{-i\vec{k}\vec{r} + i\omega_k t}) \tag{1.9}$$

and magnetic field vector is

$$\vec{H} = \nabla \times \vec{A} = i \sum_{\vec{k}} \left[\left(\vec{k} \times \vec{A}_{\vec{k}} \right) e^{i\vec{k}\vec{r} - i\omega_k t} - \left(\vec{k} \times \vec{A}_{\vec{k}}^* \right) e^{-i\vec{k}\vec{r} + i\omega_k t} \right]. \tag{1.10}$$

1.1.2   Creation and annihilation operators

We start quantization by establishing relations between modes and operators. The vector potential operator $\hat{\vec{A}}_k$ can be expressed in terms of the generalized coordinate operator $\hat{Q}_k$ and the generalized momentum operator $\hat{P}_k$:

$$\hat{\vec{A}}_k = \vec{e}\hat{A}_k = \left(4\varepsilon_0 V \omega_k^2\right)^{-1/2} \left(\omega_k \hat{Q}_k + i\hat{P}_k\right), \tag{1.11}$$

here $\vec{e}$ is the unit polarization vector, ε_0 is the vacuum permittivity, V is the volume, $\hat{Q}_k^* = \hat{Q}_k$, $\hat{P}_k^* = \hat{P}_k$, and

$$\hat{A}_k^\dagger = \left(4\varepsilon_0 V \omega_k^2\right)^{-1/2} \left(\omega_k \hat{Q}_k - i\hat{P}_k\right). \tag{1.12}$$

(For the sake of simplicity, the sign of vector in the index k is omitted.) The energy operator of the mode can be written as

$$H_k = \hat{E}_k^2 + \hat{H}_k^2 = 4\omega_k^2 |A_k|^2 = \frac{1}{V} \left(\omega_k^2 \hat{Q}_k^2 + \hat{P}_k^2\right) \quad (\varepsilon_0 = 1),$$

which gives the *Hamiltonian of the electromagnetic field*

$$H = \sum_k \left(\omega_k^2 \hat{Q}_k^2 + \hat{P}_k^2\right). \tag{1.13}$$

> The energy of EM-field is the sum of the energies of harmonic oscillators. Consequently, each mode of the field is dynamically equivalent to a harmonic oscillator.

Quantization can be done, if we assume that $\hat{Q}_k$ and $\hat{P}_k$ are the operators that satisfy the following commutation relations:

$$\begin{aligned} \left[\hat{Q}_k, \hat{P}_{k'}\right] &= i\hbar\delta_{kk'}, \\ \left[\hat{Q}_k, \hat{Q}_{k'}\right] &= \left[\hat{P}_k, \hat{P}_{k'}\right] = 0. \end{aligned} \tag{1.14}$$

As a next step, we go to dimensionless operators:

$$\hat{a}_k = \sqrt{\frac{\omega_k}{2\hbar}} \left(\hat{Q}_k + i\omega_k \hat{P}_k\right), \quad \hat{a}_k^\dagger = \sqrt{\frac{\omega_k}{2\hbar}} \left(\hat{Q}_k - i\omega_k \hat{P}_k\right).$$

The creation operator $\hat{a}^\dagger$ is the Hermitian conjugate of the annihilation operator $\hat{a}$. It follows from Equation 1.14 that the commutator of these operators is

$$\left[\hat{a}_k, \hat{a}_k^\dagger\right] = 1.$$

Note that operators of the different modes commute:

$$\left[\hat{a}_k, \hat{a}_{k'}^\dagger\right] = [\hat{a}_k, \hat{a}_{k'}] = \left[a_k^\dagger, a_{k'}^\dagger\right] = 0, \quad k \neq k'.$$

Thus, for

$$\hat{Q}_k = \sqrt{\frac{\hbar}{2\omega_k}}\left(\hat{a}_k + \hat{a}_k^\dagger\right) \tag{1.15}$$

and

$$\hat{P}_k = -i\sqrt{\frac{\hbar\omega_k}{2}}\left(\hat{a}_k - \hat{a}_k^\dagger\right) \tag{1.16}$$

we get (see Equation 1.8)

$$\hat{\vec{A}} = \sum_{\vec{k}} \hat{\vec{A}}_{\vec{k}} = \sum_{\vec{k}} \sqrt{\frac{\hbar}{2\varepsilon_0 V \omega_k}} \vec{e}\left[\hat{a}_{\vec{k}}e^{i\vec{k}\vec{r}-i\omega t} + \hat{a}_{\vec{k}}^\dagger e^{-i\vec{k}\vec{r}+i\omega t}\right]. \tag{1.17}$$

The field energy is defined by the Hamiltonian

$$\hat{H} = \sum_{k} \hat{H}_{\vec{k}} = \sum_{k} \hbar\omega_k\left(\hat{a}_{\vec{k}}^\dagger \hat{a}_{\vec{k}} + \frac{1}{2}\right). \tag{1.18}$$

The vector potential $\vec{A}$ (see Equation 1.17) defines the potentials of the electromagnetic field in second quantization formalism:

$$\hat{\vec{E}} = i\sum_{\vec{k}} \vec{e}\sqrt{\frac{\hbar\omega_k}{2\varepsilon_0 V}}\left[\hat{a}_{\vec{k}}e^{i\vec{k}\vec{r}-i\omega_k t} - \hat{a}_{\vec{k}}^\dagger e^{-i\vec{k}\vec{r}+i\omega_k t}\right], \tag{1.19}$$

$$\hat{\vec{H}} = i\sum_{\vec{k}} (\vec{k} \times \vec{e}_k)\sqrt{\frac{\hbar}{2\varepsilon_0 V \omega_k}}\left[\hat{a}_{\vec{k}}e^{i\vec{k}\vec{r}-i\omega_k t} - \hat{a}_{\vec{k}}^\dagger e^{-i\vec{k}\vec{r}+i\omega_k t}\right]. \tag{1.20}$$

Note that $\hat{\vec{A}}_{\vec{k}}$, $\hat{H}_{\vec{k}}$, $\hat{\vec{E}}$, $\hat{\vec{H}}$ are all Hermitian.

Let us prove that the operators $\hat{a}^\dagger$ and $\hat{a}$ act as the creation and annihilation operators of photons.

To do that, we define the operator $\hat{n} = \hat{a}^\dagger \hat{a}$. This operator has eigenstates $|n\rangle$, such that

$$\hat{n}|n\rangle = n|n\rangle.$$

Let us see how operator $\hat{a}^\dagger$ affects the state $|n\rangle$. The energy operator (Hamiltonian) is given below (for simplicity we consider a 1-mode case):

$$\hat{H} = \hbar\omega\left(\hat{n} + 1/2\right).$$

In stationary state $\hat{H}|n\rangle = E_n|n\rangle = \hbar\omega\left(n + 1/2\right)|n\rangle$, thus

$$\hat{n}\hat{a}^\dagger|n\rangle = \hat{a}^\dagger\hat{a}\hat{a}^\dagger|n\rangle = \hat{a}^\dagger(\hat{a}^\dagger\hat{a} + 1)|n\rangle = (n+1)\hat{a}^\dagger|n\rangle$$

and

$$\hat{H}\hat{a}^\dagger|n\rangle = \hbar\omega(\hat{a}^\dagger\hat{a} + 1/2)\hat{a}^\dagger|n\rangle = \hat{a}^\dagger\hbar\omega((\hat{n}^\dagger + 1) + 1/2)|n\rangle = (E_n + \hbar\omega)\hat{a}^\dagger|n\rangle.$$

We just showed that that the state $a^\dagger|n\rangle$ is a stationary state with energy higher than the energy of state $|n\rangle$. The operator $a^\dagger$ is the *creation operator,* which rises the energy by a quantum $\hbar\omega$. Similarly, we find that operator $\hat{a}$ is the *annihilation operator*:

$$\hat{H}\hat{a}|n\rangle = \hbar\omega(\hat{a}^\dagger\hat{a} + 1/2)\hat{a}|n\rangle = \hat{a}\,\hbar\omega((\hat{a}^\dagger\hat{a} - 1) + 1/2)|n\rangle = (E_n - \hbar\omega)\hat{a}|n\rangle.$$

The energy of a harmonic oscillator cannot be negative, since both potential and kinetic energies are assigned to a square of measurables (real quantities). Repeatedly applying the annihilation operator, we reach the minimum energy state, denoted by $|0\rangle$. Since there are no states with lower energy, $\hat{a}|0\rangle = 0$. Repeatedly applying the creation operator to the state $|0\rangle$, we obtain n positive integers $1, 2, 3...$ and equidistant energy levels $E_n = \hbar\omega(n + 1/2)$.

The state of lowest energy ($n = 0$) has energy $\hbar\omega/2$. This energy is known as *zero-point energy*. It should be noted that the existence of zero-point energy is a purely quantum phenomenon: it disappears at the boundary of classical physics $\hbar \to 0$.

1.1.3   Planck scale: energy, time and length

From known physical constants: c (speed of light in vacuum), G (gravitational constant), $h = 2\pi\hbar$ (*Planck constant*) one can derive quantities with the dimension of energy, length and time. For example, we can take a length dimensional quantity

$$L_P \approx \sqrt{\hbar G/c^3} \sim 10^{-35}\text{m},$$

known as *Planck length*. There is reason to believe (see below) that Planck length is the smallest possible length. By dividing L_P with the speed of light, we get the *Planck time*

$$t_P = L_P/c \approx 5 \times 10^{-44}\text{s}.$$

This time also determines *Planck energy*

$$E_P \sim \hbar/t_P = \sqrt{\frac{\hbar c^5}{G}} \approx 1.22 \times 10^{19}\text{GeV} \approx 1.956 \times 10^9\text{J} \approx 0.5433\text{ MWh}.$$

We can summarize as follows (Table 1.1):

Table 1.1: Planck scale

Quantity	Equation	SI units
Planck energy	$E_P = \sqrt{\dfrac{\hbar c^5}{G}}$	1.22×10^{19} GeV
Planck time	$t_P \approx \sqrt{\dfrac{\hbar G}{c^5}}$	5.39121×10^{-44} s
Planck length	$L_P \approx \sqrt{\dfrac{\hbar G}{c^3}}$	1.616252×10^{-35} m
Planck mass	$M_P = \dfrac{E_P}{c^2}$	2.177×10^{-8} kg

1.2   Zero-point energy and Casimir effect

1.2.1   Zero-point energy of electromagnetic field

In the stationary state, the energy of mode $\vec{k}$ is

$$E_{\vec{k}} = \hbar\omega_k\left(n_{\vec{k}} + 1/2\right) \qquad n_{\vec{k}} = 0, 1, 2, ...$$

(in each mode there are $n_{\vec{k}}$ photons), which gives the total energy of the field

$$E = \sum_{\vec{k}} \hbar \omega_k \left(n_{\vec{k}} + 1/2 \right).$$

In the zero-state, all $n_{\vec{k}} = 0$ (there are no photons) and the *zero-point energy* (vacuum energy) yields

$$E_0 = \sum_{\vec{k}} \hbar \omega_k / 2.$$

Other fields also contribute to the energy of the vacuum, for example, in the Standard Model, the gauge fields, the fermion field and also the Higgs field.

Zero-point energy arises from the Heisenberg *uncertainty principle* - there is no state in which the system is immobile in the bottom of the potential well - the coordinate and momentum cannot be precisely determined simultaneously. The lowest energy state (the ground state) must have a coordinate and momentum distribution that satisfies the uncertainty principle. In other words, the energy of the system must be higher than the minimum of the potential well.

Let us estimate the value of the zero-point energy. Since L_P is the minimal possible length, π / L_P is the maximum possible k. The *zero-point energy density* is

$$\rho_0 = \frac{E_0}{V} = \frac{\hbar c}{2} \int_0^{L_P^{-1}} k \rho_k dk = \frac{\hbar c}{2\pi^2} \int_0^{L_P^{-1}} k^3 dk = \frac{E_P}{8\pi^2 L_P^3} \tag{1.21}$$

where *Planck density* is

$$\rho_P = E_P / L_P^3.$$

This is a tremendous amount of energy, $\sim 10^{107}$ Joule per cubic centimeter of vacuum.

Historically it was assumed that vacuum corresponds to the minimum possible energy that does not occur in real processes. In 1948 the Dutch physicist Henrik B.G. Casimir pointed out the fact that the vacuum state can be altered by changing its energy. He showed that a typical optical resonator affects electromagnetic modes and therefore their zero-point energy. For example, in the case of the simplest resonator - two parallel reflective (metallic) plates - the zero-point energy decreases with the distance between the plates. As a result, the distance between the plates shrinks (the *Casimir effect*), and the corresponding attractive force (called the *Casimir force*), although it is very weak, was nevertheless measured.

1.2.2 One-dimensional Casimir effect

Allowed k-values give the zero-point energy

$$E_0 = \sum_k \frac{\hbar \omega_k}{2} = \sum_k \frac{\hbar c k}{2} = \frac{\hbar c \pi}{2a} \sum_{n=1}^{n_{\max}} n. \tag{1.22}$$

If $a \to \infty$, then the sum is replaced by the integral

$$E'_0 = \frac{\hbar c}{2} \int_0^{k_{\max}} k dk. \tag{1.23}$$

To calculate the Casimir force, we need to find the difference between two gigantic numbers $E_0 - E'_0$. In order to avoid infinity, the procedure of the quantum field theory called regularization is used. We introduce a parameter dependent variable, which makes the sum finite, and eliminates this parameter from the theory by choosing the suitable limits. Casimir added an exponential damping factor to this sum by replacing the regular value

$$\sum_n n \to \sum_{n=0}^{\infty} n e^{-\gamma n},$$

where $\gamma = \alpha \pi / a$, α is a cutoff parameter (of length dimension),

$$\sum_{n=0}^{\infty} n e^{-\gamma n} = -\frac{\partial}{\partial \gamma} \sum_{n=0}^{\infty} e^{-\gamma n} = -\frac{\partial}{\partial \gamma} \frac{1}{1 - e^{-\gamma}} = \frac{e^{-\gamma}}{(1 - e^{-\gamma})^2} = \frac{1}{(e^{\gamma/2} - e^{-\gamma/2})^2}.$$

We get

$$E_0 = \frac{\hbar c \pi}{2a} \frac{1}{(e^{\gamma/2} - e^{-\gamma/2})^2}.$$

By series expansion for small γ,

$$\frac{1}{(e^{\gamma/2} - e^{-\gamma/2})^2} \approx \frac{1}{\gamma^2} - \frac{1}{12} + \left(\frac{1}{240}\right)\gamma^2 - O(\gamma^4).$$

Thus,

$$E_0 = \frac{\hbar \pi c}{2a} \left(\frac{1}{\gamma^2} - \frac{1}{12} + ... \right),$$

which has a regular, cutoff-independent part

$$E_{\text{reg}} = -\frac{\pi \hbar c}{24a}. \tag{1.24}$$

In the one-dimensional case, we get the Casimir force

$$F_{\text{cas}} = -\frac{\partial E}{\partial a} = -\frac{\pi \hbar c}{24 a^2}. \tag{1.25}$$

A modern approach uses the *Abel-Plana formula*, which allows to calculate the sum using an integral (see Appendix A):

$$\sum_{n=1}^{\infty} F(n) = \int_0^{\infty} F(t) dt - \frac{1}{2} F(0) + i \int_0^{\infty} \frac{F(it) - F(-it)}{e^{2\pi t} - 1} dt.$$

In the one-dimensional case $D = 1$, $F(n) = n$ and the regular part of zero-point energy equals

$$E_{reg} = \frac{\pi \hbar c}{2a} i \int_0^{\infty} \frac{(it - (-it)) dt}{e^{2\pi t} - 1} = -\frac{\pi \hbar c}{2a} \frac{B_2}{2}, \tag{1.26}$$

where B_2 stays for *Bernoulli number*. Bernoulli numbers are determined by the integral

$$B_{2n} = (-1)^{n-1} 4n \int_0^{\infty} \frac{t^{2n-1} dt}{e^{2\pi t} - 1}, \tag{1.27}$$

$$B_0 = 1, B_1 = -1/2, B_2 = 1/6, B_3 = 0, B_4 = 1/30,$$

hence $E_{\text{reg}} = -\pi \hbar c / (24a)$, and the Casimir force is

$$F_{\text{cas}} = -\frac{\partial E}{\partial a} = -\frac{\pi \hbar c}{24 a^2}.$$

1.2.3   Casimir effect in three dimensions

Let us have two infinitely large, plane-parallel metal plates (for the boundary conditions to be as simple as possible) with an area of zy-plane as L^2. The spatial dependence of the field between the plates is given by Equation 1.4. It follows that

$$k_x = \frac{\pi \nu_x}{a}, k_y = \frac{\pi \nu_y}{L}, k_z = \frac{\pi \nu_z}{L},$$

$$\nu_x, \nu_y, \nu_z = 0, \pm 1, \pm 2, ...,$$

$$E_\alpha(t) = E_{\alpha 0} e^{i\omega t}.$$

When $L \to \infty$, the density of modes is $\rho(k) = k^2/\pi^2$, where the wave vector is a continuous variable:

$$k = \sqrt{k_x^2 + k_y^2 + k_z^2} = \sqrt{\left(\frac{\pi n}{a}\right)^2 + k_y^2 + k_z^2}, \quad \omega = ck.$$

The zero-point energy yields

$$E_0 = \frac{\hbar c}{2} \sum_{\vec{k}} k = \frac{\hbar c}{2} \int dk_y \int dk_z \sum_{n=0}^{\infty} \sqrt{\left(\frac{\pi n}{a}\right)^2 + k_y^2 + k_z^2}.$$

In the limit $L \to \infty$,

$$E_0 = \frac{\hbar c}{2} \int_0^{\infty} \frac{kdk}{\pi} \sum_{n=0}^{\infty} \sqrt{\left(\frac{\pi n}{a}\right)^2 + k^2}.$$

Here $k^2 = k_y^2 + k_z^2$. Introducing a dimensionless quantity

$$q = \frac{a}{\pi} k \quad \to \quad dq = \frac{a}{\pi} dk,$$

yields

$$E_0 = \frac{\hbar c}{2} \int_0^{\infty} \frac{kdk}{\pi} \sum_{n=0}^{\infty} \sqrt{\left(\frac{\pi}{a}\right)^2 (n^2 + q^2)} = \frac{\hbar c}{2\pi} \left(\frac{\pi}{a}\right)^3 \int_0^{\infty} q \, dq \sum_{n=0}^{\infty} \sqrt{n^2 + q^2}.$$

We use the Abel-Plana formula to find the regular value of energy:

$$E_{0,\text{reg}} = \frac{\hbar c \pi^2}{2a^3} \int_0^{\infty} q dq \left[i \int_0^{\infty} dt \frac{\sqrt{(it)^2 + q^2} - \sqrt{(-it)^2 + q^2}}{e^{2\pi t} - 1} \right] = \frac{\hbar c \pi^2}{2a^3} \sigma.$$

Let us calculate σ :

$$\sigma = \int_0^{\infty} q dq \left[i \int_0^{\infty} dt \frac{\sqrt{(it)^2 + q^2} - \sqrt{(-it)^2 + q^2}}{e^{2\pi t} - 1} \right]$$

$$= \int_0^{\infty} q dq \left[i^2 \times 2 \int_q^{\infty} dt \frac{\sqrt{t^2 - q^2}}{e^{2\pi t} - 1} \right].$$

We change the order of integration and introduce a new integration variable x:

$$q = tx, \ dq = t \, dx,$$

$$\sigma = -2 \int_0^\infty dt \frac{1}{e^{2\pi t} - 1} \int_0^t dq\, q \sqrt{t^2 - q^2} = -2 \int_0^\infty dt \frac{t^3}{e^{2\pi t} - 1} \int_0^1 dx\, x \sqrt{1 - x^2}$$

We get

$$\sigma = -\frac{2}{3} \int_0^\infty dt \frac{t^3}{e^{2\pi t} - 1},$$

where the integral over t is the Bernoulli number $B_4/8 = 1/240$ (see Equation 1.27), thus $\sigma = -1/360$ and the corresponding zero-point energy is

$$E_{0,\mathrm{reg}} = -\frac{\hbar c \pi^2}{720 a^3}, \tag{1.28}$$

which gives the Casimir force per unit area (i.e. pressure)

$$F_{\mathrm{cas}} = -\frac{\partial E_{0,\mathrm{reg}}}{\partial a} = -\frac{\pi^2 \hbar c}{240 a^4}. \tag{1.29}$$

If $L = 10$ cm (hence the size of the plate is $L^2 = 10^{-2} \mathrm{m}^2$) and the gap between the plates is $a = 10^{-7}$m, then

$$F_{\mathrm{cas}} \sim 0.13\,\mathrm{N}$$

$$\Rightarrow P_{\mathrm{cas}} \sim 1.3 \times 10^{-4} \mathrm{atm} \sim 13\,\mathrm{Pa}.$$

As we can see, the Casimir force is proportional to the Planck constant, so it lacks an analogy in classical physics.

1.2.4   Casimir force in experiment

The first measurement attempt was made by M.J. Sparnaay in 1958, but only at the beginning of 1997, Steven K. Lamoreaux announced the first correct attempt to test Casimir force. *Apparently, zero-point energy can be directly observed in the experiment and this energy is affected by the matter.*

How does the zero-point energy of an electromagnetic field change if you place two plane-parallel metal plates at a distance of a?

Consider the zero-point energy of the electromagnetic field per unit area (see Figure 1.1). This energy depends on the distance between the plates. The waves propagating between the conductive plates must satisfy the boundary conditions: the cross-component of the electric field must be zero at the surface of the conducting plate; on the conducting surface there is a nodal point of the wave. Therefore, there can be only plane waves between the plates having integer number of half-wavelengths. In other words, only waves of length $\lambda_k = 2a/n$ are allowed to propagate between the plates. Allowed wave vector values are $k = 2\pi/\lambda = \pi n/a$.

If we reduce the distance of a twice, half of the modes disappear, thus reducing the zero-point energy between the plates and creating an attractive force. At a distance $1\,\mu m$, this force is $\simeq 10^{-8} N$.

Casimir force can be considered as a special case of the van der Waals forces, which generally act on a small distance between macroscopic bodies whose surfaces form partially open resonators.
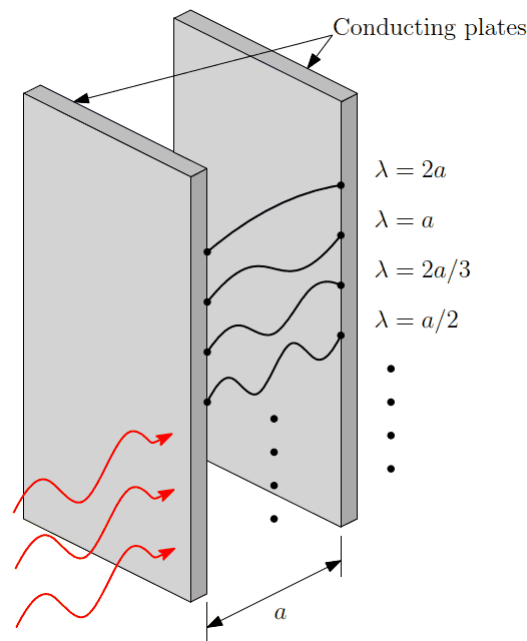
Figure 1.1: Casimir force between two parallel plates.
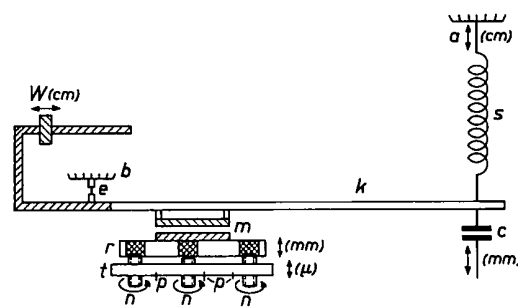
Figure 1.2: Casimir effect measurements (from Sparnaay, 1958).

The following device has been proposed for experimental verification of the Casimir effect [32].

In the experiment, the voltage drop has been measured when moving a tiny wagon (see Figure 1.2). Despite the large measurement error (~ 50 %), the force has been registered. Later tests have been performed many times. The distance between the plates has been reduced down to $2-3$ Å.

Vacuum energy often manifests itself in experiments:

- between two plane-parallel plates, one of which oscillates;

- with a vibrating mirror;

- with accelerated moving detector;

- with the black hole radiation (vacuum decay).

1.3   Energy of vacuum

1.3.1   Universe as a quantum fluctuation

USA theoretical physicist Edward Tryon (see [33]) presented a model according to which our Universe is a quantum fluctuation with a zero net value of energy. Let summarize his hypothesis.

Universe appeared from nowhere around 10^{10} years ago. At this point there was no need to break the conservation laws of physics. It means that in such Universe the net value of all conserved quantities must be zero.

There are two kinds of conserved quantities: continuous and discrete. Discrete quantities characterize elementary particles (electric charge, etc.), they have the same magnitude, but a different sign for particle and antiparticle. The discrete conservation laws require that the Universe created from nowhere must equally contain both matter and antimatter.

For cosmology, the most important is the energy conservation law. Although matter and energy can be converted to each other, the total energy must remain constant, even if each part of matter gets energy mc^2.

The Universe has a huge amount of rest mass energy, which seems to prevent creation of the Universe from nothing! But let's not forget that there is another important form of energy for cosmology, namely the potential energy of gravity. The interaction of the mass m with the rest of the Universe produces the gravitational energy

$$E_G \approx -GmM/R,$$

where M is the total mass of the Universe limited by the Hubble radius $R = c/H$, H is the Hubble constant. The star on a distance D moves away at a speed of $v = H \cdot D$, $H = 77\,\text{km/s} \cdot \text{Mpc} = 2.5 \times 10^{-18}\text{s}^{-1} \rightarrow R \approx 10^{28}\text{cm}$ (here Mpc = megaparsec).

$$1\,\text{Mpc} = \text{megaparsec} = 3.08567758 \times 10^{22}\text{m}.$$

The critical density of the mass of the Universe limited by the Hubble radius is

$$\rho_c = \frac{3H^2}{8\pi G} = \frac{3c^2}{8\pi R^2 G} = \frac{3}{8\pi}\frac{mc^2 R}{mMG}\frac{M}{R^3} = -\frac{mc^2/2}{E_G}\frac{M}{4\pi R^3/3} = -\frac{mc^2/2}{E_G}\rho_c. \tag{1.30}$$

Consequently,

$$E_G \approx -mc^2/2.$$

The negative gravitational energy of each particle is sufficient to compensate for the positive rest mass energy mc^2. Thus, the mass of the Universe is compensated by the mass-induced gravitational energy, so that their total energy is zero or close to zero. With this compensation, Tryon asserts that the energy of the vacuum, as well as of the whole Universe, is zero (or close to it).

Tryon argues that the possibility of generating the Universe with the zero-point energy arises from the quantum field theory. According to quantum electrodynamics, the electron, positron, and photon can spontaneously appear in a vacuum. If this happens, these three particles can exist only in a short period of time and then annihilate without leaving a trace. The conservation of energy would be broken, but only during the lifetime Δt of the particle, which is allowed with the uncertainty $\Delta E \Delta t \sim \hbar$, where ΔE is the total energy of three particles. This temporary spontaneous particle creation is called *vacuum fluctuation*.

Tryon suggests that our Universe arose as an energy fluctuation of a vacuum, and continues to expand.

The Universe expands because the vacuum energy density of it is slightly less than 0. In Tryon's model, this is obvious when considered the particle-free vacuum. Indeed, particles have been created in the initial fluctuation. Total energy is 0. Part of that energy belonged to particles, and it is a positive energy. Consequently, the vacuum energy, excluding the particle energy, must be negative in the case of initial fluctuation and must remain slightly negative in order to support further expansion.

1.3.2 Gravitational energy of small wave packet

Below the arguments are presented that vacuum energy is a balance between two gigantic energy of the opposite sign. One of them is the zero-point energy of the fundamental bosons, which is positive. Another is the gravitational energy of Planck length particles, which we assume to exist.

First, we show that Planck energy indeed corresponds to the maximum possible absolute value of one particle's energy.

Consider a single particle with an extremely small wave packet length L. From the Heisenberg uncertainty principle, it follows that in the order of magnitude

$$\Delta x \Delta p \geq \hbar \quad \rightarrow \quad L \Delta p \geq \hbar.$$

If L is rather small, then the momentum $p \sim \hbar / L$ corresponds to a very large relativistic (kinetic) energy of the order of

$$E_k = pc = \frac{\hbar c}{L}.$$

Normally, gravity is not taken into account, but here there is a wave packet with a very high energy and mass, so one should also take into account the gravitational energy of the packet

$$E_G \sim -G \frac{m^2}{L},$$

where the mass m is determined by the total energy: $m = E/c^2$, $E = (E_k + E_G)$. Thus, in the order of magnitude

$$E_G = -G \frac{(E_k + E_G)^2}{c^4 L} = -G \frac{E^2}{c^4 L}.$$

The full energy of the wave packet is

$$E = E_k + E_G = \frac{\hbar c}{L} - G \frac{E^2}{c^4 L},$$
$$\Rightarrow \left(E - \frac{\hbar c}{L} \right) \frac{c^4 L}{G} + E^2 = 0, \tag{1.31}$$
$$\Rightarrow E^2 + \frac{c^4 L}{G} E - \frac{\hbar c^5}{G} = 0.$$

There are two solutions of this equation:

$$E_\pm = \pm \sqrt{\frac{\hbar c^5}{G} + \left(\frac{c^4 L}{2G} \right)^2} - \frac{c^4 L}{2G} = E_P \left(\pm \sqrt{1 + \left(\frac{L}{2L_P} \right)^2} - \frac{L}{2L_P} \right). \tag{1.32}$$

Here $E_P = \sqrt{\hbar c^5 / G} = 1.22 \times 10^{19}$ GeV is the *Planck energy*. It is the maximum possible absolute value of energy of a single particle, and gravity does not allow more.

A hypothetical particle of maximum possible positive energy E_P and mass $M_P = E_P/c^2 = 2.177 \times 10^{-8}$ kg is called *Planck particle*. For comparison, one of the heaviest observed elementary particles - the Higgs boson - is about 125 GeV.

It should be noted that the maximum energy of a particle comes from the positive energy solution of Equation 1.31 (the negative energy solution will be given later). As we saw previously, the electromagnetic field zero-energy is given by Equation 1.21

$$E_0 = V \frac{\hbar c}{2} \int\limits_0^{k_{\max}} k \rho_k \, dk = V \frac{E_P}{8\pi^2 L_P^3},$$

where $k_{\max} = 1/L_P$ is the maximum value of wave number determined by the reciprocal Planck length. The corresponding energy density is

$$\rho_0 = E_0/V_0 = E_P/(8\pi^2 L_P^3).$$

Photons are not the only fundamental bosons, there are some others that also contribute to the zero-point energy of the vacuum. That is why the energy density (zero-energy of electromagnetic field per unit volume) is usually given as

$$\rho_{\text{vac}}^+ = \alpha E_P/L_P^3,$$

where $\alpha = Z/16\pi^2$, and Z is the total number of bosonic spin states (including anti-particles), E_P is *Planck energy*, L_P is *Planck length*. This giant energy density exceeds by 10^{102} times the average energy density of the mass in the Universe.

1.3.3   Planck-scale wave packets of particles with negative gravitational energy

Let us return to the vacuum energy and its density. It seems reasonable to search for the gravitational interaction as the compensation for the huge boson-caused zero-point energy $\sim 10^{107} \, J/cm^3$, which, as we we assume, exist. In this, we rely on the negative energy solution obtained above

$$E_- = -E_P \left(\sqrt{1 + \left(\frac{L}{2L_P}\right)^2} + \frac{L}{2L_P} \right) \tag{1.33}$$

We assume that this solution corresponds to particles with negative energy that are trapped in their own gravitational field. At first glance, it seems that this assumption is not physical (it cannot correspond to reality), since it leads to an arbitrarily large absolute value of the negative energy density E_-/L^3. However, this conclusion is not true. Here are two facts to consider:

- Planck length L_P is the only quantity of such magnitude with the dimension of length; there are no smaller quantities we know of. Similarly, the energy density of negative energy particles should not have a significantly greater absolute value than E_P/L_P^3 (see the next paragraph to justify these generally accepted statements;

- energetically it is benefical if such particles of negative energy exist everywhere in space and do not overlap. In other words, the considered particles of negative energy are repelled at the Planck limit.

The last property follows from the consideration of compound wave packets consisting from $N > 1$ packets of small size. According to above equation, a wave packet $L \gg L_P$ consisting of $N > 1$ completely overlapping particles has approximately L/L_P times higher negative energy and $(L/L_P)^3$ times greater volume than one particle of size L_P. In the same volume $\sim (L/L_0)^3$ particles can be placed, separated by the distance L_0 (which is greater, but comparable to L_P), having $\sim (L/L_P)^2$ times larger total negative energy than the single wave packet of size $\sim L_0$. Thus, it is energetically favorable to place aforementioned packets of the size $\sim L_P$ in a space separated from each other by a distance of $L_0 > L_P$. Negative energy particles form a superstructure of vacuum on Planck scale.

The parameter L_0 of the superstructure can be found if to suppose that the negative energy density compensates for the density of the positive vacuum energy density $10^{107} J/cm^3$. Here we proceed from the Tryon's hypothesis that only the Universe whose total energy density is close to zero can exist. According to the above arguments, the vacuum, in addition to zero-point fluctuations of the bosons, should contain hypothetical particles of size $\sim L_P$ and energy $\sim -E_P$. The energy density of these particles is huge and negative, and it compensates for the huge positive energy density of zero-point fluctuations of bosons.

Here we assume that this generally accepted value of the energy density of the zero-point state of bosons is not essentially influenced by gravitational interaction due to homogeneous distribution of the zero-point energy in space.

1.3.4 Repulsion interaction in Planck scale

According to above presented consideration, the hypothetical particles (fluctuations) with negative energy should have small size of the order of L_P. To find this size, we take into account that $-E_P/L_P^3$ is the smallest possible energy density of the negative energy fluctuations. This means that there should exist a mechanism which works against the gravitational collapse of the fluctuations under consideration. For this mechanism may stand an inherent repulsive interaction. Such interaction is known in the standard model (see [13]), it is given by the following fourth order nonlinear energy term in the Lagrangian of the quantum field ϕ:

$$U_{\text{rep}} = \lambda(\phi^\dagger \phi)^2, \tag{1.34}$$

where $\lambda = 1/2$ is the dimensionless interaction parameter (for the value of λ, see Appendix B). We suppose that this-type repulsion interaction exists also for the particles under consideration.

In the Heaviside units ϕ has the dimension of energy. In these units in the Planck limit $\phi_P = E_P$ and $l_P = E_P^{-1}$. Then the self-repulsion energy E_{rep} is

$$E_{\text{rep}} \sim \lambda E_P (L_P/L)^3 \tag{1.35}$$

For an arbitrary ϕ we get in SI units

$$E_{\text{rep}}(L) = \lambda E_P L_P^3 \int dV \phi^4.$$

Unlike the gravitacional interaction which is also a nonlinear one and is considered in classical limit, $E_{\text{rep}}(L)$ is of a purely quantum origin. Therefore a rigorous consideration of both nonlinear interactions simultaneously is possible only within the frames of the quantum theory of gravity which is not yet available. However, as it follows from Equations

1.33-1.34 for small $L < L_P$ the quantum repulsion is much stronger than the gravitational attraction while for large $L > L_P$ the ratio of them is just the opposite. Therefore, to describe the large and small L one may consider both nonlinear interactions to be independent.

Let us consider the Gaussian wave packets

$$\phi(r) = (2/\pi)^{3/4} L^{-3/2} e^{-r^2/L^2}, \tag{1.36}$$

where r is the radial coordinate, $L/2$ is the root-mean-square deviation of r. One gets

$$E_{\text{rep}} = \lambda E_{\text{P}} (L_{\text{P}}/\sqrt{\pi} L)^3, \tag{1.37}$$

$$E_G = -\pi^{3/2} G E^2 / 8 L c^4, \quad E_{\text{kin}} = 3\hbar c/L,$$

$$E_- = -4 E_{\text{P}} \pi^{-3/2} \left(L/L_{\text{P}} + \sqrt{L^2/L_{\text{P}}^2 + 3\pi^{3/2}/2} \right). \tag{1.38}$$

This gives the following energy density of the negative enery particles:

$$\rho_{\text{vac}}^- = \pi \left(E_{\text{rep}} + E_- \right) / 3\sqrt{2} L_0^3, \tag{1.39}$$

where L_0 is the distance between the wave packets under consideration (the factor $3\sqrt{2} L_0^3/\pi$ stands for the volume of the unit cell of the close-packed structure). The dependence of the energy density of the fluctuations with negative energy on the distance L_0 between them for $\lambda = 1/2$ (see Appendix B) and three different values of $L_1 = L_0 - L/2$ is given in Figure 1.3.
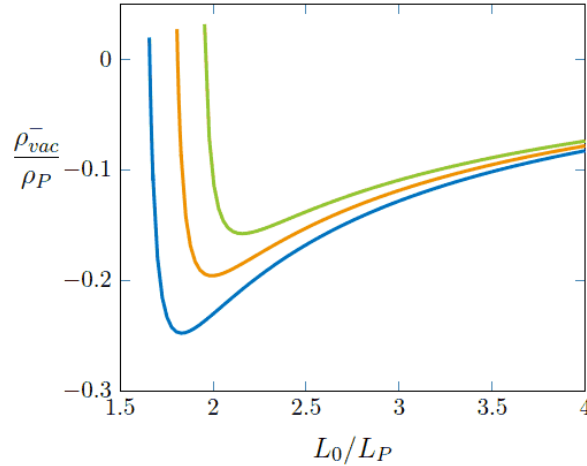
Figure 1.3: The energy density of the quantum fluctuations with negative energy for three values of $L_1 = L_0 - L/2$ (L is the space size of the fluctuation): 1) $1.9 L_P$ (upper curve), 2) $1.75 L_P$ (middle curve), 3) $1.6 L_P$ (lower curve); L_0 is the distance between the fluctuations.

For $L_1 = 1.75 L_P$ the absolute value of the minimum of the calculated negative density of energy coincides with the energy density of the zero-point fluctuations of bosons $\approx 0.2 \rho_P$ (middle curve), and the total energy density of vacuum is zero. In our model the size of the fluctuations equals $L = 0.5 L_P$ and the distance between them is $L_0 = 2 L_P$. (Here we assume that this generally accepted value of the energy density of the zero-point state of bosons takes into account the influence of gravitational self-action of this state.)

To find the actual value of L_0 (and ρ_{vac}^-), we proceed from Tryon's argument that the Universe could only have appeared with zero (or close to zero) energy. Taking that both positive and negative energy contributions to vacuum energy coincide and cancel, we get the following vacuum energy density dependence on distance L_0 between negative energy particles (see Figure 1.4). The minimum of energy density gives the value of L_0, that corresponds to the Tryon's zero energy.
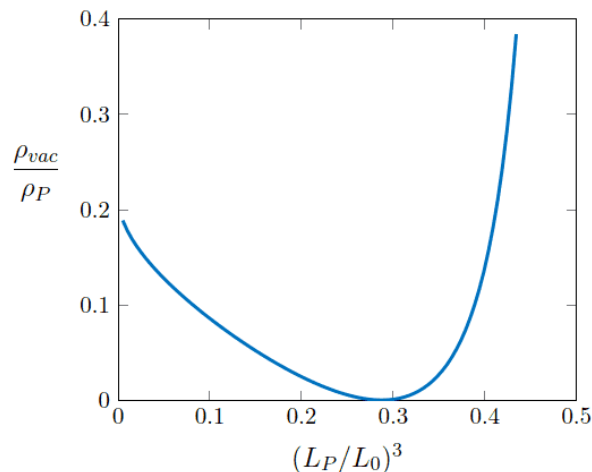
Figure 1.4: Dependence of vacuum energy density ρ_{vac} on the volume L_0^3 of vacuum superstructure.

1.3.5 Quantum vacuum in Planck limit

It was shown above that on Planck limit vacuum has a structure. In addition to the homogeneously distributed in space zero-point field of bosons of huge positive energy, it contains Planck-size particles with negative energy. These particles give all together the same huge contribution to the energy, but of opposite sign. The total energy density of vacuum is zero or close to zero.

> The constant density of zero-point energy is easy to verify if we recall that a monochromatic wave of circular polarization everywhere has the same energy density.

It is interesting to note the possibility of various not entirely accurate compensations for the contributions of the zero-point energy of bosons and particles with negative energy, considered here in different regions of Universe. This inaccurate compensation may be the cause of the so-called dark cosmological energy, different in different areas of Universe.

To characterize the structure of vacuum on Planck scale, we introduced two new fundamental lengths characterizing the Universe:

- the length of negative energy fluctuations L,

- intra-fluctuation distance L_0.

We got the values

$$L \approx 0.5\, L_{\text{P}},$$
$$L_0 \approx 2\, L_{\text{P}}. \tag{1.40}$$

To derive the values of these quantities, we introduced the dimensionless parameter λ, that describes the repulsion of quantum field on Planck scale. We have found it

$$\lambda = 1/2. \tag{1.41}$$

The almost exact balance of the positive energy of the zero point boson field and the energy of the negative particle allows one to consider the creation and destruction of particles without violating the law of conservation of energy. Such processes can lead to expansion of the Universe (see Appendix D and Appendix E).

Quantum states of radiation field

2.1 Phase operator

One of the characteristics of classical vibrational processes is the phase. In quantum theory, the phase operator is introduced to describe similar properties of quantum systems. Below we define a phase operator describing all states of the system except the 0-state. So, in this chapter we are going to talk about the *excited states*. Then it's easy to define a phase operator.

We consider the classical (vector) field $\vec{A} = \sum_{\vec{k}} \vec{A}_{\vec{k}}$, where

$$\vec{A}_{\vec{k}}(\vec{r}, t) = \vec{A}_{0\vec{k}} e^{i\vec{k}\vec{r} - i\omega_k t + i\varphi_k} + Cc,$$

φ denotes the initial phase (i.e. the phase of the field at the point $\vec{r} = 0, t = 0$).

In quantum theory (see Equation 1.17)

$$\hat{\vec{A}}_{\vec{k}}(\vec{r}, t) = \left(\frac{\hbar}{2\varepsilon_0 V \omega_k}\right)^{1/2} \vec{e}_k \left(\hat{a}_k e^{i\vec{k}\vec{r} - i\omega_k t} + \hat{a}_k^+ e^{-i\vec{k}\vec{r} + i\omega_k t}\right),$$

where operators a_k and $a_k^\dagger$ are amplitude and phase-dependent. Further we skip the index k, then

$$\hat{a} = (\hat{n} + 1)^{1/2} \hat{e}^{i\varphi}, \tag{2.1}$$

$(\hat{n} + 1)^{1/2}$ is a normalization coefficient, $\hat{e}^{i\varphi}$ is the *phase operator*, defined by the equation

$$\hat{e}^{i\varphi} = (\hat{n} + 1)^{-1/2} \hat{a}, \tag{2.2}$$

where $\hat{n} = \hat{a}^\dagger \hat{a}$ is a *particle-number operator*:

$$\hat{n}|n\rangle = n|n\rangle.$$

Phase operator is *not Hermitian*, since $\hat{a}$ is not. *Adjoint* (or Hermitian conjugate) phase operator is

$$\hat{e}^{-i\varphi} \equiv (\hat{e}^{i\varphi})^\dagger = \hat{a}^\dagger (\hat{n}+1)^{-1/2}. \tag{2.3}$$

These operators generally do not commute because a_k and $a_k^\dagger$ do not commute either:

$$\left[\hat{e}^{i\varphi}, \hat{e}^{-i\varphi}\right] \neq 0.$$

Let us check this:

$$\hat{e}^{i\varphi}\hat{e}^{-i\varphi} = (\hat{n}+1)^{-1/2}\hat{a}\hat{a}^\dagger(\hat{n}+1)^{-1/2} = (\hat{n}+1)^{-1/2}(\hat{n}+1)(\hat{n}+1)^{-1/2} = 1,$$

$$\hat{e}^{-i\varphi}\hat{e}^{i\varphi} = \hat{a}^\dagger(\hat{n}+1)^{-1/2}(\hat{n}+1)^{-1/2}\hat{a} \neq 1.$$

There is a reason why there are two phase operators in quantum mechanics: one operator corresponds to the coordinate, and the other to the momentum.

Let us find how the phase operator acts on the well-defined energy state:

$$\hat{e}^{i\varphi}|n\rangle = (\hat{n}+1)^{-\frac{1}{2}}\hat{a}|n\rangle = (\hat{n}+1)^{-\frac{1}{2}}\sqrt{n}|n-1\rangle = \sqrt{n}(\hat{n}+1)^{-\frac{1}{2}}|n-1\rangle =$$

$$= \sqrt{n}(n-1+1)^{-1/2}|n-1\rangle = \begin{cases} |n-1\rangle, & n > 0, \\ 0, & n = 0. \end{cases}$$

This corresponds to the *normalized annihilation operator*. Similarly, the adjoint operator

$$\hat{e}^{-i\varphi}|n\rangle = \hat{a}^\dagger(\hat{n}+1)^{-\frac{1}{2}}|n\rangle = (n+1)^{-\frac{1}{2}}\hat{a}^\dagger|n\rangle = \sqrt{n+1}(n+1)^{-\frac{1}{2}}|n+1\rangle = |n+1\rangle$$

corresponds to the *normalized creation operator*. These operators do not commute with each other or with $\hat{n}$, since

$$[\hat{n}, \hat{a}] = \left[\hat{a}^\dagger\hat{a}, \hat{a}\right] = \hat{a}^\dagger\hat{a}\hat{a} - \hat{a}\hat{a}^\dagger\hat{a} = -\hat{a},$$

$$\left[\hat{n}, \hat{a}^\dagger\right] = \hat{a}^\dagger.$$

Thus,

$$\left[\hat{n}, \hat{e}^{i\varphi}\right] = -\hat{e}^{i\varphi},$$

$$\left[\hat{n}, \hat{e}^{-i\varphi}\right] = \hat{e}^{-i\varphi}.$$

The quantity defined by the phase operator cannot be measured simultaneously with the energy operator. In other words, *in a stationary state, the phase is not well-defined.*

It is still possible to define *Hermitian phase operators* (can be considered as quantum mechanical operators that describe the phase properties of an electromagnetic field), that do not commute

$$\widehat{\cos}\varphi = \frac{1}{2}\left(\hat{e}^{i\varphi} + \hat{e}^{-i\varphi}\right), \quad \widehat{\sin}\varphi = \frac{1}{2i}\left(\hat{e}^{i\varphi} - \hat{e}^{-i\varphi}\right). \tag{2.4}$$

The operator is Hermitian, when $\hat{A} = \hat{A}^\dagger$. The operators commute, when $[\hat{A}, \hat{B}]\psi \equiv \hat{A}\hat{B}\psi - \hat{B}\hat{A}\psi = 0$.

From quantum mechanics, we know that $[A, B] = iC$, then $\Delta A \,\Delta B = \langle C \rangle /2$, where

$$\Delta A = \sqrt{\left\langle A^2 \right\rangle - \langle A \rangle^2}.$$

Let us check commutation relations for "phase and energy" ("phase and number of particles"):

$$\left[\hat{n}, \widehat{\cos}\varphi\right] = -i\,\widehat{\sin}\varphi,$$
$$\left[\hat{n}, \widehat{\sin}\varphi\right] = i\,\widehat{\cos}\varphi,$$

i.e. the number of particles and the phase are not defined simultaneously:

$$\Delta n \Delta \cos\varphi \geq \frac{1}{2}\left\langle \sin\varphi \right\rangle,$$
$$\Delta n \Delta \sin\varphi \geq \frac{1}{2}\left\langle \cos\varphi \right\rangle.$$

We compare this result with the classical harmonic oscillator having $x \sim \cos\omega t$ and $p \sim \sin\omega t$, it follows that the coordinate and momentum phase difference is exactly π. If we know the coordinate, we also know the momentum at the same time. But in the quantum mechanics $\Delta x \Delta p > \hbar/2$.

We consider the particle at the stationary state, or in other words, we study the phase properties in a state with a well-defined energy (number of particles)

$$\left\langle \cos\varphi \right\rangle = \langle n | \widehat{\cos}\varphi | n \rangle = 0,$$
$$\left\langle \sin\varphi \right\rangle = \langle n | \widehat{\sin}\varphi | n \rangle = 0.$$

$$\overline{\cos^2\varphi} = \langle n | (\widehat{\cos}\varphi)^2 | n \rangle = \frac{1}{4}\langle n | (\hat{e}^{i\varphi})^2 + \hat{e}^{i\varphi}\hat{e}^{-i\varphi} + \hat{e}^{-i\varphi}\hat{e}^{i\varphi} + (\hat{e}^{-i\varphi})^2 | n \rangle =$$
$$= \frac{1}{4}\begin{cases} 2, & n > 0, \\ 1, & n = 0. \end{cases}$$

In a stationary state one gets

$$\left\langle \cos^2\varphi \right\rangle = \begin{cases} \frac{1}{2}, & n > 0, \\ \frac{1}{4}, & n = 0. \end{cases} \tag{2.5}$$

$$\left\langle \sin^2\varphi \right\rangle = \begin{cases} \frac{1}{2}, & n > 0 \\ \frac{1}{4}, & n = 0. \end{cases} \tag{2.6}$$

Factor $\frac{1}{2}$ means that the phase is totally undefined. In all excited states with a well-defined energy the phase is completely undefined.

In Figure 2.1 one can see a circular trajectory of particle movement in phase space. According to classical physics, the particle is located at a specific point at any time. The quantum theory asserts that in the stationary state the particle is located on the entire circle at any time.
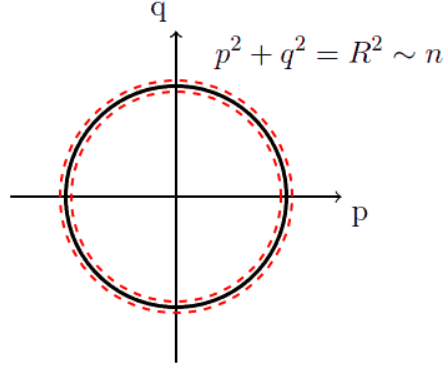
Figure 2.1: Trajectory of a particle in the phase space.

2.2   States with a well-defined phase

The states with a well-defined phase are the *phase operator eigenstates*:

$$\hat{e}^{i\varphi}\left|\varphi\right\rangle = e^{i\varphi}\left|\varphi\right\rangle.$$

These are abstract (fictitious) states that can only be approximated to real states. The phase of the classical harmonic movement is precisely defined at each moment of time. In quantum mechanics, we introduce a state

$$\left|\varphi\right\rangle = \lim_{s\to\infty}(s+1)^{-1/2}\sum_{n=0}^{s}e^{in\varphi}\left|n\right\rangle. \tag{2.7}$$

Let us show that this is the phase operator eigenstate:

$$\hat{e}^{i\varphi}\left|\varphi\right\rangle = \lim_{s\to\infty}(s+1)^{-1/2}\sum_{n=0}^{s}e^{in\varphi}\hat{e}^{i\varphi}\left|n\right\rangle =$$

$$= \lim_{s\to\infty}(s+1)^{-1/2}\sum_{n=1}^{s}e^{in\varphi}\left|n-1\right\rangle =$$

$$= \lim_{s\to\infty}(s+1)^{-1/2}\sum_{m=0}^{s-1}e^{i(m+1)\varphi}\hat{e}^{i\varphi}\left|m\right\rangle =$$

$$= e^{i\varphi}\lim_{s\to\infty}(s+1)^{-1/2}\sum_{n=0}^{s}e^{im\varphi}\left|m\right\rangle = e^{i\varphi}\left|\varphi\right\rangle.$$

Similarly,

$$\hat{e}^{-i\varphi}\left|\varphi\right\rangle = e^{-i\varphi}\left|\varphi\right\rangle.$$

Let us look at the time dependence of this state

$$e^{-itH/\hbar}\left|\varphi\right\rangle = \lim_{s\to\infty}(s+1)^{-1/2}\sum_{n=0}^{s}e^{in\varphi}e^{-itH/\hbar}\left|n\right\rangle =$$

$$= \lim_{s\to\infty}(s+1)^{-1/2}\sum_{n=0}^{s}e^{in\varphi}e^{-(it/\hbar)\cdot\hbar\omega(n+\frac{1}{2})}\left|n\right\rangle =$$

$$= e^{-it\omega/2}\lim_{s\to\infty}(s+1)^{-1/2}\sum_{n=0}^{s}e^{in(\varphi-\omega t)}\left|n\right\rangle =$$

$$= e^{-it\omega/2}\left|\varphi-\omega t\right\rangle,$$

i.e. the phase is linear in time.

The *mean energy* of this state is

$$\bar{E} = \frac{\hbar\omega}{2} + \hbar\omega\bar{n}_\varphi\,,$$

whilst the average number of photons in this state

$$\bar{n}_\varphi = \langle\varphi|\,\hat{n}\,|\varphi\rangle = \lim_{s\to\infty}(s+1)^{-1/2}\lim_{s'\to\infty}(s'+1)^{-1/2}\sum_{n=0}^{s}\sum_{n'=0}^{s'}e^{i(n-n')\varphi}\langle n'|\hat{n}|n\rangle =$$

$$= \lim_{s\to\infty}(s+1)^{-1/2}\lim_{s'\to\infty}(s'+1)^{-1/2}\sum_{n=0}^{s}\sum_{n'=0}^{s'}e^{i(n-n')\varphi}n\delta_{nn'} =$$

$$= \lim_{s\to\infty}(s+1)^{-1}\sum_{n=0}^{s}n = \lim_{s\to\infty}(s+1)^{-1}\frac{s(s+1)}{2} = \lim_{s\to\infty}\frac{s}{2}\to\infty.$$

Therefore, the state with a well-defined phase is *not a physical state* ($\bar{n}_\varphi \to \infty$). Energy and phase are not precisely measurable simultaneously. These states cannot be produced with a sufficient accuracy.

We can find a *dispersion**

$$\Delta n = \sqrt{(n_\varphi^2)_{\text{avg.}} - \bar{n}_\varphi^2} = \lim_{s\to\infty}\sqrt{\frac{s(2s+1)}{6} - \frac{s^2}{4}} = \lim_{s\to\infty}\frac{s}{2\sqrt{3}},$$

where

$$(n_\varphi^2)_{\text{avg.}} = \langle\varphi|\,\hat{n}^2\,|\varphi\rangle = \lim_{s\to\infty}(s+1)^{-1}\sum_{n=0}^{s}n^2 = \lim_{s\to\infty}\frac{s(s+1)(2s+1)}{3!(s+1)},$$

and

$$\frac{\Delta n}{\bar{n}_\varphi} = \frac{1}{\sqrt{3}}.$$

2.3 Coherent states

There are states which, by their properties (phase and energy are simultaneously well defined), are close to the classical states. These are *coherent states*. Such states are generated by lasers.

Coherent states are defined as *annihilation operator eigenstates* (i.e. the states of the interaction between the electromagnetic field and the matter):

$$\hat{a}|\alpha\rangle = \alpha|\alpha\rangle\,,$$

where α is a complex number. The adjoint operator satisfies the equation

$$\langle\alpha|\,a^\dagger = \alpha\langle\alpha|\,.$$

We may present such state by the series expansion (a wave packet) of the stationary states:

$$|\alpha\rangle = e^{-\frac{1}{2}|\alpha|^2}\sum_{n=0}^{\infty}\frac{\alpha^n}{\sqrt{n!}}|n\rangle\,. \tag{2.8}$$

This state is actually an annihilation operator eigenstate,

$$\hat{a}\,|\alpha\rangle = e^{-\frac{1}{2}|\alpha|^2} \sum_{n=0}^{\infty} \frac{\alpha^n}{\sqrt{n!}} \hat{a}\,|n\rangle =$$

$$= e^{-\frac{1}{2}|\alpha|^2} \sum_{n=1}^{\infty} \frac{\alpha^n}{\sqrt{n!}} \sqrt{n}\,|n-1\rangle =$$

$$= e^{-\frac{1}{2}|\alpha|^2} \sum_{m=0}^{\infty} \frac{\alpha^{m+1}}{\sqrt{m!}}\,|m\rangle = \alpha\,|\alpha\rangle .$$

Here, we introduce some useful formulas for linear operators, for which commutator is a constant. Keep in mind that in the product of operators, each factor acts on the quantity standing to the right of it. In the following, we need an expression

$$e^{\tau\hat{a}}\hat{b}e^{-\tau\hat{a}},$$

with the given commutator being constant: $[\hat{a}, \hat{b}] = c$. It follows that

$$\frac{d}{d\tau}e^{\tau\hat{a}}\hat{b}e^{-\tau\hat{a}} = e^{\tau\hat{a}}(\hat{a}\hat{b} - \hat{b}\hat{a})e^{-\tau\hat{a}} = c,$$

$$e^{\tau\hat{a}}\hat{b}e^{-\tau\hat{a}} = \hat{b} + c\tau.$$

Let us show that for the operator $\hat{f} = e^{\hat{a}}e^{\hat{b}}$ the *Weyl identity* holds, that is

$$\hat{f} = e^{\hat{a}+\hat{b}}e^{\frac{1}{2}[\hat{a},\hat{b}]}.$$

Proof. Let

$$\hat{F}_\tau = e^{\tau(\hat{a}+\hat{b})} = e^{\tau\hat{a}}e^{\tau\hat{b}}e^{f(\tau)},$$

then

$$\frac{d}{d\tau}\hat{F}_\tau = \left(\hat{a} + \hat{b}\right)\hat{F}_\tau = \hat{a}\hat{F}_\tau + \hat{F}_\tau\hat{b} + f'(\tau)\hat{F}_\tau .$$

Considering

$$\hat{b}e^{\tau(\hat{a}+\hat{b})} = e^{\tau(\hat{a}+\hat{b})}e^{-\tau(\hat{a}+\hat{b})}\hat{b}e^{\tau(\hat{a}+\hat{b})} = e^{\tau(\hat{a}+\hat{b})}(\hat{b} - \tau\left[\hat{a},\hat{b}\right]),$$

one gets

$$\frac{d}{d\tau}\hat{F}_\tau = (\hat{a} + \hat{b} + f'(\tau) + \tau\left[\hat{a},\hat{b}\right])\hat{F}_\tau,$$

$$f'(\tau) = -\tau\left[\hat{a},\hat{b}\right] \rightarrow f(\tau) = -\frac{\tau^2}{2}\left[\hat{a},\hat{b}\right],$$

$$\tau = 1: \quad e^{\hat{a}+\hat{b}} = e^{\hat{a}}e^{\hat{b}}e^{-\frac{1}{2}[\hat{a},\hat{b}]}.$$

We present a coherent state (see Equation 2.8) in a different form using

$$|n\rangle = \frac{\hat{a}^\dagger}{\sqrt{n}}\,|n-1\rangle = \frac{(\hat{a}^\dagger)^n}{\sqrt{n!}}\,|0\rangle ,$$

then

$$|\alpha\rangle = e^{-\frac{1}{2}|\alpha|^2} \sum_{n=0}^{\infty} \frac{\alpha^n}{\sqrt{n!}}\,|n\rangle = e^{-\frac{1}{2}|\alpha|^2} e^{\alpha\hat{a}^\dagger}\,|0\rangle . \tag{2.9}$$

The operator $e^{-\frac{1}{2}|\alpha|^2}e^{\alpha\hat{a}^\dagger}$ generates a coherent state from the 0-state. Taking $\hat{a}|0\rangle = 0$, and using Weyl identity, we obtain

$$|\alpha\rangle = e^{-\frac{1}{2}|\alpha|^2}e^{\alpha\hat{a}^\dagger}e^{-\alpha^*\hat{a}}|0\rangle = e^{\alpha\hat{a}^\dagger - \alpha^*\hat{a}}|0\rangle. \tag{2.10}$$

We denote the operator that generate a coherent state from 0-state

$$\hat{D}(\alpha) = e^{\alpha\hat{a}^\dagger - \alpha^*\hat{a}}.$$

In the case of real α, $\alpha = \alpha^*$. Then $|\alpha\rangle = e^{\alpha(\hat{a}^\dagger - \hat{a})}|0\rangle$. Recall Equation 1.14:

$$\begin{cases} \hat{Q}_k &= \sqrt{\frac{\hbar}{2\omega_k}}\left(\hat{a}_k + \hat{a}_k^\dagger\right) \\ \hat{P}_k &= -i\sqrt{\frac{\hbar\omega_k}{2}}\left(\hat{a}_k - \hat{a}_k^\dagger\right) \end{cases} \Rightarrow \begin{cases} \hat{a} = \frac{1}{\sqrt{2\hbar\omega}}\left(\omega\hat{Q} + i\hat{P}\right) \\ \hat{a}^\dagger = \frac{1}{\sqrt{2\hbar\omega}}\left(\omega\hat{Q} - i\hat{P}\right) \end{cases}$$

From the difference of the operators

$$\hat{a}^\dagger - \hat{a} = -\frac{2i\hat{P}}{\sqrt{2\hbar\omega}} = -\sqrt{\frac{2\hbar}{\omega}}\frac{\partial}{\partial Q}$$

and the definition of the momentum operator $\hat{P} = -i\hbar\frac{\partial}{\partial Q}$, we get

$$|\alpha\rangle = e^{\alpha\sqrt{\frac{2\hbar}{\omega}}\frac{\partial}{\partial Q}}|0\rangle. \tag{2.11}$$

The coherent state with the real parameter α is simply the shifted 0-state of the harmonic oscillator. The wave function of the 0-state of the harmonic oscillator is a Gaussian,

$$\Psi_0(Q) = |0\rangle = C\exp\left(-\frac{\omega}{2\hbar}Q^2\right),$$

where the full width at half maximum (FWHM) is $(2\omega/\hbar)^{1/2}$ and $C = (\omega/\pi\hbar)^{1/4}$.

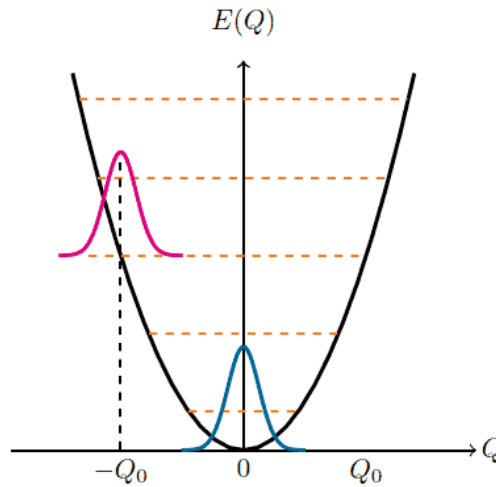The coherent state (or the shifted 0-state) has the minimal (P,Q)-uncertainty.

Figure 2.2: Harmonic oscillator.

If α is real, the operator $D(\alpha)$ is the *displacement operator*. Thus, $|\alpha\rangle$-state in Q-representation yields

$$\Psi_\alpha(Q) = e^{-Q_0 \frac{\partial}{\partial Q}} \Psi_0(Q) = \Psi_0(Q - Q_0),$$

where $Q_0 = \sqrt{2\hbar/\omega}\,\alpha$.

Let us consider the time dependence of the coherent states. According to the definition, the time dependence of a linear operator (in Schröodinger representation) is given by

$$\hat{A}(t) = e^{\frac{iHt}{\hbar}} \hat{A} e^{-\frac{iHt}{\hbar}}$$

Taking $H = \hbar\omega(n+1/2)$, the time-dependent annihilation operator yields $\hat{a}(t) = e^{it\omega\hat{n}} \hat{a} e^{-it\omega\hat{n}}$ and

$$\frac{d\hat{a}(t)}{dt} = i\omega e^{it\omega\hat{n}}[\hat{n}, \hat{a}] e^{-it\omega\hat{n}} = -i\omega a(t) \quad \Rightarrow \quad \hat{a}(t) = \hat{a} e^{-it\omega}.$$

Similarly,

$$\hat{a}^\dagger(t) = \hat{a}^\dagger e^{it\omega}.$$

The operators $\hat{a}$ and $\hat{a}^\dagger$ depend on the time so that their phase changes linearly over time:

$$\hat{a}\,|\alpha(t)\rangle = \hat{a} e^{-\frac{i}{\hbar}tH}\,|\alpha\rangle = e^{-\frac{i}{\hbar}tH} e^{\frac{i}{\hbar}tH} \hat{a} e^{-\frac{i}{\hbar}tH}\,|\alpha\rangle =$$

$$= e^{-\frac{i}{\hbar}tH} \hat{a}(t)\,|\alpha\rangle = e^{-i\omega t} e^{-\frac{i}{\hbar}tH} \hat{a}\,|\alpha\rangle = \alpha e^{-i\omega t}\,|\alpha(t)\rangle.$$

Since, by definition, $\hat{a}\,|\alpha(t)\rangle = \alpha(t)\,|\alpha(t)\rangle$, it follows that $\alpha(t) = \alpha e^{-i\omega t}$ oscillates in time with frequency ω. One can write in the same way

$$|\alpha(t)\rangle = e^{-\frac{i}{\hbar}\hat{H}t}\,|\alpha\rangle = e^{-\frac{1}{2}|\alpha|^2} e^{-\frac{i}{\hbar}\hat{H}t} e^{\alpha\hat{a}^\dagger - \alpha^*\hat{a}}\,|0\rangle =$$

$$= e^{-\frac{1}{2}|\alpha|^2} e^{-\frac{i}{\hbar}\hat{H}t} e^{\alpha\hat{a}^\dagger - \alpha^*\hat{a}} e^{\frac{i}{\hbar}\hat{H}t} e^{-\frac{i}{\hbar}\hat{H}t}\,|0\rangle =$$

$$= e^{-\frac{1}{2}|\alpha|^2} \exp\left[\alpha e^{-i\omega t} \hat{a}^\dagger - \alpha^* e^{i\omega t} \hat{a}\right]\,|0\rangle =$$

$$= e^{-\frac{1}{2}|\alpha|^2} e^{\alpha(t)\hat{a}^\dagger - \alpha^*(t)\hat{a}}\,|0\rangle.$$

Consequently, *the coherent state remains coherent in time.*

We can find the *coherent state energy*

$$E_n = \hbar\omega\,(n + 1/2),$$

$$E = \sum_n |c_n|^2 E_n = \frac{\hbar\omega}{2} + \hbar\omega \sum_n |c_n|^2 n = \frac{\hbar\omega}{2} + \hbar\omega\bar{n}, \quad \text{where} \quad \sum_n |c_n|^2 = 1.$$

By definition,

$$\bar{n} = \langle\alpha|\,\hat{n}\,|\alpha\rangle = \langle\alpha|\,\hat{a}^\dagger\hat{a}\,|\alpha\rangle = |\alpha|^2\,\langle\alpha|\alpha\rangle = |\alpha|^2.$$

Thus,

$$\bar{E} = \frac{\hbar\omega}{2} + \hbar\omega|\alpha|^2. \tag{2.12}$$

The *uncertainty of energy* is given by

$$\Delta n = \sqrt{\overline{n^2} - \bar{n}^2},$$

$$\overline{n^2} = \langle\alpha|\,\hat{n}^2\,|\alpha\rangle = \langle\alpha|\,\hat{a}^\dagger\hat{a}\hat{a}^\dagger\hat{a}\,|\alpha\rangle =$$

$$= \langle\alpha|\,\hat{a}^{\dagger 2}\hat{a}^2\,|\alpha\rangle + \langle\alpha|\,\hat{a}^\dagger\hat{a}\,|\alpha\rangle = |\alpha|^4 + |\alpha|^2.$$

Hence

$$\Delta n = \sqrt{|\alpha|^4 + |\alpha|^2 - |\alpha|^4} = |\alpha|,$$

and

$$\frac{\Delta n}{n} = \frac{1}{|\alpha|} = \frac{1}{\sqrt{\bar{n}}}.$$

If $|\alpha| \gg 1$, then $\bar{E} \gg \hbar\omega$, and the relative uncertainty of energy decreases.

The *uncertainty of phase* is given by

$$\overline{\cos\varphi} = \langle \alpha | \widehat{\cos}\varphi | \alpha \rangle.$$

Using

$$|\alpha\rangle = e^{-\frac{1}{2}|\alpha|^2} \sum_{n=0}^{\infty} \frac{\alpha^n}{\sqrt{n!}} |n\rangle,$$

one gets

$$\overline{\cos\varphi} = e^{-|\alpha|^2} \sum_{n,n'=0}^{\infty} \langle n' | \frac{\alpha*^n \alpha^{n'}}{\sqrt{n'!n!}} \widehat{\cos}\varphi | n\rangle,$$

$$\widehat{\cos}\varphi = \frac{1}{2}\left(\widehat{e^{i\varphi}} + \widehat{e^{-i\varphi}}\right),$$

$$\widehat{e^{i\varphi}}|n\rangle = |n-1\rangle,$$

$$\langle n'|\widehat{e^{-i\varphi}} = \langle n'-1|.$$

It follows that

$$\overline{\cos\varphi} = e^{-|\alpha|^2} \sum_{n=0}^{\infty} \frac{|\alpha|^{2n}}{\sqrt{n!}} \frac{\alpha^* + \alpha}{2\sqrt{n+1}}.$$

Here $\alpha = |\alpha|e^{i\Theta}$, Θ is the phase of α. Then $\operatorname{Re}\alpha = |\alpha|\cos\Theta$, and one gets

$$\overline{\cos\varphi} = \cos\Theta e^{-|\alpha|^2} \sum_{n=0}^{\infty} \frac{|\alpha|^{2n+1}}{n!\sqrt{n+1}} = |\alpha|\cos\Theta \sum_{n=0}^{\infty} P_n/\sqrt{n+1}.$$

We take into account that

$$\frac{1}{\sqrt{n+1}} = \frac{2}{\sqrt{\pi}} \int_0^{\infty} e^{-x^2(n+1)} dx$$

is a Poisson integral;

$$P_n = \frac{e^{-|\alpha|^2}|\alpha|^{2n}}{n!}.$$

In the case of large α,

$$\overline{\cos\varphi} \approx \cos\Theta(1 - \frac{1}{8|\alpha|^2} + ...),$$

$$\overline{\cos^2\varphi} - \overline{\cos\varphi}^2 = \frac{\cos^2\varphi - 1/2}{2|\alpha|^2},$$

$$\Delta(\cos\varphi) = \sqrt{\overline{\cos^2\varphi} - \overline{\cos\varphi}^2},$$

i.e the phase is practically precisely determined.

We introduce the *dimensionless coordinate and momentum* ($\hbar\omega = 1$)

$$\begin{cases} \hat{x} &= \frac{1}{\sqrt{2}}(\hat{a} + \hat{a}^\dagger) \\ \hat{p} &= \frac{i}{\sqrt{2}}(\hat{a}^\dagger - \hat{a}) \end{cases}$$

where $[\hat{p}, \hat{x}] = -i$. We find the mean value and uncertainty of these quantities in the state of the well-defined phase $\alpha(t)$:

$$\bar{x} = \langle \alpha | \hat{x} | \alpha \rangle = \frac{1}{\sqrt{2}} \langle \alpha | (\hat{a} + \hat{a}^\dagger) | \alpha \rangle = \frac{1}{\sqrt{2}} (\alpha + \alpha^*) = \frac{1}{\sqrt{2}} \operatorname{Re}(\alpha),$$

$$\bar{p} = \langle \alpha | \hat{p} | \alpha \rangle = i \frac{1}{\sqrt{2}} \langle \alpha | (\hat{a}^\dagger - \hat{a}) | \alpha \rangle = i \frac{1}{\sqrt{2}} \operatorname{Im}(\alpha),$$

$$\langle \alpha(t) | \hat{a}^\dagger = \alpha^*(t) \langle \alpha(t) |,$$
$$\hat{a} | \alpha(t) \rangle = \alpha(t) | \alpha(t) \rangle.$$

Thus,
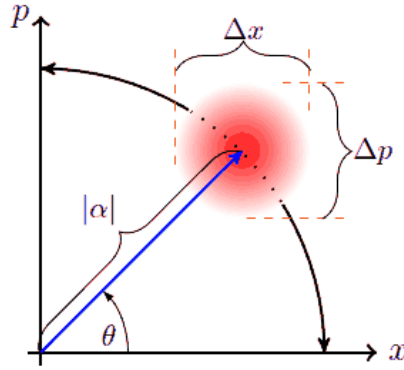
Figure 2.3: Coherent state: a circle of unit radius $((\Delta x)^2 + (\Delta p)^2 = 1)$ moves along a circular path in the phase space (dimensionless units, $\hbar = 1$).

$$\bar{x} = \frac{2}{\sqrt{2}} \operatorname{Re}(\alpha(t)) = \sqrt{2} \operatorname{Re}(\alpha(t)) = 2\sqrt{2} |\alpha| \cos(\omega t),$$

$$\bar{p} = \sqrt{2} \operatorname{Im}(\alpha(t)) = \frac{1}{\sqrt{2}} \langle \alpha(t) | (\hat{a} - \hat{a}^\dagger) | \alpha(t) \rangle = 2\sqrt{2} |\alpha| \sin(\omega t),$$

$$(\Delta x)^2 = \overline{x^2} - \bar{x}^2,$$

$$(\Delta p)^2 = \overline{p^2} - \bar{p}^2,$$

$$\hat{x}^2 = \frac{1}{2} (\hat{a}^2 + \hat{a}\hat{a}^\dagger + \hat{a}^\dagger \hat{a} + \hat{a}^{\dagger 2}) =$$

$$= \frac{1}{2} (\hat{a}^2 + 2\hat{a}^\dagger \hat{a} + \hat{a}^{\dagger 2}) + \frac{1}{2},$$

$$\langle \alpha(t) | \hat{x}^2 | \alpha(t) \rangle \equiv \overline{\hat{x}^2} = \frac{1}{2} (\alpha(t) + \alpha^*(t))^2 + \frac{1}{2} = \bar{x}^2 + \frac{1}{2},$$

$$\overline{p^2} = \bar{p}^2 + \frac{1}{2},$$

$$\begin{cases} \overline{x^2} - \bar{x}^2 = \frac{1}{2} \equiv (\Delta x)^2 \\ \overline{p^2} - \bar{p}^2 = \frac{1}{2} \equiv (\Delta p)^2 \end{cases} \quad \Rightarrow \quad (\Delta x \Delta p)^2 = \frac{1}{4}.$$

The uncertainty $(\Delta x \Delta p) = 1/2$ is the *minimum possible uncertainty*, the same as in the 0-state, and $\Delta x = \Delta p$. According to the Heisenberg uncertainty relation, $\Delta x \Delta p \geq 1/2$.

In a coherent state, the coordinate and momentum uncertainty is the smallest possible.

2.4 Squeezed states

If we have two Hermitian operators A and B whose commutator is $[A, B] = iC$, then, in accordance with the Heisenberg uncertainty relation, the product of the uncertainties (of the average values of the operators) equals

$$\Delta A \Delta B \geq \frac{1}{2}|\langle C \rangle|.$$

We call the state of the system *squeezed*, if the uncertainty of one variable (for example, A) satisfies the equation

$$(\Delta A)^2 < \frac{1}{2}|\langle C \rangle|.$$

In the squeezed state, the quantum fluctuations of one variable decrease, but due to the increase of the fluctuations of the complementary variable, the uncertainty relation remains valid. In the phase diagram (see Figure 2.4), we have an ellipse instead of circle.

(a) Phase squeezing   (b) Amplitude squeezing   (c) Quadrature squeezing
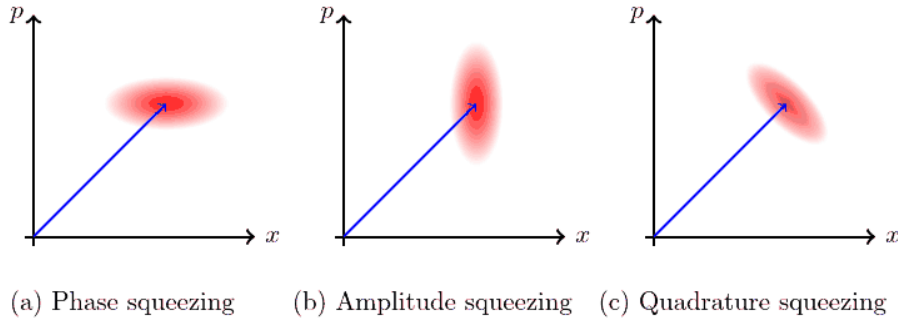
Figure 2.4: Squeezed states.

The *squeezed state* is given by

$$|\alpha, \xi\rangle = \hat{D}(\alpha)\hat{S}(\xi)|0\rangle \tag{2.13}$$

where ξ is the *squeezing parameter*,

$$\hat{D}(\alpha) = \exp\left(\alpha\hat{a}^\dagger - \alpha^*\hat{a}\right)$$

is the *coherent state generator* (emits photons one by one, due to the linear operators a and $a^\dagger$ in the exponent),

$$\hat{S}(\xi) = \exp\left(\frac{1}{2}\xi\hat{a}^{\dagger 2} - \frac{1}{2}\xi^*\hat{a}^2\right)$$

is the *squeezed state generator* (emits two photons at once, due to the squared operators in the exponent).

The coherent state is a superposition of all photon states:

$$|\alpha\rangle = e^{-\frac{1}{2}|\alpha|^2} \sum_n \frac{\alpha^n}{n!} a^{\dagger n}|0\rangle =$$

$$= e^{-\frac{1}{2}|\alpha|^2}\left(1 + \alpha a^\dagger + \frac{\alpha^2}{2}a^{\dagger 2} + \dots\right)|0\rangle.$$

The first term in brackets corresponds to a pure vacuum state, the second to the one-photon state, the third to the two-photon state, etc.

When $\alpha = 0$, we get a *pure squeezed state*:

$$|0, \xi\rangle = \exp\left(\frac{1}{2}\xi\hat{a}^{\dagger 2} - \frac{1}{2}\xi^*\hat{a}^2\right)|0\rangle$$
$$= \left[1 + \frac{1}{2}\left(\xi\hat{a}^{\dagger 2} - \xi^*\hat{a}^2\right) + \frac{1}{8}\left(\xi\hat{a}^{\dagger 2} - \xi^*\hat{a}^2\right)^2 + ...\right]|0\rangle.$$

A pure squeezed state takes place when there are only two-photon states, so it is called a *two-photon coherent state*. We introduce a new ("squeezed") annihilation operator:

$$\hat{\tilde{a}} \equiv \hat{S}(\xi)\hat{a}\hat{S}^{-1}(\xi) = e^{\hat{A}}\hat{a}e^{-\hat{A}}, \tag{2.14}$$

where

$$\hat{A} = \frac{1}{2}\left(\xi\hat{a}^{\dagger 2} - \xi^*\hat{a}^2\right).$$

Taking into account that

$$[\hat{A}, \hat{a}] = \left[\frac{1}{2}\left(\xi\hat{a}^{\dagger 2} - \xi^*\hat{a}^2\right), \hat{a}\right] = -\xi\hat{a}^{\dagger},$$

we get

$$e^{\hat{A}}\hat{a}e^{-\hat{A}} = \sum_n \frac{1}{n!}\underbrace{\left[\hat{A}, \left[\hat{A}, ... \left[\hat{A}, \hat{a}\right]\right]\right]}_{n} =$$
$$= \sum_{n=0}^{\infty}\left[\frac{1}{(2n)!}|\xi|^{2k}\hat{a} - \frac{1}{(2k+1)!}|\xi|^{2k+1}e^{i\Theta}\hat{a}^{\dagger}\right] =$$
$$= \text{ch}\,|\xi|\,\hat{a} - \text{sh}\,|\xi|\,\hat{a}^{\dagger}e^{i\Theta} = \mu\hat{a} + \nu\hat{a}^{\dagger}.$$

The squeezed state operators are connected with the former (coherent state) operators using *Bogolyubov transformation* (has a wide range of application in theoretical physics, superconductivity, superfluidity, astrophysics, etc.):

$$\hat{\tilde{a}} = \mu\hat{a} + \nu\hat{a}^{\dagger},$$
$$\hat{\tilde{a}}^{\dagger} = \mu^*\hat{a}^{\dagger} + \nu^*\hat{a}, \tag{2.15}$$

where $|\mu|^2 - |\nu|^2 = 1$. In our case, $\mu = \text{ch}(|\xi|)$, $\nu = \text{sh}(|\xi|)e^{i\Theta}$. Due to Bogolyubov transformation, new linear operators have the same commutation properties (Bose operators):

$$\left[\hat{\tilde{a}}, \hat{\tilde{a}}^{\dagger}\right] = |\mu|^2 - |\nu|^2 = 1$$

Since $\hat{\tilde{a}}|0\rangle \neq 0$, there are particles in the squeezed vacuum state.

The squeezed state is the operator $\hat{\tilde{a}}$ eigenstate: $\hat{\tilde{a}}|\alpha, \xi\rangle = d|\alpha, \xi\rangle$, where $d = d(\alpha, \xi)$. We may show that. Using the relation $e^{A}Be^{-A} = B + [A, B]$, one gets

$$\hat{\tilde{a}}|\alpha, \xi\rangle = D(\alpha)D(\alpha)^{-1}(\mu\hat{a} + \nu\hat{a}^{\dagger})\hat{D}(\alpha)S(\xi)|0\rangle =$$
$$= \hat{D}(\alpha)(\mu(\hat{a} + \alpha^*) + \nu(\hat{a}^{\dagger} + \alpha))\hat{S}(\xi)|0\rangle$$
$$= \hat{D}(\alpha)\left(\hat{\tilde{a}} + d\right)\hat{S}(\xi)|0\rangle = d|\alpha, \xi\rangle + \hat{D}(\alpha)\hat{\tilde{a}}\hat{S}(\xi)|0\rangle,$$

where $d = \mu\alpha^* + \nu\alpha$. Since $\hat{\tilde{a}} = \hat{S}(\xi)\hat{a}\hat{S}^{-1}(\xi)$, then

$$\hat{\tilde{a}}\,|\alpha,\xi\rangle = d\,|\alpha,\xi\rangle + \underbrace{\hat{D}(\alpha)\hat{S}(\xi)\hat{a}\,|0\rangle}_{=0} = d\,|\alpha,\xi\rangle\,.$$

The squeezed state is, in fact, a coherent state, only for the squeezed annihilation operator:

$$\hat{\tilde{a}} = \mu\hat{a} + \nu\hat{a}^\dagger = \operatorname{ch}(|\xi|)\hat{a} + e^{i\Theta}\operatorname{sh}(|\xi|)\hat{a}^\dagger \tag{2.16}$$

here μ is real, besides $\mu \geq \nu$ (there is no eigenstate for $\hat{a}^\dagger$, so it cannot dominate). Maximum possible squeezing is obtained when $\operatorname{ch} \cong \operatorname{sh}$.

Let us calculate the coordinate and momentum uncertainty for the squeezed state. We use dimensionless operators and find them for the squeezed state.

$$\begin{aligned}
\hat{x} &= \frac{1}{\sqrt{2}}\left(\hat{a} + \hat{a}^\dagger\right) \rightarrow \hat{x} = \frac{1}{\sqrt{2}}\left((\mu^* - \nu^*)\hat{\tilde{a}} + (\mu - \nu)\hat{\tilde{a}}^\dagger\right), \\
\hat{p} &= \frac{1}{\sqrt{2}}\left(\hat{a} - \hat{a}^\dagger\right) \rightarrow \hat{p} = \frac{1}{\sqrt{2}}\left((\mu^* - \nu^*)\hat{\tilde{a}} - (\mu - \nu)\hat{\tilde{a}}^\dagger\right).
\end{aligned} \tag{2.17}$$

Here it is considered that $\hat{a} = \mu\hat{\tilde{a}} - \nu^*\hat{\tilde{a}}^\dagger$ and $\hat{a}^\dagger = \mu\hat{\tilde{a}}^\dagger - \nu\hat{\tilde{a}}$. If $\Theta = 0$, then

$$\begin{cases}
\hat{x} &= \frac{1}{\sqrt{2}}e^{|\xi|}\left(\hat{\tilde{a}} + \hat{\tilde{a}}^\dagger\right) \\
\hat{p} &= \frac{1}{\sqrt{2}}e^{-|\xi|}\left(\hat{\tilde{a}} - \hat{\tilde{a}}^\dagger\right)
\end{cases}$$

If $\Theta = \pi$, then

$$\begin{cases}
\hat{x} &= \frac{1}{\sqrt{2}}e^{-|\xi|}\left(\hat{\tilde{a}} + \hat{\tilde{a}}^\dagger\right) \\
\hat{p} &= \frac{1}{\sqrt{2}}e^{|\xi|}\left(\hat{\tilde{a}} - \hat{\tilde{a}}^\dagger\right)
\end{cases}$$

If $\Theta = 0$, then

$$\begin{cases}
\bar{x} &= \frac{1}{\sqrt{2}}e^{|\xi|}2\operatorname{Re}d \\
\bar{p} &= \frac{1}{\sqrt{2}}e^{-|\xi|}2\operatorname{Im}d
\end{cases} \Rightarrow \begin{cases}
\Delta x = \frac{1}{\sqrt{2}}e^{|\xi|} \\
\Delta p = \frac{1}{\sqrt{2}}e^{-|\xi|}
\end{cases}$$

and, consequently, $\Delta x \Delta p = \frac{1}{2}$. If $\Theta = \pi$, then

$$\begin{cases}
\Delta x &= \frac{1}{\sqrt{2}}e^{-|\xi|} \\
\Delta p &= \frac{1}{\sqrt{2}}e^{|\xi|}
\end{cases}$$

and $\Delta x \Delta p = 1/2$.

The product of the uncertainties is the smallest possible, thereto the uncertainties are not equal. The quantum noise increases in one variable and decreases in the other.

In communication, one can use squeezed states instead of coherent states, thus reducing the quantum noise; on detection, one can choose, which signal to use.

The mean energy of the squeezed state tends to $\bar{n}$:

$$\begin{aligned}
\bar{n} &= \langle\alpha,\xi|\,\hat{\tilde{a}}^\dagger\hat{\tilde{a}}\,|\alpha,\xi\rangle = \langle 0|\,\hat{S}^{-1}\hat{D}^{-1}\hat{a}^\dagger\hat{D}\hat{D}^{-1}\hat{a}\hat{D}\hat{S}\,|0\rangle = \\
&= \langle 0|\,\hat{S}^{-1}(\hat{a}^\dagger + \alpha)(\hat{a} + \alpha)\hat{D}\hat{S}\,|0\rangle\,.
\end{aligned}$$

Given $\langle 0|\,\hat{S}^{-1}\hat{a}\hat{S}\,|0\rangle = 0$ (linear terms cancel each other, since S, S^{-1} contain an even number of operators, and $\langle 0|$ even-number-of-operators $|0\rangle = 0$), one gets

$$\bar{n} = \underbrace{\langle 0| \hat{S}^{-1} \hat{a}^\dagger \hat{a} \hat{S} |0\rangle}_{\bar{n}_{\text{pure-squeezed}}} + \underbrace{|\alpha|^2}_{\bar{n}_{\text{coherent}}}$$

The part containing the pure squeezed states is, therefore

$$\bar{n}_{\text{pure-squeezed}} = \langle 0| (\mu^* \hat{a}^\dagger + \nu \hat{a})(\mu \hat{a} + \nu^* \hat{a}^\dagger) |0\rangle = |\nu|^2 = (sh\,|\xi|)^2,$$

when ξ is large, this is not a tiny number after all: $\bar{n}_{\text{pure-squeezed}} \to \frac{1}{4} e^{2|\xi|}$. Eventually,

$$\bar{n} = |\nu|^2 + |\alpha|^2.$$

There is no operator $\hat{a}^\dagger$ eigenstate (this would be a state with an infinitely large squeezing!). Larger squeezing means larger energy.

2.5   Density matrix and mixed states

So far, we looked at the eigenstates of a certain operator, which are described by the wave functions, the so-called *pure states*. Quantum systems can also have other type of states, i.e. the *mixed states*, described by the density matrices.

The density matrix is convenient to introduce by studying the *subsystem*. Assume that the whole system is determined by the wave function $\Psi(q, x)$, where the set of coordinates x describes the subsystem, and the set of q describes the rest of the system. It is our interest to measure only the subsystem, the rest does not interest us. In order to get the necessary information, we should calculate the average value of the corresponding operator:

$$\bar{f} = \iint \Psi^*(q, x) \hat{f} \Psi(q, x) dq dx. \tag{2.18}$$

We take into account that the operator $\hat{f}$ does not affect the coordinates q, but only affects x. So we introduce the following quantity

$$\rho(x', x) = \int \Psi^*(q, x') \Psi(q, x) dq. \tag{2.19}$$

This is a density matrix in the *coordinate representation*.
The probability to find the system in the point with coordinate x is

$$\rho(x, x) = \int \Psi^*(q, x) \Psi(q, x) dq = \int |\Psi(q, x)|^2 dq.$$

One can obtain the average value of an operator using the density matrix:

$$\bar{f} = \int \left(\hat{f} \rho(x', x) \right)\Big|_{x=x'} dx. \tag{2.20}$$

Since $\hat{f} = \hat{f}(x)$,

$$\hat{f} \rho(x', x) = \int \hat{f} \Psi^*(q, x') \Psi(q, x) dq = \int \Psi^*(q, x') \hat{f} \Psi(q, x) dq.$$

We can rearrange $\hat{f}$, because it does not depend on x'.

Generally, a density matrix can be introduced in any presentation. For example, we can choose a representation given by the functions $\psi_n(x)$, that form a complete orthonormal set

of functions, that is, any function can be presented as a superposition of other functions. This means that

$$\rho(x, x') = \sum_n \varphi_n(x')\psi_n(x). \tag{2.21}$$

On the other hand, $\varphi_n(x')$ can be also expanded in a series in ψ_m,

$$\varphi_n(x') = \sum_m \rho_{nm}\psi_m^*(x').$$

Then

$$\rho(x', x) = \sum_{nm} \rho_{nm}\psi_m^*(x')\psi_n(x). \tag{2.22}$$

Here ρ_{nm} is a density matrix in the *arbitrary representation.* To find this matrix, we multiply the Equation 2.22 by $\psi_{m'}(x')\psi_{n'}^*(x)$ and integrate over x and x':

$$\iint \psi_{m'}(x')\psi_{n'}^*(x)\rho(x', x)dxdx' = \sum_{nm} \rho_{nm} \int \psi_{m'}(x')\psi_m^*(x')dx' \int \psi_{n'}^*(x)\psi_n(x)dx.$$

Using the orthonormality condition,

$$\int \psi_{m'}^*(x')\psi_m(x)dx = \delta_{mm'},$$

$$\int \psi_{n'}^*(x')\psi_n(x)dx = \delta_{nn'},$$

$$\Rightarrow \iint \psi_{m'}(x')\psi_{n'}^*(x)\rho(x', x)dxdx' = \sum_{nm} \rho_{nm}\delta_{nn'}\delta_{mm'} = \rho_{n'm'}.$$

Thus, we obtain a density matrix in the arbitrary representation expressed through the density matrix $\rho(x', x)$ in the coordinate representation:

$$\rho_{nm} = \iint \psi_{m'}(x')\psi_{n'}^*(x)\rho(x', x)dxdx' = \iint \psi_n^*(x)\psi_m(x')\rho(x', x)dxdx'. \tag{2.23}$$

The quantity $\bar{f}$ can also be presented using density matrix in the arbitrary representation:

$$\bar{f} = \sum_{nm} \rho_{nm} \int \left(\hat{f}\psi_m^*(x')\psi_n(x) \right) \Big|_{x=x'} dx = \sum_{nm} \rho_{nm} \int \psi_m^*(x)\hat{f}\psi_n(x)dx.$$

Since

$$\int \psi_m^*(x)\hat{f}\psi_n(x)dx = f_{mn},$$

then

$$\bar{f} = \sum_{nm} \rho_{nm}f_{mn} = \sum_n \left(\rho f\right)_{nn} = \text{Sp}(\rho f) = \text{Sp}(f\rho). \tag{2.24}$$

The average value of the physical quantity can be calculated as a trace of the product of the density matrix and the given physical quantity:

$$\bar{f} = \text{Sp}(f\rho).$$

$\text{Sp}(f\rho)$ is a representation-independent *invariant*. Indeed,

$$\text{Sp}(A) \Rightarrow \text{Sp}(\tilde{A}) = \text{Sp}(UAU^{-1}) = \text{Sp}(U^{-1}UA) = \text{Sp}(A), \bar{f} = \sum_{ll'} f_{ll'}\rho_{l'l} = \sum_{l} f_{ll}\rho_{ll},$$

where ρ_{ll} is the probability of finding the system in a given state.

The density matrix is also a Hermitian operator (its diagonal elements are real):

$$\rho_{nm} = \rho_{mn}^{*},$$

$$\rho(x, x') = \rho^{*}(x', x) = \int \Psi^{*}(q, x')\Psi(q, x)dq.$$

The density matrix can always be diagonalized:

$$u = \{u_{lm}\},$$

$$uu^{\dagger} = 1,$$

$$\left(u\rho u^{-1}\right)_{ll'} = \rho_{ll}\delta_{ll'}.$$

This means that $u_{lm}\rho_{mn}u_{nl'}^{-1} = \delta_{ll'}\rho_{ll}$. Here $u_{nl'}^{-1} = u_{l'n}^{*}$ is a transform that diagonalizes the density matrix. The diagonal element

$$\rho_{ll} = \begin{pmatrix} \rho_{11} & 0 & \dots \\ 0 & \rho_{22} & \dots \\ \dots & \dots & \dots \end{pmatrix}$$

is the probability of finding the subsystem in the state 1, which is the matrix ρ eigenstate ($\rho_{ll} \geq 0$). In a pure state, one can present ρ in the form

$$\rho \to \begin{pmatrix} 0 & 0 & 0 & \dots \\ 0 & 0 & 0 & \dots \\ 0 & 0 & 1 & \dots \\ \dots & \dots & \dots & \dots \end{pmatrix}.$$

A state described by the density matrix having only one non-zero component ($\rho_{l_0 l_0} = 1$, $\rho_{ll} = 0$, when $l \neq l_0$) is a *pure state* (i.e. there is no statistical uncertainty). Otherwise, if more than one diagonal element is different from zero, it is a *mixed state* (another uncertainty is added to the Heisenberg uncertainty).

In the case of a pure state, $\rho^n = \rho$ (diagonal), $\sum_n \rho_{nn} = 1$ and $\sum_n \rho_{nn}^2 = 1$.

In the mixed state, $\rho^n \neq \rho$, $\sum_n \rho_{nn}^2 \leq 1 \Rightarrow Sp(\rho^2) < 1$.

If the density matrix factorizes, $\rho_{mn} = c_m c_n$, then we have a pure state: $\Psi = \sum_m c_m \psi_m$.

Often an additional uncertainty of the mixed state is called statistical. This is not entirely correct. The usual statistical uncertainty applies only to the ensembles of particles (the measured values are different in each sequential measurement). The mixed state applies also to a single system, i.e this is the property of the system itself. This question will be additionally discussed in the section of entangled states.

Density matrix in thermal equilibrium

Consider the case of thermal equilibrium, described by the Boltzmann distribution of energy. Then the state of the system is described by the diagonal density matrix in energetic representation:

$$\rho_{nn} = Z^{-1} e^{-E_n/k_B T}, \tag{2.25}$$

where $Z = \sum_n e^{-E_n/kT}$. $\rho_{nn'} \neq 0$, if $n \neq n'$. In a state of thermal equilibrium, the off-diagonal elements of the density matrix are averaged to zero. In operator notation,

$$\rho = Z^{-1} e^{-H/k_B T} \tag{2.26}$$

Time dependence of the density matrix

Let us have a mixed state at the initial moment, and after the interaction is turned off, the mixed state remains steady. If ψ_n is the eigenstate of the subsystem,

$$\hat{H}\psi_n = E_n \psi_n.$$

It is preferable to study the time dependence of the density matrix in the energy representation, since then the time dependence of the wave function is known:

$$\psi_n(x, t) = \psi_n(x) e^{-\frac{i}{\hbar} E_n t},$$

and

$$\rho(x', x, t) = \sum_{mn} \rho_{nm} e^{i(E_m - E_n)t/\hbar} \psi_m^*(x') \psi_n. \tag{2.27}$$

This is the *time dependence of the density matrix*. It can be written in a different way:

$$\rho(x', x; t) = \sum_{mn} \psi_n^*(x') e^{\frac{i}{\hbar} E_n t} \rho_{nm} e^{-\frac{i}{\hbar} E_m t} \psi_m(x) =$$

$$= \sum_{mn} \psi_n^*(x') e^{\frac{i}{\hbar} \hat{H} t} \rho_{nm} e^{-\frac{i}{\hbar} \hat{H} t} \psi_m(x) =$$

$$= \sum_{mn} \psi_n^*(x') \hat{\rho}(t) \psi_m(x).$$

where

$$\hat{\rho}(t) = e^{\frac{i}{\hbar} \hat{H} t} \rho_{nm}(0) e^{-\frac{i}{\hbar} \hat{H} t}.$$

In a differential form,

$$i\hbar \frac{\partial \hat{\rho}}{\partial t} = \left[\hat{H}, \hat{\rho} \right]. \tag{2.28}$$

This is *von Neumann equation*. An analogous equation also applies to other operators. (This is somewhat more general than the Schrödinger equation.) As the time-dependent Schrödinger equation

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

describes the evolution of the pure state over time, so von Neumann equation (Also known as the Liouville-von Neumann equation) determines the evolution of the density operator. Using this equation, we can find the mean value of any physical quantity.

2.6   Entangled states

The word "entangled" generally applies to the compound systems having more than one coordinate. Ideally, only pure states participate in the entanglement, with a single non-zero element in the density matrix, thus $\rho^2 = \rho$. Here, we consider the states of the subsystems in this ideal case, if the compound system is in pure state.

We consider a system of 2 coordinates and 2 degrees of freedom. An *entangled state* is defined as a state that is not separable (cannot be presented as the product of the wave functions of subsystems):

$$\Psi(x_1, x_2) \neq \Psi'(x_1)\Psi(x_2). \tag{2.29}$$

In the case of such a system (the sign $\otimes$ denotes the tensor product)

$$\rho \neq \rho_1 \otimes \rho_2. \tag{2.30}$$

We assume that these subsystems do not interact (are far from each other), but the Equation 2.29 still applies, since the subsystems were interacting in the past.

Example: Two two-level systems

$$|\Psi_1\rangle = c_{10}|\uparrow\rangle_1 + c_{11}|\downarrow\rangle_1 = c_{10}|0\rangle_1 + c_{11}|1\rangle_1,$$
$$|\Psi_2\rangle = c_{20}|\uparrow\rangle_2 + c_{21}|\downarrow\rangle_2 = c_{20}|0\rangle_2 + c_{21}|1\rangle_2,$$

$$|c_{10}|^2 + |c_{11}|^2 = 1, \qquad |c_{20}|^2 + |c_{21}|^2 = 1,$$

where the amplitudes c_{ij} can be arbitrary (even complex) numbers. If

$$\Psi(x_1, x_2) = \Psi'(x_1)\Psi(x_2),$$

then it is a *coherent state*:

$$\langle\Psi_1|\Psi_2\rangle = (c_{10}|\uparrow\rangle_1 + c_{11}|\downarrow\rangle_1)(c_{20}|\uparrow\rangle_2 + c_{21}|\downarrow\rangle_2) =$$
$$= c_{10}c_{20}|\uparrow\rangle_1|\uparrow\rangle_2 + c_{10}c_{21}|\uparrow\rangle_1|\downarrow\rangle_2 + c_{11}c_{20}|\downarrow\rangle_1|\uparrow\rangle_2 + c_{11}c_{21}|\downarrow\rangle_1|\downarrow\rangle_2.$$

If the wave function Ψ cannot be presented in such a form (the product of wave functions), then it is an *entangled state*.

Let us take as an example the most famous entangled state called the *EPR-state* (named by Einstein, Podolsky and Rosen):

$$|\Psi_{EPR}\rangle = \frac{1}{\sqrt{2}}[|\uparrow\rangle_1|\downarrow\rangle_2 - |\downarrow\rangle_1|\uparrow\rangle_2] \equiv \frac{1}{\sqrt{2}}[|0\rangle_1|1\rangle_2 - |1\rangle_1|0\rangle_2]. \tag{2.31}$$

In principle, this state cannot be decomposed into the product of two states. The state corresponds to the maximum entanglement (the total spin is 0, the spin product is -1). If we measure one atom and find it in the state $|\downarrow\rangle$, then the other one is definitely in the state $|\uparrow\rangle$, even if it is far away. This is the additional information that applies to our quantum system, the so-called *quantum information resource* (or hidden quantum information).

In general, we consider the state

$$\Psi(x_1, x_2) = \sum_{mn} c_{nm}\psi_m(x_1)\psi_n(x_2),$$

where m and n are some quantum numbers of subsystems. Since in general $c_{mn} \neq c_n c_m$, this state cannot be presented as a product. However, one can write

$$\Psi(x_1, x_2) = \sum_n \psi_n(x_2) u_n(x_1), \tag{2.32}$$

where

$$u_n(x_1) = \sum_m c_{nm} \psi_m(x_1).$$

If the measurement of the second subsystem gives the value of the physical quantity f_n, which corresponds to the eigenstate $\psi_n(x_2)$, then the first subsystem is definitely in the state $u_n(x_1)$ (by measurement we have fixed the state of the first subsystem). If we have measured another value $f_{n'}$, which corresponds to the eigenstate $\psi_{n'}(x_2)$, then the first subsystem will necessarily be in the state $u_{n'}(x_1)$. In general, this state is different from the previous one, although there is no interaction between the subsystems. Such a result seems controversial. However, for quantum systems, this can be true. The states with such properties are known as the *entangled states*.

One can measure the entanglement of the subsystems' states by calculating the entropy. The *quantum entropy* is

$$\varepsilon = -\mathrm{Sp}(\rho \ln \rho). \tag{2.33}$$

In the case of a pure state, one diagonal element of ρ is equal to one, while others are zeros. Therefore, in the pure state, $\varepsilon = 0$. The measure of entanglement is the entropy of the subsystems:

$$\begin{aligned} \varepsilon_1 &= -\mathrm{Sp}_1(\rho_1 \ln \rho_1), \\ \varepsilon_2 &= -\mathrm{Sp}_2(\rho_2 \ln \rho_2). \end{aligned} \tag{2.34}$$

Consider the entangled state $|\Psi_{\mathrm{EPR}}\rangle$. The density matrix reads

$$\hat{\rho} = |\Psi_{\mathrm{EPR}}\rangle \langle \Psi_{\mathrm{EPR}}| = \frac{1}{2} \big[|\uparrow\rangle_1 |\downarrow\rangle_2 - |\downarrow\rangle_1 |\uparrow\rangle_2 \big] \big[{}_1\langle\uparrow| \, {}_2\langle\downarrow| - {}_1\langle\downarrow| \, {}_2\langle\uparrow| \big],$$

$$\rho_{nm} = \langle m| \hat{\rho} |n\rangle,$$
$$|m\rangle = |0\rangle, |1\rangle, |2\rangle, |3\rangle,$$

$$\hat{\rho} = \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & \frac{1}{2} & -\frac{1}{2} & 0 \\ 0 & -\frac{1}{2} & \frac{1}{2} & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} \tag{2.35}$$

This is the density matrix of a pure EPR-state. Diagonalization yields

$$\hat{\rho} = \frac{1}{2} \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} + \frac{1}{2} \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}$$

$$\Rightarrow \frac{1}{2} \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} - \frac{1}{2} \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} = \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}$$

Thus, in a diagonal form, just one element of $\hat{\rho}$ is different from zero. As expected, it is a pure state.

However, in the $|\Psi_{\mathrm{EPR}}\rangle$-state, each spin is individually in a mixed state, although both spins are in a pure state. Let us show it. It follows that

$$\rho_1 = \mathrm{Sp}_2 \hat{\rho}_{\mathrm{EPR}} = {}_2\langle\uparrow|\rho_{\mathrm{EPR}}|\uparrow\rangle_2 + {}_2\langle\downarrow|\rho_{\mathrm{EPR}}|\downarrow\rangle_2.$$

Recall that

$$\hat{\rho}_{\mathrm{EPR}} = \frac{1}{2}\left[|\uparrow\rangle_1|\downarrow\rangle_2 - |\downarrow\rangle_1|\uparrow\rangle_2\right]\left[{}_1\langle\uparrow|_2\langle\downarrow| - {}_1\langle\downarrow|_2\langle\uparrow|\right].$$

We take into account that

$$\begin{cases} {}_i\langle\uparrow|\uparrow\rangle_{i'} = \delta_{ii'}, \\ {}_i\langle\uparrow|\downarrow\rangle_{i'} = 0, \end{cases} \qquad \text{where} \quad i, i' = 1, 2.$$

One gets

$$\rho_1 = {}_2\langle\uparrow|\rho|\uparrow\rangle_2 + {}_2\langle\downarrow|\rho|\downarrow\rangle_2 = \frac{1}{2}\left(|\downarrow\rangle_{11}\langle\downarrow| + |\uparrow\rangle_{11}\langle\uparrow|\right).$$

Thus,

$$\rho_1 = \frac{1}{2}\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

is the *maximally entangled state* in which the spin is with equal probability in the state $|\downarrow\rangle$ and $|\uparrow\rangle$. Here

$$\varepsilon_1 = -\mathrm{Sp}(\rho_1 \ln \rho_1) = -\frac{1}{2}\mathrm{Sp}(\ln \rho_1) = -\frac{1}{2}\mathrm{Sp}(\ln\frac{1}{2} + \ln I) = -\ln\frac{1}{2} = \ln 2$$

is the maximum possible entropy of the two-level system. Analogously,

$$\rho_2 = \frac{1}{2}\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

and one obtains again the maximum entropy $\varepsilon_2 = \ln 2$. Therefore, the entire system has zero entropy, whilst both subsystems have the maximum entropy.

There are different entangled states. For example, the general equation of EPR-state is

$$|\psi\rangle = \cos\varphi|\uparrow\rangle_1|\downarrow\rangle_2 + e^{i\varphi}\sin\varphi|\downarrow\rangle_1|\uparrow\rangle_2.$$

As an example of multi-spin systems, one can take a state

$$|\Psi_{\mathrm{cat}}\rangle = \frac{1}{\sqrt{2}}\left(\underbrace{|000..0\rangle}_{N} + \underbrace{|111..1\rangle}_{N}\right).$$

When N is a macroscopically large number, this state is called the Schrödinger's *cat state*. All the phases here are well-defined. Over time, the interaction with the surroundings creates fluctuations that damage each spin's phase. Therefore, the cat state is getting destroyed the faster the larger the cat is (the more subsystems it has). The larger the "cat", the "shorter" is its lifespan. In fact, the lifespan decreases exponentially with the increase in the number of subsystems.

The degree of entanglement in large compound systems cannot grow because of interaction. One of the most important applications of entangled states is quantum computing.
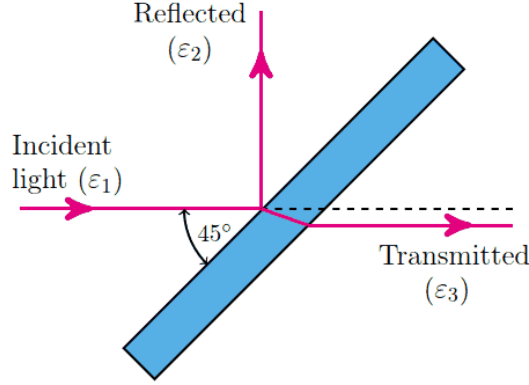
Figure 2.5: Beam splitter. The initial beam falls to the semi-transparent plate at an angle of $45°$, with probability $1/2$ it is reflected at an angle of $90°$ and with probability $1/2$ passes through ($|\varepsilon_1|^2 = |\varepsilon_2|^2/2 = |\varepsilon_3|^2/2$, ε_n is the electric field strength).

2.7 Beam splitter and photons

Interesting entangled photon states can be obtained using a *beam splitter* (BS) - a plate which with probability $1/2$ transmits the light and with probability $1/2$ reflects it at an angle of $90°$ (see Figure 2.5).

We are interested in the photon wave function in this process. It must be taken into account that, in reflection, the photon phase changes by $\pi/2$. To make sure, we change the direction of the arrows in Figure 2.5 to the opposite and consider the intensity of light $\propto |\varepsilon'_1|^2$, when $|\varepsilon'_2| = |\varepsilon'_3| = \varepsilon'$. We denote a phase change with φ. We also assume that the plate is thin, thus the phase shift of the transmitted light can be ignored. In this case, we get the field strength

$$\varepsilon'_1 = \left(\varepsilon_2 e^{i\varphi} + \varepsilon_3\right)/\sqrt{2} = \varepsilon'\left(e^{i\varphi} + 1\right)/\sqrt{2},$$

which gives

$$|\varepsilon'_1|^2 = \varepsilon'^2(1 + \cos\varphi).$$

If $\varphi = \pi/2$, one gets the required value $|\varepsilon'_1|^2 = \varepsilon'^2$.

In the quantum theory, such field transformations correspond to the following transformation of the photon creation operators:

$$\begin{aligned}
\hat{a}_0^\dagger &= \frac{1}{\sqrt{2}}\left(\hat{a}_2^\dagger + i\hat{a}_3^\dagger\right), \\
\hat{a}_1^\dagger &= \frac{1}{\sqrt{2}}\left(i\hat{a}_2^\dagger + \hat{a}_3^\dagger\right).
\end{aligned} \tag{2.36}$$

Here, i (the imaginary unit) accounts for the phase change at the reflection, the lower index 0 corresponds to the photons that fall from the bottom, the index 1 to the photons that fall from the left, 2 to the photons propagating to the right, and 3 to the photons propagating downwards.

Consequently, the states are transformed as follows

$$\begin{aligned}
|0\rangle_0|1\rangle_1 &\rightarrow \frac{1}{\sqrt{2}}\left(\hat{a}_2^\dagger + i\hat{a}_3^\dagger\right)|0\rangle_2|0\rangle_3 = \frac{1}{\sqrt{2}}\left(|1\rangle_2|0\rangle_3 + i|0\rangle_2|1\rangle_3\right), \\
|1\rangle_0|0\rangle_1 &\rightarrow \frac{1}{\sqrt{2}}\left(i\hat{a}_2^\dagger + \hat{a}_3^\dagger\right)|0\rangle_2|0\rangle_3 = \frac{1}{\sqrt{2}}\left(i|1\rangle_2|0\rangle_3 + |0\rangle_2|1\rangle_3\right).
\end{aligned} \tag{2.37}$$

This means that one photon is always below *or* to the right, and never below *and* to the right at the same time after it leaves the plate.
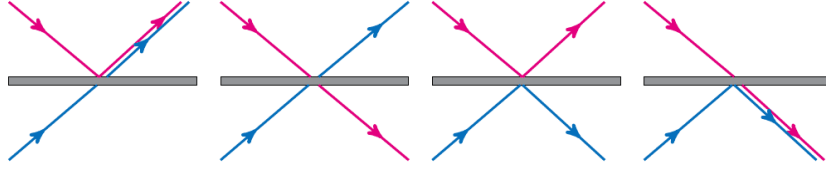
Figure 2.6: Four possibilities for the photons to behave; two middle processes cancel each other.

Let us now look at two identical photons falling on the plate at the same time: one from the top and the other from the bottom. The corresponding initial state $|1\rangle_0|1\rangle_1$ is transformed as follows:

$$
\begin{aligned}
|1\rangle_0|1\rangle_1 &= \frac{1}{2}\left(\left(\hat{a}_2^\dagger + i\hat{a}_3^\dagger\right)\left(i\hat{a}_2^\dagger + \hat{a}_3^\dagger\right)\right)|0\rangle_2|0\rangle_3 = \\
&= \frac{i}{2}\left(\hat{a}_2^{\dagger 2} + \hat{a}_3^{\dagger 2}\right)|0\rangle_2|0\rangle_3 = \frac{i}{\sqrt{2}}\left(|2\rangle_2|0\rangle_3 + |0\rangle_2|2\rangle_3\right).
\end{aligned}
\tag{2.38}
$$

Therefore, both the photons get to one side. Note that the term $\hat{a}_2^\dagger\hat{a}_3^\dagger$ is cancelled out. The described process is called Hong-Ou-Mandel interference; it is schematically depicted in Figure 2.6.

The state obtained in Equation 2.38 is the *Schrödinger's cat state* (or simply the *cat state*). If, however, the initial photons were not identical (for example, they would have a different polarization), they would have been found on the right and below at the same time.

Two-level atoms in electromagnetic field

3.1 Interactions of photons with two-level atoms and Einstein coefficients

The model of two-level atoms interacting with light is widely used in quantum theory. First time it was used by Einstein in 1915. Already in this early work he obtained very important results (stimulated radiation), that is before the quantum theory was completely formulated. Einstein applied this model to consideration of interaction of atoms with thermal (black body) radiation.

In 1900, Max Planck completed the formula for the spectrum of an absolutely black body. He assumed that electromagnetic radiation can be emitted or absorbed only in discrete packets, the energy quanta $E_n = nh\nu$, for which the Planck constant h was introduced for the first time. This assumption ensured the correct shape of the spectral distribution function.

Let us consider the modes of the radiation field in the state of thermal equilibrium. The probability to find the mode on the level n at temperature T is given by

$$P_n = \frac{e^{-\beta n\hbar\omega}}{\sum_n e^{-\beta n\hbar\omega}} = e^{-\beta n\hbar\omega}\left\{1 - e^{-\beta\hbar\omega}\right\}, \tag{3.1}$$

where $\beta = 1/k_B T$, and k_B is the Boltzmann constant.

The *average number of photons* excited at temperature T is

$$\bar{n} = \sum_n n P_n = \frac{1}{e^{\beta \hbar \omega} - 1}. \tag{3.2}$$

Given the density of modes $\rho_\omega = \omega^2/\pi^2 c^3$ (see Equation 1.7) in the frequency range $(\omega, \omega + d\omega)$, and the mean energy of a single mode $\bar{n} \hbar \omega$, we obtain the Planck formula for the *average density of thermal radiation*

$$W_T(\omega) = \bar{n} \hbar \omega \rho_\omega = \frac{\hbar \omega^3}{\pi^2 c^3} \frac{1}{e^{\hbar \omega/(k_B T)} - 1}. \tag{3.3}$$

Planck considered the electromagnetic field in a cavity. Einstein (1916) studied the state of equilibrium in more detail. According to him, in this cavity, photons are constantly absorbed and emitted, furthermore, the photon absorption rate equals the emission rate. Einstein considered that absorption and emission of a photon with frequency $\omega = (E_2 - E_1)/\hbar$ take place as a result of transition between the levels with energies E_1 and E_2.
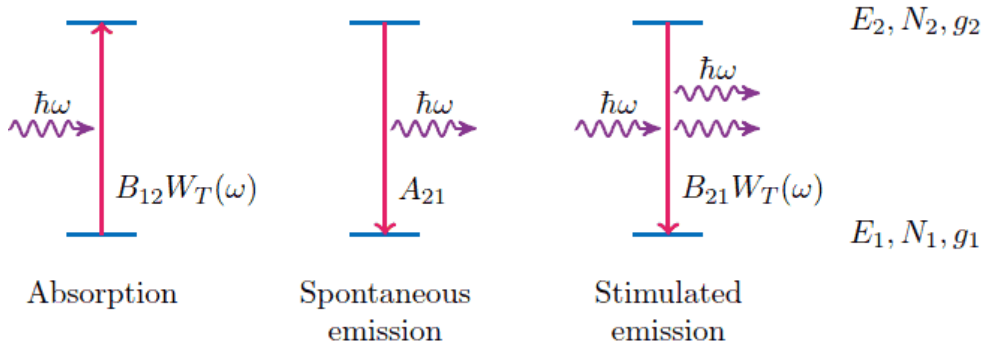
Figure 3.1: The processes occurring in the formation of atomic spectra.

The field state is a stationary: the radiation process takes place all the time, so that the emission of photons is dynamically balanced with the absorption. The spontaneous emission A_{21} is accompanied by the stimulated emission $W_T(\omega)B_{21}$, that is $W_{21} = A_{21} + W_T(\omega)B_{21}$. Here the coefficients A_{21}, B_{21}, B_{12} are the Einstein coefficients (see [10]).

In the state of equilibrium, three processes should be introduced:

- spontaneous emission (A_{21});

- photon absorption, which is proportional to the radiation power ($B_{12} \times W_T(\omega)$);

- stimulated emission ($B_{21} \times W_T(\omega)$).

Without stimulated emission, equilibrium cannot be achieved. The equilibrium equation requires that (N_1, N_2 - the occupancy of states 1 and 2)

$$\frac{dN_1}{dt} = N_2(A_{21} + B_{21}W) - N_1 B_{12}W = -\frac{dN_2}{dt}. \tag{3.4}$$

In thermal equilibrium, $dN_1/dt = dN_2/dt = 0$, which only happens when $W = W_T$. From

$$N_2(A_{21} + B_{21}W_T) - N_1 B_{12}W_T = 0,$$

it follows that

$$\frac{N_1}{N_2} = e^{\hbar\omega/(k_B T)}\frac{g_1}{g_2},$$

where g_1, g_2 are the statistical weights, which are equal to the degeneracy of states 1 and 2. We get

$$W_T = \frac{A_{21}}{e^{\hbar\omega/(k_B T)}\frac{g_1}{g_2}B_{12} - B_{21}}. \tag{3.5}$$

This equation coincides with the Planck formula, if $(g_1/g_2)B_{12} = B_{21}$:

$$g_1 B_{12} = g_2 B_{21} \qquad (1^{\text{st}} \text{ condition}) \tag{3.6}$$

When the stimulated emission occurs,

$$W_T(\omega) = \frac{A_{21}/B_{21}}{e^{\hbar\omega/kT} - 1}, \tag{3.7}$$

and hence it follows that $(A_{21}/B_{21}) = \hbar\omega^3/(\pi^2 c^3)$:

$$B_{21} = \frac{\pi^2 c^3}{\hbar\omega^3}A_{21} \qquad (2^{\text{nd}} \text{ condition}) \tag{3.8}$$

From Equation 3.6 and Equation 3.8, one gets

$$A_{21} = B_{12}\frac{g_1}{g_2}\frac{\hbar\omega^3}{\pi^2 c^3}.$$

Consequently, only one of Einstein's coefficients is independent: there is only one parameter that determines the transition rates between two levels. Thus, before the creation of quantum mechanics, Einstein introduced a process that was not known - *stimulated emission* - which is crucial for lasers.

We emphasize again that without the introduction of stimulated emission, it is impossible to explain the thermal radiation or get the Planck formula.

3.2 Second quantization of atomic Hamiltonian

In this section, we consider the interaction of atom with photons. We start with the Schrödinger equation of the system,

$$i\hbar\frac{\partial\Psi}{\partial t} = \hat{H}\Psi. \tag{3.9}$$

If there are stationary states $(\hat{H}\psi_i = E_i\psi_i)$, then $d\psi_i/dt = -(i/\hbar)E_i\psi_i$ and

$$\psi_i(t) = e^{-\frac{i}{\hbar}E_i t}\psi_i. \tag{3.10}$$

Next, we use a Dirac notation for the stationary Schrödinger equation:

$$H|i\rangle = E_i|i\rangle, \tag{3.11}$$

where $E_i = \hbar\omega_i$. The closure relation[1] $\sum_i |i\rangle\langle i| = 1$ yields $\sum_i \psi_i(x)\psi_i(x') = \delta(x - x')$, and the orthonormality condition yields $\sum_i \langle i|i\rangle = 1$.

Let us continue in the *Hilbert space*. An arbitrary state Ψ is a Hilbert space vector. The scalar product $\langle k'|k\rangle = \delta_{kk'}$ is orthonormal (here $k = 1, 2, ... N$). In 2-dimensional space, the state is a unit vector[2] $(|c_1|^2 + |c_2|^2 = 1)$.

---

[1] The resolution of identity.

[2] In general, basis states are not necessarily real.

An arbitrary quantum mechanical state is a unit vector in the Hilbert space.

The Hamiltonian can be presented in the basis of discrete states:

$$H = \sum_i \sum_j |i\rangle \langle i| H |j\rangle \langle j| = \sum_{ij} H_{ij} |i\rangle \langle j|. \tag{3.12}$$

One can introduce the creation and annihilation operators $\hat{b}_i^+, \hat{b}_j$, such as

$$|i\rangle \langle j| = \hat{b}_i^\dagger \hat{b}_j \qquad \Rightarrow \qquad \sum_{ij} H_{ij} \hat{b}_i^\dagger \hat{b}_j.$$

Applying these operators to the state $|l\rangle$ yields

$$\langle i|j\rangle |l\rangle = \delta_{jl} |i\rangle,$$

i.e. we lost the state $|l\rangle$ and created the state $|i\rangle$. This representation is called the *second quantization.*

In the representation, where the states are vector in Hilbert space, one can use a *matrix notation* for vectors:

$$|j\rangle = \begin{pmatrix} c_1 \\ c_2 \\ \vdots \\ c_n \end{pmatrix}, \quad \langle i| = \begin{pmatrix} c_1 & c_2 & \cdots & c_n \end{pmatrix} \qquad \sum_i |c_i|^2 = 1. \tag{3.13}$$

Hereafter, the *Heisenberg representation* will be used, in which the state $\Psi = \sum_k c_k |k\rangle$ is presented as a series of eigenstates of some operator.

3.2.1   Interaction of a two-level atom with radiation

The corresponding Hamiltonian consists of atomic (**A**tomic), electromagnetic (**R**adiation) and interaction (**int**eraction) parts (see [30]):

$$H = H_A + H_R + H_{int}. \tag{3.14}$$

We denote the states of the atom (g = **g**round, e = **e**xcited) as follows:

$$|1\rangle \equiv |e\rangle \equiv \ldots \equiv |\uparrow\rangle \rightarrow \begin{pmatrix} 1 \\ 0 \end{pmatrix}$$
$$\Rightarrow \qquad \begin{matrix} E_e = \hbar\omega_0 \\ E_g = 0 \end{matrix}$$
$$|2\rangle \equiv |g\rangle \equiv \ldots \equiv |\downarrow\rangle \rightarrow \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

In a representation in which the states are two-component vectors, the Hamiltonians are 2×2 matrices:

$$H_A = \sum_{i=1}^{2} \hbar\omega_i |i\rangle \langle i|, \qquad H_A = \begin{pmatrix} \hbar\omega_0 & 0 \\ 0 & 0 \end{pmatrix}. \tag{3.15}$$

Indeed,

$$\begin{pmatrix} \hbar\omega_0 & 0 \\ 0 & 0 \end{pmatrix} \begin{pmatrix} 0 \\ 1 \end{pmatrix} = 0, \qquad \begin{pmatrix} \hbar\omega_0 & 0 \\ 0 & 0 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \hbar\omega_0 \begin{pmatrix} 1 \\ 0 \end{pmatrix}.$$

We can express a 2×2 matrix as the sum of the unit matrix and the Pauli matrix:

$$\begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} = \frac{1}{2} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + \frac{1}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}.$$

Recall the definition of *Pauli matrices*:

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \qquad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \qquad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}.$$

Let us bring here the *quasi-spin matrices*

$$S_i = \frac{1}{2}\sigma_i, \qquad [S_i, S_j] = i e_{ijk} S_k,$$

where e_{ijk} is the Levi-Civita symbol. In *dipole approximation*, the interaction Hamiltonian equals $H_{\text{int}} = \hat{E} \cdot \hat{d}$. Thus,

$$\begin{aligned}
H_{\text{A}} &= \frac{\hbar\omega_0}{2} I + \frac{\hbar\omega_0}{2}\sigma_z = \frac{\hbar\omega_0}{2} I + \hbar\omega_0 S_z, \\
H_{\text{R}} &= \sum_k \hbar\omega_k (a_k^+ a_k + 1/2), \\
H_{\text{int}} &= \hat{E} \cdot \hat{d} \quad (d = e_0 \vec{r}).
\end{aligned} \tag{3.16}$$

Here the matrix $\hat{d}$ is a 2×2 matrix:

$$\{d_{ij}\} = \begin{pmatrix} d_{11} & d_{12} \\ d_{21} & d_{22} \end{pmatrix},$$

where

$$d_{11} = \langle e | e_0 r | e \rangle = e_0 \int d^3 r \psi_e^*(r) r \psi_e(r) = e_0 \int d^3 r |\psi_e(r)|^2 r = 0,$$

since d_{11} is the integral of odd function; similarly, $d_{22} = 0$. Only off-diagonal elements are different from zero:

$$\begin{aligned}
d_{12} &= \langle e | \hat{d} | g \rangle \equiv d \neq 0, \\
d_{21} &= \langle g | \hat{d} | e \rangle \equiv d^*.
\end{aligned}$$

Since d is a physical quantity, the corresponding matrix is Hermitian. In our case

$$\hat{d} \equiv \{d\} = d \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}. \tag{3.17}$$

Taking into account that $\hat{E} = \sum_k \hat{E}_k$, where

$$\hat{E}_k = \left(\frac{\hbar\omega_k}{2V}\right)^{1/2} i\left(\hat{a}_k - \hat{a}_k^\dagger\right),$$

we obtain

$$\begin{aligned}
H_{\text{int}} &= i d \sum_k \left(\frac{\hbar\omega_k}{2V}\right)^{1/2} (\hat{a}_k - \hat{a}_k^\dagger)\sigma_x = \\
&= \frac{i\hbar}{2} \sum_k q_k (a_k - a_k^\dagger)(S_+ + S_-),
\end{aligned} \tag{3.18}$$

where $q_k = (2\omega_k/(\hbar V))^{1/2}$ is the interaction parameter (with the dimension of frequency), and

$$S_+ = \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}, \qquad S_- = \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}.$$

What is the purpose of the operators S_+ and S_-? If we act on the ground state with the operator S_+, then

$$S_+ \begin{pmatrix} 0 \\ 1 \end{pmatrix} = \begin{pmatrix} 1 \\ 0 \end{pmatrix},$$

i.e. the operator S_+ is the *creation operator of electronic excitation*. Analogously,

$$S_- \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \begin{pmatrix} 0 \\ 1 \end{pmatrix},$$

thus, the operator S_- is the *annihilation operator of electronic excitation*. These operators are related to Pauli matrices:

$$S_+ + S_- = 2S_x = \sigma_x.$$

The operators S_+ and S_- act as ladder operators, since they increase (raise) or decrease (lower) a quantum number associated with the state of a system.

3.2.2   Rotating Wave Approximation (RWA)

We continue with a two-level atoms in a resonant electromagnetic quantum field (see Equations 3.16 - 3.18):

$$H = H_A + H_R + H_{int}.$$

We restrict ourselves to one electromagnetic mode. It seems like a nonsense, but not quite. This is possible, e.g. in the case of a strongly excited mode in a resonator. We take in account that there are modes in a resonator, and if the resonator is small, then the frequency difference is large. For example, if the resonator length is 1 mm, then $\Delta\omega \sim 10^{13}\text{sec}^{-1}$. Consider the case when the length is large enough. Let us have one 2-level atom, and the transition frequency is approximately in resonance with the electromagnetic mode.
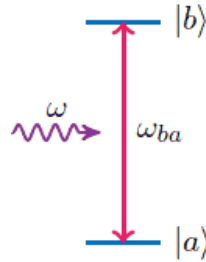
Figure 3.2: The interaction of a single two-level atom with a single mode of the EM-field (here $\hbar = 1$).

Since $\gamma \sim 10^8\text{s}^{-1}$ is a natural line width ($\gamma \ll \Delta\omega$), we can restrict ourselves to only one mode (in a resonance). Other modes are far from the resonance.

The parts of Hamiltonian are

$$H_R = \hbar\omega \, (a^\dagger a + 1/2),$$

$$H_A = \frac{\hbar\omega_0}{2} I + \hbar\omega_0 S_z,$$

$$H_{int} = \frac{i\hbar}{2} \sum_k q_k (a_k - a_k^\dagger) (S_+ + S_-) =$$

$$= \frac{i\hbar}{2} \sum_k q_k \left(a_k S_+ + a_k S_- - a_k^\dagger S_+ - a_k^\dagger S_- \right).$$

In the latter expression, important terms are the first (the photon disappears, the electronic excitation is created) and the fourth (the photon is created, the electronic excitation is annihilated), because in them the number of excitations is conserved. The second and third terms are non-resonant, thus decreasing and increasing energy by $\omega + \omega_0$.

Considering only resonant terms, we get the interaction Hamiltonian in the *rotating wave approximation* (RWA):

$$H_{\text{int}}^{\text{RWA}} = \frac{i\hbar}{2} \sum_k q_k \left(a_k S_+ - a_k^+ S_- \right). \tag{3.19}$$

The whole Hamiltonian in this approximation yields

$$H_{\text{RWA}} = H_A + H_R + H_{\text{int}}^{\text{RWA}} \tag{3.20}$$

3.3 Dressed states

We proceed with a two-level atom, which is located in the field of a single strongly excited mode, whose frequency is close to the energy of electronic excitation ($\omega \approx \omega_0$). All other modes are unexcited.

When can we use this model?

1. If there is a small resonator (cavity) ($\omega = \pi/a$, where a is the size of resonator).

2. If there is a photon with the laser-excited level ($N \sim 10^3 \div 10^6$), that is, one mode is highly excited, while others are not excited at the same time.

3.3.1 Non-interacting states

If there is no interaction between the electromagnetic field and the atom,

$$H_0 = H_A + H_R = \frac{\hbar\omega_0}{2} I + \frac{\hbar\omega_0}{2} \sigma_z + \hbar\omega \left(a^\dagger a + 1/2 \right). \tag{3.21}$$

We are trying to solve the stationary Schrödinger equation $H\Psi = E\Psi$ in the basis of H_0 eigenstates. These are of 2 types, and we introduce quantum numbers N = number-of-photons and the number of atomic excitations:

$$\Psi_{1N} = \left| g \right\rangle | N \rangle,$$
$$\Psi_{2N} = i \left| e \right\rangle | N - 1 \rangle,$$

where i is connected to the phase and added in order to avoid the complex numbers further in text. Corresponding energy levels are

$$E_{1N} = \hbar\omega \left(N + 1/2 \right),$$
$$E_{2N} = \hbar\omega \left(N - 1 \right) + \hbar\omega/2 + \hbar\omega_0 = \hbar\omega_0 + \hbar\omega \left(N - 1/2 \right),$$
$$\Rightarrow E_{1N} = E_{2N} - \hbar\omega + \hbar\omega_0 \equiv E_{2N} + \hbar\Delta.$$

where $\Delta = \omega - \omega_0 \ll \omega$.

The states $|e\rangle, |g\rangle$ are the eigenstates of σ_z, where $N = 0, 1, 2, \dots$. There is an infinite number of states, thereby 2 times more than for the harmonic oscillator, because there are two atomic states.
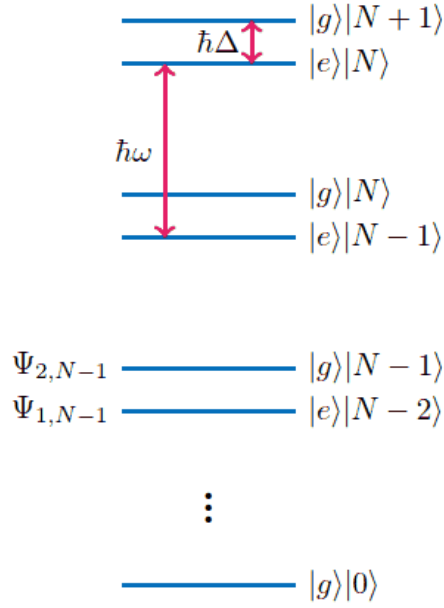
Figure 3.3: Dressed states.

The state of the lowest energy is $|g\rangle|0\rangle$. The corresponding line is single (not double). All other levels form the two-step ladder of states with the gap $\hbar\Delta$ between the two neighboring levels (if there is no interaction). The interaction part of the Hamiltonian overlaps the $\hbar\Delta$-separated states. In the case of exact resonance ($\omega = \omega_0$), the states 1 and 2 would coincide.

If $H_{\text{int}} = 0$, we get an infinite diagonal matrix of the Hamiltonian H:

$$
H = H_0 = \begin{pmatrix}
\cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\
\cdot & E_{1N} & 0 & 0 & 0 & \cdot \\
\cdot & 0 & E_{2N} & 0 & 0 & \cdot \\
\cdot & 0 & 0 & E_{1N-1} & 0 & \cdot \\
\cdot & 0 & 0 & 0 & E_{2N-1} & \cdot \\
\cdot & \cdot & \cdot & \cdot & \cdot & \cdot
\end{pmatrix}.
\tag{3.22}
$$

3.3.2   Interaction Hamiltonian

We add an interaction between the laser mode and the atom:

$$
\begin{aligned}
\left(H_{\text{int}}^{\text{RWA}}\right)_{N,N';\,1,2} &= \frac{q\hbar}{2} \langle N-1|\langle e| \left(a S_+ - a^\dagger S_-\right) |g\rangle |N'\rangle = \\
&= \frac{\hbar}{2} q \langle N-1|a|N'\rangle = \frac{\hbar}{2} q \sqrt{N}\,\delta_{NN'}
\end{aligned}
\tag{3.23}
$$

Analogously

$$
\left(H_{\text{int}}^{\text{RWA}}\right)_{N,N';2,1} = \frac{\hbar}{2} q \sqrt{N}\,\delta_{NN'}
$$

Hence,

$$
\langle \Psi_{1N}| H_{\text{int}} |\Psi_{2N}\rangle = \langle \Psi_{2N}| H_{\text{int}} |\Psi_{1N}\rangle = \frac{\hbar q}{2}\sqrt{N},
$$

where N is the number of photons. All other terms are equal to zero, i.e.

$$
\langle \Psi_{1N}| H_{\text{int}} |\Psi_{1N-1}\rangle = 0
$$

Now the Hamiltonian in RWA approximation and matrix representation equals

$$\mathbf{H} = \begin{pmatrix} \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \mathbf{H_{N+1}} & \mathbf{0} & \mathbf{0} & \cdot \\ \cdot & \mathbf{0} & \mathbf{H_N} & \mathbf{0} & \cdot \\ \cdot & \mathbf{0} & \mathbf{0} & \mathbf{H_{N-1}} & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \end{pmatrix}, \tag{3.24}$$

it is a quasi-diagonal matrix whose elements are 2×2 matrices:

$$\mathbf{H_N} = \hbar\omega \left(\mathbf{N} + \mathbf{1/2}\right)\hat{\mathbf{I}} + \frac{\hbar}{2}\begin{pmatrix} \Delta & \Gamma_N \\ \Gamma_N & -\Delta \end{pmatrix} = \hbar\omega\left(\mathbf{N} + \mathbf{1/2}\right)\hat{\mathbf{I}} + \mathbf{H'_N}, \tag{3.25}$$

where $\Gamma_N = q\sqrt{N}$ - the interaction with the laser mode leads to the splitting of energy levels, and $\mathbf{0}$ is a 2×2 *zero matrix*.

To diagonalize $\mathbf{H_N}$, we need to find the states ϕ_{iN}:

$$\phi_{iN} = \sum_{i'=1,2} \Psi_{i'N} c_{i,i'}.$$

Let us find the matrices $\mathbf{c} = \{\mathbf{c_{i,i'}}\}$ that satisfy the equation

$$\mathbf{H'_N} \cdot \mathbf{c} \equiv \frac{\hbar}{2}\begin{pmatrix} \Delta & \Gamma_N \\ \Gamma_N & -\Delta \end{pmatrix}\begin{pmatrix} c_{i,1} \\ c_{i,2} \end{pmatrix} = \mathbf{E_i}\begin{pmatrix} c_{i,1} \\ c_{i,2} \end{pmatrix}.$$

In Hilbert space, our states are rotated by φ, so this is a 1-parameter task:

$$\begin{array}{l} \phi_{1N} = \Psi_{1N}\cos\varphi + \Psi_{2N}\sin\varphi \\ \phi_{2N} = -\Psi_{1N}\sin\varphi + \Psi_{2N}\cos\varphi \end{array} \quad \text{and} \quad \mathbf{c} = \begin{pmatrix} \cos\varphi & -\sin\varphi \\ \sin\varphi & \cos\varphi \end{pmatrix}. \tag{3.26}$$

The states $\left|\phi_{iN}\right\rangle$ are orthogonal, i.e. $\left\langle\phi_{1N}\middle|\phi_{2N}\right\rangle = 0$. If $\varphi = (1/2)\arctan(\Gamma_N/\Delta)$, then rows of the matrix $\mathbf{c}$ are the eigenstates of $\mathbf{H'_N}$, i.e. the following equations are satisfied:

$$\begin{array}{l} \dfrac{\hbar}{2}\begin{pmatrix} \Delta & \Gamma_N \\ \Gamma_N & -\Delta \end{pmatrix}\begin{pmatrix} \cos\varphi \\ \sin\varphi \end{pmatrix} = E_1\begin{pmatrix} \cos\varphi \\ \sin\varphi \end{pmatrix}, \\[3mm] \dfrac{\hbar}{2}\begin{pmatrix} \Delta & \Gamma_N \\ \Gamma_N & -\Delta \end{pmatrix}\begin{pmatrix} -\sin\varphi \\ \cos\varphi \end{pmatrix} = E_2\begin{pmatrix} -\sin\varphi \\ \cos\varphi \end{pmatrix}, \end{array} \tag{3.27}$$

where the eigenvalues are

$$E_{1,2} = \pm\frac{\hbar}{2}\sqrt{\Delta^2 + \Gamma_N^2} = \pm\frac{\hbar}{2}\Omega_N, \qquad \Omega_N = \sqrt{\Delta^2 + \Gamma_N^2} \quad \text{is the Rabi frequency.} \tag{3.28}$$

Indeed, the first line of the first matrix in Equation 3.27 gives $\Delta\cos\varphi + \Gamma_N\sin\varphi = \Omega\cos\varphi$. Here and below $\Omega \equiv \Omega_N$. Multiplying by $\cos\varphi$ and using trigonometric identities (Double angle identities: $\cos 2\varphi = 2\cos^2\varphi - 1$, $\sin 2\varphi = 2\sin\varphi\cos\varphi$), we get $\Delta + \Delta\cos 2\varphi + \Gamma_N\sin 2\varphi = \Omega + \Omega\cos 2\varphi$. We take into account that $\tan 2\varphi = \Gamma_N/\Delta$ and, correspondingly, $\sin 2\varphi = \Gamma_N/\Omega$ and $\cos 2\varphi = \Delta/\Omega$. This gives $\Delta + \Delta^2/\Omega + \Gamma_N^2/\Omega = \Omega + \Delta$, and hence $\Delta^2 + \Gamma_N^2 = \Omega^2$. Analogously, one can obtain other matrix relations in Equation 3.27.

We also note that in the expression

$$\mathbf{c^T} \cdot \begin{pmatrix} \Delta & \Gamma_N \\ \Gamma_N & -\Delta \end{pmatrix} \cdot \mathbf{c} = \begin{pmatrix} \Gamma_N\sin 2\varphi + \Delta\cos 2\varphi & \Gamma_N\cos 2\varphi - \Delta\sin 2\varphi \\ \Gamma_N\cos 2\varphi - \Delta\sin 2\varphi & -\Gamma_N\sin 2\varphi - \Delta\cos 2\varphi \end{pmatrix}$$

the non-diagonal elements get to zero, while diagonal elements equal $\pm\Omega$:

$$\mathbf{c}^{\mathbf{T}}\begin{pmatrix} \Delta & \Gamma_N \\ \Gamma_N & -\Delta \end{pmatrix}\mathbf{c} = \Omega\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}.$$

From $\Delta\cos\varphi + \Gamma_N\sin\varphi = \Omega_N\cos\varphi$, it follows that $\sin\varphi = \sqrt{(\Omega_N - \Delta)/(2\Omega_N)}$. The new states

$$\begin{aligned} \Psi_1 &= \sqrt{\frac{\Omega_N + \Delta}{2\Omega_N}}\,|e\rangle\,|N-1\rangle + \sqrt{\frac{\Omega_N - \Delta}{2\Omega_N}}\,|g\rangle\,|N\rangle \\ \Psi_2 &= -\sqrt{\frac{\Omega_N - \Delta}{2\Omega_N}}\,|e\rangle\,|N-1\rangle + \sqrt{\frac{\Omega_N + \Delta}{2\Omega_N}}\,|g\rangle\,|N\rangle \end{aligned} \tag{3.29}$$

are mixed states (a *superposition* of states), these are the so-called *dressed states* in which the atom is "dressed" in photons. (If N is large, then the dependence on N is small, and one can ignore the index.)

We now have the following picture (see Figure 3.4).
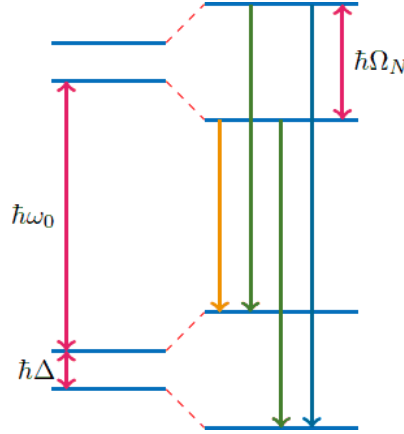
Figure 3.4: Interaction Hamiltonian.

We can see that the interaction leads to splitting. The situation can change if there is the third energy level.

If there is an exact resonance ($\Delta = 0$), then $\sin\varphi = 2^{-1/2}$ and, in this case, Equation 3.26 changes to the form:

$$\begin{aligned} \phi_{1N} &= \frac{1}{\sqrt{2}}\left(\Psi_{1N} + \Psi_{2N}\right) \\ \phi_{2N} &= \frac{1}{\sqrt{2}}\left(\Psi_{1N} - \Psi_{2N}\right). \end{aligned}$$

Are the dressed states observable in the experiment?

Yes, these states are experimentally observable. If a strong laser mode is in a resonance with atomic transition frequency, then the *dynamical Stark effect* (see [2]) takes place.

In a strong laser field, the spectral lines split into 3 components when the laser field is in a resonance with the transition frequency of spectral line of atom (see Figure 3.5). In other words, in the absence of an interaction, there is only one line at the frequency ω_0, and after the interaction, there are two additional peaks at the frequency $\omega_0 \pm \Omega$. The dynamical Stark effect is also known in spectroscopy as the Autler-Townes effect).
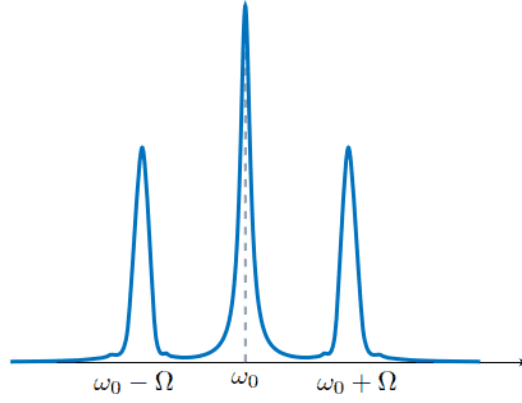
Figure 3.5: Strong laser fields.

3.4 Oscillations of atomic inversion

The matrix $\sigma_z = 2S_z$ is also called the *operator of atomic inversion.* Let us see how this operator's mean value changes over time, i.e. investigate the evolution of atomic inversion. Suppose that the atom is in the field of the monochromatic laser. We use quasi-spin matrices:

$$S_x = \frac{1}{2}\sigma_x = \frac{1}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad S_y = \frac{1}{2}\sigma_y = \frac{1}{2}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad S_z = \frac{1}{2}\sigma_z = \frac{1}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}.$$

The Hamiltonian is

$$H_{\text{RWA}} = \hbar\omega(a^\dagger a + 1/2) + \hbar\omega_0 S_z + \underbrace{\frac{i\hbar q}{2}\left(aS_+ - a^\dagger S_-\right)}_{H_{\text{int}}}.$$

We introduce the particle number operator $\hat{N} = \hat{a}^\dagger \hat{a} + S_z$, then the Hamiltonian yields

$$H_{\text{RWA}} = \frac{\hbar(\omega + \omega_0)}{2} + \hbar\omega(a^\dagger a + S_z) + \hbar\Delta S_z + H_{\text{int}},$$

where $\Delta = \omega_0 - \omega$. We select the energy of the ground state $\hbar(\omega + \omega_0)/2$. Then

$$H_{\text{RWA}} = \hbar\omega\hat{N} + \hbar\Delta S_z + \frac{i\hbar q}{2}\left(aS_+ - a^\dagger S_-\right).$$

We get

$$\dot{S}_z = \frac{i}{\hbar}[H, S_z] = -\frac{q}{2}\left([S_+, S_z]\, a - [S_-, S_z]\, a^\dagger\right).$$

We also take into account that

$$[S_z, S_+] = S_+, \qquad [S_z, S_-] = -S_-, \qquad \dot{S}_z = \frac{q}{2}\left(S_+ a + S_- a^\dagger\right),$$

here $q \simeq \gamma$ is a natural line width. We also find

$$\ddot{S}_z = \frac{i}{\hbar}[H, \dot{S}_z] = i\frac{q\Delta}{2}\left[S_z, \left(S_+ a + S_- a^\dagger\right)\right] - \frac{q^2}{4}\left(\left[S_+ a^\dagger, S_- a\right] - \left[S_- a^\dagger, S_+ a\right]\right)$$

$$= i\frac{q\Delta}{2}\left(S_+ a - S_- a^\dagger\right) - \frac{q^2}{4}\left[S_+ a, S_- a^\dagger\right] = \frac{\Delta}{\hbar}H_{\text{int}} - \frac{q^2}{4}\left[S_+ a, S_- a^\dagger\right].$$

The commutator yields

$$\left[S_+ a, S_- a^\dagger \right] = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} \left(a^\dagger a + 1 \right) - \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix} a^\dagger a$$

$$= 2 S_z a^\dagger a + S_z + \frac{1}{2}$$

$$= 2 S_z \left[\left(a^\dagger a + S_z \right) + \frac{1}{2} \right],$$

$$\left[S_+ a, S_- a^\dagger \right] = 2 S_z (\hat{N} + 1/2).$$

Expressing the H_{int} through the H_{RWA}, we obtain the derivative of the inversion operator

$$\ddot{S}_z = \frac{\Delta}{\hbar} (H_{\text{RWA}} - \hbar \omega N - \hbar \Delta S_z) - q^2 S_z (\hat{N} + 1/2)$$

$$= \frac{\Delta}{\hbar} (H_{\text{RWA}} - \hbar \omega N) - S_z (\Delta^2 + q^2 (\hat{N} + 1/2)).$$

We find the averages $\langle \ddot{S}_z \rangle$ and $\langle S_z(t) \rangle$. We consider that $\langle \hat{N} \rangle$ is constant over time. Therefore,

$$\langle \hat{N} \rangle = \langle \hat{N} \rangle_0 = n + m + 1/2,$$

where n is the number of photons at the initial moment, m is the initial inversion ($m = -1/2$ corresponds to the ground state of atom, while $m = +1/2$ corresponds to the excited state). We get

$$\langle \ddot{S}_z \rangle = -\Omega^2 \langle S_z \rangle + \frac{\Delta}{\hbar} \langle H_{RWA} - \hbar \omega N \rangle ,$$

where

$$\Omega^2 = \Omega_{nm}^2 = \Delta^2 + q^2 (\hat{N} + 1/2),$$

here Ω is the Rabi frequency. The equation has a solution

$$S_z(t) = S_z(0) \left[\left(1 - \frac{\Delta^2}{\Omega^2} \right) \cos \Omega t + \frac{\Delta^2}{\Omega^2} \right].$$

Consequently, in a strong field (large N) atom oscillates rapidly (with the Rabi frequency) between the ground and excited electronic states. Oscillations reach the maximum in the case of resonance ($\Delta = 0$). Out of the resonance ($\Delta \gg qn$) the oscillations are weak. If $S_z(0) = 0$, there are no oscillations.

$$\Omega_{n,1/2}^2 - \Omega_{n,-1/2}^2 = q^2,$$

i.e. the transitions accelerate due to spontaneous emission: $q = A_{21} = \gamma$.

3.5 Optical Bloch equation and π–pulses

Let us consider the interaction of a two-level atom with a light pulse (not one mode, but a wave packet).

In the case of 1mJ-pulse, there are 10^{16} photons)

We consider the field classically and do not take into account the quantum effects. More precisely, we introduce an averaging over the electromagnetic quantum field:

$$\underbrace{\left\langle \hat{E}(t) \right\rangle}_{\text{approx. coherent state}} \quad \rightarrow \quad \underbrace{E(t)}_{\text{usual classical field}}$$

and suppose that this field is in the almost classical coherent state. In this approximation, the Hamiltonian yields

$$H = \frac{1}{2}\hbar\omega_0\sigma_z + \hat{d}E(t) = \frac{1}{2}\hbar\omega_0\sigma_z + d\sigma_x E(t), \tag{3.30}$$

where

$$E(t) = \varepsilon(t)e^{i\omega t} + cc = 2\varepsilon(t)\cos(\omega t)$$

and d is a dipole matrix element.

For a monochromatic excitation, the field strength is $\varepsilon(t) = \varepsilon_0 = $ const. In the case of quasi-monochromatic excitation, the factor $\varepsilon(t)$ depends slowly on time, in comparison with the factor $\cos(\omega t)$. This is a normal case - even femto-pulses are quasi-monochromatic. Here it is considered that

$$\hat{d} = d\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} = d\sigma_x.$$

We can estimate the field strength, which corresponds to the intensity of the light I_0:

$$\varepsilon_0 = \sqrt{I_0 Z_0}. \tag{3.31}$$

Here $Z_0 = 376.7\,\Omega$ is the impedance of vacuum. To obtain the field $\varepsilon_0 \sim 10^6$ V/cm (about a hundred times weaker than the natural atomic field), the light pulse of the intensity 10^{10} W/cm^2 is needed.

Next, we introduce a new interaction constant $\kappa = 2d/\hbar$. In this case the Hamiltonian gets the following form:

$$H = \frac{1}{2}\hbar(\omega_0\sigma_z + \kappa\sigma_x E). \tag{3.32}$$

Let us investigate how atomic states change over time (this is determined by Pauli matrices)

$$\dot{\sigma}_\alpha = \frac{i}{\hbar}[H,\sigma_\alpha], \qquad [\sigma_\alpha,\sigma_\beta] = 2i\sigma_\gamma e_{\alpha\beta\gamma}, \qquad \alpha = x,y,z,$$

or

$$\begin{aligned} \dot{\sigma}_x &= -\omega_0\sigma_y, \\ \dot{\sigma}_y &= \omega_0\sigma_x - \kappa E\sigma_z, \\ \dot{\sigma}_z &= \kappa E\sigma_y. \end{aligned} \tag{3.33}$$

We are interested in states and not in operators. Let us introduce $S_\alpha(t) = \langle\sigma_\alpha(t)\rangle$, where $\langle\cdots\rangle$ denotes the averaging of the atomic state. We want to find how the state changes over time, seeking the equations that describe the quasi-spin $\dot{S} = [H,S]$. This is determined by the Bloch equations:

$$\begin{cases} \dot{S}_x = -\omega_0 S_y \\ \dot{S}_y = \omega_0 S_x - \kappa E S_z \\ \dot{S}_z = \kappa E S_y \end{cases}$$

or, in a compact vector form,

$$\frac{d}{dt}\vec{S}(t) = \vec{\Omega} \times \vec{S}(t),$$ (3.34)

where

$$\Omega_x = \kappa E, \quad \Omega_y = 0, \quad \Omega_z = \omega_0, \qquad \vec{\Omega} \in (\kappa E, 0, \omega_0),$$

$$(\vec{A} \times \vec{B})_x = A_y B_z - A_z B_y.$$

Historically, this model was primarily considered by Bloch and Rabi. From these equations it follows that in the absence of an external field, the vector $\vec{S}$ revolves around a z-axis at a high angular velocity ω_0. When the external field is turned on, the rotation axis oscillates in zx-plane with the amplitude $\kappa\varepsilon$.

We continue with the RWA-approximation. The field $E(t) = 2\varepsilon(t)\cos\omega t$ is considered to be quasi-monochromatic: $\varepsilon(t) \neq$ const is a slowly dependent function of time. The vector $\vec{\Omega}$ oscillates at the frequency ω_0 in xz-plane (although $\varepsilon(t)$ violates it). Let's assume that the field is weak: $|\kappa E| \ll \omega_0$. If $\kappa E \sim \omega_0$, then the field strength would be 10^8 V/cm, which corresponds to to the radiation intensity $I > 10^{15}$W/cm^2. Thus, we consider the case when $|E| \ll 10^8$V/cm. Then the spin axis oscillates at a low amplitude in zx-plane near the z-axis. This oscillation can be presented as the sum of two oscillations around z-axis. Mathematically this means that

$$\vec{\Omega} = \vec{\Omega}_0 + \vec{\Omega}_+ + \vec{\Omega}_-,$$ (3.35)

where the rotation is in xy-plane (around the z-axis), and $\bar{\kappa} \equiv \kappa/2$:

$$\begin{aligned}
\vec{\Omega}_0 &= (0, 0, \omega_0), \\
\vec{\Omega}_+ &= (\bar{\kappa}\varepsilon\cos\omega t, \bar{\kappa}\varepsilon\sin\omega t, 0), \\
\vec{\Omega}_- &= (\bar{\kappa}\varepsilon\cos\omega t, -\bar{\kappa}\varepsilon\sin\omega t, 0).
\end{aligned}$$ (3.36)

We can ignore the following terms

$$\begin{cases}
\sin 2\omega t & \to 0 \\
\cos 2\omega t & \to 0 \\
\sin(\omega + \omega_0)t & \to 0
\end{cases}$$

since they give almost zero contribution after averaging over the period, and only consider the $(\omega - \omega_0)$-type terms.

In rotating wave approximation, $\vec{\Omega}_{RWA} = \vec{\Omega}_0 + \vec{\Omega}_+$ and the equations are

$$\begin{cases}
\dot{S}_x &= -\omega_0 S_y + \bar{\kappa}\varepsilon S_z \sin\omega t \\
\dot{S}_y &= \omega_0 S_x - \bar{\kappa}\varepsilon S_z \cos\omega t \\
\dot{S}_z &= \bar{\kappa}\varepsilon(S_y \cos\omega t - S_x \sin\omega t)
\end{cases}$$ (3.37)

We go ahead and introduce a new (basis) vector $\vec{\rho}$ in a system that revolves around a z-axis at the frequency of ω:

$$\vec{\rho} = (u, v, w) = (\text{rotation matrix}) \times \vec{S},$$

$$\begin{pmatrix} u \\ v \\ w \end{pmatrix} = \begin{pmatrix} \cos\omega t & \sin\omega t & 0 \\ -\sin\omega t & \cos\omega t & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} S_x \\ S_y \\ S_z \end{pmatrix}.$$ (3.38)

We find the time dependence of the components u, v and w:

$$u = \cos(\omega t)S_x + \sin(\omega t)S_y,$$
$$v = -\sin(\omega t)S_x + \cos(\omega t)S_y,$$
$$w = S_z.$$

The time derivative (see Equation 3.38) yields

$$\dot{u} = -\omega\sin(\omega t)S_x + \omega\cos(\omega t)S_y + \cos(\omega t)\dot{S}_x + \sin(\omega t)\dot{S}_y =$$
$$= -\omega\sin(\omega t)S_x + \omega\cos(\omega t)S_y - \omega_0\cos(\omega t)S_y + \omega_0\sin(\omega t)S_x =$$
$$= -\Delta v,$$

where $\Delta \equiv \omega_0 - \omega$. We get

$$\begin{cases} \dot{u} & = -\Delta v \\ \dot{v} & = \Delta u - \bar{\kappa}\varepsilon w \\ \dot{w} & = \bar{\kappa}\varepsilon v \end{cases} \tag{3.39}$$

The rapid time dependencies (double-degenerate terms) are gone. These are Bloch equations in a rotating reference frame. In a compact form,

$$\dot{\vec{\rho}} = \vec{\Omega}' \times \vec{\rho}, \tag{3.40}$$

where $\vec{\Omega}' \in (\kappa\varepsilon, 0, \Delta)$. The coefficients here are smaller. We did not account the fast oscillating terms, since they disappear on the averaging. This system of equations leads to some interesting conclusions.

1. A case of resonance ($\Delta = 0$).

Then

$$\begin{cases} \dot{u} = 0 \\ \dot{v} = -\bar{\kappa}\varepsilon w \\ \dot{w} = \bar{\kappa}\varepsilon v \end{cases} \rightarrow \begin{cases} u(t) = const \rightarrow 0 \\ v(t) = v_0\cos\theta(t) - w_0\sin\theta(t) \\ w(t) = v_0\sin\theta(t) + w_0\cos\theta(t) \end{cases} \tag{3.41}$$

where

$$\theta(t) = \bar{\kappa}\int_{-\infty}^{t} \varepsilon(t')dt'$$

is the accumulated interaction strength (action) of the light pulse with the two-level system.

The solutions are periodic, with the period of 2π. The vector $\vec{\rho}$ is rotated by the angle θ.

What does the pulse do to the atomic system? What happens when $t \rightarrow \infty$ (after the pulse)? The corresponding integral is

$$\theta(t) = \bar{\kappa}\int_{-\infty}^{\infty} \varepsilon(t')dt',$$

and $\kappa \times$ (integrated amplitude) is a constant.

Here the concept of π-**pulse** should be introduced.

If $\theta = 2\pi n$, then nothing happens (final state = initial state). $n = 1$: the front of the pulse excites the system, the back part returns to its original state; $n > 1$: everyting repeats n times.

If $\theta = \pi + 2\pi n$, then the inversion of the system takes place (for this the duration of the π-pulse must be much shorter than the time of relaxation): if $t = 0$ and $u = v = 0, w = 1/2$, then for $t \to \infty$ one gets $u = v = 0, w = -1/2$.

The angle of $\theta = \pm\pi/2 + 2\pi n$ generates a coherent state - both the levels are occupied with a specific phase difference, the initial and final energy levels are equally occupied and the phase is fixed. The equality of occupancies in the ground and excited states makes the medium transparent, and it is used in laser mode-locking. The experiments confirm the theory.

2. Non-resonant case ($\Delta \neq 0$).

Rabi considered a non-resonant case, by taking a monochromatic wave ($\varepsilon = const$):

$$\dot{\vec{\rho}} = \begin{pmatrix} \dot{u} \\ \dot{v} \\ \dot{w} \end{pmatrix} = \begin{pmatrix} 0 & -\Delta & 0 \\ \Delta & 0 & -\bar{\kappa}\varepsilon \\ 0 & \bar{\kappa}\varepsilon & 0 \end{pmatrix} \begin{pmatrix} u \\ v \\ w \end{pmatrix}, \tag{3.42}$$

where $\dot{\vec{\rho}} = \tilde{\vec{\Omega}} \times \vec{\rho}$ and $\tilde{\vec{\Omega}} = (\bar{\kappa}\varepsilon, 0, \Delta)$. Then we get a solution in the limit case of dressed states.

Let us introduce a new vector $\vec{\rho}' = S\vec{\rho}$, which is rotated by the angle of χ around y-axis:

$$S = \begin{pmatrix} \cos\chi & 0 & \sin\chi \\ 0 & 1 & 0 \\ -\sin\chi & 0 & \cos\chi \end{pmatrix} \tag{3.43}$$

where $\tan\chi = \Delta/\kappa\varepsilon$. The solution is the same as before, with a minor change:

$$\begin{cases} u(t) & = const \to 0 \\ v'(t) & = v_0'\cos\Omega t - w_0'\sin\Omega t \\ w'(t) & = v_0'\sin\Omega t + w_0'\cos\Omega t \end{cases} \tag{3.44}$$

where $\Omega = \sqrt{\Delta^2 + (\bar{\kappa}\varepsilon)^2}$. Since in the case of the large number of photons $\varepsilon \propto \sqrt{N}$, then $\kappa = \Gamma\sqrt{N}$ and we get the Rabi frequency, i.e. the atomic state oscillates again. (This solution was first obtained by Rabi.)

We can estimate the Rabi frequency. Assuming that $d \sim er_0$, where $r_0 \sim 10^{-8}$cm is a characteristic size of atoms, and taking $\varepsilon_0 \sim 10^6$V/cm (corresponds to the intensity of the pulse 10^{10}W/cm^2), we get $\Omega \sim 10^{-2}$eV.

3.6   Self-induced transparency

By irradiating the substance containing two-level atoms with a laser pulse being in resonance with the atoms, it is possible that the substance does not absorb it at all, but the pulse passes through the substance, while keeping its original form. This is when we have a 2π-*pulse*. The shape of the pulse is important, in the region of resonance there may be solitons[3], i.e the waves that propagate without changing their shape.

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[3]Note that light pulses described by solitons exist also in highly transparent optical fibers (waveguides) in near infrared region. They are used to reduce the losses of the light pulse energy. The light solitons in fibers can propagate thousands of kilometers, thus being very important in modern communications.

Soliton as a phenomenon was discovered in England. It was on August 12, 1834, when engineer Scott Russell, riding along a narrow channel, watched the barge carried by two horses. The barge stopped suddenly, but the water continued its course along the channel, preserving its original shape 9 m long and 40 cm in height at a speed of 14km/h for 2-3 kilometers. Russell named this phenomenon as the "wave of translation".

Consider a set of two-state atoms (e.g., glass) and the light pulses propagating in this complex, and take into account non-linearity, which compensates the dispersion-caused expansion. Let us have a first 1-dimensional z-directional plane wave, described by the equation:

$$\left(\frac{\partial^2}{\partial z^2} - \frac{1}{c^2}\frac{\partial^2}{\partial t^2}\right)E(t,z) = \frac{4\pi}{c^2}\frac{\partial^2}{\partial t^2}P(t,z) \tag{3.45}$$

Field amplitude

$$E(t,z) = \underbrace{\varepsilon(t,z)}_{\substack{\text{changes}\\\text{slowly}}}\underbrace{e^{i\omega t - ikz}}_{\substack{\text{rapidly}\\\text{oscillates}}} + cc$$

describes the pulse, not the monochromatic field. A slow change in time and space allows us to limit ourselves to only first order derivatives. The same for $P(t,z) = p(t,z)e^{i\omega t + ikz}$. Thus,

$$-2i\left(\frac{\partial}{\partial z} + \frac{1}{c}\frac{\partial}{\partial t}\right)\varepsilon(t,z) \simeq \frac{4\pi\omega}{c}p(t,z). \tag{3.46}$$

We use a solution for 2-level atom, $p = Nd\langle S_x\rangle$ (in the case of 1 atom, $ed\langle S_x\rangle$). Further, we define for simplicity $S_x \equiv \langle S_x\rangle = u\cos\omega t - iv\sin\omega t$. We assume that the matter before the excitation was in the ground state, then $u = 0$, $S_x = -v\sin\omega t$. Hence, it follows that $p = -Ndv\sin\omega t$.

The wave equation in a resonant medium yields

$$\left(\frac{\partial}{\partial z} + \frac{1}{c}\frac{\partial}{\partial t}\right)\varepsilon(t,z) \simeq \frac{2\pi\omega}{c}Ndv(t). \tag{3.47}$$

The solution for $v(t)$ is $v(t) = -\sin\Theta(t)$, where $\Theta(t) = \kappa\int_{-\infty}^{t}\varepsilon(t')dt'$, $\kappa = \varepsilon d/\hbar$ is the constant of interaction, which contains a dipole moment. Taking into account that $\partial\Theta(t)/\partial t = \kappa\varepsilon(t)$, we get

$$\left(\frac{\partial}{\partial z} + \frac{1}{c}\frac{\partial}{\partial t}\right)\frac{\partial}{\partial t}\Theta(t,z) \simeq \beta\sin\Theta(t,z) \tag{3.48}$$

where the constant $\beta = 2\pi\omega c^{-1}Nd\kappa \sim d^2{>}0$. Here $\beta > 0$ is because we choose the ground state as the initial state, but if we were to take the excited state as the initial state, then $\beta < 0$.

We have got the sine-Gordon equation, one solution of which is a soliton. So, we assume that a soliton-type solution exists. In that case $\theta(t)$ is independent of t and z, but depends on the linear combination of these variables $\zeta = t - z/v$ (the solution moves in time with a constant velocity).

$$\begin{cases}\frac{\partial}{\partial z} = \frac{\partial\zeta}{\partial z}\frac{\partial}{\partial\zeta} = -\frac{1}{v}\frac{\partial}{\partial\zeta}\\\frac{\partial}{\partial t} = \frac{\partial\zeta}{\partial t}\frac{\partial}{\partial\zeta} = \frac{\partial}{\partial\zeta}\end{cases}$$

$$\Rightarrow \frac{\partial^2}{\partial z\partial t} + \frac{1}{c}\frac{\partial^2}{\partial t^2} = -\frac{1}{v}\frac{\partial^2}{\partial\zeta^2} + \frac{1}{c}\frac{\partial^2}{\partial\zeta^2} = -\frac{1}{c}\left(\frac{c}{v} - 1\right)\frac{\partial^2}{\partial\zeta^2}.$$

If there is a soliton-type solution, then it is described by the equation

$$\frac{\partial^2}{\partial\zeta^2}\Theta = -\Omega'^2\sin\Theta \tag{3.49}$$

where $\Omega'^2 = \beta c(c/v - 1)^{-1}$. We get the equation of the *physical pendulum.*

In the case of high initial speed, the pendulum rotates, while in the case of low initial speed, it only oscillates. If $\Theta = 2\arcsin(\text{th}(\Omega'\zeta))$, then

$$\varepsilon = \frac{1}{\kappa}\frac{\partial}{\partial\zeta}\Theta = \frac{2\hbar\Omega'}{2d}\frac{1}{\sqrt{1-\text{th}^2(\Omega'\zeta)}}\frac{1}{\text{ch}^2(\Omega'\zeta)} = \frac{\hbar\Omega'}{d}\frac{1}{\text{ch}(\Omega'\zeta)}$$

– it is typical for the soliton.

So far, the speed v was undetermined. It can be connected with the properties of the solution, e.g. the maximum pulse amplitude

$$\varepsilon(0) = \varepsilon_{\max} = \frac{\hbar\Omega'}{d} \qquad \rightarrow \qquad v = \frac{c}{1 + \dfrac{4\beta c}{\kappa^2\varepsilon_{\max}^2}}.$$

A few remarks:

- the speed depends on the maximum pulse amplitude;

- the higher the pulse, the higher the speed.

This is a 2π-pulse: the front of the pulse is absorbed, the rear (part) is restored. This phenomenon is called the *self-induced transparency.* The theory of self-induced transparency was presented in the 1960s by S.L. McCall and E.L. Hahn (see *Phys.Rev.* 183, 457-485, 1969).

McCall-Hahn theorem

If the pulse area Θ is within range $(2\pi n - \pi, 2\pi n + \pi)$, then each pulse transforms into a soliton. If $\Theta < \pi$, the soliton disappears (gets absorbed).

In the range of $(2\pi n - \pi, 2\pi n + \pi)$, the pulse transforms into a $2\pi n$-pulse, and the last transforms into a $n \times 2\pi$-pulse. This is what happens. If there are several solitons with the area $2\pi n$, then the sub-solitons usually have different velocities (depending on $\varepsilon_{\max}$), so they run away from each other. The sharper the soliton, the faster it propagates. The asymptotic solution: the solitons run through each other without interaction (soliton shape does not change). Such solitons have been experimentally observed.

If the atoms are initially in the ground state, then the soliton velocity c is always lower than the speed of light. But if the atoms are initially in the excited state, then $v > c$ ($\beta < 0$). It has been observed experimentally (in the 1960s, Prohhorov et al., $v \sim 3c$). Is it a violation of the *principle of causality*? In fact, not. The pulse front is amplified by stimulated emission, the rear is absorbed, and the pulse reshaping takes place. (If the atoms are initially in the 0-state, then the pulse front will disappear and the back will reappear.)

All of this applies if the theory is valid. The theory does not take into account the spontaneous emission, the interaction between the atoms, or the atomic collisions. If the initial pulses are very short, then the relaxation of the two-state atoms does not happen (then spontaneous emission is not important). The spontaneous emission time is $\sim 10^{-8}$ s, so the duration of the pulse in this region must be $< 10^{-8}$ s.

3.7 Dicke superradiance

Consider the system of N identical two-state atoms on a distance $< \lambda$ from each other, which is excited with a short pulse. Suppose that after the excitation the system is inverted and there is no light coming out. If one atom is in an excited state, it will radiate. In the case of N atoms,

$$H = \frac{1}{2}\hbar\omega_0 \sum_i \sigma_{zi} + \hat{d}E \sum_i S_{xi} + H_R. \tag{3.50}$$

In 1954, Dicke showed that such a system can spontaneously migrate to the ground state in a time of $\tau_c \sim 1/N$, which is proportional to the inverse number of atoms. The atoms radiate coherently and the radiation intensity is $I \sim N\hbar\omega_0/\tau_c \sim N^2$. Dicke colllective spontaneous emission is different from an ordinary spontaneous emission, when the atoms independently relax to the ground state with the spontaneous decay time T_1, and $I \sim N\hbar\omega_0/T_1 \sim N$. The collective spontaneous emission of Dicke was called the superradiance. The effect is due to a correlation between sources of radiation that interact with each other via an electromagnetic field.

Here we use the Fermi's golden rule to find the probability of radiative transitions of the superradiance.

At the beginning, we start with a case when $N = 1$. By γ we denote the radiation decay constant of single atom ($\gamma \sim 10^8 \text{s}^{-1}$, $\gamma \ll \omega_0$):

$$\gamma = \frac{4}{3}\frac{\pi^2\omega_0 d^2}{\hbar}\rho(\omega_0) = \frac{4}{3}\frac{\omega_0^3 e^2 d^2}{\hbar c^3}. \tag{3.51}$$

where $\rho(\omega_0) \sim \omega_0^2/(\hbar c^3)$ is the density of states of photons.

3.7.1 Bright and dark states

If there are 2 identical atoms ($N = 2$),

$$|0\rangle = |g_1\rangle|g_2\rangle$$
$$|1\rangle = |e_1\rangle|g_2\rangle$$
$$|2\rangle = |g_1\rangle|e_2\rangle$$
$$|3\rangle = |e_1\rangle|e_2\rangle$$

As a result of any interaction, we obtain two coherent states (not fixed where excitation takes place):

$$|I\rangle = \frac{1}{\sqrt{2}}(|1\rangle + |2\rangle),$$
$$|II\rangle = \frac{1}{\sqrt{2}}(|1\rangle - |2\rangle).$$

We compare the transition $|1\rangle \to |0\rangle$, in which the second atom does not participate in the process (here it is considered that $\langle g_2|d_2|g_2\rangle = 0$):

$$\gamma_1 \sim |\langle e_1 g_2|ed|g_1 g_2\rangle|^2 = |\langle e_1 g_2|e(d_1 + d_2)|g_1 g_2\rangle|^2 = |\langle g_2|g_2\rangle\langle e_1|ed_1|g_1\rangle|^2 = \gamma,$$

with optical transition from the coherent state $|I\rangle \to |0\rangle$

$$\gamma_I = \underbrace{\frac{4}{3}\frac{\omega_0^3}{\hbar c^3}}_{A}|\langle 0|\hat{d}|I\rangle|^2 = \frac{1}{2}A|\langle g_1|\langle g_2|\hat{d}_1 + \hat{d}_2\left[|e_1\rangle|g_2\rangle + |g_1\rangle|e_2\rangle\right]|^2$$

$$= \frac{1}{2}A|\langle g_1|d_1|e_1\rangle + \langle g_2|d_2|e_2\rangle|^2 = 2\gamma.$$

We see that the coherent state $|I\rangle$ radiates twice as fast as $|1\rangle$. It is called the *bright state.*
The state $|II\rangle$ is metastable (does not radiate). It is called the *dark state.*

If there is a phase relaxation, then the phases of the atomic states become random. This
can be considered by replacing $|2\rangle \Rightarrow e^{i\varphi}|2\rangle$, where φ is a (random) phase difference. Averaging over this phase difference cancels all the terms that contain the product $\langle g_1|d_1|e_1\rangle\langle g_2|d_2|e_2\rangle$.
We get the same result as if each atom radiates separately. But if the number N of simultaneously excited atoms is large, then $\gamma_1 = N\gamma$, and the radiation is so fast that the phase cannot
get damaged.

3.7.2   The spin Hamiltonian of Dicke superradance

Dicke noticed that in the Hamiltonian Equation 3.50, the square of total spin is a conserved
quantity. The transitions do not happen between all the levels, but only between those where
the total spin is conserved.

$$\hat{S}^2 = \sum_i S_i^2 = \sum_i S_{xi}^2 + S_{yi}^2 + S_{zi}^2.$$

Spin components satisfy the following relations:

$$[S_x, S_y] = iS_z; [S_\alpha, S^2] = 0.$$

The operator $\hat{S}^2$ commutes with Hamiltonian, $[H, S^2] = 0$ (there are non-collapsing states).
Let us take a closer look. For a single two-state system,

$$S^2 = \frac{3}{4}\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} = \frac{3}{4} = \text{const}, \qquad S^2 = j(j+1).$$

This relationship also applies when there is more than one two-state system at a time.
The quantum number of the total spin j is conserved also in this case, but the quantum
number $m = -j\ldots j$, corresponding to S_z, changes with the emission of photons..

3.7.3   The pulse of Dicke superradiance

If we have N excited atoms, then $j = m = N/2$, i.e. it has the maximum possible value. To find
the probability that the system emits photons, one need to find the probability of (radiative)
transition $|j, m\rangle \to |j, m-1\rangle$:

$$\gamma_{jm} = A|\langle j, m-1|\hat{d}|j, m\rangle|^2.$$

Let us bring the operators

$$S_+ = S_x + iS_y \qquad \textbf{(rises)}$$
$$S_- = S_x - iS_y \qquad \textbf{(lowers)}$$

It follows that
$$|\langle m-1|S_-|m\rangle|^2 = \langle m|S_+|m-1\rangle\langle m-1|S_-|m\rangle.$$

We consider that $\langle m|S_+|m-1\rangle$ and $\langle m-1|S_-|m\rangle$ are the only non-zero matrix elements
of the operators S_+ and S_-. Therefore,

$$\langle m|S_+|m-1\rangle\langle m-1|S_-|m\rangle = \langle m|S_+ \sum_{m'}|m'\rangle\langle m'|S_-|m\rangle$$
$$= \langle m|S_+S_-|m\rangle = \langle m|S^2 - S_z^2 + S_z|m\rangle,$$

and

$$\gamma_{jm} = \frac{d^2}{4} j(j+1) - m^2 + m = \frac{d^2}{4}(j+m)(j-m+1).$$

Here we take into account that

$$S_+ S_- = (S_x + iS_y)(S_x - iS_y) = S_x^2 + S_y^2 - i\left[S_x, S_y\right] = S_x^2 + S_y^2 + S_z = S^2 - S_z^2 + S_z.$$

If all N atoms are excited ($j = N/2$), then

$$\gamma^{(N)} \equiv \gamma_{N/2,m} = \gamma\left(\frac{N}{2} + m\right)\left(\frac{N}{2} - m + 1\right) \tag{3.52}$$
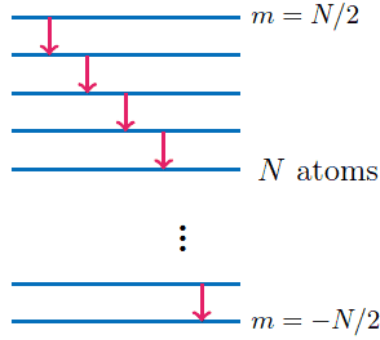
Figure 3.6: Superradiance.

We can find the analytical shape of the pulse. To do this, we look at the kinetics process. The probability that a photon is emitted in a transition $|m\rangle \to |m-1\rangle$ is

$$\dot{m} = \gamma|\langle m| d |m-1\rangle|^2 = \gamma(j+m)\left(j-m+1\right), \tag{3.53}$$

where $\gamma = 4/3\omega_0^3 d^2/(\hbar c^3)$. Consider the case when all the atoms are excited ($j = N/2$):

$$\frac{dm}{dt} = -\gamma^{(N,m)},$$
$$\frac{dm}{dt} = -\gamma\left(\frac{N}{2} + m\right)\left(\frac{N}{2} - m + 1\right),$$

where γ is the decay rate of one atom; $t_0 = \gamma^{-1} \sim 10^{-8}$s is the spontaneous emission rate of an atom. This is a standard differential equation for m:

$$\frac{dm}{(N/2 + m)(N/2 - m + 1)} = -\gamma\, dt.$$

Using

$$\frac{1}{(a+x)(b-x)} = \frac{1}{a+b}\left(\frac{1}{a+x} - \frac{1}{b-x}\right),$$

we obtain

$$dm\left(\frac{1}{N/2 + m} - \frac{1}{N/2 + 1 + m}\right) = -\gamma(N+1)\, dt,$$

which gives a linear equation for m

$$\ln\left(\frac{m + N/2}{m - N/2 - 1}\right) = -\gamma(N+1)t + c \quad \to \quad \frac{m + N/2}{m - N/2 - 1} = e^{-\gamma(N+1)t} \times c.$$

We get

$$m(t) = \frac{N+1}{2} th\left(\frac{t-t_{0N}}{2t_N}\right), \quad \text{where} \begin{cases} t_N = \frac{1}{\gamma(N+1)} \\ t_{0N} = t_N \ln N \end{cases} \tag{3.54}$$

We are interested in the factor

$$\dot{m}(t) = \frac{\gamma(N+1)^2}{4ch^2\left(\frac{t-t_{0N}}{2t_N}\right)}, \tag{3.55}$$

describing the intensity of emission. Consequently, there is a very short and fast pulse.

Which N values are actually possible?

There is an important limitation: identical atoms should be closely spaced, i.e. the scope of the object must be less than λ. In the case of nuclear magnetic resonance, this is not a problem because it is radio waves. In optics, the situation is different. The effective number of atoms is $N_{\text{ef}} = \mu N$, where $\mu \ll 1$.

Let us have a cylindrical object of length L and cross-section area S. An important parameter is the Fresnel number $N_F = S/(L\lambda)$.

- If there is a short wide cylinder, i.e. $N_F \gg 1$, then $\mu = (3/8)\pi^{-1}(\lambda^2/S)$, the only a part of cylinder with cross-section $\sim \lambda^2$ radiates coherently;

- If there is a long narrow fiber, i.e. $N_F \ll 1$ and $\mu = (3/8)\pi^{-1}(\lambda/L)$, then coherently radiates as many atoms as fits in λ. In this case radiation is directed strictly along the fiber.

In fact, there are lasers that work on this principle - these are the *mirrorless lasers.*

Hawking-Unruh radiation

4.1   Hawking radiation of black holes

Hawking radiation (also known as Hawking-Gribov radiation) is blackbody radiation, which was predicted to emerge from black holes, due to quantum effects near the event horizon.

Stephen Hawking justified theoretically the possibility of black hole radiation in 1974, after visiting Moscow in 1973, where Jakov Zeldovich had shown that a rotating black hole could generate and radiate particles. Hawking, however, found that the non-rotating black hole also could emit particles. The idea that a black hole should radiate particles was already developed by the Russian theorist Vladimir Gribov. In 1976, William George Unruh presented a mathematically more simple explanation.

This is again an effect of the zero-point energy, which could also be called a *dynamic Casimir effect*. A black hole emits thermal radiation, with a temperature T depending on the mass.

In 1972, Jacob Bekenstein reached the conclusion that the black hole has temperature.

According to classical physics, the black hole does not radiate because the light can not pass through the Schwarzschild radius. Gravity changes the frequency (of photon) to zero: in the gravitational field, the wavelength of the photon increases until the energy finally approaches zero. Each object with a mass has a Schwarzschild radius $r = 2MGc^{-2}$. If the radius of a star is $R < r$, then, according to classical theory, the light never escapes the star. Considering the quantum effects, the situation changes - the thermal radiation of the black hole appears.

Indeed, in quantum theory, the time dependence of the operators must be considered; in the case of annihilation operators, the time-dependent frequency is positive, while in the case of creation operators, it is negative. Gravity changes the time dependence of field operators. Namely, reducing the value of the gravitational field reduces the photons' frequency; this holds true until at the Schwarzschild radius the frequency changes to zero and then goes to negative. This means that, according to quantum theory, an annihilation operator turns into a creation operator. The creation operator, acting on the vacuum state, gives a non-zero state, unlike the annihilation operator. This means that the black hole emits photons.

In particular, due to the gravity of Schwarzschild's radius leads to the Bogolyubov transformation of operators (Equation 2.15)

$$\hat{\bar{a}} = \mu \hat{a} + \nu \hat{a}^{\dagger},$$
$$\hat{\bar{a}}^{\dagger} = \mu^* \hat{a}^{\dagger} + \nu^* \hat{a},$$

where $|\mu|^2 - |\nu|^2 = 1$ ja $\nu \neq 0$. Now the particle number in the initial vacuum

$$n = \langle 0| \hat{\bar{a}}^{\dagger} \hat{\bar{a}} |0\rangle = |\nu|^2$$

is greater than zero: black hole emits photons. The given by $|\nu|^2$ intensity of emission depends on frequency; this dependence corresponds to the thermal radiation (see Unruh radiation below).

4.2 Thermal emission of black holes

The conclusion that the black hole radiates can be obtained also differently. The black hole entropy increases as the object falls into the black hole. The corresponding formula (Bekenstein, 1972) is

$$\frac{S}{k_B T} = \frac{4\pi G}{\hbar c} M^2. \tag{4.1}$$

From thermodynamics, we know that $k_B T = k_B \cdot (\partial U / \partial S)$, where $U = Mc^2 \sim \sqrt{S} \rightarrow k_B T = \hbar c^3 / (8\pi G M)$. Also, $T \sim dU/dS \sim S^{-1/2} \sim M^{-1}$, the smaller the black hole, the hotter it is. If there is temperature, then radiation must be there as well! According to the Stefan-Boltzmann law, $dM/dt \sim -T^4 r^2 \sim M^{-4} M^2 = M^{-2}$.
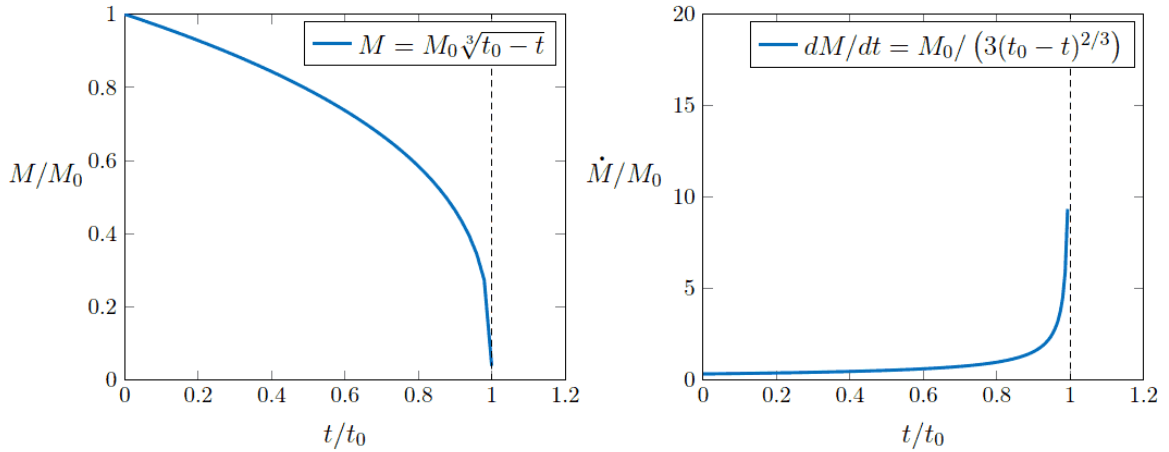
Figure 4.1: Hawking radiation.

At the moment t_0 the black hole evaporates; in the final phase there is explosive radiation. The small black holes that formed in the Big Bang have all been evaporated nowadays. *Hawking radiation has not been detected by now!*

Primordial black hole - a hypothetical type of black hole formed during the high-density, inhomogeneous phase of the Big Bang due to the gravitational collapse of important density fluctuations. The concept was first proposed in 1971 by Stephen Hawking, who

introduced the idea that black holes may exist that are smaller than stellar mass, and are thus not formed by stellar gravitational collapse.

Let us note that the Planck particle radius is smaller than its Schwarzschild radius $r = 2MGc^{-2}$. Thus, the Planck particle forms a black hole, and therefore, according to Hawking, evaporates. Its evaporation time is $t_{PBH} = 5120\pi t_P = 8.67 \times 10^{-40}$s, or 16085 times longer than Planck time.

4.3   Unruh radiation in accelerated reference frame

Hawking radiation is related to the Unruh effect. Unruh considered an *accelerated reference frame* where a photodetector is located. It turns out that an accelerated photodetector registers photons that correspond to the blackbody radiation.

Unruh effect: an accelerating observer sees blackbody radiation while the inertial viewer does not.

Unruh came to the conclusion that the spectrum recorded by an accelerating photodetector corresponds to the thermal radiation at a temperature $T = a/(2\pi k_B)$ (here a is acceleration). Let us show it. We compare the vacuum in an inertial reference frame (Minkowski space) to the vacuum in an accelerated reference frame (Rindler space).

Interval in the 2-dimensional Minkowski space is

$$ds^2 = dt^2 - dx^2 = d\bar{u}\, d\bar{v},$$

where

$$\bar{u} = t - x, \qquad \bar{v} = t + x.$$

Let us introduce now the Rindler space with coordinates η and ξ satisfying the relations (see [3])

$$
\begin{aligned}
t &= \alpha^{-1} e^{\alpha\xi} \mathrm{sh}(\alpha\eta) \\
x &= \alpha^{-1} e^{\alpha\xi} \mathrm{ch}(\alpha\eta)
\end{aligned}
\quad \rightarrow \quad
\begin{aligned}
u &= \eta - \xi \\
v &= \eta + \xi
\end{aligned}
\quad \rightarrow \quad
\begin{aligned}
\bar{u} &= -\alpha^{-1} e^{-\alpha u} \\
\bar{v} &= \alpha^{-1} e^{\alpha v}
\end{aligned}
$$

We find the interval in the new coordinates

$$d\bar{u}\, d\bar{v} = e^{\alpha(v-u)} du\, dv = e^{2\alpha\xi} du\, dv = e^{2\alpha\xi} \left(d\eta^2 - d\xi^2 \right)$$

Thus,

$$ds^2 = e^{2\alpha\xi} \left(d\eta^2 - d\xi^2 \right),$$

Consequently η is a timelike and ξ is a spacelike variable (coordinate).

Consider the point $\xi = $ const in Rindler coordinates. We find $x^2 - t^2 = \alpha^{-2} e^{2\alpha\xi} = $ const. This is a hyperbole. Therefore, if $\xi = $ const, then the point moves along the hyperbolic path.

The motion is accelerated. Indeed, if we take $x = x_0 + y$, where $x_0 = \alpha^{-1} e^{\alpha\xi}$ corresponds to x at the initial moment $t = 0$, and we look at small y, then we get $\left(x_0 + y \right)^2 - t^2 = x_0^2$. This follows from the case of small y: $y \simeq at^2/2$, where $a = x_0^{-1} = \alpha e^{-\alpha\xi} = $ const. This is a *proper acceleration*, since

$$ds^2 = e^{2\alpha\xi} d\eta^2 = g_{00} d\eta^2,$$

where g_{00} is a *metric tensor*. Therefore, in the case of $\xi = $ const one gets the motion with constant acceleration, and the proper time is $\tau = e^{-\alpha\xi} t$. In this case, the point in the Figure 4.2 will never get to the left side of the coordinate system. The classical system moves only in the right-hand wedge. The dashed lines corresponds to the Rindler event horizon.
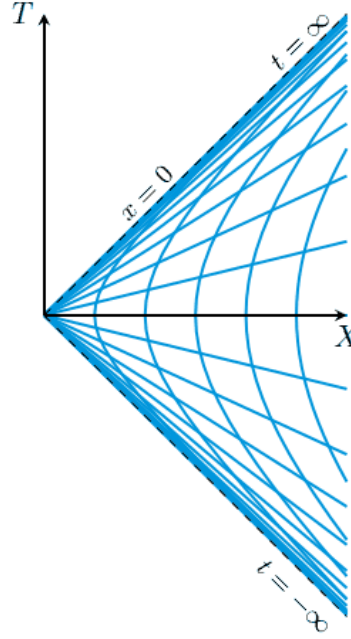
Figure 4.2: Rindler space coordinates. The hyperbolic curves correspond to a potential Rindler observer, written in Cartesian coordinates. Rindler space coordinates are only defined on the right side of the x-axis. The boundary line corresponds to the Rindler events horizon in classical physics.

> For classical objects in Rindler space, only the half-space is available. Information from the other side is missing. The quantum particle can pass to the other half, changing the time sign.

In L-space ('L' for **L**eft) one gets

$$t = -\alpha^{-1}e^{\alpha\xi}\text{sh}(\alpha\eta),$$
$$x = -\alpha^{-1}e^{\alpha\xi}\text{ch}(\alpha\eta).$$

Unruh idea

We quantize the electromagnetic field in both spaces. Modes in the normal Minkowski space satisfy the wave equation

$$\left(\frac{\partial^2}{\partial t^2} - \frac{\partial^2}{\partial x^2}\right)\Phi = 0, \tag{4.2}$$

or

$$\frac{\partial^2\Phi}{\partial\bar{u}\partial\bar{v}} = 0. \tag{4.3}$$

Using coordinates,

$$\begin{cases} u = \eta - \xi \\ v = \eta + \xi \end{cases} \Rightarrow \begin{cases} \bar{u} = -\alpha^{-1}e^{-\alpha u} \\ \bar{v} = \alpha^{-1}e^{-\alpha v} \end{cases} \Rightarrow \begin{cases} \frac{\partial}{\partial\bar{u}} = e^{-\alpha u}\frac{\partial}{\partial u} \\ \frac{\partial}{\partial\bar{v}} = e^{\alpha v}\frac{\partial}{\partial v} \end{cases}$$

the wave equation in Rindler space yields

$$e^{2\alpha\xi}\left(\frac{\partial^2}{\partial\eta^2} - \frac{\partial^2}{\partial\xi^2}\right)\Phi = 0 \quad \rightarrow \quad \left(\frac{\partial^2}{\partial\eta^2} - \frac{\partial^2}{\partial\xi^2}\right)\Phi = 0. \tag{4.4}$$

These equations also apply to the field operators. Therefore, the field operators satisfy the wave equation in the left and right Rindler wedges. However, the equations are satisfied everywhere in the Minkowski space, and thus the solutions are continuously changing everywhere. This means that operators (solutions of wave equations) in Rindler space have to swap on $L - R$ border, in order to be valid in the Minkowski space, and this operation should give continuous operators.

> The condition of continuity can be fullfilled if properly add the creation/destruction operator of R-space to the destruction/creation operator of L-space. As a result, we get a continuous (Minkowski) creation operator as a proper linear combination of a creation operator in L-space and a destruction operator in R-space. The mentioned linear combination gives the Bogolubov transformation for Minkowski/Rindler space operators. This allowed Unruh to find the number of particles in R/L-space for the Minkowsi vacuum state.
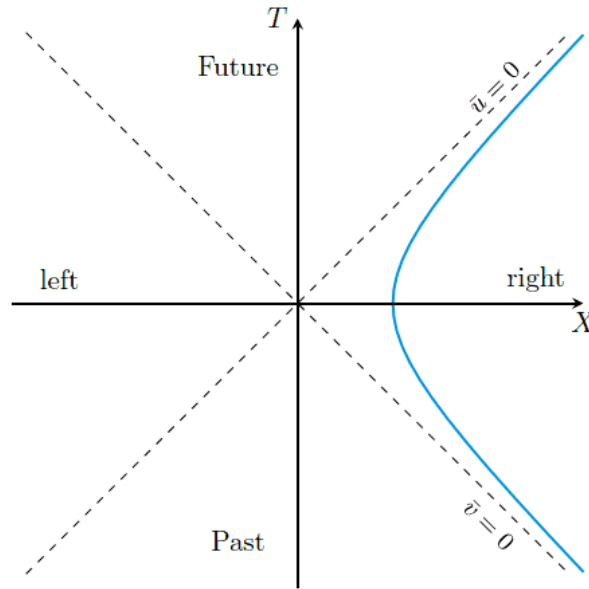
Figure 4.3: Minkowski space.

Let us consider the quantum states (quantum modes). The field operators in the Minkowski space yield

$$\hat{\Phi} = \sum_{k=-\infty}^{\infty} \hat{\Phi}_k$$

In the positive direction of propagation ($k > 0$, $k = \omega/c$, taking $c = 1$, $k = \omega$),

$$\hat{\Phi}_k = e^{-i\omega(t-x)} \hat{a}_k = e^{-i\omega \bar{u}} \hat{a}_k.$$

In the negative direction ($k < 0$),

$$\hat{\Phi}_{-k} = e^{-i\omega(t+x)} \hat{a}_{-k} = e^{-i\omega \bar{v}} \hat{a}_{-k}.$$

Similarly, we can define an adjoint operators

$$\hat{\Phi}_k^+ = e^{i\omega \bar{u}} \hat{a}_k^\dagger, \qquad \hat{\Phi}_{-k}^+ = e^{i\omega \bar{v}} \hat{a}_{-k}^\dagger.$$

In the vacuum of Minkowski space,

$$\begin{cases} \hat{a}_k \, |0\rangle = 0 \\ \hat{a}_{-k} \, |0\rangle = 0 \end{cases}$$

Let us now consider those operators in Rindler space. Similarly to the Minkowski space, in the *R-space vacuum* ("R" for **R**ight) the field operators are

$$\hat{\Phi}_k^R = e^{-i\omega u}\hat{b}_k^R, \qquad \hat{\Phi}_k^{R+} = e^{i\omega u}\hat{b}_k^{R+},$$
$$\hat{\Phi}_{-k}^R = e^{-i\omega v}\hat{b}_{-k}^R, \qquad \hat{\Phi}_{-k}^{R+} = e^{i\omega v}\hat{b}_{-k}^{R+}, \tag{4.5}$$

and in *L-space vacuum*:

$$\hat{\Phi}_k^L = e^{i\omega v}\hat{b}_k^L, \qquad \hat{\Phi}_k^{L+} = e^{-i\omega v}\hat{b}_k^{L+},$$
$$\hat{\Phi}_{-k}^L = e^{i\omega u}\hat{b}_{-k}^L, \qquad \hat{\Phi}_{-k}^{L+} = e^{-i\omega u}\hat{b}_{-k}^{L+}. \tag{4.6}$$

Note that the operators in *R*- and *L*-spaces have the opposite signs of ω in the exponent. The corresponding annihilation operators (for two vacuums) are

$$\begin{cases} \hat{b}_{k/-k}^R \, |0\rangle = 0 \\ \hat{b}_{k/-k}^L \, |0\rangle = 0 \end{cases}$$

Consequently, we have *three vacuums*: a Minkowski vacuum and two Rindler vacuums. Thereat the Minkowski space vacuum includes two Rindler space vacuums (*R* and *L*).

We need to find a connection between the annihilation operators in different vacuums.

Let us see how the operators u and v change in $R \leftrightarrow L$ transition. From $\bar{u} = -\alpha^{-1}e^{-\alpha u}$, we get $u = \alpha^{-1}(\ln\alpha + \ln(-\bar{u}))$, where $\ln(-\bar{u})$ is not uniquely defined, since $\ln(-1) = \pm i\pi$. We are interested in the lower complex half-plane $\bar{u}$, and take $\ln(-1) = -i\pi$.

We consider,

- in *R*-space,

$$t = \alpha^{-1}e^{\alpha\xi}sh(\alpha\eta) = \frac{1}{2\alpha}\left(e^{\alpha(\xi+\eta)} - e^{\alpha(\xi-\eta)}\right),$$
$$x = \alpha^{-1}e^{\alpha\xi}ch(\alpha\eta) = \frac{1}{2\alpha}\left(e^{\alpha(\xi+\eta)} - e^{\alpha(\xi-\eta)}\right),$$

  which gives

$$\bar{u} = -\alpha^{-1}e^{-\alpha u},$$
$$\bar{v} = \alpha^{-1}e^{\alpha v}.$$

- in *L*-space,

$$t \to -t, \quad x \to -x, \quad \eta \to -\eta,$$

  which corresponds to

$$\bar{u} = \alpha^{-1}e^{-\alpha u},$$
$$\bar{v} = -\alpha^{-1}e^{\alpha v}.$$

Hence,

in *R*-space: $\begin{cases} u = -\alpha^{-1}(\ln\alpha + \ln\bar{u} + i\pi) \\ v = -\alpha^{-1}(\ln\alpha + \ln\bar{v}) \end{cases}$

in *L*-space: $\begin{cases} u = -\alpha^{-1}(\ln\alpha + \ln\bar{u}) \\ v = -\alpha^{-1}(\ln\alpha + \ln\bar{v} + i\pi) \end{cases}$

Variables u and v change their phase by π in the transition $R \leftrightarrow L$, i.e. a phase jump takes place. One should compensate this phase jump, in order to get a continuous wave. We should add a proper factor ς to operators, when making a transition from R to L. Namely, the following wave combinations behave continuously

$$\Psi_k^R + e^{-\pi\omega/\alpha}\Psi_{-k}^{*L}, \qquad \text{if} \quad \begin{cases} R: & \Psi_k^R = \varsigma e^{-i\omega u} \\ L: & \Psi_k^R = 0 \end{cases}$$

$$\Psi_{-k}^{*R} + e^{\pi\omega/\alpha}\Psi_k^L, \qquad \text{if} \quad \begin{cases} L: & \Psi_{-k}^L = \varsigma e^{i\omega u} \\ R: & \Psi_{-k}^L = 0 \end{cases}$$

where $\varsigma = (4\pi\omega)^{-1/2}$. Consequently, it can be used to describe waves in the Minkowski space, and the annihilation operator can be presented as

$$\Phi_k' = \left(2sh\left(\frac{\pi\omega}{\alpha}\right)\right)^{-1/2}\left[\begin{array}{l} d_k^{(1)}\left(e^{\pi\omega/2\alpha}\Psi_k^R + e^{-\pi\omega/2\alpha}\Psi_{-k}^{*L}\right) \\ + d_k^{(2)}\left(e^{\pi\omega/2\alpha}\Psi_{-k}^{*R} + e^{-\pi\omega/2\alpha}\Psi_k^L\right) \end{array}\right], \tag{4.7}$$

where $d^{(1)}, d^{(2)}$ are the Minkowski space operators that correspond to waves that are analytical everywhere.

We may establish a connection with $\hat{b}_k$:

$$A\left[d_k^{(1)}e^{\pi\omega/\alpha} + d_{-k}^{(2)+}\right]\Psi_k^R = b_k^R\Psi_k^R, \qquad \text{where} \quad A = e^{-\pi\omega/2\alpha}(2sh(\pi\omega/\alpha))^{-1/2},$$

$$b_k^R = (2sh(\pi\omega/\alpha))^{-1/2}\left[e^{\pi\omega/2\alpha}d_k^{(1)} + e^{-\pi\omega/2\alpha}d_{-k}^{(2)+}\right].$$

This relation is analogous to Bogolyubov transformation , where

$$v = (2sh(\pi\omega/\alpha))^{-1/2}e^{-\pi\omega/2\alpha}.$$

Number of particles in Minkowski space:

$$N_k = \langle 0|\hat{b}_k^R\hat{b}_{-k}^R|0\rangle =$$
$$= (sh(\pi\omega/\alpha))^{-1}\left[e^{\pi\omega/\alpha}\langle 0|d^{(1)+}d^{(1)}|0\rangle + e^{\pi\omega/\alpha}\langle 0|d^{(2)+}d^{(2)}|0\rangle\right] =$$
$$= |v|^2 = (sh(\pi\omega/a))^{-1}e^{-\pi\omega/\alpha}.$$

Thus,

$$N_k = \frac{1}{e^{\pi\omega/\alpha} - 1}. \tag{4.8}$$

Unruh-Hawking effect: acceleration produces radiation with the spectrum analogous to Planck's thermal radiation, having

$$n_M = \frac{1}{e^{\hbar\omega/(kT_0)} - 1}. \tag{4.9}$$

The temperature that the photodetector measures is $T_0 = \alpha/(2\pi k)$. Acceleration plays the same role as the temperature: the larger the acceleration $a = \alpha e^{-\alpha\xi}$, the greater the number of particles. In the accelerated reference frame, the temperature measured by the accelerated observer is given by the Tolman's formula

$$T = (g_{00})^{-1/2}T_0 = e^{-\alpha\xi}T_0 = \alpha e^{-\alpha\xi}/(2\pi k_B) = \hbar a/(2\pi k_B). \tag{4.10}$$

We conclude that the vacuum in the accelerated reference frame is no longer vacuum; there are already particles - real photons.

Considering the quantum vacuum in a purely dynamical way, we did not introduce statistical arguments, but we received radiation that corresponds to the thermal radiation. Why is this so? In an accelerated reference frame, on R-side, we do not have any information about L-side; it remains behind the events horizon. We lose information about half-space. However, by losing information from the L-side, we do not know exactly what the wave is on the R-side. In this case, the quantum state of an electromagnetic field can not be described by wave functions; it is a mixed state. This state can be described with a density matrix: there is no information about the phases, but there is balance of photons going in and out at event horizon, resulting in the temperature distribution.

How high is the temperature of Unruh radiation? And how many photons does the detector read?

We take $a = dv/dt \sim 0.1c\,\omega$, were $\omega \approx 10^{15}\text{s}^{-1}$, i.e. speed increment of $0.1c$ during 10^{-15}s, that is a huge acceleration! In this case

$$T \sim 0.1 \frac{\hbar\omega}{2ak_B} \sim 100K$$

It's not very high temperature. The corresponding radiation is in infrared spectral region. This means that under the realistic situation, where acceleration is much smaller, Unruh radiation is practically missing (the vacuum does not give us anything).

However, in a nonlinear environment, the femto-pulse (A femtosecond is the SI unit of time equal to 10^{-15} of a second) changes the refractive index by $\Delta n = 0.1$. For waves, this rapid change in refractive index is equivalent to a highly accelerated reference frame. In this case, infrared or even visible light is emitted [11], [36].

Hence, it is possible to measure Unruh photons in nonlinear optics, for example, by taking the oscillating mirrors: $n(t) = n_0 + n'_0 \cos(\omega t)$, where $\cos(\omega t) = (1/2)(e^{i\omega t} - e^{-i\omega t})$. The negative energy term changes a positive time dependence of the annihilation operator to the negative one. It also explains why in the case of time-dependent $n(t)$ the emission appears. This radiation is called a *dynamical Casimir effect* [5], [14]. When the optical path length (eikonal) rapidly changes in time, then the strong and high-frequency emission is generated:

$$\frac{d\Delta l}{dt} = n'_0 l\omega.$$
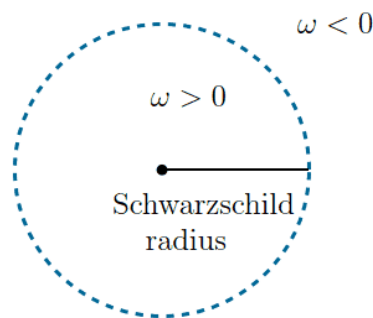
Figure 4.4: Black hole.

In concluding remarks on the black hole physics, given the **event horizon** (in Figure 4.4, the circle), which is determined by the Schwarzschild radius. When it is crossed by a photon,

$\omega > 0$ becomes $\omega < 0$, and the annihilation operator gets replaced by the creation operator. That means the black hole is radiating.

Hawking showed that this radiation is analogous to the blackbody radiation. The acceleration in the Schwarzschild radius determines the radiation temperature. The smaller the black hole mass, the higher is the radiation temperature

$$kT = \frac{\hbar c^3}{8\pi MG}$$

and the more it radiates. The total radiation (the loss of mass) is $\sim M^{-4}$, that is, the lifetime is finite.

Resonant secondary radiation and Raman scattering

5.1   Kramers-Heisenberg equation

Below we consider the optical processes (absorption, radiation, scattering) in ordinary crystals, where optical spectra are significantly broadened due to the interaction between optical electrons of impurity centers and crystal atoms (ions).

In previous chapters, describing the interaction between radiation and matter, we limited ourselves to two-level systems. Such a model can be used for strong monochromatic excitation, resonant with narrow absorption bands. Hereby the spectral width of the absorption band should be smaller than the Rabi frequency. In condensed matter, this condition is difficult to fulfill because of broad absorption bands (characteristic width is $0.01 \div 1$ eV).

To increase the Rabi frequency, it is necessary to use the excitation strength up to (see Equation 3.31)

$$I_0 = |E_0|^2 / Z_0 \sim (10^8 \text{ V/cm})^2 / 376.7\, \Omega \sim 10^{13} \text{W/cm}^2.$$

In ordinary experiments, many times weaker excitations are used. Hence, the usual two-level model is not suitable for crystals with impurity centres. The model used here must

be more general - the electron and vibrational levels that take part in electronic transitions should be taken into account, but at the same time, it can be simpler because the interaction of substance and radiation can be described by perturbation theory. Such a theory can be based on the Kramers-Heisenberg dispersion formula for the *cross section of scattering of a photon* by an atomic electron (the formula for second order quantum processes):

$$\frac{d^2\sigma}{d\Omega_{k'}d(\omega'_k)} = \frac{\omega'_k}{\omega_k} \sum_{|f\rangle} \left| \sum_{|n\rangle} \frac{\langle f | T^\dagger | n \rangle \langle n | T | i \rangle}{E_i - E_n + \hbar\omega_k + i\frac{\Gamma_n}{2}} \right|^2 \delta\left(E_i - E_f + \hbar\omega_k - \hbar\omega'_k\right).$$

The formula determines the probability of emission of photons of energy $\hbar\omega'_k$ in the solid angle $\hbar\Omega_{k'}$ (centered in the k' direction), after the excitation of the system with photons of energy $\hbar\omega_k$; $|i\rangle, |n\rangle, |f\rangle$ denote the initial, intermediate and final states of the system with energies E_i, E_n, E_f respectively; the δ-function ensures the energy conservation during the whole process. T is the relevant transition operator; Γ_n denotes the intrinsic linewidth of the intermediate state.

It was derived before the advent of quantum mechanics by Hendrik Kramers and Werner Heisenberg in 1925, based on the correspondence principle applied to the classical dispersion formula for light. The quantum mechanical derivation was given by Paul Dirac in 1927.

Let us note that under the sum over $|n\rangle$ there is another member with $-\hbar\omega_k$ instead of $\hbar\omega_k$. This is so-called nonresonant member that can be ignored in resonant processes.

In the scattering process most of photons are absorbed and emitted without changing the state of the atom or molecule, this is the elastic *Rayleigh scattering* with unchanged wavelength, whereas a small number (one per 10^7) of photons scatters inelastic way with changed frequency. Their part of secondary radiation is called *Raman scattering*.

In the case of nonresonant excitation when the frequencies of photons do not coincide with the vibronic frequencies, the secondary radiation consists only of Rayleigh and Raman scattering. In this case the denominators in the Kramers-Heisenberg formula can be taken as constants, only the nominators depend on vibronic states. The corresponding theory has been developed by Placzek (1936).

The situation changes appreciably in the resonant case, when the excitation photons fall into the domain of vibronic transitions. The corresponding theory, called the *theory of resonant secondary radiation* (RSR) has been developed in Tartu, in the Institute of Physics [15] - [21].

5.2   Vibronic states of impurity centers in crystals

In this chapter we apply the Kramers-Heisenberg formula for the description of the interaction of light with impurity centers in crystals (see, e.g. [8]). Optical properties of these systems can be considered in a rather simple model. Hereby the results of the consideration have a great amount of generality and may serve as a basis for understanding the interaction of reasonably weak light with condensed matter.

5.2.1   Adiabatic approximation

The states $|i\rangle, |f\rangle, |n\rangle$ in the Heisenberg-Kramers formula in our case are the electron-vibrational states of the optical electrons of the impurity center in the crystal interacting with vibrations

of atoms (ions) of the crystal. The Hamiltonian of this system can be taken as follows:

$$H = \frac{1}{2m} \sum_l \hat{p}_l^2 + \frac{1}{2} \sum_{n,\alpha} \frac{\hat{P}_{n,\alpha}^2}{M_n} + V(r,R), \tag{5.1}$$

where l counts electronic degrees of freedom, n is the number of the atom (ion) in the crystal, $\alpha = x, y, z$ denote the Cartesian coordinates of atoms, m and M_n are the masses of the electron and atoms, $\hat{p}_l$ and $\hat{P}_{n,\alpha}$ are the corresponding operators of momenta, r and R denote the sets of coordinates of the electrons and the nuclei of atoms, $V(r,R)$ is the potential energy of the interaction of the electrons and the nuclei. Solutions of the stationary Schrödinger equation

$$H\Psi(r,R) = E\Psi(r,R) \tag{5.2}$$

give the energies and the wave functions of the system. Corresponding states are called the *vibronic* (electronic-vibrational) states. The basic approximation used for the description of the vibronic states is the *adiabatic approximation* (see [8]), which relies on very large difference of the masses of the electron and nuclei $m_e \lesssim 10^{-5} M_n$. The vibronic wave function in this approximation is considered as the product of electronic and vibrational wave functions

$$\Psi(r,R) = \phi(r,R)\psi(R). \tag{5.3}$$

Here the electronic and vibrational wave functions satisfy the equations

$$\left(\frac{1}{2m} \sum_l \hat{p}_l^2 + V(r,R)\right)\phi_e(r,R) = U_e(R)\phi_e(r,R), \tag{5.4}$$

$$\left(\frac{1}{2} \sum_{n,\alpha} \frac{\hat{P}_{n,\alpha}^2}{M_n} + U_e(R)\right)\psi_{e,k}(R) = E_{e,k}\psi_{e,k}(R). \tag{5.5}$$

Equation 5.4 describes the electronic state number e with energy $U_e(R)$ and corresponds to the electronic motion for staying (immobile) nuclei in the configuration R. Equation 5.5 describes the quantum motion of nuclei in the electronic state number e. The electronic energy $U_e(R)$ stands for the potential energy of nuclei. One can find corrections to this approximation by substituting Equation 5.3 into Equation 5.2 and taking into account the terms stemming from the commutators $[\hat{P}_{n,\alpha}^2/M_n, \phi(r,R)]$ (so-called non-adiabaticity operators). These terms are small as compared to the terms stemming from the commutators $[p_l^2/m, \phi(r,R)]$ which govern the quantum motion of the electrons described by Equation 5.4. A simple improvement of the approximation one gets if to use the potential energy operator instead of $U_e(R)$

$$\tilde{U}_e(R) = U_e(R) + \frac{1}{2} \sum_{n,\alpha} \frac{1}{M_n} \int dr \phi_e(r,R)\hat{P}_{n,\alpha}^2\phi_e(r,R). \tag{5.6}$$

The second term here describes the averaged kinetic energy operator of nuclei in the electronic state $\phi_e(r,R)$. We assume that it is a small correction to the operator $U_e(R)$.

The adiabatic approximation Equation 5.3 works well for non-degenerate electronic states. However, if the electronic state under consideration is degenerate (e.g., due to high symmetry of the center) then it may not work. In this case one should take into account the mixing of the degenerate electronic states by vibrations of nuclei which may result in lowering of symmetry of the center (the Jahn-Teller effect) and in other phenomena (usually called the *dynamical Jahn-Teller effect* (see, e.g., Slonczewski J., Theory of the Dynamical Jahn-Teller Effect, *Phys.Rev.* 131, 1596, 1963). Here we consider only the case of nondegenerate electronic state where the adiabatic approximation is well applicable.

5.2.2   Vibration of crystal

From presented above Equations 5.2 - 5.5 it follows that the solution of the problem of find-
ing of the vibronic states of an impurity center in a crystal in the adiabatic approximation is
reduced to the solution of two simpler problems:

1. to find the solution of the electronic equation 5.4 for the important values of the nu-
   clear coordinates;

2. to characterize vibrations of atoms (ions) described by the Equation 5.5 with the known
   (found) $U_\nu(R)$.

To solve the first problem one can take into account that an impurity center causes
change only of a small part of the potential energy of the entire crystal, i.e. the changes de-
pend only on few local displacements of the nearest atoms to the impurity atom (molecule).
This allows one to solve this problem in two steps:

1. to find the potential energy of the perfect crystal;

2. to find the local corrections of it caused by the impurity center in different electronic
   states of it.

The first problem nowadays is solved by *ab-initio* calculations of the perfect crystal, e.g.,
by means of the density functional theory (DFT). The periodic structure of the crystal makes
these calculations possible and sometimes even easy. The second problem can be solved
by applying the *crystal field theory* (also known as ligand field theory (LFT). Alternatively,
the potential energy of the center in the ground electronic states can be also calculated by
applying the supercell size scaling of DFT.

The basic approximation used for the description of vibrations of crystal lattices in the
given electronic state ν is the approximation of small amplitudes, allowing one to expand
the potential energy U of vibrations into the series of the displacements $u_{m\kappa}^\alpha$ of atoms (ions)
in the lattice from their equilibrium position. Here m is the number of the given elementary
cell, κ is the number of the atom in the elementary cell, α is the number of the Cartesian
coordinate of the atom. In the basic, so-called *harmonic approximation* only the second-
order term with respect to $u_{m\kappa}^\alpha$ are included into consideration. Then, up to a constant the
Hamiltonian of vibrations of atoms in the crystal lattice gets the form

$$H = \frac{1}{2} \sum_{m,\kappa,\alpha} \frac{\hat{P}_{m\kappa}^{\alpha\,2}}{M_{m\kappa}} + \frac{1}{2} \sum_{m,m'} \sum_{\kappa,\kappa'} \sum_{\alpha,\alpha'} \Phi_{m\kappa,m'\kappa'}^{\alpha\alpha'} u_{m\kappa}^\alpha u_{m'\kappa'}^{\alpha'}. \tag{5.7}$$

Here $\Phi_{m\kappa,m'\kappa'}^{\alpha\alpha'}$ is the second derivative of the potential energy of vibrations with respect
to $u_{m\kappa}^\alpha$ and $u_{m'\kappa'}^{\alpha'}$, $\hat{P}_{m\kappa}^\alpha$ is the operator of the α-component of momentum of atom (m,κ).

The Hamiltonian (Equation 5.7) can be presented in the diagonal form. To this end we
introduce the reduced displacements $\bar{u}_{m\kappa}^\alpha = u_{m\kappa}^\alpha \sqrt{M_{m\kappa}}$ and momentum operators

$$\hat{P}_{m\kappa}^\alpha = \hat{P}_{m\kappa}^\alpha / \sqrt{M_{m\kappa}}.$$

Then the vibrational Hamiltonian in the harmonic approximation gets the form

$$H = \frac{1}{2} \sum_{m,\kappa,\alpha} \hat{P}_{m\kappa}^{\alpha\,2} + \frac{1}{2} \sum_{m,m'} \sum_{\kappa,\kappa'} \sum_{\alpha,\alpha'} D_{m\kappa,m'\kappa'}^{\alpha\alpha'} \bar{u}_{m\kappa}^\alpha \bar{u}_{m'\kappa'}^{\alpha'}, \tag{5.8}$$

where

$$\mathrm{D}^{\alpha\alpha'}_{m\kappa,m'\kappa'} = \sqrt{\Phi^{\alpha\alpha'}_{m\kappa,m'\kappa'}} \Big/ \sqrt{M_{m\kappa}M_{m'\kappa'}}$$

is the *dynamical matrix* of the crystal. The operator potential energy for reduced momenta is in diagonal unite form. Now to get the entire vibrational Hamiltonian H in the diagonal form one should diagonalize the dynamical matrix D. This is done by means of the orthogonal transformation $\bar{u}^{\alpha}_{m\kappa} = \sum_j e_{\alpha m\kappa,j} x_j$, where $x_j = \sum_{m,\kappa,\alpha} e_{\alpha m\kappa,j} \bar{u}^{\alpha}_{m\kappa}$ is the *normal coordinate* of the mode j, the coefficients of the transformation satisfy the equation

$$\sum_{m,\kappa,\alpha} \mathrm{D}^{\alpha\alpha'}_{m\kappa,m'\kappa'} e_{m\kappa\alpha,j} = \omega_j^2 e_{m'\kappa'\alpha',j} \tag{5.9}$$

and the orthogonality conditions

$$\sum_{m\kappa\alpha} e_{\alpha m\kappa,j} e_{\alpha m\kappa,j'} = \delta_{jj'},$$
$$\sum_j e_{\alpha m\kappa,j} e_{\alpha'm'\kappa',j} = \delta_{mm'}\delta_{\kappa\kappa'}\delta_{\alpha\alpha'}.$$

Here ω_j^2 and $e_{\alpha m\kappa,j}$ are the eigenvalues and the eigenvectors of the dynamical matrix. After this transformation H gets the form of sum of independent harmonic oscillators (modes)

$$H = \frac{1}{2}\sum_j \left(-\hbar^2 \partial^2/\partial x_j^2 + \omega_j^2 x_j^2\right) = \hbar \sum_j \omega_j \left(a_j^\dagger a_j + 1/2\right), \tag{5.10}$$

where ω_j is the frequency of the *normal mode j*,

$$a_j = \sqrt{1/2\hbar\omega_j} \left(i\partial/\partial x_j + \omega_j x_j\right)$$

is the destruction operator of this mode. The quantum of a normal mode is called *phonon*.

5.2.3 Phonon spectrum of perfect lattice

Equation 5.9 can be solved for molecular systems with $N < 10^4 \div 10^5$ atoms (ions). In case of crystals, however, one needs to consider much larger number of atoms. Nevertheless, the problem can be solved due to the fact that a perfect crystal lattice is periodic. Due to this property the dynamical matrix of a crystal depends only on difference of the numbers of the elementary cells m and m':

$$\mathrm{D}^{\alpha\alpha'}_{m\kappa,m'\kappa'} = \mathrm{D}^{\alpha\alpha'}_{(m-m')\kappa,0\kappa'} \equiv \bar{\mathrm{D}}^{\alpha\alpha'}_{\kappa\kappa',m-m'}.$$

This allows one to take $\vec{u}_{m\kappa,j}$ as a plane wave $\vec{u}_{m\kappa,j} = \vec{\eta}_\kappa e^{i\vec{k}\vec{l}_m}/\sqrt{3N}$, where $\vec{l}_m$ is the radius vector of the position of the elementary cell m, and $\vec{k}$ is the reciprocal lattice vector, $N \sim N_A \approx 6\cdot 10^{23}$, where N_A is the Avogadro constant. Now U gets the form

$$U = \frac{1}{2}\sum_{\kappa,\kappa'}\sum_{\alpha,\alpha'} d^{\alpha\alpha'}_{\kappa,\kappa'}(\vec{k})\eta_{\kappa\alpha}\eta'_{\kappa'\alpha'}, \tag{5.11}$$

where we introduced the dynamical matrix in $\vec{k}$-representation $d^{\alpha\alpha'}_{\kappa,\kappa'}(\vec{k}) = \sum_m \bar{\mathrm{D}}^{\alpha\alpha'}_{\kappa\kappa',m} e^{i\vec{k}\vec{l}_m}$. This is $3v \times 3v$ matrix where v is the number of atoms in the elementary cell. This matrix is by far smaller than $3N\times 3N$ dynamic matrix $\mathrm{D}^{\alpha\alpha'}_{m\kappa,m'\kappa'}$ with $N \sim N_A$. E.g., in NaCl crystal there are two atoms in the elementary cell, and $d^{\alpha\alpha'}_{\kappa,\kappa'}(\vec{k})$ is 6×6 matrix. Diagonalization of

this matrix can be achieved by means of the unitary transformation $x_{\vec{k},\zeta} = \sum_{\kappa,\alpha} b_{\kappa\alpha}(\vec{k},q)\eta_{\kappa\alpha}$, giving

$$U = \frac{1}{2}\sum_{\vec{k}}\sum_{q=1}^{3\nu} \omega_{\vec{k}q}^2 x_{\vec{k},q}^2. \tag{5.12}$$

Here $\omega_{\vec{k}q}$ is the frequency and $\vec{b}_\kappa(\vec{k},q)$ is polarization vector of the phonon with the wave vector $\vec{k}$ of the branch q satisfying the equation

$$\sum_{\kappa,\alpha} d_{\kappa,\kappa'}^{\alpha\alpha'}(\vec{k})\, b_{\kappa'\alpha'}(\vec{k},q) = \omega_{\vec{k}q}^2\, b_{\kappa'\alpha'}(\vec{k},q) \tag{5.13}$$

There are all-totally 3ν branches: three acoustic with $\omega_{\vec{k}} \to 0$, $k \to 0$ and $3\nu-3$ optical with $\omega_{\vec{k}} > 0$; in symmetry directions ν branches are longitudinal and 2ν branches are transversal. The dependence of ω_q on $\vec{k}$ is called the *dispersion law* of the phonon branch q. The density of states (DOS) of phonons

$$\rho(\omega) = \frac{1}{3N}\sum_{\vec{k},q}\delta(\omega - \omega_{\vec{k}q}) = \sum_{\alpha q}\left|\partial k_\alpha/\partial\omega_{\vec{k}q}\right|, \quad N \to \infty, \tag{5.14}$$

ranges from $\omega = 0$ untill the maximum phonon frequency $\omega_m \lesssim 10^{13}\ sec^{-1}$; it may have several peaks reflecting different branches of the phonons, see Figure 5.1, with the dispersion laws and DOS for NaCl.
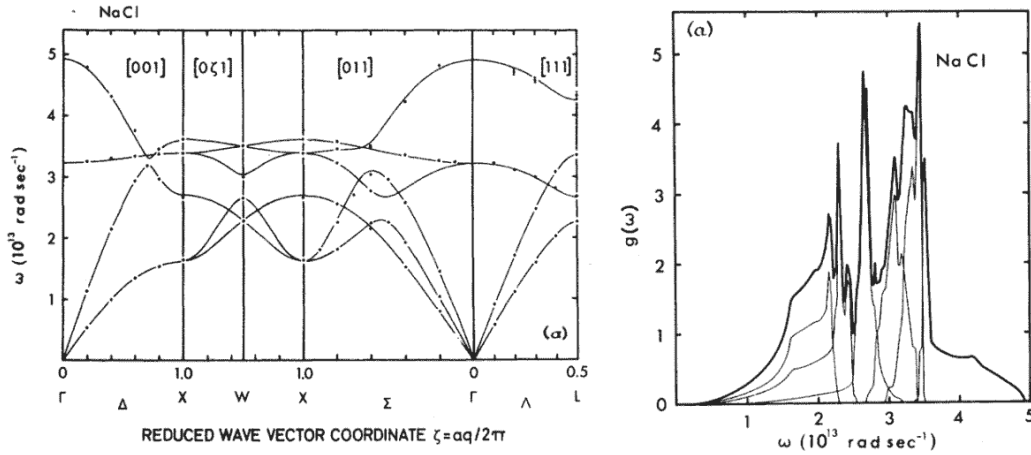
Figure 5.1: Phonon spectrum in NaCl. Dependence of frequencies of phonon branches on directions of the wave vector $\vec{k}$ in reciprocal crystal lattice (*left*) and DOS (*right*); thin lines depict contributions of different branches of phonons [G.Raunio, and S.Rolandson, *PRB* 2, 2098, 1970; G.G.Zavt, private communication]

The phonon spectrum of crystals consisting of atoms (ions) with essentially different masses usually has gaps separating different phonon bands. Van Hove has shown that in the D-dimensional lattice for ω close to a limit frequency ω_s

$$\rho_D(\omega) \propto \omega^{D-2}\sqrt{\left|\omega_s^2 - \omega^2\right|}.$$

Besides, the DOS $\rho(\omega)$ and its first derivative may have singularities (so-called *van Hove singularity*). For the low-frequency part of the spectrum (the part of acoustic phonons) ($\omega_s = 0$) it gives $\rho_{ac} \propto \omega^{D-1}$.

5.2.4 Vibrations of crystal with point defect and Lifshitz method

A point defect in a crystal radically changes the dynamic problem while it removes the periodicity of the lattice. An essential feature of the problem in this case is the circumstance that the perturbation introduced by the defect is not weak which does not allow one to apply the ordinary perturbation theory. Nevertheless, as it was shown by Lifshitz (see I.M. Lifshitz, *JETP* 12, 117, 1942) the problem can be solved due to the fact that the perturbation is localized in a small region Ω of the lattice. Indeed, in case of a defect Equation 5.9 gets the form

$$\omega^2 e_{l\alpha} = \sum_{l',\beta} D^{(0)}_{l\alpha,l'\beta} e_{l'\beta} + \sum_{l_1,\beta_1} V_{l\alpha,l_1\beta_1} e_{l_1\beta_1}. \tag{5.15}$$

Here l numbers both the cells and the atoms in the cells, $D^{(0)}_{l\alpha,l'\beta}$ is the dynamical matrix of ideal lattice, $V_{l\alpha,l_1\beta_1}$ is its perturbation by the defect, l_1 belongs to the perturbed area Ω. Using the Green's function of the ideal lattice

$$G_{l\alpha,l'\beta}(\omega) = \frac{1}{3N} \sum_{\vec{k},q} \frac{b_{\kappa'\alpha'}(\vec{k},q) b_{\kappa'\alpha'}(\vec{k},q)}{\omega_{\vec{k}q}^2 - \omega^2} e^{i\vec{k}(\vec{l}-\vec{l'})}, \tag{5.16}$$

Equation 5.15 gets the form

$$e_{l\alpha} = -\sum_{l',\beta} \sum_{l_1\beta_1} G_{l\alpha,l'\beta}(\omega) V_{l',\beta,l_1,\beta_1} e_{l_1\beta_1}. \tag{5.17}$$

Due to localization of the perturbation, the sums in Equation 5.17 are taken over the atoms in the defect area. Consequently, the Green's function extends the solution in the defect area on the entire crystal. Besides, it allows one to find the solution in the defect area; to this end one should take in Equation 5.17 l in the defect area Ω which gives a system of linear equations for $e_{l\alpha}$ in the defect area Ω. The condition for the solvability of this system

$$\det \left| \delta_{ll'} \delta_{\alpha\beta_1} + \sum_{l_1\beta_1} G_{l\alpha,l'\beta}(\omega) V_{l',\beta,l_1,\beta_1} \right| = 0, \quad l, l', l_1 \in \Omega \tag{5.18}$$

gives the equation for the frequencies of the perturbed lattice. Consequently, in the Lifshitz method all necessary information about the perfect lattice is contained in the Green's function of the perfect crystal lattice $G(\omega)$. At present this function has been calculated for many different crystals.

5.2.5 Local modes

From the definition 5.16 it follows that $G(\omega)$ is discontinuous in $3N - \nu$ points $\omega^2 = \omega_{\vec{k}q}^2$ abruptly changing there from ∞ to $-\infty$. In case of $3D$-lattices, at the limits ω_s of the phonon bands and in the forbidden gaps G has finite values. From these properties of G it follows that $3N - \nu$ frequencies ω_j being the solutions of Equation 5.18 lie inside of the phonon spectrum; they are the new frequencies, although being almost the same frequencies of phonons (the changes are of the order of $1/N$). However, ν of the frequencies $\omega_{j_{loc}}$ may lie outside of allowed phonon spectrum. The basic property of these solutions of Equation 5.18 is that the amplitudes $e_{l\alpha,j_{loc}}$ essentially differ from zero for l in the defect area. Such a property of the solutions is obvious: far from the defect can exist only vibrations with the frequencies of the phonon spectrum. These solutions describe the local modes.

Thus, a defect may result in appearance of vibrational excitations, which are totally different from phonons: they are localized in the defect area and they correspond to vibrations of atoms in the defect area which do not decay in time. In perfect lattice such localization of vibrational energy on one or few atoms is impossible: stationary vibrations correspond to phonons which are spread over all crystal. Note that if to take anharmonicity of vibrations into account then all vibrations, including the local ones will decay due to creation of two or more different phonons. However, usually this decay is rather slow: its characteristic time is of the order of hundreds vibrational periods.

For the occurrence of the local modes in $3D$-lattices it is necessary to have a finite (usually quite large) perturbation. This immediately follows from Equation 5.18, if to take into account that in $3D$ lattices the Green's function has finite values for the frequencies forbidden for phonons. In particular, for the appearance of a local mode above the phonon spectrum one needs to have rather light impurity or a remarkable enlargement of the elastic constants by the impurity. If there are gaps in the phonon spectrum then, to get a local mode with the frequency in the gap, as a rule, the perturbation introduced by the defect may be less.

5.2.6   Pseudo-local modes

There exist cases when the spectrum of vibrations of impurity center has a sharp and narrow peak. Small spectral width of the corresponding DOS means that this vibration has long lifetime (as compared to the mean period of vibrations), i.e. for a long time this vibration is localized. This vibration is called the pseudolocal vibration. To describe such a vibration we introduce the configurational coordinate x_0 - a linear combination of few coordinates of atoms participating in this weakly decaying vibration. The Hamiltonian of vibrations can be presented in the form [26]

$$H = \hbar\omega_0 a_0^\dagger a_0 + H_{ph} + \mu(a_0^\dagger + a_0) \sum_{j \geq 1} \bar{e}_j(a_j^\dagger + a_j), \tag{5.19}$$

where ω_0 is the frequency of the pseudolocal vibration, $a_0 = \sqrt{\hbar/2\omega_0}\, x_0 - \sqrt{\omega_0/2\hbar}\, \partial/\partial x_0$ is the destruction operator of it, H_{ph} is the Hamiltonian of phonons. The last term in Equation 5.19 stands for the interaction of the pseudo-local vibration with phonons, $\bar{e}_j = \left(\hbar/2\sqrt{\omega_0\omega_j}\right) e_{0j}$, μ is the interaction strengths, which is supposed to be small. The straightforward calculations give in this model the following equation:

$$\langle 0|\, a_0 a_0^\dagger(t)\, |0\rangle \approx e^{i\bar{\omega}_0 t - \Gamma|t|}, \tag{5.20}$$

describing the time-evolution of the pseudo-local vibration in the zero-point state $|0\rangle$ of all vibrations. Here $\bar{\omega}_0 = \omega_0 + \Delta$, $\Delta = \mu^2 P \sum_j \bar{e}_j^2/(\omega_0 - \omega_j)$ describes the phonon-induced renormalization of the frequency of the mode, $\Gamma = \pi\mu^2 \sum_j \bar{e}_j^2 \delta(\omega_0 - \omega_j)$ is decay of the mode in time. Both, Δ and Γ are small: $\Delta, \Gamma \ll \omega_0$. The DOS of this mode has the Lorentzian shape

$$\rho_0(\omega) \approx \Gamma\pi^{-1}\big/\big((\omega - \bar{\omega}_0)^2 + \Gamma^2\big). \tag{5.21}$$

5.3   Basic formulae and classification of resonant secondary radiation

The radiation emitted by photoexcited sample is called *secondary radiation*. In the case of a nonresonant excitation (outside of electronic transition), the secondary radiation is a relatively weak scattered light, however at a resonant excitation, there is several orders of magnitude more intense radiation that consists of

- the ordinary and hot luminescence,

- the Rayleigh and Raman scattering.

The classification of resonant secondary radiation is an important problem in the physics of the optical properties of a matter.
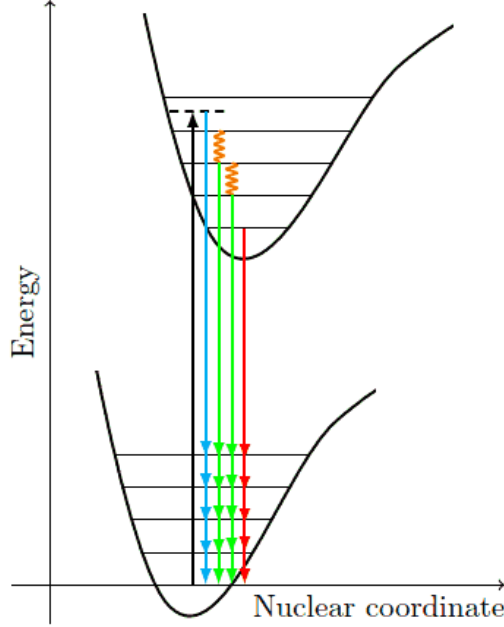
Figure 5.2: Resonance scattering

In the case of a resonant excitation ($\omega_0 \approx \Omega_{21} \approx (E_2 - E_1)/\hbar$), the secondary radiation consists of three components that differ in spectral characteristics and relaxation times. The luminescence is the most intense of them (red arrows), Rayleigh and Raman scattering always occur (blue arrows), and it is often possible to distinguish hot luminescence (green arrows) - luminescence from partly relaxed vibrational states.

> The secondary radiation is produced by two-photon processes described by the second-order perturbation theory of interaction between light and matter.

Let us examine the spectrum of light scattered by an impurity centre in crystal where in case of excitation with a monochromatic wave of light, the transition $|0\nu\rangle \to |1\nu''\rangle \to |0\nu'\rangle$ takes place. Here $|0\rangle$ and $|1\rangle$ denote the ground and excited (intermediate) electronic states, ν is the vibrational state of the system crystal+impurity. As usually, we examine the process in adiabatic approximation. The intensity of scattered light (per unit of the solid angle) is determined by the formula

$$W(\omega_0, \Omega) = \frac{\omega_0 \Omega^3}{2\pi c^3} \sum_{\alpha\beta\gamma\delta} n_\alpha n_\beta \varepsilon_\gamma \varepsilon_\delta \, i_{\alpha\beta,\gamma\delta}(\omega_0, \Omega), \tag{5.22}$$

where ω_0 and Ω are respectively the frequencies of excitation and scattered radiation, $n_{\alpha(\beta)}$ is the unit vector of polarization of the scattered radiation, $\varepsilon_{\gamma(\delta)}$ denotes the amplitudes of the electromagnetic field of excitation (primary radiation), and $i_{\alpha\beta,\gamma\delta}$ is determined by the tensor of polarizability $P_{\alpha\beta}$ in the following way:

$$i_{\alpha\beta,\gamma\delta}(\omega_0, \Omega) = \sum_{\nu,\nu'} w(\nu) \langle \nu | P_{\alpha\gamma} | \nu' \rangle \langle \nu' | P_{\delta\beta}^* | \nu \rangle \delta(\Omega - \omega_0 + \omega_{\nu\nu'}). \tag{5.23}$$

Here v and v' denote initial and final vibrational states, $\omega_{vv'} = (E_v - E_{v'})/\hbar$ is the frequency of the corresponding transition, $w(v)$ is the Boltzmann factor. In the resonant case, the second term in the Heisenberg-Kramers formula can be omitted (due to the large denominator it is small compared to the first term). Taking into account only one excited resonant electronic state, the polarizability tensor can be written as

$$P_{\alpha\gamma} = \sum_{v''} \frac{M_\alpha^* |v''\rangle \langle v''| M_\gamma}{\Omega_{21} + \omega_{v''} - \omega_v - \omega_0 + i\gamma}. \tag{5.24}$$

Here M_α is the matrix element of electronic transition $|1\rangle \rightarrow |2\rangle$, γ denotes the radiative width of the excited electronic transition, $\Omega_{21} = (E_2 - E_1)/\hbar$ is the frequency of pure electronic (zero-phonon) transition (hereafter $\hbar = 1$).

There are computational and conceptual problems when using Equations 5.23-5.24 in this representation. Sum $\sum_{v''}$ over discrete electron-vibrational (vibronic) states is difficult to calculate when the number of vibrational modes increases. Therefore, it is limited usually to one or two-three modes. This is not a solution to the problem, especially in the case of continuous spectra.

As regards conceptual issues, it should be noted that due to frequency representation the formula 5.23 does not reflect the photon emission and absorption as distinguished in time processes - it cannot be deduced from here for how long the system was in the virtual intermediate state. The problem will be solved by converting the formula to temporal representation, into a triple integral in time domain.

By using in Equation 5.23 integral representation of δ-function

$$\delta(x) = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\mu\, e^{ix\mu},$$

we get

$$i_{\alpha\beta,\gamma\delta}(\omega_0, \Omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\mu\, e^{i(\Omega - \omega_0)\mu} \left\langle P_{\alpha\gamma}(\mu) P_{\delta\beta}^* \right\rangle_1, \tag{5.25}$$

where $P_{\alpha\gamma}(\mu)$ is the polarizability tensor in Heisenberg representation:

$$P_{\alpha\gamma}(\mu) = e^{iH_1\mu} P_{\alpha\gamma} e^{-iH_1\mu}. \tag{5.26}$$

The sum

$$\langle ... \rangle_0 = Z^{-1} \sum_v e^{-E_v/(kT)} \langle v| ... |v\rangle$$

denotes the quantum mechanical average over initial vibrational states $|v\rangle$,

$$Z = \sum_v \exp(-E_v/kT)$$

is the statistic sum; here it is taken into account that $\exp(itE_v)|v\rangle = \exp(itH_1)|v\rangle$, where H_1 is the vibrational Hamiltonian of the ground electronic state. Further we use the integral representation for resolvents of polarizability operators in Equation 5.24. Considering again $\exp(itE_{v''})|v''\rangle = \exp(itH_2)|v''\rangle$ (H_2 is the vibrational Hamiltonian of the excited electronic state) and the completeness requirement $\sum_{v''} |v''\rangle \langle v''| = 1$, we get

$$P_{\alpha\gamma} = \int_0^{\infty} d\tau\, e^{-i\omega_0\tau} M_\alpha^\dagger e^{iH_2\tau - \gamma\tau} M_\gamma e^{-iH_1\tau}, \tag{5.27}$$

which gives us the Kramers-Heisenberg formula in the integral representation

$$i_{\alpha\gamma,\beta\delta}(\omega_0,\Omega) = \frac{1}{2\pi} \int\limits_{-\infty}^{\infty} d\mu \int\limits_{0}^{\infty} d\tau \int\limits_{0}^{\infty} d\tau' e^{i\Omega\mu - i\omega_0(\mu+\tau'-\tau)} A_{\alpha\gamma\delta\beta}(\mu,\tau,\tau'),$$ (5.28)

where the three-time dependent correlation function is determined as follows:

$$A_{\alpha\gamma\delta\beta}(\mu,\tau,\tau') = e^{i\Omega_{21}(\tau'-\tau)} \times$$
$$\times \left\langle M_\alpha^* e^{iH_2\tau'-\gamma\tau'} M_\gamma e^{iH_1\mu} M_\delta e^{-iH_2\tau-\gamma\tau} M_\beta^* e^{-iH_1(\mu+\tau'-\tau)} \right\rangle_1.$$ (5.29)

Integration variables μ, τ and τ' in Equation 5.29 have physical meaning, related to relaxation processes. Variables τ and τ' correspond to the time from the absorption of the exciting/primary photon until the radiation of the secondary photon in two probability amplitudes, and μ is the difference between times of two amplitudes after emission of the secondary photon. The average time of two amplitudes

$$s = (\tau + \tau')/2$$ (5.30)

is lifetime of the excited state, the difference

$$s' = \tau' - \tau$$ (5.31)

describes the difference of phases of amplitudes, which arose during lifetime of the excited intermediate state; time μ describes the phase difference, which arose during conversion of the source photon to secondary.

If we consider the process in two steps

1. the preparation of intermediate state,

2. presence of system in the intermediate state,

then time s' describes the phase difference that arose in the first stage, time $\mu - s'$ - the phase difference arosen in the second stage, time μ - the total phase difference that arose passing both stages. Correlator $A(\mu - s')$ describes the phase correlation in excitation process, dependence on μ determines the phase correlation in emission, dependence on s - extinction of phase correlation between absorption and emission. So $A(s')$ describes the phase relaxation of system in the intermediate state phase relaxation, and $A(s)$ - the energetic relaxation in the same state.

The physical meaning of integration variables as relaxation times solves the classification problem of the resonant secondary radiation (RSR). The distinction of phase and energetic relaxation in resonant case permits, in turn, to distinguish in the secondary radiation 3 components: the ordinary luminescence, the hot luminescence and the resonant scattering (see [21], [15], [16], [27]).

1. **Ordinary luminescence** is the radiation from relaxed vibrational state (in thermal equilibrium), i.e. after phase and energetic relaxation.

2. **Hot luminescence** is the radiation from the state, where phase relaxation has already taken place, however, energetic relaxation has not yet happened.

3. **Resonant scattering** is the radiation from the state, which has the phase memory

of the excitation, i.e. the scattering takes place before the phase and energetic relaxation.

It is obvious that separation of the entire resonance secondary radiation to the components mentioned (scattering, hot luminescence, ordinary luminescence) is possible due to the essential difference of the characteristic rates of phase relaxation, energy relaxation and decay rate of the excited electronic state. By definition, this separation can be done only approximately. However, as a rule this separation is very well achievable.

In crystals and molecules the relaxation rates of phase (Γ_{ph}) and energy (Γ_{en}) are very high compared to speed of radiational transition (γ): $\Gamma_{ph} \sim 10^{13} \text{sec}^{-1}$, $\Gamma_{en} \sim 10^{11} - 10^{12} \text{sec}^{-1}$, $\gamma \sim 10^4 - 10^8 \text{sec}^{-1}$. Therefore, usually (e.g., in the case of impurity centres of crystals) the ordinary luminescence dominates in RSR. The rest RSR - scattering and hot luminescence - is much less intense, but still observable in experiment: the spectrum is distinct, containing important information that cannot be obtained from the ordinary luminescence spectrum. Note that usually the difference of the rates of phase and energy relaxation is not so big; however, at low temperatures phase relaxation may become very slow - smaller than the rate of radiative transitions γ.

In cases where the duration of phase relaxation is considerably shorter than that of energetic relaxation, the radiation from the excited vibration state before the loss of phase memory can be well distinguished from the radiation after phase relaxation but before energetic relaxation. The first stage radiation is similar to the properties of nonresonant scattering. This part of the radiation is resonant Rayleigh and Raman scattering.

The second stage radiation - after loss of phase memory of excitation - reminds luminescence, but unlike ordinary luminescence, there are transitions from non-equilibrium vibrational states. This is hot luminescence. It follows from the foregoing that the formulas 5.28-5.29 describe resonant scattering in a short period, $s \sim |s'| \sim \Gamma_{ph}^{-1}$, hot luminescence in a period $\Gamma_{ph}^{-1} \ll s \sim \Gamma_{en}^{-1}$, and ordinary luminescence in longer times $\Gamma_{en}^{-1} \ll s \sim \gamma^{-1}$.

Note. Equations 5.22-5.28 are derived for non-degenerate electronic states. If in these formulas operators are treated as matrix operators, they also apply to degenerate (and quasi-degenerate) states.

5.4   Separation of luminescence

The second-order formulas of perturbation theory are well-known for describing two-photon processes like scattering. Let us show how these formulas describe the 3-steps process: absorption, relaxation, luminescence.

For simplicity, we consider the most used model - the *basic model* - which includes:

1. adiabatic approximation,

2. non-degenerate electronic states,

3. harmonic vibration of nuclei,

4. the Condon approximation ($\vec{M} = \text{Const}$),

5. linear vibronic (electron-vibrational) interaction.

Linear vibronic interaction causes the variation of equilibrium positions of nuclei in electronic transition. In this case Hamiltonians are associated by the shift operator ∇:

$$H_2 = e^{\nabla} H_1 e^{-\nabla},$$

where

$$\nabla = \sum_j \nabla_j, \qquad \nabla_j = x_{0j}\left(\partial/\partial x_j\right) = \xi_j(a_j - a_j^\dagger),$$

$\xi_j = x_{0j}\sqrt{\hbar/2\omega_j}$ - dimensionless parameter of vibronic interaction, j is phonon number, $\xi_j \sim N^{-1/2}$, $N \sim 10^{23}$ - number of vibrational freedom degrees of environment (crystal/solution) of impurity.

Now we can provide the correlation function (Equation 5.29) in the form:

$$
\begin{aligned}
A\left(\mu,\tau,\tau'\right) &= e^{i\Omega_{21}(\tau'-\tau)-\gamma(\tau'+\tau)}\left\langle e^\nabla e^{i\tau' H_1} e^{-\nabla} e^{i\mu H_1} e^\nabla e^{-i\tau H_1} e^{-\nabla} e^{i(\mu+\tau'-\tau)H_1}\right\rangle \\
&= e^{i\Omega_{21}(\tau'-\tau)-\gamma(\tau'+\tau)}\left\langle e^\nabla e^{-\nabla(\tau')} e^{\nabla(\mu+\tau')} e^{-\nabla(\mu+\tau'-\tau)}\right\rangle.
\end{aligned}
\tag{5.32}
$$

Further we use the Bloch-deDominicis theorem (see Appendix C) and the approximation of pair correlators. We get

$$A\left(\mu,\tau,\tau'\right) = e^{i\Omega_{21}(\tau'-\tau)-\gamma(\tau'+\tau)} e^{g(\mu)+g(\mu+\tau'-\tau)+g(\tau')+g(-\tau)-g(\mu+\tau')-g(\mu-\tau)} \tag{5.33}$$

where

$$
\begin{aligned}
g(\mu) &= \left\langle\nabla^2\right\rangle - \left\langle\nabla\nabla(\mu)\right\rangle = \\
&= \sum_j \xi_j^2\left[(\bar{n}_j+1)(e^{i\mu\omega_j - \Gamma_j|\mu|}-1) + \bar{n}_j(e^{-i\mu\omega_j-\Gamma_j|\mu|}-1)\right],
\end{aligned}
\tag{5.34}
$$

$\bar{n}_j = \left(e^{\omega_j/kT}-1\right)^{-1}$ is the phonon occupancy Bose-Einstein factor.

> Function $g(t)$ determines the Fourier transform of one-phonon transition spectrum.

Let us note that there is a continuous phonon spectrum in crystals. Therefore, Equation 5.34 can be represented as an integral

$$g(\mu) = \int_0^{\omega_M} d\omega\,\xi^2(\omega)e^{-\Gamma|\mu|}\left[(n(\omega)+1)\,e^{i\omega\mu} + n(\omega)e^{-i\omega\mu}\right], \tag{5.35}$$

where ω_M is the phonon maximum frequency. The width of phonon spectrum of ordinary vibronic systems Γ is much broader than the radiative width γ, that is $\Gamma/\gamma \sim 10^5 - 10^8$. In this case $g(\mu)$ differs significantly from zero only for small $|\mu|$, estimated $|\mu| \leq \Gamma^{-1} \sim 10^{-13}$ sec. The most intense part of the resonant secondary radiation is formed at large times $\tau, \tau' \sim \gamma^{-1}$, while the time difference is small: $|s'| \approx |\tau - \tau'| \approx \Gamma^{-1}$. In the limit case $|\mu| \leq \Gamma^{-1} \ll \gamma^{-1}$ function $g(\tau') + g(-\tau) - g(\mu+\tau') - g(\mu-\tau)$ approaches zero and remains

$$A_L\left(\mu,\tau,\tau'\right) \simeq e^{i\Omega_{21}(\tau'-\tau)-\gamma(\tau'+\tau)}\exp[g\left(\mu\right) + g\left(\mu+\tau'-\tau\right)], \tag{5.36}$$

This allows $W(\omega_0,\Omega)$ to be presented in the form of product: (**luminescence spectrum**) × (**absorption probability of initial photon**). Let us show it.

The *integral intensity* of RSR spectrum is determined by

$$
\begin{aligned}
\kappa(\omega_0) &= \sum_\Theta \int d\Omega W(\omega_0,\Omega) = \\
&= \sum_\Theta \frac{B}{2\pi}\int d\Omega \int_{-\infty}^\infty d\mu \int_0^\infty d\tau \int_0^\infty d\tau' e^{i\Omega\mu - i\omega_0(\mu+\tau'-\tau)} A(\mu,\tau,\tau').
\end{aligned}
\tag{5.37}
$$

The integral over Ω gives $2\pi\delta(\mu)$, and we get:

$$
\kappa(\omega_0) = \sum_{\Theta} B \int\limits_0^\infty \int\limits_0^\infty d\tau\, d\tau'\, e^{i(\Omega_{21}-\omega_0)(\tau'-\tau)-\gamma(\tau'+\tau)} \exp\left[g\left(\tau'-\tau\right)\right] =
$$
$$
= \sum_{\Theta} B \int\limits_0^\infty ds\, e^{-2\gamma s} \int\limits_{-s}^{s} ds'\, e^{i(\Omega_{21}-\omega_0)s'} \exp\left[g\left(s'\right)\right].
$$
(5.38)

Here

$$
B = \frac{\omega_0 \bar{\Omega}^3}{2\pi c^3} \left|\left(\vec{E}\vec{M}\right)\left(\vec{n}\vec{M}\right)\right|^2.
$$

The main contribution to integrals occurs at times $s = (\tau + \tau')/2 \sim \gamma^{-1}$ and $|s'| = |\tau' - \tau| \sim \Gamma^{-1}$.

In the case of regular vibronic spectra, the phonon spectral width Γ is much larger than the radiation width γ (the ratio is $\Gamma/\gamma \approx 10^4 - 10^6$), then the integration paths $\pm s$ in the Equation 5.38 can be replaced by $\pm\infty$:

$$
\kappa(\omega_0) = \sum_{\Theta} \frac{B}{2\gamma} \int\limits_{-\infty}^{\infty} ds'\, e^{i(\Omega_{21}-\omega_0)s'} \exp\left[g\left(s'\right)\right]
$$
(5.39)

> The integral intensity of RSR spectrum is the absorption probability of initial photon.

Going back to Equation 5.36, we see that it gives us $W(\omega_0,\Omega)$ (see Equation 5.22 and Equation 5.28) as the product of the absorption probability and luminescence spectrum:

$$
W(\omega_0,\Omega) = \kappa(\omega_0) I_L(\Omega),
$$
(5.40)

where the normalized luminescence spectrum is determined by Fourier integral:

$$
I_L(\Omega) = \frac{1}{2\pi} \int\limits_{-\infty}^{\infty} d\mu\, e^{i(\Omega-\Omega_{21})\mu} \exp\left[g\left(\mu\right)\right].
$$
(5.41)

The excitation in phonon wing gives an intense luminescence which does not depend on the excitation frequency. The rapid decay of the phonon correlation function $g(t)$ is caused by the broad phonon wing of absorption spectrum.

> The energetic relaxation always causes also the phase relaxation. The factorized shape of RSR in Equation 5.40 confirms the absence of phase relaxation between excitation and luminescence. Let us note here that the same result - the luminescence - we get from the frequency representation of the Kramers-Heisenberg formula (see Equations 5.23-5.24), if we take into account only diagonal terms in the sum over intermediate states ν''.

The rest part of RSR, that cannot be classified as luminescence, is determined by the difference $\Delta A = A(\mu,\tau,\tau') - A_L(\mu,\tau,\tau')$. ΔA as a function of lifetime $s = (\tau + \tau')/2$ of the excited electronic state describes the relaxation of the system in this state, depending at the same time on the phase relaxation time $s' = \tau' - \tau$. It is known that duration of phase relaxation may differ significantly from the duration of energy relaxation, in that case $\Gamma_{ph}^{-1} \leq \Gamma_{en}^{-1}$. If the phase relaxation is much faster than the energy relaxation it is possible to distinguish the radiation before the loss of phase memory from the radiation which occurs after phase relaxation but during the energy relaxation. The first is analogous to nonresonant scattering, the second one is similar to the ordinary luminescence which occurs after the phase relaxation, due to the transitions from non-equilibrium vibrational levels.

The first part of RSR (radiation in time interval $s \sim \Gamma_{ph}^{-1}$) can be classified as *Rayleigh and Raman scattering,* the second part (radiation in time interval $\Gamma_{ph}^{-1} \ll s \approx \Gamma_{en}^{-1}$) - as *hot luminescence.*

5.4.1   Arbitrary Hamiltonians

Separation of luminescence in Equations 5.22 and 5.28 can be easily done also in general case. Here we can demonstrate that for arbitrary vibrational Hamiltonians in Condon approximation.

In this approximation, up to a constant multiplier, correlation function A can be presented as

$$A\left(\mu,\tau,\tau'\right) = e^{-\gamma(\tau+\tau')}\left\langle e^{i\tau' H_2} e^{-i\mu H_1} e^{i\mu H_2} e^{-i\tau' H_2} e^{i\nu H_2} e^{-i\nu H_1} e^{-\frac{H_1}{kT}} e^{\frac{H_2}{kT}} \right\rangle_2 \frac{z_2}{z_1},$$

where $\nu = \mu + \tau' - \tau$, $\langle \cdots \rangle_2 = Tr\left(\cdots e^{-H_2/(kT)}\right) z_2^{-1}$, $z_i = Tr\left(e^{-H_i/(kT)}\right)$.

Let us consider the limit $\tau' \to \infty$ and finite ν. Taking into account relation

$$\left\langle e^{i\tau' H_2} A e^{-i\tau' H_2} B \right\rangle_2 = \langle A \rangle_2 \langle B \rangle_2, \qquad \tau' \to \infty,$$

we get

$$A\left(\mu,\tau,\tau'\right)\big|_{\tau' \to \infty} = \left\langle e^{-i\mu H_1} e^{i\mu H_2} \right\rangle_2 \left\langle e^{i\nu H_2} e^{-i\nu H_1} \right\rangle_1.$$

This equation describes the correlation function A after vibrational relaxation in the excited electronic state. Inserting this equation into Equations 5.22 and 5.28, we get

$$W\left(\omega_0, \Omega\right) = \kappa(\omega_0) I_L(\Omega),$$

where

$$\kappa(\omega_0) = \sum_{\Theta} \frac{B}{2\gamma} \int_{-\infty}^{\infty} d\nu \, e^{i(\omega_0 - \Omega_{21})\nu - \gamma|\nu|} \left\langle e^{i\nu H_2} e^{-i\nu H_1} \right\rangle_1$$

describes absorption,

$$I_L(\Omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\mu \, e^{i(\Omega - \Omega_{21})\mu - \gamma|\mu|} \left\langle e^{-i\mu H_1} e^{i\mu H_2} \right\rangle_2$$

stands for the luminescence [22].

5.5   Total RSR spectrum. Model of damped vibrational oscillator

Let us look at the RSR spectrum in the model, which allows us to accurately distinguish between all three RSR components. The model assumes two non-degenerate electronic states and one exponentially decaying (local or pseudolocal) vibration. At the electron transition, both the displacement of the equilibrium position and the change in frequency of the vibration occur.

In addition the condition $\omega_1 \gg |\omega_2 - \omega_1| \gg \Gamma$ is fulfilled. Introducing different frequencies of the vibration in different electronic states satisfying the given conditionb is important

because in this case the lines of resonant scattering do not coincide with the lines of hot and ordinary luminescence. This allows one to easily distinguish the Raman lines from the lines of hot and ordinary luminescence. Such a model, for example, will be realized for the impurity molecule NO_2^- in the alkali-halide crystals – an object where hot luminescence was recorded for the first time ([15], [16]).

Vibrational Hamiltonians in ground and excited electron states are presented as follows:

$$H_1 = \sum_j \omega_{1j} a_{1j}^\dagger a_{1j} + H_{\text{anh}}, \tag{5.42}$$

$$H_2 = e^{\xi(a_\lambda - a_\lambda^\dagger)}(H_1 + \Delta\omega(a_\lambda^\dagger a_\lambda + 1/2))e^{-\xi(a_\lambda - a_\lambda^\dagger)} + \Omega_{21}, \tag{5.43}$$

here i denotes normal vibrations (crystal and local modes), $a_i^\dagger(a_i)$ are the ordinary phonon creation (annihilation) operators, H_{anh} - anharmonicity operator; ξ^2 - dimensionless Stokes losses, $e^{\xi(a_\lambda - a_\lambda^\dagger)}$ - shift operator of local mode (we will omit the index λ later), $\Delta\omega = \omega_2 - \omega_1$ is change in the frequency of the local mode at the electron transition.

In calculating the correlator $A(\mu, \tau, \tau')$, we again use the approximation of pair correlators. In addition, we assume that the temperature $T \ll \omega/k$ and the local mode is exponentially decaying, i.e. $\langle aa^\dagger(t) \rangle = \exp(i\omega t - \Gamma|t|)$. According to these approximations

$$\begin{aligned} A(\mu, \tau, \tau') = e^{i\Omega_{21}(\tau' - \tau)} \exp\big[g(\mu) + \bar{g}_1(\tau') + \bar{g}_1(-\tau) \\ - \bar{g}_2(\mu + \tau') - \bar{g}_2(\mu - \tau) + \bar{g}_3(\mu + \tau' - \tau) \big] \end{aligned} \tag{5.44}$$

where

$$g(\mu) = \xi^2 \exp(i\omega_1 \mu - \Gamma|\mu|),$$

$$\bar{g}_1(\tau') = \xi^2 \exp(i\omega_2 \tau' - \Gamma|\tau'|),$$

$$\bar{g}_2(\mu + \tau') = g(\mu + \tau') + i\Delta\omega \xi^2 \exp(i\omega_1(\mu + \tau')) \times$$

$$\times \int_0^{\tau'} ds \exp(i\Delta\omega s - \Gamma(s + |\mu + \tau' - s|)),$$

$$\bar{g}_3(\mu + \tau' - \tau) = g(\mu + \tau' - \tau) + i\Delta\omega \xi^2 e^{i\omega_1(\mu + \tau' - \tau)} \times$$

$$\times \left\{ \int_0^{\tau'} ds\, e^{i\Delta\omega s - \Gamma(s + |\mu + \tau' - \tau - s|)} \right.$$

$$- \int_0^{\tau} ds\, e^{-i\Delta\omega s - \Gamma(s + |\mu + \tau' - \tau + s|)} \tag{5.45}$$

$$\left. - i\Delta\omega \int_0^{\tau'} ds' \int_0^{\tau} ds\, e^{-i\Delta\omega(s' - s) - \Gamma(s + s' + |\mu + \tau' - \tau - s' + s|)} \right\}.$$

Using Equation 5.45 in the representation

$$e^{-\Gamma|x|} = (\Gamma/\pi) \int_{-\infty}^{\infty} dy\, e^{ixy}/(x^2 + \Gamma^2),$$

we will integrate the function $\bar{g}_2$ and $\bar{g}_3$ expressions over s, s and y. We get

$$
\begin{aligned}
A(\mu, \tau, \tau') = e^{-\xi^2} \exp\{\xi^2 [e^{i\omega_1 \mu - \Gamma|\mu|} (e^{i\omega_2 \tau' - \Gamma\tau'} - 1)(e^{-i\omega_2 \tau - \Gamma\tau} - 1) + \\
+ e^{i\omega_2 \tau' - \Gamma\tau'} + e^{-i\omega_2 \tau - \Gamma\tau} + e^{i\omega_2(\mu + \tau' - \tau)}(e^{-\Gamma|\mu + \tau' - \tau|} + \\
+ e^{-\Gamma|\mu| + \tau' - \tau} - e^{-\Gamma|\mu + \tau'| - \tau} - e^{-\Gamma|\mu - \tau| + \tau'})]\}
\end{aligned}
\tag{5.46}
$$

Replacing Equation 5.46 in RSR spectrum

$$
W(\omega_0, \Omega) = \frac{B}{2\pi} \int\limits_{-\infty}^{\infty} d\mu \int\limits_{0}^{\infty} d\tau \int\limits_{0}^{\infty} d\tau' \, e^{i\Omega\mu - i\omega_0(\mu + \tau' - \tau)} A(\mu, \tau, \tau')
\tag{5.47}
$$

we divide the integration area into six parts: 3 parts in region $\mu \geq 0$: ($\tau \in (0, \mu)$, $\tau' \in (0, \infty)$; $\tau \in (\mu, \infty)$, $\tau' \in (0, \mu - \tau)$ ja $\tau' \in (\mu - \tau, \infty)$) and analogous 3 parts in region $\mu < 0$. We get

$$
\begin{aligned}
W(\omega_0, \Omega) = \frac{B}{2\pi} e^{-2\xi^2} \sum_{m,m',l,l',p,k=0}^{\infty} (-1)^{l+l'} \frac{\xi^{2(m+m'+l+l'+p+k)}}{m!\, m'!\, l!\, l'!\, p!\, k!} f(m+l+k) f^*(m'+l'+k) \times \\
\times \left\{ -\left[i\left(\Omega - \omega_0 + \omega_1(p+k+l+l')\right) - \Gamma(p+k+l+l') \right]^{-1} + \right. \\
+ \left[i\left(\Omega - \Omega_{21} + \omega_1(p+k+l+l') - \omega_2(m+l+k)\right) - \gamma - \Gamma(p+m+l'+2l+2k) \right]^{-1} - \\
- \sum_{k_1=0}^{k} (-1)^{k_1} \binom{k}{k_1} \sum_{k_2=0}^{k_1} (-1)^{k_2} \binom{k_1}{k_2} \frac{i\omega_2(m'+l'-m-l) - 2\gamma - \Gamma(m+m'+l+l'+2k)}{i\omega_2(m'+l'-m-l) - 2\gamma - \Gamma(m+m'+l+l'+2k-2k_2)} \times \\
\left. \times \left[i\left(\Omega - \Omega_{21} + \omega_1(p+k+l+l'-k_1) - \omega_2(m+l+k-k_1)\right) - \gamma - \Gamma(p+m+l'+2l+2k) - 2k_1 \right]^{-1} + cc \right\},
\end{aligned}
\tag{5.48}
$$

where

$$
f(m+l+k) = \left[-i(\Omega_{21} - \omega_0 + \omega_2(m+l+k)) - \gamma - \Gamma(m+l+k) \right]^{-1}.
$$

Equation 5.48 represents the **total RSR spectrum**!

Let us distinguish the most intense part of the spectrum W_0, which corresponds to fixed indexes $m = m' = l = l' = 0$ and $k_1 = k_2 = k$:

$$
\begin{aligned}
W_0(\omega_0, \Omega) = \frac{B}{2\pi\gamma} e^{-2\xi^2} \sum_{k=0}^{\infty} \frac{\xi^{2k}}{k!} \frac{2\Gamma k}{(\Omega_{21} - \omega_0 + \omega_2 k)^2 + (\Gamma k)^2} \times \\
\times \sum_{p=0}^{\infty} \frac{\xi^{2p}}{p!} \frac{2(\Gamma p + \gamma)}{(\Omega - \Omega_{21} + \omega_1 p)^2 + (\Gamma p + \gamma)^2}.
\end{aligned}
\tag{5.49}
$$

This is a spectrum of *ordinary luminescence* multiplied by the probability of absorption!

Let us look at this part of the spectrum that has an intensity $\sim \Gamma/\gamma$ times weaker than luminescence. Now we fix index combinations: $N = m + l + k = m' + l' + k$, $L_2 = m + l + k - k_2$, $L_1 = p + l + l' + k - k_1$. M denotes the number of vibration level, to which the impurity center is excited, L_2 is the number of the initial level of radiadion transition (in the excited electronic state 2), L_1 - final level of radiation transition. In the case of monochromatic excitation this

part of spectrum (Rayleigh + Raman scattering (RS) and hot luminescence (HL)) is described by the formula:

$$W_{RS+HL}(\omega_0, \Omega) = \frac{B\kappa_N |\langle L_2|L_1\rangle|^2}{2\gamma\Gamma L_2} \left\{ \frac{2\Gamma L_1 \delta_{L_2 N}}{(\Omega - \omega_0 + \omega_1 L_1)^2 + (\Gamma L_1)^2} + \right.$$
$$\left. + \frac{2\Gamma(L_1 + L_2)(1 - \delta_{L_2 N})}{(\Omega - \Omega_{21} + \omega_1 L_1 - \omega_2 L_2)^2 + \Gamma^2(L_1 + L_2)^2} \right\},$$

(5.50)

where

$$\kappa_N = \frac{|\langle 0|N\rangle|^2 \Gamma N}{(\Omega_{21} - \omega_0 + \omega_2 N)^2 + (\Gamma N)^2}$$

(5.51)

is the *probability of absorption* during the transition $0 \to N$,

$$|\langle 0|N\rangle|^2 = \frac{e^{-\xi^2} \xi^{2N}}{N!}$$

is the *Franck-Condon factor of absorption,*

$$|\langle L_2|L_1\rangle|^2 = e^{-\xi^2} \sum_{n=0}^{L_1} \sum_{l=0}^{L_1 - n} \sum_{l'=0}^{L_1 - n - l} (-1)^{l+l'} \times$$
$$\times \frac{\xi^{2(L_1 + L_2 - 2n - l - l')} L_2!}{n! \, l! \, l'! \, (L_1 - l - l' - n)! \, (L_2 - l - n)! \, (L_2 - l' - n)!}$$

is the *Franck-Condon factor of radiative transition* $L_2 \to L_1$. The first term in brackets {...} of Equation 5.50 gives us the spectral lines of transition $N \to L_1$, with maximums at frequency $\Omega = \omega_0 - \omega_1 L_1$ and halfwidths ΓL_1. These correspond to scattering transitions: $L_1 = 0$ is the Rayleigh line of shape $\delta(\Omega - \omega_0)$, $L_1 = 1$ is the first order Raman line etc.

The second term in brackets {...} of Equation 5.50 corresponds to the transition from level $L_2 < N$ to level L_1, it is the hot luminescence. Hot luminescence lines are Lorentzians with maximums at frequencies $\Omega = \Omega_{21} - \omega_1 L_1 + \omega_2 L_2$ and with halfwidths $\Gamma(L_1 + L_2)$.

The intensity of resonant scattering and hot luminescence lines is determined by lifetime of the initial level $(\Gamma L_2)^{-1}$.

We showed that in this model there are 3 *distinct components* in the RSR spectrum:

1. ordinary luminescence,
2. hot luminescence,
3. resonant Raman and Rayleigh scattering.

Ordinary luminescence corresponds to the radiation transition from the lowest vibration level $L_2 = 0$, hot luminescence is the radiation from intermediate levels L_2 ($N > L_2 > 0$) and resonant scattering takes place from the same level $L_2 = N$, to where the system was excited.

One relaxation transition $(N) \to (N - 1)$ is sufficient to corrupt the phase correlation between the first and second photons: the subsequent radiation is hot luminescence.

5.6 Rayleigh and Raman scattering. Transform method

As shown in the previous paragraph, the Raman scattering depends on the initial and final states of the light-transforming system as well as on the electronic-vibrational (vibronic) intermediate state. The latter fact allows the use of resonant Raman scattering to study the

vibrational interaction in an excited electronic states. Unlike absorption, which contains similar information, in the resonance Raman scattering it is possible to distinguish between the parameters of the vibrational interaction associated with this Raman-active vibration mode. Possibility of selective information gives Raman scattering as a method an advantage over absorption, especially for absorption spectra of continuous or complex structure (see [4]).
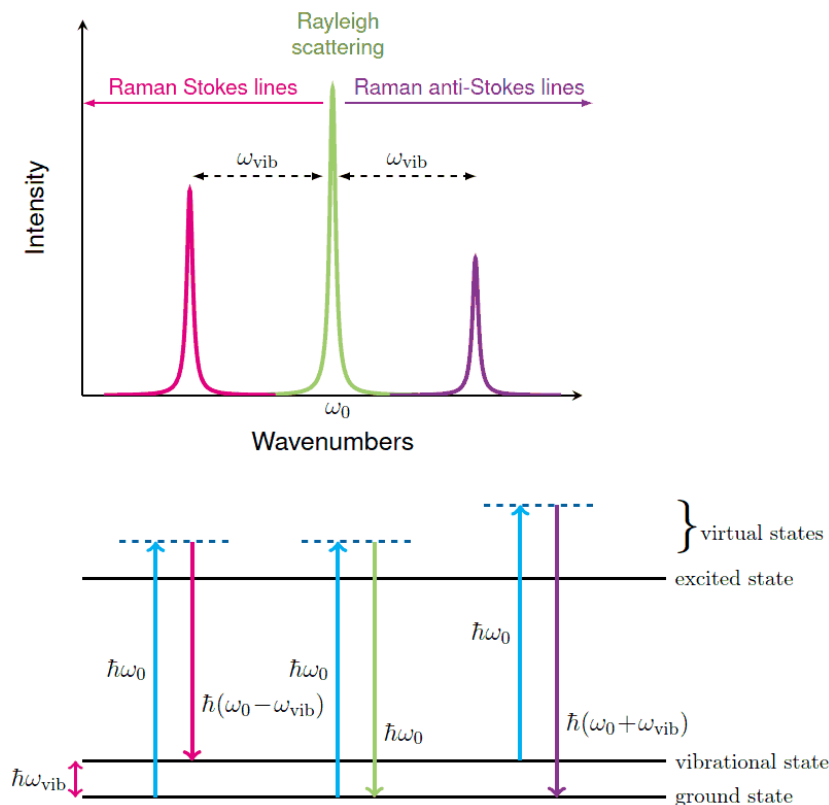

Figure 5.3: Rayleigh and Raman scattering.

In the case of Rayleigh scattering (see Figure 5.3), the scattered photon has the same energy as the initial photon (no energy exchange occurs with the substance); Raman-scattered atom/molecule can absorb energy (Stokes component) or lose energy (anti-Stokes component)

By measuring the scattering cross section at different scattering frequencies Ω, fixing the excitation frequency ω_0, we obtain the Raman spectrum, which gives us information about the ground state of the subject being examined. Changing the excitation frequency ω_0 in the case of a constant difference $\omega_0 - \Omega = \omega_j$, we obtain the excitation spectrum of the Raman scattering of the j-mode (REP=Raman excitation profile). The latter provides us with information on an excited intermediate state.

In Figure 5.4 one can see Raman and absorption spectra, that is $\sigma(\omega_L, \omega_S)$ in the case of excitation of electron transition $^1A_1 \rightarrow {}^1T_2$, $T = 5K$. The excitation profile (REP) of vibrational mode ν_1 is clearly outlined.

Measurements of Raman excitation profiles began in the 70's of the last century, thanks to scanning lasers. The class of objects extends from impurity centers in crystals to large organic molecules. However, the theoretical interpretation of the measured REP turned out to be non-trivial, since all of these vibrational modes, which contribute to the absorption band, are involved in the resonance Raman scattering. Thus, the parameters of Raman mode are dependent on the vibronic interaction as a whole.
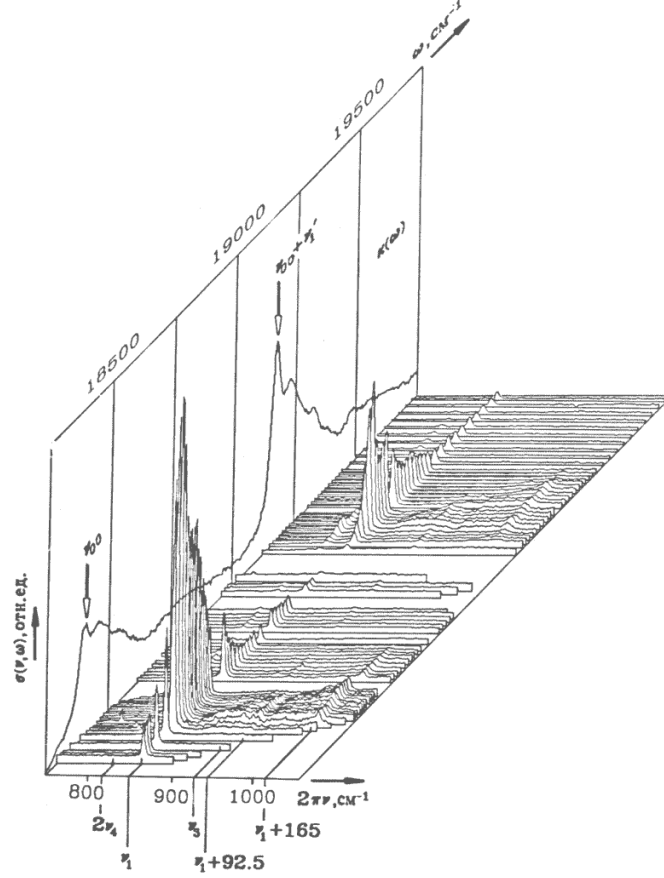
Figure 5.4: REP spectrum of KBr:MnO$_4^-$ (from Blumberg, 1988).

We have seen that a resonant Raman spectrum can be represented by the same phonon operator correlators that determine the Fourier transform of optical absorption. Thus, it turns out that two phenomena - absorption and resonant Raman scattering - can be described in terms of a single theory in which they relate to specific transformations. All vibronic transitions that are not Raman-active but participate in a resonant scattering process can be taken into account by measured absorption spectrum.

5.6.1   Rayleigh scattering. Optical theorem

The connection/correlation between the absorption and scattering is already given by an optical theorem, according to which the imaginary part of the amplitude of the (Rayleigh) forward scattering is determined by the absorption coefficient. Let us start with Rayleigh's scattering amplitude:

$$
\begin{aligned}
\alpha_{0 \to 0}(\omega_0) &= \sum_{m=0}^{\infty} \frac{\langle 0 | m \rangle \langle m | 0 \rangle}{\omega_0 - \Omega_{21} - \omega_j m - i\Gamma_m} = \\
&= \sum_{m=0}^{\infty} \frac{|\langle 0 | m \rangle|^2 \left(\omega_0 - \Omega_{21} - \omega_j m + i\Gamma_m \right)}{\left(\omega_0 - \Omega_{21} - \omega_j m \right)^2 + (\Gamma_m)^2}.
\end{aligned}
\tag{5.52}
$$

We see that the imaginary part of the Rayleigh scattering amplitude is proportional to the absorption spectrum

$$
\kappa(\omega_0) = \sum_{m=0}^{\infty} \frac{|\langle 0 | m \rangle|^2 \Gamma_m}{\left(\omega_0 - \Omega_{21} - \omega_j m \right)^2 + (\Gamma_m)^2}.
\tag{5.53}
$$

So $\mathrm{Im}\,\alpha_{0\to 0}(\omega_0) = \kappa(\omega_0)$. This relation is in agreement with the optical theorem, according to which the total cross section of the wave (scattering + absorption) in the environment is related to the imaginary part of amplitude of the elastic (Rayleigh) scattering:

$$\mathrm{Im}\,\alpha_{0\to 0}(\omega_0) = \kappa(\omega_0).$$

This is a general law that does not depend on the vibronic interaction: the imaginary part of the amplitude of the forward scattering leads to weakening of this scattering. We can generalize this relation by using the function $\Phi(\omega) = n(\omega) + i\kappa(\omega)$ - complex refractive index, the real part of which is determined via the Kramers-Kronig dispersion relation by imaginary part

$$\mathrm{Re}\,\Phi(\omega) = \frac{1}{\pi} P \int dx \frac{\mathrm{Im}\,\Phi(x)}{x - \omega}. \tag{5.54}$$

We get Rayleigh scattering intensity:

$$I_R^0(\omega_0) = |\Phi(\omega_0)|^2. \tag{5.55}$$

5.6.2 From REP to absorption: Fourier amplitude method

In the case of non-elastic Raman scattering, a Raman active vibration quantum/mode is created (or destructed) in the substance, the shape of the vibronic interaction becomes important and therefore, there is no general connection/relationship between absorption and scattering spectrum. The shape of the transformation relationship depends on the chosen vibrational interaction model. So, comparing the calculated and measured Raman profiles, it is possible to check the validity of the model for this system.

We proceed from Raman amplitude in adiabatic approximation (see [17])

$$\alpha_{if}(\omega_0) = C \sum_m \frac{\langle i| M_1 |m\rangle \langle m| M_2 |f\rangle}{E_i + \omega_0 - E_m - i\gamma}. \tag{5.56}$$

Using the integral representation of resolvent

$$\frac{1}{E_i + \omega_0 - E_m - i\gamma} = -i \int\limits_0^\infty dt\, e^{i(E_m - \omega_0 - E_i)t - \gamma t}$$

and keeping in mind $e^{itE_m}|m\rangle = e^{itH_2}|m\rangle$ and $e^{-itE_i}|i\rangle = e^{-itH_1}|i\rangle$, and the condition of completeness $\sum_m |m\rangle\langle m| = 1$, we get

$$\alpha_{if}(\omega_0) = C \int\limits_{-\infty}^\infty dt\, e^{-i\omega_0 t - \gamma t} A_{if}(t), \tag{5.57}$$

where

$$A_{if}(t) = i\Theta(t)\langle i| e^{-itH_1} M_1 e^{itH_2} M_2 |f\rangle \tag{5.58}$$

is the Fourier transform of the resonance Raman amplitude (hereinafter Raman Fourier amplitude) and $\Theta(t)$ - the Heaviside function, which takes into account the principle of causality, i.e. the scattering follows an excitation.

In the harmonic approximation

$$H_1 = \sum_j \omega_{1j}\left(a_{1j}^\dagger a_{1j} + 1/2\right),$$

$$H_2 = \sum_k \omega_{2k}\left(a_{2k}^\dagger a_{2k} + 1/2\right) + \Omega_{21}.$$

First-order Raman Fourier amplitude for the Stokes component is determined as follows

$$A_j^{(S)}(t) = i\Theta(t)\langle i| S(t)a_{1j}^{\dagger}|i\rangle\left(n_j + 1\right)^{-1/2},\tag{5.59}$$

where n_j is the number of phonons of the Raman-active mode j, and

$$S(t) = e^{-itH_1}M_1 e^{itH_2}M_2\tag{5.60}$$

is an operator of Fourier transform $F(t)$ of absorption, i.e. $F(t) = \langle S(t)\rangle$. The Equation 5.59 also applies in the case of $T \neq 0$, in the state of thermal equilibrium, if the quantum mechanical averaging is replaced by quantum statistical averaging

$$A_j^{(S)}(t) = i\Theta(t)\left(\bar{n}_j + 1\right)^{-1/2}\left\langle e^{-itH_1}M_1 e^{itH_2}M_2 a_{1j}^{\dagger}\right\rangle.\tag{5.61}$$

Fourier amplitude for anti-Stokes Raman scattering is manifested through the Stokes component

$$A_j^{(a)}(t) = \exp\left[-\omega_j\left(it + \frac{1}{2}kT\right)\right]A_j^{(S)}(t).\tag{5.62}$$

Using the Raman Fourier amplitude, you can easily find transform relationship between Raman scattering and absorption. We show it for the *basic model* of standard assumptions (nondegenerate electron states, adiabatic and Condon approximation, harmonic vibrations, and linear vibronic interaction). In this model

$$H_2 = H_1 + V_0 + \sum_j \xi_j\omega_j(a_j + a_j^{\dagger}).$$

Phonon operators of ground and excited $a_{1j}^{\dagger}$ and $a_{2j}^{\dagger}$ differ only in the constant, which is the dimensionless vibrational interaction parameter ξ_j, $a_{1j}^{\dagger} = a_{2j}^{\dagger} - \xi_j$, $\omega_j = \omega_{1j} = \omega_{2j}$.

The first-order RRS is determined by Equations 5.59-5.60:

$$\begin{aligned}
\left\langle S(t)a_{1j}^{\dagger}\right\rangle &= \left\langle S(t)\left(a_{2j}^{\dagger} - \xi_j\right)\right\rangle\\
&= \left\langle e^{-itH_1}a_{1j}^{\dagger}e^{itH_2}\right\rangle e^{it\omega_j} + \xi_j\left(e^{it\omega_j} - 1\right)\langle S(t)\rangle\\
&= e^{-\omega_j/kT}\left\langle S(t)a_{1j}^{\dagger}\right\rangle + \xi_j\left(e^{it\omega_j} - 1\right)F(t).
\end{aligned}$$

Here it is considered that

$$e^{itH_2}a_{2j}^{\dagger} = a_{2j}^{\dagger}e^{it(\omega_{2j}+H_2)}.$$

Solving the simple equation above, we obtain the following relation between the Fourier transform of absorption $F(t) = \langle S(t)\rangle$ and the Raman Fourier amplitude:

$$A_j^{(S)}(t) = i\Theta(t)\left(\bar{n}_j + 1\right)^{1/2}\xi_j\left(e^{it\omega_j} - 1\right)F(t).\tag{5.63}$$

Fourier transform of formula 5.63 gives Raman amplitude in frequency space:

$$\alpha_j(\omega_0) = \left(\bar{n}_j + 1\right)^{1/2}\xi_j\left[\Phi(\omega_0) - \Phi(\Omega)\right],\tag{5.64}$$

where $\Omega = \omega_0 - \omega_j$ is the frequency of scattered light,

$$\Phi(\omega) = i\int\limits_0^{\infty} dt\, e^{it\omega - \gamma t}F(t)$$

is the complex refractive index, determined by the absorption spectrum $\kappa(\omega)$ as follows:

$$\Phi(\omega) = i\pi\kappa(\omega) + P\int\limits_{-\infty}^{\infty} dx \frac{\kappa(\omega)}{x-\omega}.$$

Thus, for the first order resonance Raman excitation spectrum (Stokes component) we get:

$$I_j^{(S)}(\omega_0) \propto \left(\bar{n}_j + 1\right)\xi_j^2 \left|\Phi(\omega_0) - \Phi(\omega_0 - \omega_j)\right|^2. \tag{5.65}$$

The corresponding REP of anti-Stokes Raman scattering appears:

$$I_j^{(a)}(\omega_0) \propto \bar{n}_j\xi_j^2 \left|\Phi(\omega_0) - \Phi(\omega_0 + \omega_j)\right|^2. \tag{5.66}$$

Equations 5.65 and 5.66 are the transform relationships, which are valid in the basic model. Using the measured absorption spectrum, the function $\Phi(\omega)$ can be calculated. Substituting the found $\Phi(\omega)$ into the Equation 5.65, we can calculate the excitation profiles for all Raman-active modes. There is no additional parameter needed to get REP as a function of frequency. If the theoretical REP coincides with the measured one, it means that the standard model for this system holds. The Equation 5.65 can be used as a test of the validity of the model for the given object.

An example of calculated and measured REPs of $KBr{:}MnO_4^-$ is shown in Figure 5.5.

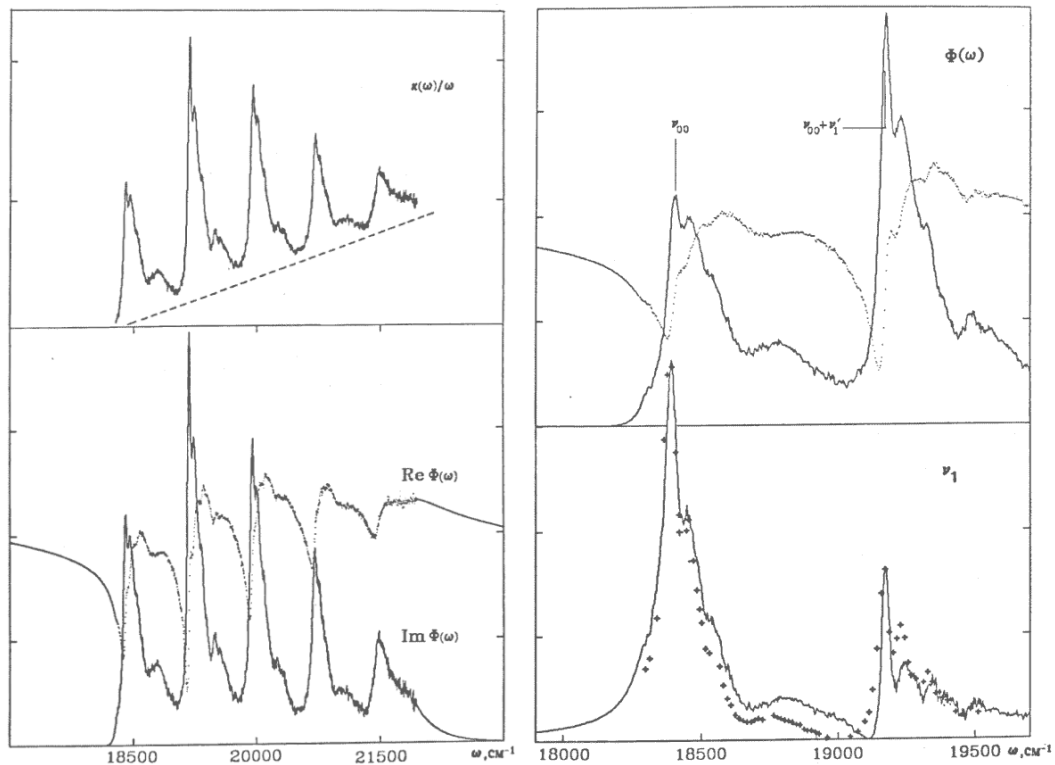*Figure 5.5:* (left) Calculation of complex function $\Phi(\omega)$ and the corresponding REP using the measured absorption spectrum of $KBr{:}MnO_4^-$, and (right) comparison with experimentally measured REP (from Blumberg, 1988).

It is clear that the basic model cannot often be used for real objects, if the Herzberg-Teller interaction (deviation from Condon approximation) or the mixing of modes and the

change in frequency at the electron transition (which manifests itself in the electron-phonon interaction through a second-order term) plays an important role.

Below the transform laws for different vibronic interactions are shown, without stopping at their derivation.

(1) Deviation from Condon approximation (electronic matrix element $M_\alpha \neq$ const), also called Herzberg-Teller interaction

$$M = m_0 + \sum_j m_j(a_j + a_j^\dagger) + ...$$

adds additional members to the basic transform law:

$$I_R^{(1)}(\omega_0) \sim (\bar{n}_j + 1)\left|\xi_j^2\left[\Phi(\omega_0) - \Phi(\omega_0 - \omega_j)\right] + m_j\left[\Phi(\omega_0) + \Phi(\omega_0 - \omega_j)\right]\right|^2. \tag{5.67}$$

We see that constructive interference is added to destructive interference, which in the continuous spectrum can lead to a sharp minimum in the Raman profile. The formula reflects the two competing, Franck-Condon and Herzberg-Teller mechanisms in the Raman process. The first one dominates in the case of excitement in the region of the maximum of the absorption band, the second interaction/term will work when the excitation is further away from the absorption region. In the limit case, the well-known Placzek's theory comes into force.

(2) The change in the frequency of vibrational modes in the electron transfer and mixing of normal modes (with close frequencies) appears on the Raman profile through the mode frequencies in the excited electron state:

$$I_R^{(1)}(\omega_0) \sim (\bar{n}_j + 1)\left|\xi_j\left[\Phi(\omega_0) - \sum_k c_{jk}\Phi(\omega_0 - \omega_{2k})\right]\right|^2. \tag{5.68}$$

Scattering resonances ($\Omega = \omega_0 - \omega_{1j}$) will return if Herzberg-Teller interaction works:

$$I_R^{(1)}(\omega_0) \sim (\bar{n}_j + 1) \times$$
$$\times \left|\xi_{1j}\left[\Phi(\omega_0) - \sum_k c_{jk}\Phi(\omega_0 - \omega_{2k})\right] + m_j\left[\Phi(\omega_0) + \Phi(\omega_0 - \omega_{1j})\right]\right|^2. \tag{5.69}$$

Historical remark. The main transform law was derived and published in 1967 (see [21]), but it took more than 10 years before it was used, because REP measurements began only in the 1970s. The first applications took place in the United States, with the β-carotene and cyanocobalamin molecules. It turned out that in the first case, the basic model worked, while for cyanocobalamin additional minimum in REP indicated that the model was not valid. The use of the transform method in interpreting measured REPs, in turn, stimulated further development of the theory - the derivation of transform laws for more complicated vibrational interaction models.

5.7   Coherent Raman scattering: CARS and CSRS

In 1965, a new phenomenon, later called CARS (Coherent Anti-Stokes Raman Scattering) was announced by Maker and Terhune. They used a ruby laser pulse to explore the third-order response of various materials. To do this, the second pulse frequency $\omega - \omega_j$ was generated

additionally to the primary pulse of the laser, and then 2 rays were sent simultaneously to the object. When the two pulses overlapped in time and space, there could be seen the signal at frequency $\omega + \omega_j$. The signal was amplified significantly when the frequency difference coincided with the Raman frequency of the object.

CARS (**C**oherent **A**nti-Stokes **R**aman **S**cattering) is a third-order nonlinear optical process (see Figure 5.6), which uses three laser beams: a pump-ray ω_{pump}, a Stokes ray ω_{Stokes} and a probe beam ω_{probe} (see [18]). Interaction with the object generates a coherent optical signal at the anti-Stokes frequency $\omega_{\text{probe}} + \omega_{\text{Stokes}} - \omega_{\text{pump}}$. The latter is amplified resonantly, when the frequency difference $\omega_{\text{pump}} - \omega_{\text{Stokes}}$ coincides with the Raman-active frequency.
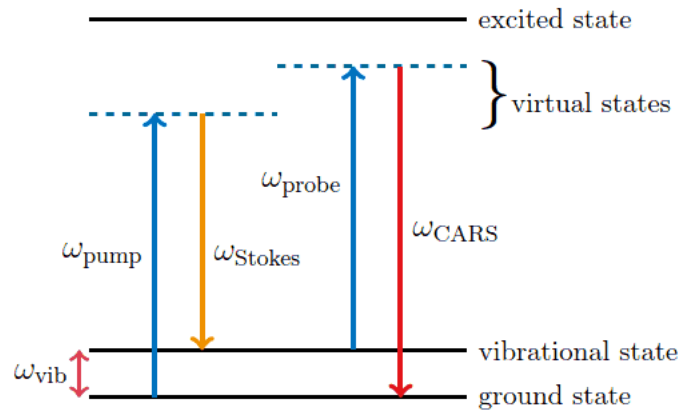
Figure 5.6: CARS.

$$\omega_{\text{pump}} - \omega_{\text{Stokes}} = \omega_j \text{ (anti-Stokes Raman)} \quad \Rightarrow \quad \omega_{\text{CARS}} = 2\omega_{\text{pump}} - \omega_{\text{Stokes}} \text{ (CARS signal)}$$

The coherent signal generated by CARS exceeds the spontaneous Raman radiation intensity several times.

Similarly, **CSRS** (**C**oherent **S**tokes **R**aman **S**cattering) can be generated (see Figure 5.7):

$$\text{CSRS signal:} \quad \omega_{\text{CSRS}} = 2\omega_{\text{Stokes}} - \omega_{\text{pump}}$$

Figure 5.7: CSRS.

Figure 5.8: The scheme of absorption spectrum and of CARS and CSRS excitation profiles. CARS signal is registered at frequency $\Omega = \omega_p + \omega_j$, CSRS at $\Omega = \omega_p - 2\omega_j$. Excitation profiles are obtained when pump-frequency and Stokes frequency are scanned with fixed difference $\omega_p - \omega_s = \omega_j$.
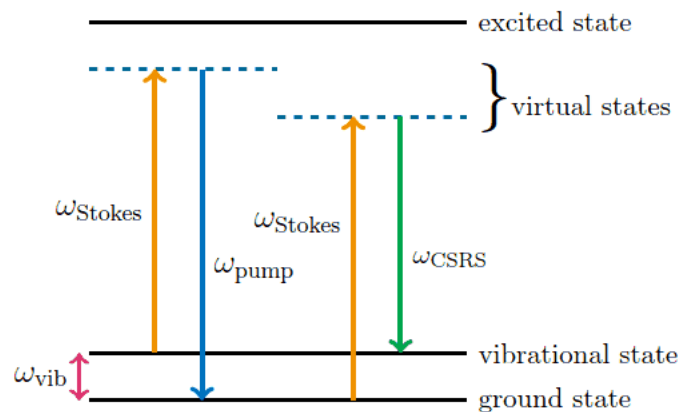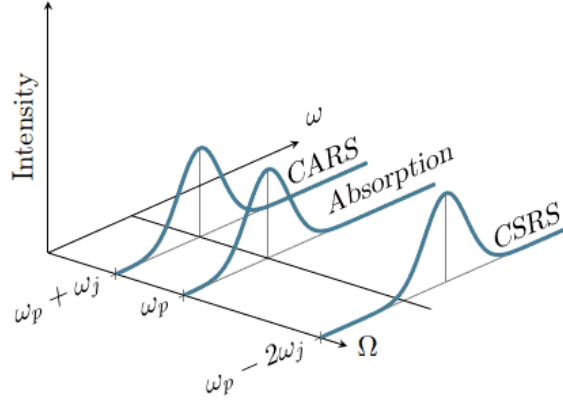
Let us take a look at CARS and CSRS below if there are molecules (impurity centers) in the system that have vibrational modes in those processes.

CARS as the third-order process is determined by the third-order susceptibility X_{CARS} (square of module $|X_{\text{CARS}}|^2$ determines the excitation profile of CARS):

$$
\begin{aligned}
X_{\text{CARS}} = \text{Av}_i(j) \sum_m & \frac{\langle i|m\rangle\langle m|i+1_j\rangle}{E_m - \omega_0 - E_i - i\gamma} \times \\
& \times \text{Av}_{i'}(j) \sum_{m'} \frac{\langle i'|m'\rangle\langle m'|i'+1_j\rangle}{E_{m'} - \omega_j - \omega_0 - E_{i'} - i\gamma},
\end{aligned}
\tag{5.70}
$$

where $\text{Av}_i(j)$ marks the averaging over all of the vibrational modes, except CARS-active j-mode, which is in a strongly excited coherent state. Here it is considered that the mode j on collective mode with wave vector $\vec{q} = \vec{k}_0 - \vec{k}_A$, where $\vec{k}_0$ is the wave vector of the exciting (pump) light and $\vec{k}_A$ is the wave vector of the scattered light. This vibrational mode interacts with electrons of the impurity (molecule).

In the Equation 5.70, the amplitudes of coherent scattering are considered to be the result of a long-time and large-space averaging, therefore, both amplitudes in Equation 5.70 are averaged independently. Let us go to the integral representation we used for the spontaneous Raman scattering. For CARS,

$$
X_{\text{CARS}} = \int_{-\infty}^{\infty} dt\, e^{-i(\omega_0 - \Omega_{21})t - \gamma t} A(t) \int_{-\infty}^{\infty} dt'\, e^{-i(\omega_0 - \Omega_{21} + \omega_j)t' - \gamma t'} A(t'),
\tag{5.71}
$$

where

$$
A(t) = \text{Av}_i(j)\langle i| e^{-itH_1} e^{itH_2} |i+1_j\rangle.
\tag{5.72}
$$

In the case $T = 0$, the Fourier amplitude is equal to the resonance Raman amplitude, which is determined by the absorption Fourier transform (case of basic model)

$$
A(t) = i\Theta(t)\xi_j\left(e^{it\omega_j} - 1\right)F(t).
\tag{5.73}
$$

Similarly, the CSRS is defined by the formula

$$X_{\text{CSRS}} = \text{Av}_i(j) \sum_m \frac{\langle i|m\rangle \langle m|i+1_j\rangle}{E_m - \omega_0 - E_i - i\gamma} \times$$
$$\times \text{Av}_{i'}(j) \sum_{m'} \frac{\langle i'|m'\rangle \langle m'|i'+1_j\rangle}{E_{m'} - \omega_j - \omega_0 - E_{i'} + i\gamma},$$

then it follows that

$$X_{\text{CSRS}} = \int\limits_{-\infty}^{\infty} dt e^{-i(\omega_0 - \Omega_{21})t - \gamma t} A(t) \int\limits_{-\infty}^{\infty} dt' e^{-i(\omega_0 - \Omega_{21} + \omega_j)t' - \gamma t'} A^*(t'). \tag{5.74}$$

At zero temperature $T = 0$ both amplitudes are related to the spontaneous Raman scattering amplitude $\alpha(\omega)$ as follows:

$$X_{\text{CARS}} = \alpha(\omega_0)\alpha(\omega_0 + \omega_j), \tag{5.75}$$

$$X_{\text{CSRS}} = \alpha(\omega_0)\alpha^*(\omega_0 - \omega_j), \tag{5.76}$$

which gives CARS and CSRS excitation profiles

$$I_{\text{CARS}} \propto |\Delta_{\text{CARS}}|^2 \sim \left| \left[\Phi(\omega_0) - \Phi(\omega_0 - \omega_j)\right] \left[\Phi(\omega_0 + \omega_j) - \Phi(\omega_0)\right] \right|^2, \tag{5.77}$$

$$I_{\text{CSRS}} \propto |\Delta_{\text{CSRS}}|^2 \sim \left| \left[\Phi(\omega_0) - \Phi(\omega_0 - \omega_j)\right] \left[\Phi(\omega_0 - \omega_j) - \Phi(\omega_0 - 2\omega_j)\right] \right|^2. \tag{5.78}$$

Here it is immediately seen that in our case, in the case of identical molecule ensembles, the shapes of excitation profiles are exactly identical, the CSRS has only been shifted towards higher frequencies by the Raman mode (substitute in Equation 5.78 $\omega_0 \Rightarrow \omega_0 + \omega_j$).

However, if molecules are in an inhomogeneous environment, such as molecules in solutions or impurity centers in crystals, local fluctuations cause inhomogeneous expansion of spectral lines. Modeling such a system, it is assumed that inhomogeneities affect, in particular, the energy of pure electron transfer, leaving vibrational dynamics unchanged. Since coherent radiation from different scattering centers interferes, the convolution of coherent scattering amplitude X_{CARS} with pure-electronic transition distribution function $\rho(\Omega_{21})$ must be calculated, integrating over frequencies of electronic transitions Ω_{21}:

$$I_{\text{CARS}}^{\text{inh}}(\omega_0) = \left| \int d\Omega_{21} X_{\text{CARS}}(\omega_0, \Omega_{21}) \rho(\Omega_{21} - \bar{\Omega}_{21}) \right|^2. \tag{5.79}$$

Using scattering amplitudes 5.71 and 5.74, and also the Fourier transform of the inhomogeneous distribution function $\rho(\Omega_{21} - \bar{\Omega}_{21})$, we find the inhomogeneously expanded excitation profiles of CARS and CSRS:

$$I_{\text{CARS}}^{\text{inh}} = \left| \int\limits_{-\infty}^{\infty} \int\limits_{-\infty}^{\infty} dt dt' e^{i(\omega_0 - \bar{\Omega}_{21})(t+t')} e^{i\omega_j t'} A_j(t) A_j(t') \rho(t+t') \right|^2, \tag{5.80}$$

$$I_{\text{CSRS}}^{\text{inh}} = \left| \int\limits_{-\infty}^{\infty} \int\limits_{-\infty}^{\infty} dt dt' e^{i(\omega_0 - \bar{\Omega}_{21})(t-t')} e^{i\omega_j t'} A_j(t) A_j^*(t') \rho(t-t') \right|^2. \tag{5.81}$$

From the formulas 5.80 and 5.81, we immediately see that the inhomogeneity causes a difference in the CARS and CSRS excitation profiles (compare $\rho(t+t')$ and $\rho(t-t')$). A comparative measurement of the CARS and CSRS excitation profiles opens up the possibility of determining the inhomogeneous width.

Abel–Plana formula

The Abel-Plana formula calculates the difference between a discrete sum and the corresponding integral. It is particularly useful in Casimir effect calculations involving differences between quantized and free modes.

Proof. Let us introduce two contour integrals

$$I_1 = i \oint_{C_1} \frac{F(it)}{e^{2\pi t} - 1} dt = 0,$$

$$I_2 = -i \oint_{C_2} \frac{F(-it)}{e^{2\pi t} - 1} dt = 0,$$

where function F has no singularities, integration contour C_1 covers lower half-plane and C_2 stays for upper half-plane. Integral I_1 can be presented as

$$I_1 = iP \int_{-i\infty}^{0-i\varepsilon} \frac{F(it)}{e^{2\pi t} - 1} dt + i \frac{i\pi}{2\pi} \left[\sum_{n=1}^{\infty} F(n) + \frac{1}{2} F(0) \right] + iP \int_0^{\infty} \frac{F(it)}{e^{2\pi t} - 1} dt,$$

where P denotes principal value of the integral without poles. Integral I_2 can be expressed in the same way:

$$I_2 = -iP \int_{i\infty}^{0+i\varepsilon} \frac{F(-it)}{e^{2\pi t} - 1} dt - i \frac{-i\pi}{2\pi} \left[\sum_{n=1}^{\infty} F(n) + \frac{1}{2} F(0) \right] - iP \int_0^{\infty} \frac{F(-it)}{e^{2\pi t} - 1} dt.$$

Taking into account that changing the sign of t in I_2 also changes the integration contour from C_2 to C_1,

$$I_2 = i \oint_{C_1} \frac{F(-it)}{e^{-2\pi t} - 1} dt = 0,$$

and

$$I_1 + I_2 = -i \oint_{C_1} F(it) dt = 0.$$

The proof is based on the idea that

$$\frac{1}{e^{2\pi t} - 1} + \frac{1}{e^{-2\pi t} - 1} = -1,$$

which gives

$$I_1 + I_2 = \int_0^\infty F(t)\,dt - \left[\sum_{n=1}^\infty F(n) + \frac{1}{2}F(0) \right] + i \int_0^\infty \frac{F(it) - F(-it)}{e^{2\pi t} - 1}\,dt = 0.$$

It follows that

$$\sum_{n=1}^\infty F(n) = \int_0^\infty F(t)\,dt - \frac{1}{2}F(0) + i \int_0^\infty \frac{F(it) - F(-it)}{e^{2\pi t} - 1}\,dt.$$

□

Value of the repulsion parameter and mass of Higgs boson

Let us consider the possible value of λ in Eq. 1.34. We remind that according to the Standard Model (see, e.g. [13]) the ϕ^4-type interaction determines the inherent repulsion of the scalar field. This field is an SU(2) doublet $\phi^\dagger = \left(\phi^{+*}\phi^{0*}\right)$ with the field components $\phi^+ = \left(\phi_1 + i\phi_2\right)/\sqrt{2}$ and $\phi^0 = \left(\phi_3 + i\phi_4\right)/\sqrt{2}$, where ϕ_i, $i = 1,2,3,4$ are the real components of the scalar field. In the Heaviside units $\varepsilon_0 = \mu_0 = c = \hbar = 1$ the Lagrangian of this field can be presented in the form

$$\mathcal{L} = \left(\partial_\mu \phi\right)^\dagger \left(\partial^\mu \phi\right) - \mu \left(\phi^\dagger \phi\right) - \lambda \left(\phi^\dagger \phi\right)^2$$

where

$$\left(\phi^\dagger \phi\right) = (1/2) \sum_{i=1}^{4} \phi_i^2.$$

The first term of the Lagrangian is the density in the space of the kinetic energy, while the remaining two terms stand for the the density in the space of the potential energy. Here the positive parameter λ describes the inherent repulsion, while the negative parameter μ describes the square of the imaginary mass in the symmetrical state. In the used units ϕ_i has the dimension of energy, the dimension of $\mathcal{L}$ is the fourth power of energy, the dimension of μ is square energy, λ is dimensionless.

The energy of the field ϕ has the minimum value for the state with $|\phi| = \sqrt{\sum_i \phi_i^2}$, which corresponds to spontaneous breaking of symmetry. The minimum is located at the point $\phi_{10} = \phi_{20} = \phi_{40} = 0$, $\phi_{30} = v$, where $v = \sqrt{-\mu/\lambda}$. The fields can be expanded near this point, taking $\phi_i \approx \phi_{i0} + h_i$. For small h_i last two terms in the Lagrangian equal $-\lambda v^2 h_3^2 + \lambda v^4/4$. As it follows from this equation, one boson of four, described by the field h_3, possesses the mass $m_H = \sqrt{2\lambda}\, v/c^2$; three other bosons remain massless.

The value of v is known in the standard model: $v = 246.2$ GeV (see [13]). However, the value of λ was not known before the experiments in CERN by ATLAS and CMS collaborations. Taking obtained in [1] mass $m_H = 125$ GeV/c^2, one gets $\lambda = 0.129$, which is close to 1/8. In our opinion this is not an occasional coincidence, and we present an argument for that.

Let us consider the relativistic wave packet of the ϕ field (its size satisfies the condition $l \ll \hbar/m_H c$). Such a wave packet should be fully characterized by its energy $E = 1/l$. This

means that $\phi_i = E$. Integrating $\left(\phi^\dagger\phi\right)^2$ over its volume $l^3 = E^{-3}$ we get

$$\left(\phi^\dagger\phi\right)^2 \equiv \left(\sum_i \phi_i^2\right)^2 = 4\,E.$$

The first term $\mu\left(\phi^\dagger\phi\right)$ in the potential energy gives in the relativistic limit only a negligible contribution of the order of $m_H^2 c^4/E \ll E$. Taking into account that the potential energy gives half of the total energy, we get $4\lambda E = E/2$, which gives $\lambda = 1/8$ and

$$m_H = v/2c^2 \approx 123.1 \text{ GeV}/c^2.$$

The obtained value of λ has simple meaning: the potential energy $E/2$ of the wave packet comes from four components of the field. The contribution of one of them (h_3), possessing the mass after the symmetry breaking, is just $1/8$ of the energy of the wave packet.

Presented arguments for the inherent repulsion energy and corresponding equation should hold also for the hypothetical particles under consideration. The only difference is that these particles, presumably, are singlets. This means that corresponding value of the repulsion parameter is $\lambda = 1/2$.

Bloch – de Dominicis theorem

Bloch – de Dominicis theorem is widely used for thermodynamical calculations involving harmonic oscillators. For linear operators in the state of thermal equilibrium the **thermal average** is

$$\langle A \cdot B \cdot C \cdot D \cdot F \ldots \rangle_T,$$

where $\hat{A}$ is a linear operator, $a_j^{+}(t) = a_j^{+} e^{i\omega_j t}$, $a_j(t) = a_j e^{-i\omega_j t}$, and

$$\hat{A}(t) = \sum_j \left(e_j a_j^{+}(t) + e_j' a_j(t) \right).$$

What is averaging?

$$\langle \hat{A} \hat{B} \ldots \rangle = \sum_{n_j} P_{n_j} \langle n_j | \hat{A} \hat{B} \ldots | n_j \rangle \equiv \sum_{n_j} P_{n_j} \int dq_j \Psi_{n_j}^* \hat{A} \hat{B} \ldots \Psi_{n_j}$$

is non-zero when the number of operators is even. The task is to find the average of the minimum number of operators *pair correlators*.

> **Theorem 1.** *The average value of the product of the creation and annihilation operators in the state of thermal equilibrium is equal to the sum of all possible sets of pairing of this product.*
>
> $$\langle \hat{A} \cdot \hat{B} \cdot \hat{C} \cdot \hat{D} \cdot \hat{F} \ldots \rangle_T = \langle \hat{A} \cdot \hat{B} \rangle \langle \hat{C} \cdot \hat{D} \cdot \hat{F} \ldots \rangle + \langle \hat{A} \cdot \hat{C} \rangle \langle \hat{B} \cdot \hat{D} \cdot \hat{F} \ldots \rangle + \ldots$$

Proof. (When the summation includes different operators, the proof is trivial.)

Let us consider just one pair correlator $C_k = \langle a^{+k} a^k \rangle$ from the normally-ordered product of the operators (i.e. annihilation operator on the right, creation operator on the left). In vacuum $C = 0 \Leftrightarrow T = 0$.

$$C_k = \langle a^{+k} a^k \rangle = \sum_{n=0}^{\infty} P_n \langle n | a^{+k} a^k | n \rangle,$$

where $P_n = Z^{-1} e^{-\hbar \omega n/(kT)}$ is a Boltzmann distribution. Then

$$C_k = \sum_{n=0}^{\infty} P_n \int dq \Psi_n^* a^{+k} a^k \Psi_n.$$

Using the common notation $\Psi_n = |n\rangle$ and operators

$$a|n\rangle = \sqrt{n}|n-1\rangle,$$
$$a^{+}|n\rangle = \sqrt{n+1}|n+1\rangle,$$

one gets (assuming that $n > k$)

$$a^k |n\rangle = \sqrt{n(n-1)\ldots(n-k+1)} \, |n-k\rangle,$$
$$a^{+k} a^k |n\rangle = \sqrt{n(n-1)\ldots(n-k+1)} \, a^{+k} |n-k\rangle$$
$$= \sqrt{n(n-1)\ldots(n-k+1)} \sqrt{n(n-1)\ldots(n-k+1)} \, |n\rangle$$
$$= n(n-1)\ldots(n-k+1) \, |n\rangle.$$

This gives

$$\langle n | a^{+k} a^k | n\rangle = n(n-1)\ldots(n-k+1) = \frac{n!}{(n-k)!},$$

then

$$C_k = \sum_{n=k}^{\infty} P_n \frac{n!}{(n-k)!}.$$

Introducing new summation index $m = n - k$,

$$C_k = \sum_{m=0}^{\infty} P_{m+k} \frac{(m+k)!}{m!} = \sum_{m=0}^{\infty} P_{m+k} \frac{m(m+k-1)!}{m!} + \sum_{m=0}^{\infty} P_{m+k} \frac{k(m+k-1)!}{m!}$$
$$= \sum_{m_1=0}^{\infty} P_{m_1+k+1} \frac{(m_1+k)!}{m_1!} + k \sum_{m=0}^{\infty} P_{m+k} \frac{(m+k-1)!}{m!},$$

where $m_1 \equiv m - 1$. Taking into account that $P_{m_1+k+1} = e^{-\hbar\omega/(kT)} P_{m_1+k}$, one gets

$$C_k = \frac{e^{-\frac{\hbar\omega}{kT}}}{1 - e^{-\frac{\hbar\omega}{kT}}} k \, C_{k-1} = \bar{n} \, k \, C_{k-1}.$$

The factor $\bar{n} = \langle a^+ a \rangle$ gives

$$C_k = \left\langle a^{+k} a^k \right\rangle = k \langle a^+ a \rangle \left\langle a^{+k-1} a^{k-1} \right\rangle = k \langle a^+ a \rangle C_{k-1}$$

and the task has been reduced to the product of pair correlators:

$$C_k = k(k-1)\ldots 1 \langle a^+ a \rangle^k = k! \langle a^+ a \rangle^k.$$

$\square$

Universe expansion in Planck limit

According to the Big Bang theory the observable Universe began approximately 13.8 billion years ago as a huge explosion of an extremely small spot. At present the Universe is still expanding and the expansion rate is given by the Hubble's frequency $H \sim T_U^{-1} = 2.4 \times 10^{-18} \mathrm{s}^{-1}$ (T_U^{-1} is the age of the Universe). Previously it was assumed that this frequency remains unchanged at least for the most part of the Universe. However, in the end of the last century it was found that Hubble's frequency depends on the distance. Namely, it was established that the Universe is expanding with an increasing speed.

This phenomenon is usually explained on the basis of the classical general theory of relativity with the account of the cosmological constant Λ (Lambda Cold Dark Matter model of Universe). The quantum-mechanical aspect of the problem is usually not discussed. However, we propose to pay attention to the relation

$$H = 8.5(2\pi k_B T)^2 / \hbar E_{pl}$$

which satisfies the Hubble frequency, temperature of the Universe $T = 2.7\,\mathrm{K}$ and Planck energy $E_{pl} = 1.2 \cdot 10^{28}\,\mathrm{eV}$ and which, if it is not just a coincidence of huge numbers, and which can only be explained within the framework of quantum theory.

We draw attention to the following possible interpretation of this relationship: the expansion of the Universe is due to quantum processes of Planck scale, which occur everywhere in the Universe with probability $\sim 2\pi(k_B T/E_{pl})^2 \sim 10^{-63}$ for the Planck period $t_{pl} = 2\pi\hbar/E_{pl} = 5.4 \times 10^{-44}\mathrm{s}$.

The acceleration of the expansion in this case is explained by the increase of the probability of the process with temperature (here it is taken into account that the more distant parts of the Universe are younger and have higher temperature). A somewhat different numerical multiplier can be attributed, e.g. to a faster expansion of the Universe in the early stages. In this paper, a quantum-mechanical model is considered that allows us to justify such an interpretation.

In the quantum theory, vacuum corresponds to the ground state of the fields and has no particles. Bosons in vacuum are in the zero-point state, characterized by a huge energy density $\sim \rho_{pl} = 2.9 \times 10^{133}$ eV/m^3 stemming from the zero-point fluctuations of them. In this theory, the vacuum is equivalent to a cosmological constant Λ. However, its value, stemming from the given energy density is 10^{120} times larger than its measured value [28]. This huge discrepancy may raise the question of whether the quantum theory can at all explain the expansion of the Universe.

The problem here is related to the energy conservation law: if we accept that universal constants are really constants, then we must conclude that the expansion of the Universe causes a huge increase in the zero-point energy of bosons. Consequently, if there would not be other contributions to the energy of vacuum, then the energy conservation law would be seriously violated.

A huge discrepancy of the Λ values has been actively discussed for a long time (see, e.g. [28]). As a possible solution, Coleman [7] suggested that the effects of quantum gravity should lead to the cancellation of the enormously large value of Λ. A complete cancellation (perhaps a tiny discrepancy, leading, for example, to a negative pressure in vacuum) then can be the result of the zero energy of the initial fluctuation, which, according to [33], gave rise to the Universe. Here we proceed from this statement. We take into account that gravitational forces increase with the decrease of distance. This suggests that the cancellation can occur due to the negative gravitational energy of the vacuum superstructure at the Planck limit.

This assumption is confirmed by the presented above consideration of the effect of the gravitational self-action energy $E_G = -GE^2/lc^4$ on the total energy E of the wave packet of a quantum particle of a small size l (G is the gravitational constant, c is speed of light). Taking into account the relation $E = E_G + E_{\text{kin}}$, where $E_{\text{kin}} = 3\hbar c/2l$ is the kinetic energy of the localization of the wave packet, one finds two solutions for the energy:

$$E = E_{pl}\left(\pm\sqrt{(1 + (l/2L_{pl})^2)} - l/2L_{pl}\right)$$

The solution with the plus sign corresponds to a wave packet with positive energy. It can be seen that this energy cannot exceed the value $\sim E_{pl}$, corresponding to the Planck particle.

More important in this context is the solution with the minus sign. As it was shown above (see Section 1.3.3), this solution describes particles of size $\sim L_{pl}$ with negative energy $\sim -E_{pl}$ repulsing in the Planck scale.

One can place into the volume $l^3 \gg L_{pl}^3$ altogether $\sim (l/L_{pl})^3 \gg 1$ non-overlapping wave packets. Therefore, the energy density of vacuum indeed should include a huge negative contribution of the order of $-\rho_{pl}$ coming from the particles with the negative energy $E \sim -E_{pl}$ and the size $l \sim L_{pl}$.

If such a vacuum structure is correct, then the expansion of the Universe can occur as quantum processes with the creation of particles with negative energy of the Planck scale. The created particles push apart the existing particles, which leads to increase in the size of the Universe and, thereby, to increase in the energy of zero-point fluctuations of bosons by the same but positive value. The processes proceed spontaneously everywhere with a small probability, which increases with temperature. These processes have a close analogy with zero-phonon transitions in solids [12].

Using this analogy, one can show (see Appendix E) that the rate of transition with creating a negative energy particle and subsequent change of Bose subsystem equals

$$w \sim H.$$

Thus, we have proposed a Planck-scale mechanism of the expansion of the Universe, which consists in the creation and destruction of pairs of particles (bosons) with positive and negative energy with the prevailing processes of their creation. The model is applicable to an empty, uncurved space. The effects of the space curvature (caused by matter) and the cosmological constant on the accelerated expansion of the Universe can be described in the framework of the classical general theory of relativity.

E

Quantum mechanism of the expansion of Universe

Abstract

We discuss the hypothesis that quantum processes of the Planck-scale with the Hubble frequency $H \sim 10^{-18} \text{sec}^{-1}$ are responsible for the expansion of the Universe. A model of these processes is proposed, according to which these processes correspond to zero boson transitions. Using the Lax theory, we show that these transitions lead to fast ($\sim k_B T / \hbar \sim 10^{11} \text{sec}^{-1}$) and small ($\sim L_P \sim 10^{-33} \text{cm}$) stochastic fluctuations in the volume with a very small ($\sim H$) predominance of processes with increasing volume and with the generation of cosmic background radiation with the correct value of its temperature T.

E.1   Introduction

According to Hubble's law, our Universe expands with a rate per unit length (frequency) $H \approx 2.2 \cdot 10^{-18} \text{ sec}^{-1}$ (here H^{-1} is the age of the Universe). Hubble's expansion is usually explained on the basis of the classical general theory of relativity (see, for example, [23], [35], [34], [28], [9]). However, it is generally accepted that empty space corresponds to the ground (zero-point) state of quantum fields. Thus, the expansion of the Universe means an increase in the volume of space occupied by this zero-point field. This provides the basis for the hypothesis that quantum processes should be behind this expansion. In this work, we propose a model of such processes.

In quantum theory, zero-point fluctuations of bosons make a huge contribution to the energy density of the Universe $\sim \rho_P = E_P / L_P^3 = 2.9 \times 10^{132} \text{ eV/m}^3$, where $E_P = 1.2 \times 10^{28} \text{ eV}$ and $L_P = 1.6 \times 10^{-35} \text{ m}$ are Planck energy and length, respectively. This means (provided that the fundamental physical constants do not change with time) that the expansion of the Universe causes a huge increase in the zero-point energy of the bosons. This is possible without violation of the energy conservation law, if there is another contribution to the energy of the vacuum, which compensates for this increase. It is usually assumed (see, for example, [7], [6], [25]) that the effects of gravity should lead to such compensation: gravitational forces are attractive and they increase with the decreasing distance. This suggests that compensation can occur due to the negative gravitational energy of the vacuum superstructure at the Planck limit [25]. A complete cancellation, possibly with a slight discrepancy, may be the

result of zero energy of the initial quantum fluctuation, which, according to [33], spawned the Universe.

This article takes the basis of the above assumption that this cancellation is provided by particles with negative gravitational energy of the Planck scale. This point of view is supported by the following consideration of the effect of the gravitational self-action of a wave packet of a particle of small size l, comparable with L_P, on its total energy E [20]. Assuming that gravitational interaction can be considered classically, this energy is determined by the sum of kinetic energy of localization $\sim \hbar c/l$ and the energy $E_G \sim -GE^2/lc^4$ of gravitational self-action, where G is the gravitational constant (consideration is carried out in order of magnitude). This gives the following equation for the total energy $E = \hbar c/l - GE^2/lc^4$ of the wave packet. This equation has two solutions: $E = E_P(\pm\sqrt{1 + (l/2L_P)^2} - l/2L_P)$.

The solution with the plus sign corresponds to a wave packet with the positive energy. This energy cannot exceed E_P (a hypothetical particle with $E \approx E_P$ is called a Planck particle, or maxon).

More important in the context is the solution with a minus sign, which, we assume, describes particles with negative energy. For these particles it is energetically beneficial to stay apart: indeed, in volume $l^3 \gg L_P^3$, $N \sim (l/L_P^3) \gg 1$ non-overlapping wave packets have $\sim (l/L_P)^2 \gg 1$ times larger total negative energy than the single wave packet of the same size. Therefore, it is energetically beneficial to place the aforementioned particles in a space separately from each other.

In other words, the considered particles of negative energy are repelled at the Planck limit.

The distance between particles L and the size of them L_0 can be determined if to take into account the standard repulsive interaction $\lambda(\phi^+\phi)^2$ (here $\lambda > 0$, ϕ is the wave function of the quantum field); this interaction works against gravitational collapse of particles, giving $L \approx 2L_P$ and $L_0 \approx L_P$ [20].

If such a vacuum structure is true, then the expansion of the Universe can occur as quantum processes with the creation of two excitations (particles): one with positive energy close to E_P and another with almost the same but negative energy. The created particles push apart existing particles, which leads to an increase in the size of the Universe.

E.2   The model

To determine the rate of such a process, it is considered here that both, positive and negative energy excitations correspond to bosons with energy $\pm E_0 \cong \pm E_P$ of the zero-point levels. The energy level diagram is shown in Fig. E.1.

The Hamiltonian of the system under consideration has the form

$$\hat{H} = \hat{H}_0(\hat{I} + \hat{\sigma}_z)/2 + \hat{H}_1(\hat{I} - \hat{\sigma}_z)/2 + \hat{H}_{\text{int}}, \tag{E.1}$$

where $\hat{H}_0 = H_{0+} + H_{0-}$, $H_{0\pm} = \sum_k \hbar\omega_k(\hat{a}_{k\pm}^+ \hat{a}_{k\pm} + 1/2)$ are the Hamiltonians of bosons with positive and negative zero-point energy, $\hat{a}_{k\pm}^+$ and $\hat{a}_{k\pm}$ are creation and destruction operators of bosons, $\omega_k = ck$ is the frequency of boson with the wave number k,

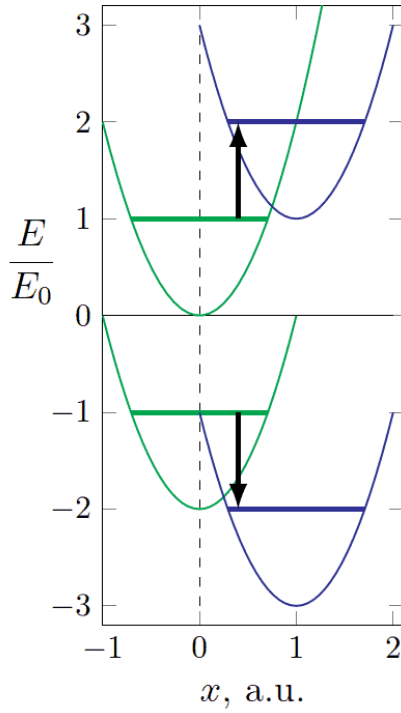$$\hat{H}_1 = \hbar\Delta + e^\nabla \hat{H}_0 e^{-\nabla} \tag{E.2}$$

Figure E.1: Energies of the particle (bosons) before and after the transition: the green horizontal lines correspond to the energies of the initial and final states of boson with positive energy, the blue horizontal lines correspond to the initial and final states of boson with negative energy, green and blue parabolas - to the initial and final potential energies of bosons. The thick arrows (up and down) - zero-boson transitions with the energies $\pm E_0 \cong \pm E_P$; x corresponds to generalized coordinate of bosons.

is the Hamiltonian of bosons after the transition, $\hbar\Delta = E_1 - E_0$ is the small energy change due to transition between zero-point states (this change is compensated by the energy of the created bosons), $\nabla = \nabla_+ + \nabla_-$ is the shift operator of bosons, $\hat{H}_{int} = V\hat{\sigma}_x$ is the interaction of bosons causing the transitions, $\hat{\sigma}_x$ and $\hat{\sigma}_z$ are the Pauli matrices, $\hat{I}$ is the 2×2 unit matrix.

Only spherical modes k are considered. In this case, the shift operator ∇ is the sum $\nabla_\pm = \sum_k \nabla_{k\pm}$ of the shift operators $\nabla_{k\pm} = x_{0k}\partial/\partial x_{k\pm}$ of these modes, where x_{0k} is the shift of the equilibrium position of the mode with the generalized coordinate $x_{k\pm} = \sqrt{\hbar/2\omega_k}(\hat{a}_{k\pm} + \hat{a}_{k\pm}^+)$. The density of these modes is $\rho(k) = 3k^2(c/\omega_P)^3$, where $\omega_P = E_p/\hbar$ is the Planck frequency. The spherical displacement $x_{r\pm}$ at the distance r can be represented as the sum of spherical modes x_k as follows:

$$x_{r\pm} = \sqrt{1/4\pi V}\, r^{-1} Im \sum_k k^2 e^{ikr} x_{k\pm}. \quad \text{(E.3)}$$

Here, it is assumed that the quantum transition leads to a finite change in the volume (Δ_V) of the fields of the zero point state. This change can be presented as $\Delta_V = 4\pi R^2 \Delta_R$, where Δ_R is the change of the radius R of the space as the result of the transition. Taking into account Equation E.3, one finds $\Delta_R \propto R^{-1} Im \int dk\, k^2 x_{0k} e^{ikR}$. The change of the volume of the zero-point

fields Δ_V is finite if $x_{0k} \propto k^{-2}$.

The derived dependence $x_{0k} \propto k^{-2}$ is analogous to the dependence of the change of a density mode on the wave number of the mode during a zero-phonon transition in superfluid helium [19] .

E.3   The rate of transitions

According to the theory of Lax [22], the rate of a quantum transition with creation of a pair of particles with total energy $E = 0$ can be presented in the form

$$W_+ = |V|^2 \int dt e^{-i\Delta t} F^2(t), \quad \text{(E.4)}$$

where

$$F(t) = \left\langle e^{\nabla_\pm} e^{-\nabla_\pm(t)} \right\rangle \quad \text{(E.5)}$$

is the Fourier transform of the spectrum of bosonic transitions followed by the shift of the equilibrium positions of bosons,

$$\nabla_\pm(t) = \sum_k \sqrt{\omega_k/2\hbar}(\hat{a}_{k\pm}e^{-i\omega_k t} + \hat{a}_{k\pm}^+ e^{i\omega_k t})$$

are the shift operators at time moment t (integrals are taken from $-\infty$ to ∞). Applying Wick's theorem, one obtains [22] $F(t) = e^{g(t)}$, where

$$\begin{aligned}
g(t) &= \langle \nabla_\pm(\nabla_\pm - \nabla_\pm(t)) \rangle = \\
&= (1/2\hbar)\sum_k \omega_k x_{0k}^2 ((n_{\omega_k}+1)(e^{i\omega_k t}-1) + n_{\omega_k}\left(e^{-i\omega_k t}-1\right)),
\end{aligned} \tag{E.6}$$

$n_\omega = (\exp(\hbar\omega/k_B T) - 1)^{-1}$ is the Planck population factor, T is the temperature of cosmic background radiation. Replacing the sum over k by the integral over the wavenumbers according to $\sum_k \to \int dk\, \rho(k)$, and using the relation $n_{-\omega} + 1 = -n_\omega$, we obtain the following simple equation:

$$g(t) = \int d\omega\, \omega^{-1}\left(e^{i\omega t}-1\right)(n_\omega + 1), \tag{E.7}$$

where the integral is taken from $-\omega_P$ to ω_P. A significant contribution to the integral E.4 is made by low frequencies $|\omega| \lesssim k_B T/\hbar$, which correspond to zero-boson transitions (ZBT) from a neighbourhood of the initial zero-point states to a neighbourhood of the final zero-point states of bosons. These transitions are analogous to the zero-phonon transitions in optical centers in crystals [31], [12]. The contribution of ZBTs is given by large values of $|t| \gg \hbar/k_B T$. To find this contribution, it is necessary to single out in the integral E.7 the term $k_B T/\hbar\omega^2$ that is divergent for $\omega \to 0$. Then, taking into account the relation $(e^{i\omega t}-1)/\omega^2 = \pi|t|(-\delta(\omega) + it^{-1}\delta'(\omega))$, $|t| \to \infty$ one gets for large $|t|$

$$g(t) = -\gamma|t| + i\alpha t/|t| - S.$$

Here $\gamma = \pi k_B T$ is the broadening of ZBT, $\alpha = \gamma/2k_B T$ is the asymmetry factor, stemming from the difference of probabilities of Stokes and anti-Stokes transitions [21],

$$S = \int\limits_0^{\omega_P} \frac{d\omega}{\omega}\left(2n_\omega + 1 - \frac{2k_B T}{\hbar\omega}\right) \cong \ln\left(\frac{E_P}{2k_B T}\right) \tag{E.8}$$

is the Huang-Rhys factor determining the probability of ZBT.

Simple calculation gives $W_+ = |V|^2 w$, where

$$w = \left(\frac{2k_B T}{E_P}\right)^2 \frac{\gamma + \alpha\Delta}{\gamma^2 + \Delta^2/4}. \tag{E.9}$$

is the normalized probability of the transition.

If $\hbar\Delta \ll k_B T$, then $W_+ = \pi^{-1}|2V/\omega_P|^2(k_B T + \hbar\Delta/2)$. The factor V, by its physical meaning is the frequency of the attempts to make a transition. Its value is not known. However, one can expect that it has the order ω_P - the only known frequency unit Planck scale. If this is so, then the rates of transitions leading to expansion of Universe are given by the equation

$$W_+ \sim k_B T/\hbar + \Delta/2. \tag{E.10}$$

Note that the boson excitation spectra upon transition (given by the Fourier transform of $F(t)$) for small $\omega \lesssim k_B T/\hbar$ are given by a similar to Equation E.9 formula

$$I(\omega) = \frac{2k_B T(\gamma + \alpha\omega)}{E_P(\gamma^2 + \omega^2)}.$$

The intensity of these spectra at zero frequency $I(0) \sim \omega_P^{-1}$ is a determining factor in the considered expansion mechanism of the Universe. Indeed, one can estimate the probability as $W_+ \sim k_B T \omega_P^2 I(0)^2/\hbar \sim k_B T/\hbar$ in agreement with Equation E.10. Here it is taken into account that w is determined by the overlapping integral of $I(\omega)$ and $I(\Delta - \omega)$. For small Δ the overlapping takes place for $|\omega| \lesssim k_B T$.

E.4 Account for reverse transitions

In addition to the transitions leading to the expansion of the Universe it is need to take into account also reverse transitions, which lead to the compression of the Universe. The rates of these transitions are given by analogous to Equation E.10 formula but with $-\Delta$ instead of Δ. Universe will, then, expand if the rate of the inverse transitions is smaller. This occurs if $\Delta > 0$. In this case the resulting rate of transitions leading to expansion of the Universe is given by the equation

$$W = H = W_+ - W_- \sim \Delta. \tag{E.11}$$

Thus, in the proposed theory, the Hubble frequency of expansion of the Universe equals to the rate W, and this rate equals to Δ, which determines the gain of the energy of vacuum as a result of the single Planck-scale process causing the expansion of the Universe.

E.5 Discussion

It was shown above that the quantum processes considered here in the Universe lead to local volume fluctuations with the amplitude $\sim L_P \sim 10^{-33}$ cm and the frequency $\omega_f \sim k_B T/\hbar \sim 10^{11}$ sec^{-1} and with a small $\sim H \sim 10^{-18}$ sec^{-1} predominance of processes with a local increase in volume.

The small ($\sim H \sim 10^{-18}$) predominance of processes with a local increase of the volume is due to the fact that the energy of the zero-point state of the Universe decreases with expansion (in one process this energy decreases by $\hbar H$). This decrease provides kinetic energy for expansion. The total energy is conserved in the processes under consideration.

According to proposed model, there exists a quantum tremor at the Planck level in the Universe with the frequency of relic radiation, and the expansion of the Universe is one of consequences of this tremor. This mechanism of the expansion makes it possible to obtain the following relation for the energy density of the created bosons in the time H^{-1} of the existence of the Universe:

$$\rho_b \sim \rho_P (k_B T/E_P)^4. \tag{E.12}$$

This gives $\rho_b \sim 0.1 \rho_c$, where $\rho_c \sim 3H^2/8\pi G \sim 10^9$ eV/m^3 is the critical value of the energy density required for the Universe to just to halt its expansion. Here it is taken into account that each transition brings an average energy $\sim |\Delta| \sim \hbar H$ of bosons with an average wavelength $L_P(E_P/k_B T)$, and that the frequency of transitions is $\sim W_\pm \sim k_B T/\hbar$. The obtained value of ρ_b is in good agreement with the known energy density of the cosmic background radiation.

Thus, the mechanism of quantum expansion of the Universe considered here allows one to explain the temperature of cosmic background radiation

$$T \sim (0.1 \rho_c/\rho_P)^{1/4} T_P \sim 2.7 \, \text{K}, \tag{E.13}$$

where $T_P = E_P/k_B$ is the Planck temperature.

This result testifies in favour of the validity of the proposed quantum model of the expansion of the Universe. In the model presented here, only massless bosons (photons) were taken into account. The case of bosons with a nonzero rest mass should be considered separately. However, one can assume that for a modern (cold) Universe with a temperature of $T = 2.7\,\text{K}$, one can neglect the processes with the creation and destruction of such bosons.

Only the case of flat space-time was considered here. Nevertheless, our model also allows us to take into account the effects of the general theory of relativity by choosing the correct local time; e.g. the actual space-time geometry can be taken into account by choosing (in appropriate units) $H = 1/2t$ in the case of radiation-dominated expansion or $H = 2/3t$ in the case of matter dominated expansion.

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