

# Deexcitation Dynamics of a Degenerate Two-Level Atom near (Inside) a Body

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## 1. Introduction

It has long been known that atomic radiation processes near a macroscopic body differ from those in free space substantially (Purcell, 1946). In particular, the lifetime of an excited state of an atom or a molecule near surface (Arnoldus & George, 1988a;b; Barnes, 1998; Chance et al., 1978; Drexhage et al., 1968; Ford et al., 1984; Fort & Grésillon, 2008; Garrett et al., 2004; Hellen & Axelrod, 1987; Kreiter et al., 2002; Lukosz & Kunz, 1977; Macklin et al., 1996; Milonni & Knight, 1973; Snoeks et al., 1995; Steiner et al., 2005; Yeung & Gustafson, 1996) or in the vicinity of (or inside) a nanoparticle (Chew, 1987; 1988; Das & Metiu, 1985; Dung et al., 2000; Gersten & Nitzan, 1981; Klimov, Ducloy & Letokhov, 1996; Klimov et al., 2001; Klimov, Ducloy, Letokhov & Lebedev, 1996; Ruppin, 1982) may be increased or decreased depending on specific conditions. This lifetime change is theoretically calculated in many papers. These calculations made in a variety of ways. Nevertheless all of these papers can be divided into two classes. The first class includes the papers that represent an excited atom as a three-dimensional damped oscillator (Chance et al., 1978; Chew, 1987; 1988; Das & Metiu, 1985; Hellen & Axelrod, 1987; Klimov, Ducloy & Letokhov, 1996; Klimov, Ducloy, Letokhov & Lebedev, 1996; Ruppin, 1982). The second class includes the papers that consider an excited atom by means of quantum mechanics (Agarwal, 1975a;b; Arnoldus & George, 1987; 1988a;b; Barnes, 1998; Dung et al., 2000; Wylie & Sipe, 1984; 1985; Yeung & Gustafson, 1996).

It is shown in the papers that are in the first class that the atomic oscillator rate of damping take a different value in the case of radial and tangential orientation of the oscillating atomic electric dipole. The magnitude of the rate of damping lies between these values in the case of another atomic dipole orientation. However the atomic or molecule decay rate is measured by the fluorescence detection after light pulse excitation of the atom or molecule. So, fluorescence is two-step process, and hence, orientation of the oscillating atomic dipole in general is not the same as exciting light polarization.

In the second class papers the problem of the atomic dipole orientation is either no discussed explicitly or reduced to partitioning of the dipole matrix element on radial and tangential parts as in the case of the classic atomic oscillator. The ratio between these two parts is either no evaluated or assumed to be in the ratio 1:2 as in the case of free space. This approach

one cannot consider as correct because of anisotropy of the atomic surroundings. The remark about fluorescence as two-step process mentioned above refers equally to the papers.

To rigorous description of the vector nature of the atomic dipole moment it is necessary to take into account the atomic angular degrees of freedom, that is degeneracy of atomic levels. As far as we know, it was done only in the papers (Arnoldus & George, 1987; 1988a;b). In the papers the steady-state fluorescence of the atom near an axial symmetrical surface was theoretically investigated and influence of the surface was expressed in terms of electric field correlation function.

The purpose of the chapter is to present the correct description of deexcitation dynamics of a degenerate two-level atom in the vicinity of arbitrary body.

We start with a quantum mechanical expression for the atomic deexcitation probability expressed in terms of the normal correlation function of the atomic dipole moment operator and the antinormal correlation function of the electric field strength operator. Then the antinormal correlation function is expressed in terms of the field susceptibility by use of the fluctuation-dissipation theorem. The atomic dipole moment operator as well as the atomic density matrix operator is expressed in terms of irreducible tensor operators. Finally, it is shown that the atomic deexcitation rate at the instant immediately after pulse excitation is proportional to a linear combination of the products of the so-called atomic polarization moments, population and alignment, and anisotropic relaxation matrix.

To find out deexcitation dynamics, a master equation for atomic density matrix is derived from an evolution equation for the total density matrix describing both atom and field. A consistent system of linear first-order ordinary differential equations for the atomic polarization moments is obtained from the master equation. Components of the anisotropic relaxation matrix describing the consistent system are expressed in terms of the field susceptibility tensor. Symmetries of the anisotropic relaxation matrix are found. It is shown that atomic deexcitation in general is multi-exponential. The simple exponential decay of the excited energy level takes place only if its total angular momentum is less than one. Deexcitation dynamics is considered in more detail for the case when the total angular momenta of the upper and lower levels are equal to 1 and 0 respectively. It is shown that in this case deexcitation dynamics also may be exponential at certain polarizations of the exciting light.

In conclusion, an intriguing issue that is why the simple model of classical oscillating dipole for description of fluorescence is in good agreement with observational evidence (Amos & Barnes, 1997; Chance et al., 1978; Drexhage et al., 1968; Fort & Grésillon, 2008; Kreiter et al., 2002; Snoeks et al., 1995; Vallée et al., 2001), is clarified.

## **2. Atomic transition rate of a degenerate two-level atom in the vicinity of a material body**

To investigate deexcitation of a degenerate two-level atom in the vicinity of a nanoparticle we consider more general problem of deexcitation of the atom in the vicinity of a material body at first.

Our approach to the problem is based on using correlation functions that appear in linear-response theory. It is about the same as used in number of works (Agarwal, 1975a; Wylie & Sipe, 1984) concerning the quantum electrodynamics and life time of a non-degenerate atom near an interface. It is most of all close to approach developed in (Klyshko, 2011).

## 2.1 Transition rate in dipole approximation vs atomic and fluctuating electric field correlation functions

We will assume that both the atom and the electromagnetic field are quantized.

Let the atom and the field be independent at the initial time moment  $t_0$ . Therefore at that instant the quantum state of the system  $|mk_i\rangle$  is equal to  $|m\rangle|k_i\rangle$ , where  $|m\rangle$ ,  $|k_i\rangle$  are the initial states of the atom and field, respectively. In the first order of the perturbation theory, the amplitude  $c_{nk}(t)$  of the transition into some state  $|nk\rangle$  is proportional to the matrix element of the interaction operator  $\hat{V}$ ,  $\langle nk|\hat{V}|mk_i\rangle$ , where  $|n\rangle$ ,  $|k\rangle$  are states of the atom and field at the final time moment  $t$ , respectively. In the dipole approximation,  $\hat{V} = -\hat{d}(t)\hat{E}(t)$ , so,

$$c_{nk} = -\frac{1}{i\hbar} \int_{t_0}^t dt' \langle nk|\hat{d}(t')\hat{E}(t')|mk_i\rangle, \quad (1)$$

where the operators of the atomic dipole moment  $\hat{d}(t)$  and the electric field strength  $\hat{E}(t)$  are considered in the interaction picture, i.e., without the account for the perturbation.

In the rotating-wave approximation (Allen & Eberly, 1975), we have

$$-\hat{V}(t) \approx \hat{d}^{(-)}(t)\hat{E}^{(+)}(t) + \hat{d}^{(+)}(t)\hat{E}^{(-)}(t), \quad (2)$$

where  $\hat{d}^{(+)}$  and  $\hat{E}^{(+)}$  are the positive-frequency parts of the operators, whereas  $\hat{d}^{(-)}$  and  $\hat{E}^{(-)}$  are negative-frequency ones. At  $t - t_0 \equiv T \gg 1/\bar{\omega}$ , fast oscillating (with approximately twice the mean frequency  $\bar{\omega}$ ) products  $\hat{d}^{(+)}\hat{E}^{(+)}$  and  $\hat{d}^{(-)}\hat{E}^{(-)}$  have no contribution into the integral (1).

The initial atomic state  $|m\rangle$  has more high energy than the final atomic state  $|n\rangle$  for the deexcitation process under consideration. That is why only the second term in (2) gives a nonzero contribution for this process. Hence, the probability of the atomic deexcitation is given by

$$P(nk|mk_i) = \frac{1}{\hbar^2} \int_{t_0}^t \int_{t_0}^t dt' dt'' \sum_{\alpha\beta} \langle m|\hat{d}_\alpha^{(-)}(t')|n\rangle \langle n|\hat{d}_\beta^{(+)}(t'')|m\rangle \\ \times \langle k_i|\hat{E}_\alpha^{(+)}(t')|k\rangle \langle k|\hat{E}_\beta^{(-)}(t'')|k_i\rangle, \quad (3)$$

where we have used the equality  $\langle r|\hat{A}^{(+)}|s\rangle = \langle s|\hat{A}^{(-)}|r\rangle^*$  for the matrix element of an operator  $\hat{A}$  between states  $|r\rangle$  and  $|s\rangle$ . We also have used the Greek letters in subscripts for the notation of the Descartes's components of the vector operators.

One should sum the expression (3) over all possible states  $|nk\rangle$  if we are not interested in what specific state the system under consideration has come. These states constitute the complete set and satisfy the completeness condition

$$\sum_{nk} |nk\rangle \langle nk| = \hat{I}. \quad (4)$$

Thus we can represent the total probability of the atomic deexcitation in the following way

$$P = \hbar^{-2} \int_{t_0}^t \int_{t_0}^t dt' dt'' \sum_{\alpha\beta} f_{\alpha\beta}^{(+)}(t', t'') g_{\alpha\beta}^{(-)}(t', t''), \quad (5)$$

where

$$f_{\alpha\beta}^{(+)}(t', t'') \equiv \langle \hat{d}_{\alpha}^{(-)}(t') \hat{d}_{\beta}^{(+)}(t'') \rangle, \quad (6)$$

$$g_{\alpha\beta}^{(-)}(t', t'') \equiv \langle \hat{E}_{\alpha}^{(+)}(t') \hat{E}_{\beta}^{(-)}(t'') \rangle$$

are normally and anti-normally ordered correlation function (CF) of the atomic dipole moment and the electric field strength in an initial state, respectively. The initial state may be pure as well as mixed, of course.

We suppose that initial unperturbed states of both interacting systems are stationary. In this case correlation functions (6) depend only on the difference of their arguments:

$$f_{\alpha\beta}^{(\pm)}(\tau) \equiv f_{\alpha\beta}^{(\pm)}(t, t + \tau) = \langle \hat{d}_{\alpha}^{(\mp)}(0) \hat{d}_{\beta}^{(\pm)}(\tau) \rangle = \left( f_{\beta\alpha}^{(\pm)}(-\tau) \right)^*, \quad (7)$$

$$g_{\alpha\beta}^{(\pm)}(\tau) \equiv g_{\alpha\beta}^{(\pm)}(t, t + \tau) = \langle \hat{E}_{\alpha}^{(\mp)}(0) \hat{E}_{\beta}^{(\pm)}(\tau) \rangle = \left( g_{\beta\alpha}^{(\pm)}(-\tau) \right)^*. \quad (8)$$

Hence, the total probability of the atomic deexcitation (5) becomes

$$P = \hbar^{-2} \int_0^T d\tau (T - \tau) \sum_{\alpha\beta} \left[ f_{\alpha\beta}^{(+)}(\tau) g_{\alpha\beta}^{(-)}(\tau) + (\tau \rightarrow -\tau) \right], \quad (9)$$

where  $T \equiv t - t_0$  is observation time. When it is much more than the atomic and field correlation time, the total probability of the atomic deexcitation (9) becomes proportional to  $T$ . So, atomic transition rate  $W \equiv P/T$  independent on time one may introduce

$$W = \hbar^{-2} \int_{-\infty}^{\infty} d\tau \sum_{\alpha\beta} f_{\alpha\beta}^{(+)}(\tau) g_{\alpha\beta}^{(-)}(\tau), \quad (10)$$

where limits of integration  $\pm T$  are extended to  $\pm\infty$ . It is convenient rewrite (10) in terms of the Fourier components of the correlation functions in the following way

$$W = \left( 1/2\pi\hbar^2 \right) \int_{-\infty}^{\infty} d\omega \sum_{\alpha\beta} f_{\alpha\beta}^{(+)}(\omega) g_{\alpha\beta}^{(-)}(-\omega), \quad (11)$$

where the Fourier transform  $A(\omega)$  of a function  $A(\tau)$  is defined by

$$A(\omega) = \int_{-\infty}^{\infty} d\tau e^{i\omega\tau} A(\tau). \quad (12)$$

## 2.2 Transition rate in terms of electric field susceptibility

It is known that total correlation function is represented as a sum of normally and anti-normally ordered correlation function in the case of stationary process. Indeed, the total correlation function of the electric field strength may be written as

$$\begin{aligned} g_{\alpha\beta}(t, t + \tau) &\equiv \left\langle \left[ \hat{E}_\alpha^{(+)}(t) + \hat{E}_\alpha^{(-)}(t) \right] \left[ \hat{E}_\beta^{(+)}(t + \tau) + \hat{E}_\beta^{(-)}(t + \tau) \right] \right\rangle \\ &= \sum_{s', s = \pm 1} \left\langle \hat{E}_\alpha^{(s')}(t) \hat{E}_\beta^{(s)}(t + \tau) \right\rangle \end{aligned} \quad (13)$$

Expressing  $\hat{E}_\alpha^{(s')}(t)$  and  $\hat{E}_\beta^{(s)}(t + \tau)$  in terms of Fourier transforms, we obtain

$$g_{\alpha\beta}(t, t + \tau) \equiv (2\pi)^{-2} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} d\omega' d\omega e^{-i\omega'\tau} e^{-i(\omega' + \omega)t} \sum_{s', s = \pm 1} \left\langle \hat{E}_\alpha^{(s')}(\omega') \hat{E}_\beta^{(s)}(\omega) \right\rangle. \quad (14)$$

Note, that

$$\hat{E}_\alpha^{(s)}(\omega) \equiv \theta(s\omega) \hat{E}_\alpha(\omega) \quad (15)$$

by definition, where  $\theta(\omega)$  is step function.

It is clear that (14) is independent on  $t$  only when expression in the angle brackets is proportional to Dirac function:

$$\left\langle \hat{E}_\alpha^{(s')}(\omega') \hat{E}_\beta^{(s)}(\omega) \right\rangle \equiv 2\pi g_{\alpha\beta}^{(s)}(\omega) \delta(\omega' + \omega), \quad (16)$$

where spectral density of the normally ordered correlation function  $g_{\alpha\beta}^{(+)}(\omega)$  and anti-normally ordered one  $g_{\alpha\beta}^{(-)}(\omega)$  are introduced respectively. In turn, (16) and (15) imply  $s' = -s$ . Hence, in (14) only two terms are nonzero, and we have

$$g_{\alpha\beta}(\tau) = g_{\alpha\beta}^{(+)}(\tau) + g_{\alpha\beta}^{(-)}(\tau). \quad (17)$$

Note that from (14), (16), and (17) it follows that relationship between  $g_{\alpha\beta}^{(\pm)}(\omega)$  and  $g_{\alpha\beta}^{(\pm)}(\tau)$  is given by the ordinary formula (12). It is clear also that ordered correlation functions  $g_{\alpha\beta}^{(\pm)}(\omega)$  are expressed in terms of the ordinary correlation function  $g_{\alpha\beta}(\omega)$  similar to relation (15):

$$g_{\alpha\beta}^{(\pm)}(\omega) = \theta(\pm\omega) g_{\alpha\beta}(\omega) \quad (18)$$

At thermal equilibrium the correlation function  $g_{\alpha\beta}(\tau)$  is simply related with symmetrized correlation function  $\{g\}_{\alpha\beta}(\tau)$  defined by

$$\{g\}_{\alpha\beta}(\tau) \equiv \frac{1}{2} \left\langle \hat{E}_\alpha(0) \hat{E}_\beta(\tau) + \hat{E}_\beta(\tau) \hat{E}_\alpha(0) \right\rangle = \frac{1}{2} \left\{ g_{\alpha\beta}(\tau) + g_{\beta\alpha}(-\tau) \right\}. \quad (19)$$

There is a simple Kubo-Martin-Schwinger's boundary condition

$$g_{\beta\alpha}(-\tau) = g_{\alpha\beta}(\tau + i\hbar\zeta), \quad (20)$$

where  $\xi \equiv 1/(kT)$ ,  $k$  and  $T$  are Boltzmann's constant and temperature respectively. It is easily proofed by using the invariance of the trace under a cyclic permutation of the operators:

$$\begin{aligned} g_{\beta\alpha}(-\tau) &= \langle \hat{E}_\beta(\tau) \hat{E}_\alpha(0) \rangle \equiv \text{tr} \left\{ \hat{\rho}_0 e^{i\hat{H}\tau/\hbar} \hat{E}_\beta e^{-i\hat{H}\tau/\hbar} \hat{E}_\alpha \right\} \\ &= Z^{-1} \text{tr} \left\{ e^{-\xi\hat{H}} e^{i\hat{H}\tau/\hbar} \hat{E}_\beta e^{-i\hat{H}\tau/\hbar} \hat{E}_\alpha \right\} \\ &= Z^{-1} \text{tr} \left\{ \hat{E}_\alpha e^{i(\xi\tau+\tau/\hbar)\hat{H}} \hat{E}_\beta e^{-i(\xi\tau+\tau/\hbar)\hat{H}} e^{-\xi\hat{H}} \right\} = g_{\alpha\beta}(\tau + i\hbar\xi), \end{aligned} \quad (21)$$

where  $\hat{\rho}_0 = Z^{-1} e^{-\xi\hat{H}}$  is the thermal equilibrium density operator,  $Z = \text{tr} \left\{ e^{-\xi\hat{H}} \right\}$ , and  $\hat{H}$  is unperturbed Hamiltonian of the system.

Using (20), we rewrite relation (19) as follows

$$\{g\}_{\alpha\beta}(\tau) = \frac{1}{2} \left\{ g_{\alpha\beta}(\tau) + g_{\alpha\beta}(\tau + i\hbar\xi) \right\}. \quad (22)$$

In turn, taking the Fourier transform, we obtain

$$\{g\}_{\alpha\beta}(\omega) = \frac{1}{2} \left\{ 1 + e^{\hbar\omega\xi} \right\} g_{\alpha\beta}(\omega). \quad (23)$$

The Fourier transform of symmetrized correlation function  $\{g\}_{\alpha\beta}(\vec{r}, \vec{r}'; \omega)$  is related with dynamical value  $G_{\alpha\beta}(\vec{r}, \vec{r}'; \omega)$ , the Fourier transform of the electric field susceptibility  $G_{\alpha\beta}(\vec{r}, \vec{r}'; \tau)$ , by the fluctuation-dissipation theorem as follows (Bernard & Callen, 1959; Callen et al., 1952; Callen & Welton, 1951; Landau & Lifshitz, 1980)

$$\{g\}_{\alpha\beta}(\vec{r}, \vec{r}'; \omega) = \frac{1}{2} i\hbar \left[ G_{\beta\alpha}^*(\vec{r}', \vec{r}; \omega) - G_{\alpha\beta}(\vec{r}, \vec{r}'; \omega) \right] \coth \left( \frac{\hbar\omega\xi}{2} \right), \quad (24)$$

where tensor  $G_{\alpha\beta}(\vec{r}, \vec{r}'; \omega)$  relates Fourier transforms of the electric dipole  $\hat{d}_\beta(\vec{r}'; \omega)$  and induced electric field  $\hat{E}_\alpha(\vec{r}; \omega)$  as follows

$$\hat{E}_\alpha(\vec{r}; \omega) = \sum_{\beta} G_{\alpha\beta}(\vec{r}, \vec{r}'; \omega) \hat{d}_\beta(\vec{r}'; \omega), \quad (25)$$

and the electric field susceptibility tensor  $G_{\alpha\beta}(\vec{r}, \vec{r}'; \tau)$  is defined by

$$G_{\alpha\beta}(\vec{r}, \vec{r}'; \tau) \equiv \frac{i}{\hbar} \theta(\tau) \left\langle \left[ \hat{E}_\alpha(\tau), \hat{E}_\beta(0) \right] \right\rangle. \quad (26)$$

Note that the same tensor  $G_{\alpha\beta}(\vec{r}, \vec{r}'; \omega)$  relates classical, not quantum, values  $E_\alpha(\vec{r}; \omega)$  and  $d_\beta(\vec{r}'; \omega)$  by the same way (25). So it can be found from the solution of the classical electrodynamic problem in the same condition.

Using (18), (23), and (24), we obtain

$$g_{\alpha\beta}^{(-)}(-\omega) = i\hbar\theta(\omega) \frac{1}{2} \left[ 1 + \coth \left( \frac{\hbar\omega\xi}{2} \right) \right] \left[ G_{\beta\alpha}^*(\vec{r}', \vec{r}; \omega) - G_{\alpha\beta}(\vec{r}, \vec{r}'; \omega) \right], \quad (27)$$

When there is no external magnetic field, tensor  $G_{\alpha\beta}(\vec{r}, \vec{r}'; \omega)$  is symmetrical one, and its imaginary part is odd in  $\omega$ . In this case (27) goes over into (Agarwal, 1975a)<sup>1</sup>

$$g_{\alpha\beta}^{(-)}(-\omega) = \hbar\theta(\omega) \left[ 1 + \coth\left(\frac{\hbar\omega\xi}{2}\right) \right] \Im \left[ G_{\alpha\beta}(\vec{r}', \vec{r}; \omega) \right], \quad (28)$$

We are interesting in only local field response because of point atom approximation used. Substituting (28) in (11) we find

$$W = (1/2\pi\hbar) \int_0^\infty d\omega \sum_{\alpha\beta} f_{\alpha\beta}^{(+)}(\omega) \left[ 1 + \coth\left(\frac{\hbar\omega\xi}{2}\right) \right] \Im \left[ G_{\alpha\beta}(\vec{r}_0, \vec{r}_0; \omega) \right], \quad (29)$$

where  $\vec{r}_0$  is radius vector of the atom.

### 2.3 Transition rate of a degenerate two-level atom

The explicit form of the atomic CF  $f_{\alpha\beta}^{(+)}(\omega)$  depends on the atomic model used. Here we consider a degenerate two-level atom. Its energy levels are degenerate on the total angular momentum projection on any axis. Suppose the excited upper energy level  $m$  and lower one  $n$  have quantum numbers  $J_m M_m$  and  $J_n M_n$  respectively, where  $J_j$  and  $M_j$  label the total angular momentum of the level  $j$  and its projection on the z-axis, respectively.

It is convenient describe vector or tensor values in terms of the circular components instead of the Descartes's one. The circular components  $v_\sigma$  of a vector  $\vec{v}$ , where  $\sigma = 0, \pm 1$ , are related with the Descartes's one  $v_i$  as follows (Varshalovich et al., 1988):

$$\begin{aligned} v_0 &= v_z, \\ v_{\pm 1} &= \mp (v_x \pm i v_y) / \sqrt{2}. \end{aligned} \quad (30)$$

The circular components of the atomic dipole operator can be expressed according to the Wigner-Eckart theorem in terms of the so-called unit irreducible tensor operators  $\hat{T}_Q^K(J_m J_n)$  in the following way (Biedenharn & Louck, 1981; Blum, 1996; Fano & Racah, 1959; Varshalovich et al., 1988):

$$\begin{aligned} \hat{d}_\sigma^{(+)}(t) &= \frac{d_{nm}}{\sqrt{3}} \hat{T}_\sigma^1(J_n J_m) \exp(-i\omega_{mn}t), \\ \hat{d}_\sigma^{(-)}(t) &= \left\{ (-1)^\sigma \hat{d}_{-\sigma}^{(+)}(t) \right\}^\dagger, \end{aligned} \quad (31)$$

where  $d_{mn}$  and  $\omega_{mn}$  are reduced matrix element of the atomic dipole moment and resonant frequency of the atomic transition, respectively. The irreducible tensor operator  $\hat{T}_Q^K(J_m J_n)$ , where  $K$  and  $Q$  are its rank and component ( $-K \leq Q \leq K$ ) correspondingly, is defined as (Biedenharn & Louck, 1981; Blum, 1996; Fano & Racah, 1959; Varshalovich et al., 1988)

$$\hat{T}_Q^K(J_m J_n) = \sum_{M_m, M_n} (-1)^{J_n - M_n} \langle J_m M_m J_n - M_n | K Q \rangle | J_m M_m \rangle \langle J_n M_n |, \quad (32)$$

where  $\langle J_m M_m J_n - M_n | K Q \rangle$  is the vector coupling (Clebsch-Gordan) coefficient. Quantities  $J_m$ ,  $J_n$ , and  $K$  of the coefficient obey triangle inequality, so  $|J_m - J_n| \leq K \leq J_m + J_n$ .

<sup>1</sup> Definition of the ordered correlation functions in this paper differs from ours one by sign of the argument  $\tau$  and, hence in sign of  $\omega$ .

**2.3.1 Properties of irreducible tensor operators and density matrix multipole components**

The operators  $\hat{T}_Q^K(JJ')$  are orthonormal in the following sense

$$\text{tr} \left[ \hat{T}_Q^{K'}(JJ') \hat{T}_Q^{K\dagger}(JJ') \right] \equiv \sum_{M'M} \langle J'M' | \hat{T}_Q^{K'}(JJ') | JM \rangle \langle JM | \hat{T}_Q^{K\dagger}(JJ') | J'M' \rangle = \delta_{K'K} \delta_{Q'Q}, \quad (33)$$

where the Hermitian conjugate operator  $\hat{T}_Q^{K\dagger}(JJ')$  is expressed in terms of  $\hat{T}_Q^K(JJ')$  as follows

$$\hat{T}_Q^{K\dagger}(JJ') \equiv (-1)^{J'-J-Q} \hat{T}_{-Q}^K(JJ'). \quad (34)$$

Set of the operators  $\hat{T}_Q^K(JJ')$  is complete. So, density operator can be decomposed into irreducible parts as follows

$$\hat{\rho} = \sum_{J'JKQ} \rho^{KQ}(JJ') \hat{T}_Q^K(JJ'). \quad (35)$$

In turn, coefficients  $\rho^{KQ}(JJ')$  known as multipole components are expressed in terms of  $\hat{T}_Q^K(JJ')$  and density operator by using (33) and (32) in the following way

$$\rho^{KQ}(JJ') = \text{tr} \left[ \hat{\rho} \hat{T}_Q^{K\dagger}(JJ') \right] = \sum_{M'M} (-1)^{J-M} \langle J'M' | J - M | KQ \rangle \langle J'M' | \hat{\rho} | JM \rangle. \quad (36)$$

It is seen that multipole components  $\rho^{KQ}(JJ')$  satisfy the following relations similar to relations (34):

$$\left[ \rho^{KQ}(JJ') \right]^* = (-1)^{J-J'-Q} \rho^{K-Q}(JJ'), \quad (37)$$

so multipole components  $\rho^{K0}(JJ)$  is real. Note also that  $\rho^{KQ}(JJ')$  transform under rotations like  $\hat{T}_Q^K(JJ')$ , and hence, are contravariant to  $\hat{T}_Q^K(JJ')$  because of property (34).

We are interesting only in states of the excited level  $m$ , so the relevant density operator  $\hat{\rho}(J_m)$  is

$$\hat{\rho}(J_m) = \sum_{KQ} \rho^{KQ}(J_m J_m) \hat{T}_Q^K(J_m J_m). \quad (38)$$

In this decomposition the rank  $K$  is in the range  $0 \leq K \leq 2J_m$  as was noted after definition (32). All multipole components  $\rho^{KQ}(J_m J_m)$  have clear physical sense (see, for example, (Biedenharn & Louck, 1981; Blum, 1996; Omont, 1977; Varshalovich et al., 1988)). In particular,  $\sqrt{2J_m + 1} \rho^{00}(J_m J_m)$  is equal to the total population of the level  $m$ , the  $\rho^{1Q}(J_m J_m)$ 's are the three standard components of what is generally called "orientation" proportional to the mean magnetic dipole of the state, and the  $\rho^{2Q}(J_m J_m)$ 's are the five standard components of the "alignment" proportional to the mean electric quadrupole moment of the state.

**2.3.2 Transition rate and material body symmetry**

Finally, after some manipulation using the relations (7), (31), and (38), and also properties of irreducible tensor operators, one can represent relation (29) in the form

$$W = \frac{1}{2} \left[ 1 + \coth \left( \frac{\hbar\omega_{m\ell}}{2} \right) \right] \sum_{KQ} \gamma_Q^K \rho^{KQ}(J_m J_m), \quad (39)$$



where

$$\gamma_Q^K \equiv 2 \frac{|d_{mn}|^2}{\hbar} (-1)^{J_m+J_n} \left\{ \begin{matrix} 1 & 1 & K \\ J_m & J_m & J_n \end{matrix} \right\} [\mathbf{G}''(\vec{r}_0, \vec{r}_0; \omega_{mn})]_Q^K \tag{40}$$

is irreducible relaxation tensor of the multipole  $\rho^{KQ}(J_m J_m)$ ,  $\left\{ \begin{matrix} 1 & 1 & K \\ J_m & J_m & J_n \end{matrix} \right\}$  is  $6 - j$  coefficient, and  $[\mathbf{G}''(\vec{r}_0, \vec{r}_0; \omega_{mn})]_Q^K$  is irreducible spherical tensor of the imaginary part of the electric field susceptibility in the  $\omega$ -representation. Irreducible spherical tensor  $G_Q^K(\vec{r}_0, \vec{r}_0; \omega_{mn})$  is related with circular components  $G_{\sigma\sigma'}(\vec{r}_0, \vec{r}_0; \omega_{mn})$  as follows

$$G_Q^K(\vec{r}_0, \vec{r}_0; \omega_{mn}) \equiv \sum_{\sigma\sigma'} \langle 1\sigma 1\sigma' | KQ \rangle G_{\sigma\sigma'}(\vec{r}_0, \vec{r}_0; \omega_{mn}). \tag{41}$$

It follows from properties of the Clebsch-Gordan coefficient  $\langle 1\sigma 1\sigma' | KQ \rangle$  that  $0 \leq K \leq 2$ . Furthermore, symmetry of the tensor  $G_{\sigma\sigma'}(\vec{r}_0, \vec{r}_0; \omega_{mn})$  under the interchange  $\sigma \rightleftharpoons \sigma'$  requires that  $K$  have to be even, so  $K = 0, 2$ . In other words, deexcitation rate depends on the total population of excited level ( $K = 0$ ) and its alignment ( $K = 2$ ). Their relative contribution depends according to (39) and (40) on quantum numbers of combining levels  $m$  and  $n$ , on the excitation type determining the value of  $\rho^{KQ}(J_m J_m)$ , and on the atom surroundings by  $G_Q^K(\vec{r}_0, \vec{r}_0; \omega_{mn})$ . Let us consider these factors in more detail.

As was noted after (38),  $K$  is in the range of values defining by  $0 \leq K \leq 2J_m$ . Consequently, if the total momentum  $J_m$  of the the excited level is equal to 0, or  $1/2$ , there is no alignment of the level. So, deexcitation is governed only by  $\gamma_0^0$  and does not depend on excitation type. In the case of  $J_m > 1/2$ , the ratio of two deexcitation rates corresponding to some two fixed excitation types, differing in initial values of  $\rho^{KQ}(J_m J_m)$ , is not universal but depends on  $J_m, J_n$ .

One can diagonalize symmetrical tensor  $G_{\alpha\beta}(\vec{r}_0, \vec{r}_0; \omega_{mn})$ . Let us label its principal axes of coordinate by  $X, Y, Z$ . In this proper basis only the following irreducible components of the tensor  $\mathbf{G}$  are not zero:

$$G_0^0 = -\frac{1}{\sqrt{3}} \text{tr}(\mathbf{G}) = -\frac{1}{\sqrt{3}} (G_{XX} + G_{YY} + G_{ZZ}), \tag{42}$$

$$G_0^2 = \sqrt{\frac{2}{3}} \left[ G_{ZZ} - \frac{1}{2} (G_{XX} + G_{YY}) \right], \tag{43}$$

$$G_{\pm 2}^2 = \frac{1}{2} (G_{XX} - G_{YY}). \tag{44}$$

As is seen from (44), components  $G_{\pm 2}^2 = 0$  if surroundings of the atom is axial symmetric (symmetry axis along  $Z$ ). In particular, this case is realized when atom is near a half-space boundary or near a spherical particle.

When surroundings of the atom is isotropic, the only nonzero component of the tensor  $\mathbf{G}$  is  $G_0^0$  one. It is just the case of an isotropic infinite medium (in particular, vacuum) or when atom is in the center of spherical particle or cavity. In this case  $(-1)^{J_m+J_n} \left\{ \begin{matrix} 1 & 1 & 0 \\ J_m & J_m & J_n \end{matrix} \right\} = -1/\sqrt{3(2J_m+1)}$  in (40). So, using relations (42), (44) we obtain from (39)

$$W_{is} = \frac{2}{3} \frac{|d_{mn}|^2}{\hbar} \Im \left( \sum_{i=X,Y,Z} G_{ii} \right) \sum_{M_m=-J_m}^{J_m} \langle J_m M_m | \hat{\rho} | J_m M_m \rangle. \tag{45}$$

Since we are here interested primarily in atomic transition energies on the order of a Rydberg that implies  $\frac{\hbar\omega_{mn}\xi}{2} \gg 1$  at room temperature, we have replaced the expression in square brackets in Eq. (39) by 2. The total population of the upper level

$$\sum_{M_m=-J_m}^{J_m} \langle J_m M_m | \hat{\rho} | J_m M_m \rangle = 1$$

because we suppose that atom is excited on level  $m$  at the initial time. For free space (Barash, 1988; Lifshitz & Pitaevskii, 1980; Nikolaev, 2006), we have

$$\Im \left( \sum_{i=X,Y,Z} G_{ii} \right) = 2 \left( \frac{\omega_{mn}}{c} \right)^3. \quad (46)$$

Substituting these two expressions in Eq. (45) we immediately obtain the well-known expression for the radiative decay rate of the excited state of an isolated atom (see, i.e., (Berestetskii et al., 2008; Sobelman, 1972)):

$$W_0 = \frac{4}{3} \frac{|d_{mn}|^2}{\hbar (2J_m + 1)} \left( \frac{\omega_{mn}}{c} \right)^3. \quad (47)$$

It should be noted that Eq. (39) describes deexcitation rate at the initial time moment just following the excitation. Density matrix multipole components  $\rho^{KQ}(J_m J_m)$  will be changed with the passage of time. It is reasonable to suggest that the expression opposite in sign to the right-hand side of Eq. (39) describes the decrease of the upper level population per unit of time. To prove the suggestion let us consider more general problem of the dynamics of the density matrix multipole components caused by interaction of the atom with quantized field.

### 3. Master equations for the excited density matrix multipole components

#### 3.1 Integro-differential equation for total density matrix operator

Let us consider a large isolated system consisting of an atom, material body and interacting with them quantum electromagnetic field. Atomic surrounding, electromagnetic field and material body that interact among themselves, we will treat as a large subsystem referred to as the thermostat. In the interaction picture representation, the density matrix  $\hat{R}$  of the total isolated system obeys the Liouville equation:

$$i\hbar \frac{d\hat{R}(t)}{dt} = [\hat{V}(t), \hat{R}(t)], \quad (48)$$

where  $\hat{V}$  is the atom-field interaction operator that in the rotating-wave approximation is given by Eq. (2). It is known that this equation can be rewritten in the integro-differential form that is suitable for perturbation technique. Indeed, formal integrating this equation in time, we obtain the integral equation:

$$\hat{R}(t) = \hat{R}(0) - (i/\hbar) \int_0^t dt' [\hat{V}(t'), \hat{R}(t')]. \quad (49)$$

Substituting this expression into Eq. (48), we get the equation for the total density matrix operator in the following form:

$$\frac{d\hat{R}(t)}{dt} = (-i/\hbar) [\hat{V}(t), \hat{R}(0)] + (-i/\hbar)^2 \int_0^t dt' [\hat{V}(t), [\hat{V}(t'), \hat{R}(t')]]. \quad (50)$$

In Eqs. (49) and (50) the lower limit we took 0 since it is assumed that the thermostat and the atom did not interact before this time moment because the atom was unexcited. Consequently, until this moment the thermostat and the atom were uncorrelated, so the total density matrix  $\hat{R}$  was equal to the direct product of the density matrices of the system:

$$\hat{R}(0) = \hat{\rho}(0)\hat{\rho}_{th}(0), \quad (51)$$

where  $\hat{\rho}$  and  $\hat{\rho}_{th}$  are the density matrix operator of the atom and thermostat, respectively.

### 3.2 Large thermostat approximation

Following the paper (Fano & Racah, 1959) (see also (Blum, 1996)), we will suppose that thermostat is always in the state of the thermal equilibrium because it has a large number of degrees of freedom and, hence, atom almost do not changes its state. The supposition implies that the total density matrix is always equal to the direct product of the density matrices of the system:

$$\hat{R}(t) = \hat{\rho}(t)\hat{\rho}_{th}(0) \quad (52)$$

This relation is referred to as the main condition of the irreversibility.

Substituting (52) in (50) and taking trace over thermostat variables, we get the equation for the reduced atomic density matrix operator,  $\hat{\rho}(t) \equiv \text{tr}_{th}\hat{R}(t)$ ,

$$\frac{d\hat{\rho}(t)}{dt} = -(i/\hbar)\text{tr}_{th} [\hat{V}(t), \hat{\rho}(0)\hat{\rho}_{th}(0)] - (1/\hbar)^2 \int_0^t dt' \text{tr}_{th} [\hat{V}(t), [\hat{V}(t'), \hat{\rho}(t')\hat{\rho}_{th}(0)]] \quad (53)$$

### 3.3 Integro-differential equation for atomic multipole components

To obtain dynamics equation for atomic multipole components, we make use of relation (36). Precisely, let us multiply both sides of (53) by  $\hat{T}_Q^{K\dagger}(J_m J_m)$  and take trace over atomic variable. So, we get

$$\begin{aligned} \frac{d\rho^{KQ}(J_m J_m)(t)}{dt} = & -(i/\hbar)\text{tr}_{all} \left\{ \hat{T}_Q^{K\dagger}(J_m J_m) [\hat{V}(t), \hat{\rho}(0)\hat{\rho}_{th}(0)] \right\} \\ & - (1/\hbar)^2 \int_0^t dt' \text{tr}_{all} \left\{ \hat{T}_Q^{K\dagger}(J_m J_m) [\hat{V}(t), [\hat{V}(t'), \hat{\rho}(t')\hat{\rho}_{th}(0)]] \right\}, \quad (54) \end{aligned}$$

where  $\text{tr}_{all}$  stands for the trace over all isolated system variables including atomic and thermostat one.

We will now transform this equation in such a way that terms include the trace of the product of  $\hat{\rho}(t')\hat{\rho}_{th}(0)$  by an operator.

To do this, we make use of the identity (Il'inskii & Keldysh, 1994)

$$\text{tr} \{ \hat{A} [ \hat{A}_1, [ \hat{A}_2, \dots [ \hat{A}_k, \hat{B} ] \dots ] ] \} = \text{tr} \{ [ \dots [ [ \hat{A}, \hat{A}_1 ], \hat{A}_2 ] \dots \hat{A}_k ] \hat{B} \} \quad (55)$$

which holds for arbitrary operators  $\hat{A}, \hat{A}_1, \hat{A}_2, \dots, \hat{B}$ .

Using identity (55) and the atomic density matrix decomposition (35), we can rewrite (54) as

$$\begin{aligned} \frac{d\rho^{KQ}(J_m J_m; t)}{dt} &= -\frac{i}{\hbar} \sum_{J'JK'Q'} \rho^{K'Q'}(J'J; 0) \text{tr}_{all} \left\{ \left[ \hat{T}_Q^{K\dagger}(J_m J_m), \hat{V}(t) \right] \hat{T}_{Q'}^{K'}(J'J) \hat{\rho}_{th}(0) \right\} \\ &\quad - \frac{1}{\hbar^2} \sum_{J'JK'Q'} \int_0^t dt' \rho^{K'Q'}(J'J; t') \text{tr}_{all} \left\{ \left[ \left[ \hat{T}_Q^{K\dagger}(J_m J_m), \hat{V}(t) \right], \hat{V}(t') \right] \hat{T}_{Q'}^{K'}(J'J) \hat{\rho}_{th}(0) \right\}. \end{aligned} \quad (56)$$

Substituting in (56) the interaction Hamiltonian (2), using (31), and also taking into account that scalar product  $\vec{d}\vec{E}$  in the circular basis (30) has the form  $\sum_{\sigma} (-1)^{\sigma} d_{\sigma} E_{-\sigma}$ , we obtain

$$\begin{aligned} \frac{d\rho^{KQ}(J_m J_m; t)}{dt} &= -\frac{d_{mn}d_{nm}}{3\hbar^2} \sum_{J'JK'Q'} \int_0^t dt' \rho^{K'Q'}(J'J; t') \sum_{\alpha\beta} \left\{ e^{i\omega_{mn}(t-t')} \left[ g_{\alpha\beta}^{(-)}(t-t) A_{\alpha\beta} \right. \right. \\ &\quad \left. \left. - g_{\alpha\beta}^{(+)}(t-t') B_{\alpha\beta} \right] + e^{-i\omega_{mn}(t-t')} \left[ g_{\alpha\beta}^{(-)}(t-t') C_{\alpha\beta} - g_{\alpha\beta}^{(+)}(t-t) B_{\alpha\beta} \right] \right\}, \end{aligned} \quad (57)$$

where  $g_{\alpha\beta}^{(\pm)}(\tau)$  are the ordered correlation functions of the fluctuating electromagnetic field (8),

$$A_{\alpha\beta} \equiv \sum_{\sigma\sigma'} (-1)^{\sigma+\sigma'} \langle \alpha | 1 - \sigma \rangle \langle \beta | 1 - \sigma' \rangle \text{tr} \left\{ \hat{T}_Q^{K\dagger}(J_m J_m) \hat{T}_{\sigma}^1(J_m J_n) \hat{T}_{\sigma'}^1(J_n J_m) \hat{T}_{Q'}^{K'}(JJ') \right\}, \quad (58)$$

$$B_{\alpha\beta} \equiv \sum_{\sigma\sigma'} (-1)^{\sigma+\sigma'} \langle \alpha | 1 - \sigma \rangle \langle \beta | 1 - \sigma' \rangle \text{tr} \left\{ \hat{T}_{\sigma}^1(J_n J_m) \hat{T}_Q^{K\dagger}(J_m J_m) \hat{T}_{\sigma'}^1(J_m J_n) \hat{T}_{Q'}^{K'}(JJ') \right\}, \quad (59)$$

$$C_{\alpha\beta} \equiv \sum_{\sigma\sigma'} (-1)^{\sigma+\sigma'} \langle \alpha | 1 - \sigma \rangle \langle \beta | 1 - \sigma' \rangle \text{tr} \left\{ \hat{T}_{\sigma}^1(J_m J_n) \hat{T}_{\sigma'}^1(J_n J_m) \hat{T}_Q^{K\dagger}(J_m J_m) \hat{T}_{Q'}^{K'}(JJ') \right\}. \quad (60)$$

In the definitions (58) – (60) symbols  $\langle \alpha | 1 - \sigma \rangle$  and  $\langle \beta | 1 - \sigma' \rangle$  are transformation matrices from the circular components to the Descartes's one, that are inverse of that given by (30), and symbol  $\text{tr} \{ \dots \}$  from now on stands for trace over atomic variables. Note that the linear on  $\hat{V}(t)$  term in (56) vanishes in our case because of the average fluctuated field is zero at the thermal equilibrium:  $\text{tr}_{th} \{ \hat{E}_{\alpha} \} \equiv \langle \hat{E}_{\alpha} \rangle = 0$ .

It should be noted that ratio of  $|g_{\alpha\beta}^{(+)}(t-t')|$  to  $|g_{\alpha\beta}^{(-)}(t-t')|$  is proportional to the mean number of photons in the thermal equilibrium,  $\langle n_{ph} \rangle \sim kT/\hbar\omega_{mn} \ll 1$ . Therefore terms that proportional to  $g_{\alpha\beta}^{(+)}(t-t')$  can be ignored in (57).

### 3.4 Master equation for multipole components in Markov-type approximation

Fluctuating field correlation functions  $g_{\alpha\beta}^{(\pm)}(t-t')$  are nonzero only for the sufficiently small time difference  $|\tau| \equiv |t-t'|$  comparable with the typical field correlation time  $\tau_c$ . We will

assume following (Loisell, 1973) that this correlation time is much less than typical variation times of the atomic multipole components. Thus, in the case of free space the lifetime of the atomic excited state much more than  $\tau_c \approx 1/\omega_{mn}$ . So, we can replace  $\rho^{K'Q'}(J'J;t')$  by  $\rho^{K'Q'}(J'J;t)$  and to take it out of the integral in (57). It is so-called Markov-type approximation.

It is also important to note that  $\hat{T}_{Q'}^{K'}(JJ')$  incoming in (58) and (60) are nonzero only if  $J = J' = J_m$  because of its definition (32) and invariance of the trace under a cyclic permutation of the operators.

Taking into account assumptions mentioned above, property (8), and by making the change of variable  $\tau \equiv t - t'$  in integration, we can represent (57) as

$$\frac{d\rho^{KQ}(J_m J_m; t)}{dt} = -\frac{d_{mnn}d_{mm}}{3\hbar^2} \sum_{K'Q'} \sum_{\alpha\beta} \left[ I_{\beta\alpha}^*(\omega_{mn}) A_{\alpha\beta} + I_{\alpha\beta}(\omega_{mn}) C_{\alpha\beta} \right] \rho^{K'Q'}(J_m J_m; t), \quad (61)$$

where

$$I_{\alpha\beta}(\omega_{mn}) \equiv \int_0^\infty d\tau g_{\alpha\beta}^{(-)}(\tau) e^{-i\omega_{mn}\tau}. \quad (62)$$

In (62) we extended upper limit from  $t$  to  $\infty$  because of  $g_{\alpha\beta}^{(\pm)}(\tau)$  is in fact zero at  $\tau \gg \tau_c$ . The error of this replacement is negligible in Markov-type approximation.

Now we will show that integral (62) is expressed in terms of retarded Green function  $G_{\alpha\beta}(\vec{r}, \vec{r}'; \omega_{mn})$ . To prove that, let us consider Fourier transform  $g_{\alpha\beta}^{(-)}(-\omega_{mn})$  of the function  $g_{\alpha\beta}^{(-)}(\tau)$  defined by (12):

$$g_{\alpha\beta}^{(-)}(-\omega_{mn}) = \int_{-\infty}^\infty d\tau g_{\alpha\beta}^{(-)}(\tau) e^{-i\omega_{mn}\tau} \quad (63)$$

Let us split this integral into two parts

$$g_{\alpha\beta}^{(-)}(-\omega_{mn}) = \int_{-\infty}^0 d\tau g_{\alpha\beta}^{(-)}(\tau) e^{-i\omega_{mn}\tau} + \int_0^\infty d\tau g_{\alpha\beta}^{(-)}(\tau) e^{-i\omega_{mn}\tau}. \quad (64)$$

Making the change of variable in integration  $\tau \rightarrow -\tau$  in the first integral and utilizing relation (8), we can rewrite (64) as

$$g_{\alpha\beta}^{(-)}(-\omega_{mn}) = \int_0^\infty d\tau (g_{\beta\alpha}^{(-)}(\tau))^* e^{i\omega_{mn}\tau} + \int_0^\infty d\tau g_{\alpha\beta}^{(-)}(\tau) e^{-i\omega_{mn}\tau}. \quad (65)$$

The second integral in (65) is just equal to  $I_{\alpha\beta}(\omega_{mn})$ , and the first one to its complex conjugation. So, (65) can be rewritten as follows

$$g_{\alpha\beta}^{(-)}(-\omega_{mn}) = I_{\alpha\beta}(\omega_{mn}) + I_{\beta\alpha}^*(\omega_{mn}). \quad (66)$$

Now comparing right-hand sides of (66) and (27), we obtain desired relation

$$I_{\alpha\beta}(\omega_{mn}) = -i\hbar \frac{1}{2} \left[ 1 + \coth \left( \frac{\hbar\omega_{mn}}{2kT} \right) \right] G_{\alpha\beta}(\vec{r}, \vec{r}'; \omega_{mn}) \tag{67}$$

It is yet mentioned after (37) that multipole components  $\rho^{KQ}(J'J)$  transform under rotations contravariant to  $\hat{T}_Q^K(J'J)$ . It is convenient to introduce co-variant multipole components  $\rho_Q^K(J'J)$  by convention

$$\rho_Q^K(J'J) \equiv (-1)^{J-J'-Q} \rho^{K-Q}(JJ') = [\rho^{KQ}(J'J)]^* \tag{68}$$

In these notations, making use of (67) and explicitly calculating traces in (58) and (60), one can finally represent (61) as follows<sup>2</sup>

$$\frac{d\rho_Q^K(t)}{dt} = -\gamma_0 \sum_{K'Q'} \Gamma_{QQ'}^{KK'} \rho_{Q'}^{K'}(t), \tag{69}$$

where

$$\gamma_0 = W_0 = \frac{4}{3} \frac{|d_{mn}|^2}{\hbar (2J_m + 1)} \left( \frac{\omega_{mn}}{c} \right)^3 \tag{70}$$

is radiation decay rate of the excited degenerate state of the atom in vacuum, dimensionless relaxation tensor  $\Gamma_{QQ'}^{KK'}$  can be represented as follows:

$$\Gamma_{QQ'}^{KK'} = \gamma_{QQ'}^{KK'} + i\Delta_{QQ'}^{KK'}, \tag{71}$$

where  $\gamma_{QQ'}^{KK'}$  and  $\Delta_{QQ'}^{KK'}$  are in general complex.

Geometrical part of  $\gamma_{QQ'}^{KK'}$  and  $\Delta_{QQ'}^{KK'}$  is represented by Clebsch-Gordan coefficient and dynamical one is proportional to retarded Green function:

$$\gamma_{QQ'}^{KK'} = \sum_{LM} \langle K'Q'LM|KQ \rangle \bar{G}_M^L(KK'L) \gamma(KK'L, J_m J_n), \tag{72}$$

$$\Delta_{QQ'}^{KK'} = \sum_{LM} \langle K'Q'LM|KQ \rangle \tilde{G}_M^L(KK'L) \gamma(KK'L, J_m J_n), \tag{73}$$

where scalar coefficient  $\gamma(KK'L, J_m J_n)$  and irreducible tensors  $\bar{G}_M^L(KK'L)$  and  $\tilde{G}_M^L(KK'L)$  are

$$\begin{aligned} \gamma(KK'L, J_m J_n) &= (-1)^{K+J_n-J_m} \frac{3}{2} (2J_m + 1) \sqrt{(2K' + 1)(2L + 1)} \\ &\times \left\{ \begin{matrix} K & K' & L \\ J_m & J_m & J_m \end{matrix} \right\} \left\{ \begin{matrix} 1 & 1 & L \\ J_m & J_m & J_n \end{matrix} \right\}, \end{aligned} \tag{74}$$

$$\bar{G}_M^L(KK'L) = \sum_{\alpha\beta\sigma\sigma'} \langle 1\sigma 1\sigma'|LM \rangle \langle 1\sigma|\alpha \rangle \langle 1\sigma'|\beta \rangle \bar{G}_{\alpha\beta}(KK'L), \tag{75}$$

$$\tilde{G}_M^L(KK'L) = \sum_{\alpha\beta\sigma\sigma'} \langle 1\sigma 1\sigma'|LM \rangle \langle 1\sigma|\alpha \rangle \langle 1\sigma'|\beta \rangle \tilde{G}_{\alpha\beta}(KK'L), \tag{76}$$

<sup>2</sup> hereinafter for simplicity we omit the dependence of  $\rho_Q^K$  on  $J_m$ :  $\rho_Q^K(t) \equiv \rho_Q^K(J_m J_m; t)$

and

$$\bar{G}_{\alpha\beta}(KK'L) = \frac{1}{2} \left[ G''_{\beta\alpha}(\omega_{mn}) + (-1)^{K+K'-L} G''_{\alpha\beta}(\omega_{mn}) \right] / \left( \frac{\omega_{mn}}{c} \right)^3, \quad (77)$$

$$\tilde{G}_{\alpha\beta}(KK'L) = \frac{1}{2} \left[ G'_{\beta\alpha}(\omega_{mn}) - (-1)^{K+K'-L} G'_{\alpha\beta}(\omega_{mn}) \right] / \left( \frac{\omega_{mn}}{c} \right)^3. \quad (78)$$

Symbol  $G'$  and  $G''$  in (77) and (78) denotes real and imaginary part of  $G$ , respectively, and symbols  $\langle 1\sigma|\alpha\rangle$  and  $\langle 1\sigma'|\beta\rangle$  are transformation matrices from the Descartes's components to the circular one, that given by (30).

### 3.4.1 Relaxation matrix symmetry

Note that  $\bar{G}_{\alpha\beta}(KK'L)$  and  $\tilde{G}_{\alpha\beta}(KK'L)$ , and consequently,  $\bar{G}_M^L(KK'L)$  and  $\tilde{G}_M^L(KK'L)$ , are symmetrical with respect to  $K$  and  $K'$ . As for the scalar  $\gamma(KK'L, J_m J_n)$ , it changes upon permutation of  $K$  and  $K'$  as follows

$$\gamma(KK'L, J_m J_n) = (-1)^{K-K'} \sqrt{\frac{2K'+1}{2K+1}} \gamma(K'KL, J_m J_n) \quad (79)$$

because of invariance of  $6-j$  symbol as regard to permutation of its columns.

Although tensor  $G_{\alpha\beta}$  in general has no symmetry with respect to permutation of subscripts, tensors  $\bar{G}_{\alpha\beta}(KK'L)$  and  $\tilde{G}_{\alpha\beta}(KK'L)$  have one, as one can see from (77) and (78),

$$\bar{G}_{\alpha\beta}(KK'L) = (-1)^{K+K'-L} \bar{G}_{\beta\alpha}(KK'L), \quad (80)$$

$$\tilde{G}_{\alpha\beta}(KK'L) = -(-1)^{K+K'-L} \tilde{G}_{\beta\alpha}(KK'L). \quad (81)$$

Irreducible tensors  $\bar{G}_M^L(KK'L)$  and  $\tilde{G}_M^L(KK'L)$  in general are complex. Using relation  $\langle 1\sigma|\alpha\rangle^* = (-1)^\sigma \langle 1-\sigma|\alpha\rangle$  and Clebsch-Gordan coefficients symmetry, one can show that

$$\left[ \bar{G}_M^L(KK'L) \right]^* = (-1)^{L+M} \bar{G}_{-M}^L(KK'L), \quad (82)$$

$$\left[ \tilde{G}_M^L(KK'L) \right]^* = (-1)^{L+M} \tilde{G}_{-M}^L(KK'L). \quad (83)$$

This relations allow to find the following symmetry of the relaxation matrix components

$$\left[ \gamma_{QQ'}^{KK'} \right]^* = (-1)^{K'-K+Q-Q'} \gamma_{-Q-Q'}^{KK'}, \quad (84)$$

$$\left[ \Delta_{QQ'}^{KK'} \right]^* = (-1)^{K'-K+Q-Q'} \Delta_{-Q-Q'}^{KK'}. \quad (85)$$

On the other hand, from hermiticity of density matrix and equation (69) it is easy to obtain

$$\left[ \Gamma_{QQ'}^{KK'} \right]^* = (-1)^{Q-Q'} \Gamma_{-Q-Q'}^{KK'}, \quad (86)$$

that can be rewrite in terms of  $\gamma_{QQ'}^{KK'}$  and  $\Delta_{QQ'}^{KK'}$  as follows

$$\left[ \gamma_{QQ'}^{KK'} \right]^* = (-1)^{Q-Q'} \gamma_{-Q-Q'}^{KK'}, \quad (87)$$

$$\left[ \Delta_{QQ'}^{KK'} \right]^* = -(-1)^{Q-Q'} \Delta_{-Q-Q'}^{KK'}. \quad (88)$$

Comparing (84) and (87) shows that  $\gamma_{QQ'}^{KK'}$  is different from zero only for even  $K + K'$ . Similarly, comparing (85) and (88) shows that  $\Delta_{QQ'}^{KK'}$  is different from zero only for odd  $K + K'$ .

These properties can be found more straightforward from symmetries (80) and (81) and definitions (75) and (76) that yield

$$\bar{G}_M^L(KK'L) = (-1)^{K+K'} \bar{G}_M^L(KK'L), \tag{89}$$

$$\tilde{G}_M^L(KK'L) = (-1)^{K+K'+1} \tilde{G}_M^L(KK'L). \tag{90}$$

Taking into account these properties that we can reformulate as  $K + K'$  is even for  $\bar{G}_{\alpha\beta}(KK'L)$  and odd for  $\tilde{G}_{\alpha\beta}(KK'L)$ , one can see from (80) and (81) that part of  $G_{\alpha\beta}$  which is symmetrical with respect to permutation of subscripts makes a contribution to  $\bar{G}_{\alpha\beta}(KK'L)$  and to  $\tilde{G}_{\alpha\beta}(KK'L)$ , and hence to  $\Gamma_{QQ'}^{KK'}$ , only when  $L$  is even. As for antisymmetrical part of  $G_{\alpha\beta}$ , it contributes to  $\Gamma_{QQ'}^{KK'}$  only when  $L$  is odd.

When tensor  $G_{\alpha\beta}$  is symmetrical (i.e., no external magnetic field), the form of tensor  $\bar{G}_{\alpha\beta}(KK'L)$  as well of tensor  $\tilde{G}_{\alpha\beta}(KK'L)$  is simplified

$$\bar{G}_{\alpha\beta}(KK'L) = \delta_{L,2l} \delta_{K+K',2n} \left(\frac{c}{\omega_{mn}}\right)^3 G''_{\alpha\beta}, \tag{91}$$

$$\tilde{G}_{\alpha\beta}(KK'L) = \delta_{L,2l} \delta_{K+K',2n+1} \left(\frac{c}{\omega_{mn}}\right)^3 G'_{\alpha\beta}, \tag{92}$$

where  $n$  and  $l$  are integer. As a consequence,  $\bar{G}_M^L(KK'L)$  and  $\tilde{G}_M^L(KK'L)$  are also simplified

$$\bar{G}_M^L(KK'L) = \delta_{L,2l} \delta_{K+K',2n} \left(\frac{c}{\omega_{mn}}\right)^3 [G'']_M^L, \tag{93}$$

$$\tilde{G}_M^L(KK'L) = \delta_{L,2l} \delta_{K+K',2n+1} \left(\frac{c}{\omega_{mn}}\right)^3 [G']_M^L. \tag{94}$$

As stated above (see Eqs. (42) - (44)), in this case there are only four nonzero components of  $G_M^L$  in the proper coordinate system.

There is additional symmetry of the relaxation tensor  $\Gamma_{QQ'}^{KK'}$  in the case. Using the fact that  $\bar{G}_M^L(KK'L)$  and  $\tilde{G}_M^L(KK'L)$  are symmetrical with respect to  $K$  and  $K'$ , evenness of  $L$ , relation (79) and also Clebsch-Gordan coefficient symmetry  $\langle K'Q'LM|KQ\rangle = (-1)^{L+M} \sqrt{\frac{2K+1}{2K'+1}} \langle K - QLM|K' - Q'\rangle$ , one can obtain

$$\Gamma_{QQ'}^{KK'} = (-1)^{K-K'+Q-Q'} \Gamma_{-Q'-Q}^{K'K} \tag{95}$$

that we can rewrite using (86) as follows

$$\Gamma_{QQ'}^{KK'} = (-1)^{K-K'} \left[ \Gamma_{Q'Q}^{K'K} \right]^*. \tag{96}$$

This is just the symmetry of  $\Gamma_{QQ'}^{KK'}$  relative to time reversal (Omont, 1977) that is natural in the absence of magnetic field.



In case of the atomic surroundings is axial symmetrical in addition, there are only two nonzero components of  $G_M^L$  in the proper coordinate system,  $G_0^0$  and  $G_0^2$ . Therefor, only irreducible tensors  $\bar{G}_0^L(KK'L)$  and  $\tilde{G}_0^L(KK'L)$  are nonzero and real in the system (see relations (82) and (83), and (93) and (94)). Consequently, only  $\gamma_{QQ}^{KK'}$  and  $\Delta_{QQ}^{KK'}$  are also nonzero and real (see relations (72 and (73)), hence,

$$\Gamma_{QQ}^{KK'} = \delta_{Q,Q'} \Gamma_{QQ}^{KK'}. \quad (97)$$

So, in this case  $\Gamma_{QQ}^{KK'}$  is real for even  $K + K'$ , imaginary for odd  $K + K'$  and

$$\Gamma_{00}^{KK'} = 0 \quad (98)$$

for odd  $K + K'$  because of the following Clebsch-Gordan coefficient symmetry

$$\langle K'0L0|K0 \rangle = (-1)^{K'+L-K} \langle K'0L0|K0 \rangle. \quad (99)$$

#### 4. Deexcitation dynamics

Deexcitation of upper level is given by (69) with  $K = Q = 0$

$$\frac{d\rho_0^0(t)}{dt} = -\gamma_0 \sum_{K'Q'} \Gamma_{0Q'}^{0K'} \rho_{Q'}^{K'}(t). \quad (100)$$

Hereinafter we suppose that there is no external magnetic field. In this case  $\gamma_0 \Gamma_{0Q'}^{0K'} = (-1)^{Q'} \gamma_{-Q'}^{K'} / \sqrt{2J_m + 1}$ , where  $\gamma_{-Q'}^{K'}$  is defined by (40), multiplier  $(-1)^{Q'}$  transforms covariant component  $\rho_{Q'}^{K'}$  into contravariant one  $\rho^{K'-Q'}$  and denominator  $\sqrt{2J_m + 1}$  reflect the fact that the right-hand side of (100) is variation in time of  $\rho_0^0$ , not of population that is  $\sqrt{2J_m + 1} \rho_0^0$  as in (39). To obtain temporal variation of the deexcitation, it is necessary to solve consistent differential equations, involving along with Eq. (100) also differential equations for  $\rho_{Q'}^{K'}(t)$ , incoming in its right-hand side.

Let us restrict themselves to the case of axial symmetrical atomic surroundings.

As it mentioned above, this case include half-space boundary and spherical particle. From (97), (98), (100), and also (99), it is follows that consistent differential equations, describing deexcitation dynamics in the proper coordinate system, include only multipole components with even  $K$  and  $Q = 0$ . The number of such components is  $[J_m] + 1$  because of  $0 \leq K \leq 2J_m$  as noted above (symbol  $[J_m]$  here and further denotes the integer part of  $J_m$ ). As the relevant  $\Gamma_{00}^{KK'}$  are real in our case, from (96) we obtain that they are symmetrical relative to  $K$  and  $K'$

$$\Gamma_{00}^{KK'} = \Gamma_{00}^{K'K}. \quad (101)$$

Hence, the number of different relevant components  $\Gamma_{00}^{KK'}$  is  $([J_m] + 1) \times ([J_m] + 2) / 2$ .

As is known, the general solution of  $[J_m] + 1$  consistent linear homogeneous differential equations is given by a linear combination of  $[J_m] + 1$  their eigen vectors, each of them varies in time exponentially with its own rate. The rates are eigen values of the consistent equations. The number of the eigen values is also in general equal to  $[J_m] + 1$ . So, the atomic deexcitation is also usually expressed as a linear sum of  $[J_m] + 1$  exponentials.

In fact, the eigenvalues are relaxation rates of populations of magnetic sublevels  $|J_m \pm M\rangle$  in the case under consideration. Indeed, relevant multipole components  $\rho_0^K$  incoming in the consistent differential equations, describing deexcitation dynamics, are linear combination of the populations of the sublevels  $|J_m M\rangle$  (see (36)). In addition, the sublevels  $|J_m M\rangle$  and  $|J_m - M\rangle$  are transformed one into another (with the sign  $(-1)^P$ , where  $P$  is parity of the level  $m$ ) under reflection in any plane through the symmetry axis (Landau & Lifshitz, 1977). Consequently, the relaxation rates of these sublevels are equal. So, the number of different relaxation rates is  $[J_m] + 1$  as stated above with respect to the eigenvalues.

#### 4.1 Deexcitation dynamics in the case of $J_m = 1, J_n = 0$

Let us consider in more detail the case when the angular momentums are  $J_m = 1$  and  $J_n = 0$ . In the case under study, deexcitation dynamics is described by only two equations

$$\frac{d\rho_0^0(t)}{dt} = -\gamma_0 \left[ \Gamma_{00}^{00} \rho_0^0(t) + \Gamma_{00}^{02} \rho_0^2(t) \right], \quad (102)$$

$$\frac{d\rho_0^2(t)}{dt} = -\gamma_0 \left[ \Gamma_{00}^{02} \rho_0^0(t) + \Gamma_{00}^{22} \rho_0^2(t) \right]. \quad (103)$$

The eigen values  $\gamma_{\pm}$  of the consistent equations are

$$\gamma_{\pm} = \gamma_0 [\Gamma_{+} \pm \Gamma], \quad (104)$$

and fundamental solution matrix are

$$S(t) = \frac{1}{2} \begin{pmatrix} \left(1 - \frac{\Gamma_-}{\Gamma}\right) e^{-\gamma_- t} + \left(1 + \frac{\Gamma_-}{\Gamma}\right) e^{-\gamma_+ t} & \frac{\Gamma_{00}^{02}}{\Gamma} (-e^{-\gamma_- t} + e^{-\gamma_+ t}) \\ \frac{\Gamma_{00}^{02}}{\Gamma} (-e^{-\gamma_- t} + e^{-\gamma_+ t}) & \left(1 + \frac{\Gamma_-}{\Gamma}\right) e^{-\gamma_- t} + \left(1 - \frac{\Gamma_-}{\Gamma}\right) e^{-\gamma_+ t} \end{pmatrix}, \quad (105)$$

where dimensionless  $\Gamma_{\pm}$  and  $\Gamma$  are defined as

$$\Gamma_{\pm} = \frac{1}{2} \left( \Gamma_{00}^{00} \pm \Gamma_{00}^{22} \right), \quad (106)$$

$$\Gamma = \sqrt{(\Gamma_-)^2 + (\Gamma_{00}^{02})^2}. \quad (107)$$

Specific solution column of the consistent equations (102)-(103), corresponding to initial conditions given by column  $c = \text{col}(\rho_0^0(0), \rho_0^2(0))$ , is obtained by multiplication of fundamental solution matrix on the right by column  $c$ .

It is known that the excited atomic states that are produced by the absorption of anisotropic resonance light are strongly polarized (Alexandrov et al., 1993; Happer, 1972; Omont, 1977). This atomic polarization results from the directionality or polarization of the light beam. So, immediately after excitation there are nonzero both  $\rho_0^0(0)$  and  $\rho_0^2(0)$ .

However, let us consider the simplest case of isotropic excitation, when there is only population  $\rho_0^0(0)$  on the upper level at the instant after excitation. So, the solution column

in the case is given by

$$\begin{pmatrix} \rho_0^0(t) \\ \rho_0^2(t) \end{pmatrix} = \frac{1}{2} \begin{pmatrix} \left(1 - \frac{\Gamma_-}{\Gamma}\right) e^{-\gamma-t} + \left(1 + \frac{\Gamma_-}{\Gamma}\right) e^{-\gamma+t} \\ \frac{\Gamma_{00}^{02}}{\Gamma} (-e^{-\gamma-t} + e^{-\gamma+t}) \end{pmatrix} \rho_0^0(0). \quad (108)$$

In the case under consideration that is  $J_m = 1, J_n = 0$ , dimensionless relaxation matrix elements are following:  $\Gamma_{00}^{00} = (1/2)(c/\omega_{mn})^3 \text{tr}(\mathbf{G}'')$ ,  $\Gamma_{00}^{02} = -(\sqrt{2}/2)(c/\omega_{mn})^3 (G''_{ZZ} - G''_{XX})$ ,  $\Gamma_{00}^{22} = \Gamma_{00}^{00} - \Gamma_{00}^{02}/\sqrt{2}$ . So, relevant dimensionless  $\Gamma_{\pm}$  and  $\Gamma$  are

$$\Gamma_+ = \frac{3}{4} \left(\frac{c}{\omega_{mn}}\right)^3 (G''_{ZZ} + G''_{XX}), \quad (109)$$

$$\Gamma_- = -\frac{1}{4} \left(\frac{c}{\omega_{mn}}\right)^3 (G''_{ZZ} - G''_{XX}), \quad (110)$$

$$\Gamma = \frac{3}{4} \left(\frac{c}{\omega_{mn}}\right)^3 (G''_{ZZ} - G''_{XX}). \quad (111)$$

Substituting (109)-(111) into (105), we obtain

$$S(t) = \frac{1}{3} \begin{pmatrix} [2e^{-\gamma-t} + e^{-\gamma+t}] & \sqrt{2} [e^{-\gamma-t} - e^{-\gamma+t}] \\ \sqrt{2} [e^{-\gamma-t} - e^{-\gamma+t}] & [e^{-\gamma-t} + 2e^{-\gamma+t}] \end{pmatrix}. \quad (112)$$

Eigen values  $\gamma_{\pm}$  in the case are

$$\gamma_+ = \frac{3}{2} \left(\frac{c}{\omega_{mn}}\right)^3 G''_{ZZ}, \quad (113)$$

$$\gamma_- = \frac{3}{2} \left(\frac{c}{\omega_{mn}}\right)^3 G''_{XX}. \quad (114)$$

In the case under consideration (i.e.,  $J_m = 1, J_n = 0$ ) it is possible such excitation conditions that upper level deexcitation is pure exponential. Such cases only three.

In the first case the atom is excited by light with linear polarization that is collinear to the symmetry axis. Such light excites only one upper sublevel with angular momentum projection on the symmetry axis  $J_{mZ} = 0$ . In this case the initial conditions column is given by

$$\mathbf{c}_0 \equiv \begin{pmatrix} \rho_0^0(0) \\ \rho_0^2(0) \end{pmatrix} = \frac{1}{\sqrt{3}} \begin{pmatrix} 1 \\ -\sqrt{2} \end{pmatrix} \rho_{00}(0),$$

where  $\rho_{00}(0)$  is population of the sublevel mentioned above. If we multiply fundamental solution matrix (112) on the right by column  $\mathbf{c}_0$ , we get the variation in the time of the population and alignment of the upper level:

$$\begin{pmatrix} \rho_0^0(t) \\ \rho_0^2(t) \end{pmatrix} = \mathbf{c}_0 e^{-\gamma t}$$

In the second case the atom is excited by circular polarized light that propagates along symmetry axis. Now the only upper sublevel with angular momentum projection on the

symmetry axis  $J_{mZ} = +1$  (or  $J_{mZ} = -1$  for the opposite circular polarization) is excited. Initial conditions column in the case is given by

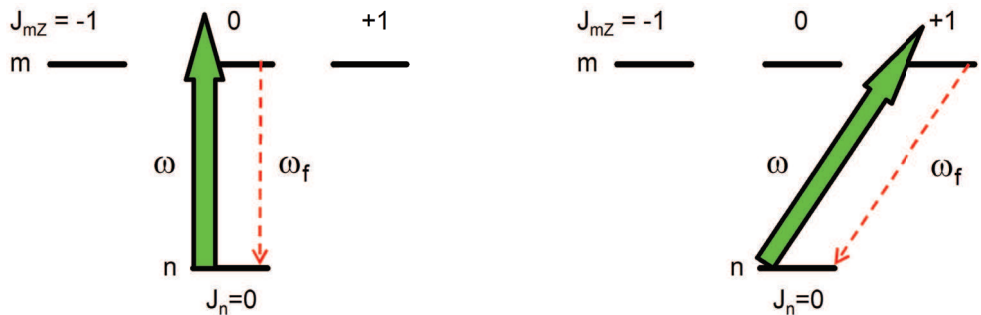
$$c_1 \equiv \begin{pmatrix} \rho_0^0(0) \\ \rho_0^2(0) \end{pmatrix} = \frac{1}{\sqrt{3}} \begin{pmatrix} 1 \\ 1/\sqrt{2} \end{pmatrix} \rho_{11}(0), \quad (115)$$

where  $\rho_{11}(0)$  is population of the excited sublevel. The solution corresponding to this column is

$$\begin{pmatrix} \rho_0^0(t) \\ \rho_0^2(t) \end{pmatrix} = c_1 e^{-\gamma t}. \quad (116)$$

Lastly, in the third case the atom is excited by light with linear polarization that is orthogonal to the symmetry axis. It has been known that such polarization can be represented by the sum of the opposite circular polarization with the same amplitude, rotating in the plane that is orthogonal to the symmetry axis. This case is reduced to the previous one because of only two upper sublevels with angular momentum projection on the symmetry axis  $J_{mZ} = \pm 1$  are excited independently with equal probability, and hence  $\rho_{11}(0) = \rho_{-1-1}(0)$ . The rates of decay of the both excited sublevels into the only low state are equal due to axial symmetry. Deexcitation dynamics in the case also given by (116).

These three exceptional cases of simple exponential deexcitation can be physically interpreted as follows. In every case the excited state transforms to the only low state by means of one channel. The decay itself is induced by the optical transition oscillating dipole that arises due to interaction of the excited atom with the electric field quantum oscillations. Both the direction of the dipole oscillation and the direction of the exciting light polarization are the same due to the one and the same channel of excitation and deexcitation (see Fig. 1).



(a) Exciting light is linear polarized along (or transversely to) the symmetry axis passing through the atom and body;  $Z$ -axis is along (or transversely to) this axis

(b) Exciting light is circular polarized and propagates along the symmetry axis that is  $Z$ -axis

Fig. 1. Exceptional polarizations of the exciting light that led to the pure exponential decay of the excited atomic state ( $\omega$  and  $\omega_f$  are frequencies of the exciting light and fluorescence respectively)

Precisely owing to this fact, experimental results of the measurement of the decay of the fluorescence signal (Amos & Barnes, 1997; Chance et al., 1978; Drexhage et al., 1968; Fort & Grésillon, 2008; Kreiter et al., 2002; Snoeks et al., 1995; Vallée et al., 2001) are in good agreement

with the simple model of the classic scattering dipole, in spite of the fact that fluorescence is the two-step process, rather than scattering.

It should be noted that consistent equations (102)-(103) describe deexcitation dynamics also in the case  $J_m = 1, J_n = 1$ , or  $J_m = 1, J_n = 2$ , and also in the case  $J_m = 3/2, J_n = 1/2$ , and either  $J_m = 3/2, J_n = 3/2$ , or  $J_m = 3/2, J_n = 5/2$ . Of course, specific values of the dimensionless  $\Gamma_{00}^{00}, \Gamma_{00}^{02}$ , and  $\Gamma_{00}^{22}$  in these cases differ from considered above.

It should be pointed out too that in the case  $J_m = 3/2$  and  $J_n = 1/2$  there is the only exciting light polarization, namely linear polarization along symmetry axis, that leads to the pure exponential decay of the excited state because of the relaxation rate equality of the excited sublevels ( $J_m Z = \pm 1/2$ ) due to the axial symmetry.

## 5. Conclusions

In the chapter we have proposed a general approach to the problem of deexcitation of a degenerate two-level atom near (inside) a body. On the basis of the approach the master equation for density matrix in the polarization moments representation was obtained.

We have shown that relaxation dynamics of a polarization moment is described in general by a consistent linear equations for all  $2J_m + 1$  polarization moments of the excited level, where  $J_m$  is the total momentum of the level. We have expressed relaxation matrix elements of the consistent linear equations in terms of the field response tensor that can be found as the electric field of the classic oscillating unit dipole situated near the body.

We have found symmetry of the relaxation matrix.

An additional relaxation matrix symmetry is recognized in the case when there is no external quasistatic magnetic field, and as a result, the field response tensor is symmetrical one. Therefore, the tensor may be diagonalized. We have shown that relaxation matrix depends only on the trace of the field response tensor, on the difference between the most principal value of the diagonal response tensor and the half-sum of two others, and also on the difference between these two.

Axial symmetric atomic surroundings gives rise to one more additional symmetry of the relaxation matrix. In this case it depends only on the trace of the field response tensor and on the difference between its two principal values.

We have shown that deexcitation dynamics of the degenerate two-level atom in the conditions under consideration represents multiexponential decay. In the case of the axial symmetric atomic surroundings, the number of the exponential is equal to  $[J_m] + 1$ , where  $[J_m]$  is the integer part of  $J_m$ . So, the simple exponential decay of the atomic excitation is possible only in two cases, namely, when  $J_m = 0$  or  $J_m = 1/2$ . We have shown that simple exponential decay of the atomic excitation is also possible in the case of  $J_m = 1, J_n = 0$  and on special polarizations of exciting light, namely on the linear polarization that is collinear or orthogonal to the axial symmetry axis, and on the circular polarizations rotating in the plane that is orthogonal to the symmetry axis. In this exceptional cases both the excitation and decay of the corresponding upper states follow the one and the same respective channel. Simple exponential decay of the atomic excitation is possible too in the case  $J_m = 3/2$  and  $J_n = 1/2$  when exciting light polarization is linear oriented along symmetry axis.

Our analysis have carried out in the absence of hyperfine structure on the combine energy levels. However, it can be easily expanded straightforward on general case by expanding

quantum states irreducible basis of the total momentum, including both the total electronic momentum and the nuclear spin, into the direct product of states irreducible bases of the the nuclear spin and the electronic momentum. Just the late basis is involved into the electromagnetic interaction in the course of the allowed optical transition.

We have considered situation when degenerate two-level atom is situated in the vicinity of a body. Nevertheless, it is clear from the consideration that our treatment is more general and results obtained are true for an atom embedded in any anisotropic medium.

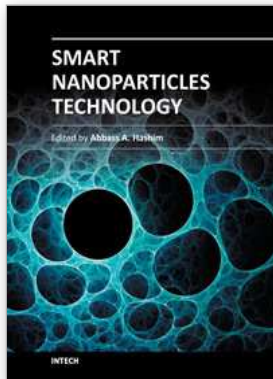
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In the last few years, Nanoparticles and their applications dramatically diverted science in the direction of brand new philosophy. The properties of many conventional materials changed when formed from nanoparticles. Nanoparticles have a greater surface area per weight than larger particles which causes them to be more reactive and effective than other molecules. In this book, we (InTech publisher, editor and authors) have invested a lot of effort to include 25 most advanced technology chapters. The book is organised into three well-heeled parts. We would like to invite all Nanotechnology scientists to read and share the knowledge and contents of this book.

### **How to reference**

In order to correctly reference this scholarly work, feel free to copy and paste the following:

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