Physica 100C (1980) 245–259

THEORY OF COHERENT TWO-PHOTON NMR: STANDARD-BASIS OPERATORS AND COHERENT AVERAGING

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Received 17 July 1979
Revised 30 November 1979

Theory of the two-photon coherent transitions for the multilevel spin system is developed by using the coherent averaging of the time-evolution operator and the spin description by the standard-basis operators. The employed formalism provides a clear picture of the interactions which cause the multi-quantum transitions and make possible to evaluate not only the two-photon but also the multiphoton transitions. The theory has been applied to the quadrupole perturbed spin-systems with $s = 1$ and $s = 3/2$ where the effective double-quantum rf field has been evaluated.

1. Introduction

When spin system absorbs the rf radiation of strong intensity, coherent transitions due to the simultaneous absorbtion of many photons can be observed [1, 2]. In this article we are discussing a new approach to the description of multi-photon coherent transition in which the spin Hamiltonian is formulated in terms of the standard-basis operators [3] and the technique of coherent averaging is employed. The substitution of the spin operators by standard-basis operators, called also the population operators [4], is naturally adapted to systems having nonequidistant energy levels in which these operators are represented by matrices whose elements are zero except for single one. They provided a clear picture of the interactions which cause interlevel transition, obscured by the use of fictitious angular momentum operators [1]. The diagonal operators play the role of the occupation number operators for the individual levels, and the nondiagonal ones act as a rising or lowering operators which generate the interlevel transitions [3].

The multi-quantum transitions are considered by the Magnus expansion of the time-development operator [4], in which zeroth-order approximation of the Hamiltonian corresponds to the one-photon transitions, the first-order approximation to the two-photon transitions, second-order to the triple-quantum transition, etc.

In section 2 the standard-basis operators are defined and applied to the various spin Hamiltonians. In particular, the Hamiltonians of spins in the magnetic or electric quadrupolar field are expressed in terms of the new operators

In section 3 the time-evolution operator governing the spin motion when the strong rf field is applied, is considered by the Magnus expansion to the first order. In sections 4 and 5 the obtained expressions for the double photon Hamiltonian are evaluated for the cases $s = 1$, and $s = 3/2$ of the quadrupole perturbed NMR.

2. The standard-basis operators and spin Hamiltonians

For an ensemble of spins having discrete nonequidistant energy levels the Hamiltonian can be written in a very simple form using the so-called standard-basis [2] or population operators [3]. These operators form a basis for the set of linear transformations on a vector space representing a state of a physical system. For the case of k discrete energy levels the set of the vectors $|\alpha\rangle$ with $\alpha = 1, 2, \ldots k$ of the form

$$|\alpha\rangle = \{0, 0, \ldots, 1_\alpha, 0, \ldots 0\}, \tag{1}$$

where α denotes the only nonzero components, constitutes the standard basis. Physically, the vector $|\alpha\rangle$ can be considered as a state vector describing a system in the state α. If the operator A represents transformation of this basis into itself, one can write

$$\hat{A}|\beta\rangle = \sum_{\alpha=1}^{k} A_{\beta\alpha}|\alpha\rangle \quad \text{for } \beta = 1, 2, \ldots k. \tag{2}$$

The set of k^2 complex numbers $A_{\beta\alpha}$ completely describes the linear transformation A. The set of the standard-base operators $n_{\alpha\beta}$ is defined as the linear transformation on $|\alpha\rangle$ vector space with matrices

$$\hat{n}_{\alpha\beta} = \begin{pmatrix} 0 & \ldots & 0 \\ \vdots & & \vdots \\ 0 \ldots & 1_{\alpha\beta} & \ldots 0 \\ \vdots & & \vdots \\ 0 & \ldots & 0 \end{pmatrix} \tag{3}$$

The subscript α and β indicates the only nonzero element which is in α row and β column position. It is clear from (1) that k^2 operators $\hat{n}_{\alpha\beta}$ are linearly independent and form the basis. Thus, any linear transformation A may be written as a linear combination of $\hat{n}_{\alpha\beta}$ operators

$$\hat{A} = \sum_{\alpha\beta} A_{\alpha\beta}\hat{n}_{\alpha\beta}. \tag{4}$$

From the definition (3) it follows that

$$\hat{n}_{\alpha\beta}|\gamma\rangle = \delta_{\beta\gamma}\,|\alpha\rangle, \tag{5}$$

where $\delta_{\beta\gamma}$ is the Kronecker delta. It is evident that the nondiagonal operators $\hat{n}_{\alpha\beta}$, $\alpha \neq \beta$, act as rising or lowering operators when $\alpha > \beta$ or $\alpha < \beta$, respectively, and their meaning is related to the transitions between levels. The diagonal operator $\hat{n}_{\alpha\beta}$ is a projection operator into the state $|\alpha\rangle$. It can be related to the occupation of the single state.

From the definition of $\hat{n}_{\alpha\beta}$ one has the relations

$$[\hat{n}_{\alpha,\alpha'}, \hat{n}_{\beta,\beta'}] = \delta_{\beta\alpha'}\hat{n}_{\alpha,\beta} - \delta_{\alpha\beta'}\hat{n}_{\beta,\alpha'} \quad \text{and} \quad \hat{n}_{\alpha,\alpha'} \cdot \hat{n}_{\beta,\beta'} = \delta_{\beta\alpha'}\hat{n}_{\alpha\beta'}. \tag{6}$$

Up to this point, the development in this section has been concerned with the properties of the standard-basis operators of the single system. In the following we shall be dealing with ensemble of N identical systems which are noninteracting in the first approximation. The set of the standard-basis operators for the ensemble of systems might be constructed in the following sense

$$\hat{N}_{\alpha,\beta} = \sum_i \hat{n}^{(i)}_{\alpha,\beta}, \tag{7}$$

where the superscript i labels different systems. By substituting the operators (7) into (6) these relations remain the same.

According to the definition, various spin Hamiltonians might be expressed in terms of new operators (7). The Hamiltonian of the quadrupole perturbed spin system

$$H_q = -\omega_0 I_z + \tfrac{1}{3}\omega_q [3I_z^2 - I(I+1)] \tag{8}$$

is diagonal in the same representation as the component of the angular momentum operator I_z. If the Hamiltonian (8) is expressed in the standard-basis operators

$$H_q = \sum_{m=-s}^{m=s} \epsilon_m N_{m,m}, \quad \text{with} \quad \epsilon_m = -\omega_0 m + \tfrac{1}{3}\omega_q [m^2 - I(I+1)], \tag{9}$$

a simple correspondence exists between the angular momentum operators and the population operators [3]

$$I_z = \sum_{m=-s}^{m=s} m N_{m,m}, \tag{10}$$

$$I^+ = \sum_{m=-s}^{m=s} A_m N_{m+1,m} \tag{11}$$

and

$$I^- = \sum_{m=-s}^{m=s} A_m N_{m,m+1}, \tag{12}$$

where $A_m = \sqrt{I(I+1) - m(m+1)}$, and $m = -s, -s+1, -s+2, \ldots, s-1, s$.

The effect of the radiofrequency magnetic field, perpendicular to the main magnetic field, is governed by

$$H_{\text{rf}} = 2\omega_1 I_x \cos\omega t = \omega_1 (I^+ + I^-) \cos\omega t, \tag{13}$$

which can be rewritten by using the new operators, such as

$$H_{\text{rf}} = \omega_1 \sum_{m=-s}^{m=s} A_m (N_{m+1,m} + N_{m,m+1}) \cos\omega t. \tag{14}$$

The definition of the standard-basis operators is less straightforward in the cases where the angular momentum component I_z is not diagonal in the same representation as the Hamiltonian, and the expansion (4) should be implemented. In the case of the pure quadrupole Hamiltonian

$$H_Q = A[3I_z^2 - I(I+1) + \eta(I_x^2 - I_y^2)], \tag{15}$$

$$\epsilon_1 = -2A, \quad \epsilon_2 = A(1-\eta), \quad \epsilon_3 = A(1+\eta) \tag{16}$$

and in the standard-basis operator representation the expression (16) becomes

$$\hat{H}_Q = \sum_{i=1}^{i=3} \epsilon_1 N_{i,i}. \tag{17}$$

According to the definition the new operators should be diagonal in the same representation as the main Hamiltonian, thus the rf field perturbation which brings about the interlevel transition is expressed as

$$\hat{H}_{\mathrm{rf}} = \sum_{i>j} (\mu_{ij} \hat{N}_{i,j} + \mu_{ij} \hat{N}_{i,j}) \cos \omega t, \tag{18}$$

where

$$\mu_{12} = \langle 1|\hat{H}_{rf}|2\rangle = \mathrm{i}H_{y1}, \quad \mu_{13} = \langle 1|\hat{H}_{\mathrm{rf}}|3\rangle = H_{x1}, \quad \mu_{23} = \langle 2|\hat{H}_{\mathrm{rf}}|3\rangle = H_{z1}$$

are the matrix elements of the $\hat{H}_{\mathrm{rf}}$ and H_{x1}, H_{y1}, H_{z1} are the rf field components.

The same procedure can be applied for any spin system where spin–spin interactions are neglected and generally it can be written as

$$H = \sum_i \epsilon_i \hat{N}_{i,i} + \sum_{i \neq j} \mu_{ij} \hat{N}_{i,j} \cos \omega t. \tag{19}$$

These forms of the Hamiltonians provide a clear picture of the eigenvalues and of the interactions which cause interlevel transition, and will be very useful in the following where the multi-quantum transitions are considered.

In the two level spin system $s = 1/2$ there is an isomorfism between the angular momentum operators and the standard-basis operators;

$$I^+ = \tfrac{1}{2} N_{1/2,\,-1/2}, \quad I^- = \tfrac{1}{2} N_{-1/2,\,1/2} \quad \text{and} \quad I_z = \tfrac{1}{2}(N_{1/2,\,1/2} - N_{-1/2,\,-1/2}). \tag{20}$$

3. Coherent averaging and double-quantum resonance

The evolution of the spin system from the thermal equilibrium, when an intense radiofrequency field is applied, can be described by using the density matrix formalism. Its density matrix at time t is

$$\rho(t) = L(t)\, \rho(0)\, L^+(t), \tag{21}$$

where $\rho(0)$ is the thermal equilibrium density matrix and

$$L(t) = T \exp\left(-\mathrm{i} \int_0^t H(t)\, \mathrm{d}t\right) \tag{22}$$

is the time-evolution operator with T being the Dyson time ordering operator [4, 5]. This operator might be divided into the part due to the static field alone if the part of $H(t)$ representing the effect of the rf field is transformated into the interaction representation

$$\mathcal{L}(t) = \mathcal{L}_s(t) \cdot \mathcal{L}_{\mathrm{rf}}(t) = \exp(-\mathrm{i}\mathcal{H}_q t) \cdot T \exp\left(\mathrm{i} \int_0^t \tilde{\mathcal{H}}_{\mathrm{rf}}(t')\, \mathrm{d}t'\right), \tag{23}$$

where

$$\tilde{\mathscr{H}}_{rf}(t) = \exp(i\mathscr{H}_q t)\mathscr{H}_{rf}(t)\exp(-i\mathscr{H}_q t). \tag{23a}$$

The time-dependence of $\tilde{\mathscr{H}}_{rf}(t)$ requires time ordering of (23) what prevents to actually perform the integration of the exponent. It can be overcome by employing the coherent averaging, i.e. if the exponent of the rf part is expanded according to Magnus (4)

$$L_{rf}(t) = \exp(-iF(t)), \quad \text{where } F(t) = F_0(t) + F_1(t) + F_2(t) + \ldots, \tag{24}$$

The first three terms of the expansion are

$$F_0(t) = \int_0^t H_{rf}(t)\,dt, \tag{25}$$

$$F_1(t) = -\frac{i}{2}\int_0^t dt_1 \int_0^t dt_2\,[H_{rf}(t_1), H_{rf}(t_2)] \tag{26}$$

and

$$F_2(t) = \frac{1}{6}\int_0^t dt_1 \int_0^t dt_2 \int_0^t dt_3\,[H_{rf}(t_1), [H_{rf}(t_2), H_{rf}(t_3)]] + [H_{rf}(t_3), [H_{rf}(t_2), H_{rf}(t_1)]]. \tag{27}$$

Thus, it is possible to integrate the above expressions explicitly obtaining a simple series expansion for $F(t)$. This can be understood as a series expansion with respect to the order of magnitude of the rf field perturbation.

The zeroth-order approximation (25) of the rf field perturbation can be found by substituting (14) into (23a) and (25)

$$F_0(t) = 2\omega_1 \sum_m A_m \int_0^t [N_{m+1,m}\exp(i\omega_m^{m+1}t) + N_{m,m+1}\exp(-i\omega_m^{m+1}t)]\cos\omega t\,dt, \tag{28}$$

with

$$\epsilon_{m+1} - \epsilon_m = \omega_m^{m+1}.$$

The form of the integrand (28) is similar to the form of the rf Hamiltonian for spin 1/2 in the rotating frame

$$H_{rf} = 2\omega_1 [S^+\exp(i\Delta t) + S^-\exp(-i\Delta t)]\cos\omega t. \tag{29}$$

As the rising operator S^+ transforms the spin state $-1/2$ into $1/2$, the $N_{m+1,m}$ makes the transition of the spin from the m to $m+1$ level. Similar correspondence exists between the lowering operators S^- and $N_{m,m+1}$. Thus the single term of (28) can be considered as the rf perturbation acting on the two-level spin system.

By integrating (28) and taking into account only one circular component of the linearly polarized rf field one obtains

$$F_0(t) = \omega_1 t \sum_m A_m [g(\Delta_m^{m+1})N_{m+1,m} + g^+(\Delta_m^{m+1})N_{m,m+1}], \tag{30}$$

with

$$g(\Delta) = \frac{\exp(i\Delta t) - 1}{i\Delta t} \quad \text{and} \quad \Delta_m^{m+1} = \omega - \omega_m^{m+1}.$$

The evaluation of the first-order correction (26) gives the expression.

$$F_1(t) = -\tfrac{1}{2}\omega_1^2 t \sum_m [f_m(t)\hat{N}_{m+1,\,m-1} + f_m^+(t)\hat{N}_{m-1,\,m+1} + 2d_m(t)\hat{N}_{m,\,m}], \tag{31}$$

with

$$f_m(t) = A_m A_{m+1}\left[\frac{\Delta_m^{m+1} - \Delta_{m-1}^m}{\Delta_{m-1}^m \cdot \Delta_m^{m+1}}\, g(\Delta_m^{m+1} + \Delta_{m-1}^m) - \frac{g(\Delta_m^{m+1})}{\Delta_{m-1}^m} + \frac{g(\Delta_{m-1}^m)}{\Delta_m^{m+1}}\right], \tag{32}$$

and

$$d_m(t) = \frac{A_m^2}{\Delta_m^{m+1}}\left[1 - \frac{\sin(\Delta_m^{m+1}t)}{\Delta_m^{m+1}t}\right] - \frac{A_{m-1}^2}{\Delta_{m-1}^m}\left[1 - \frac{\sin(\Delta_{m-1}^m t)}{\Delta_{m-1}^m t}\right]. \tag{33}$$

In the expression (31) new operators appear, $N_{m+1,\,m-1}$ and $N_{m-1,\,m+1}$, which are products of two rising operators $N_{m+1,\,m}$ and $N_{m,\,m-1}$ or two lowering operators $N_{m-1,\,m}$ and $N_{m,\,m+1}$, according to the definition (6) The new operators have only matrix elements $(m+1, m-1)$ and $(m-1, m+1)$ different from zero, thus, they can induce the forbidden transitions $\Delta m = 2$, the double-quantum transitions. In addition to this, $F_1(t)$ includes the term with $N_{m,\,m}$ which brings about the shift of the resonance line proportional to the rf field intensity, the Bloch–Siegert shift.

The rf part of the time evolution (24) operator can be expressed in terms of the effective Hamiltonian:

$$\mathscr{L}_{\mathrm{rf}}(t) = \exp\left(-\mathrm{i}\int_0^t (\mathscr{H}_{0\mathrm{rf}}(t') + \mathscr{H}_{1\mathrm{rf}}(t') + \mathscr{H}_{2\mathrm{rf}}(t') + \ldots)\,\mathrm{d}t'\right). \tag{34}$$

By substitution of (14) and (9) into (34) we obtain the effectice rf Hamiltonian which in zeroth-order approximation

$$\mathscr{H}_{0\mathrm{rf}}(t) = h\omega_1 \sum_m (a_m(t)N_m^+ + a_m(t)^* N_{m+1}^-) \tag{35}$$

gives one-photon transitions between $m \rightleftharpoons m+1$ levels, in the first-order approximation

$$\mathscr{H}_{1\mathrm{rf}}(t) = \frac{h\omega_1^2}{2}\sum_m [b_m(t)N_{m+1}^+ N_m^+ + b_m^*(t)N_{m+1}^- N_{m+2}^- + 2C_m(t)N_m(t)] \tag{36}$$

generates the two-photon transitions between $m \rightleftharpoons m+2$ and induces the Bloch–Siegert shift by the last term.

The second-order approximation

$$\mathscr{H}_{2\mathrm{rf}}(t) = \frac{h\omega_1^3}{6}\sum_m [d_m(t)N_m^+ + d_m^*(t)N_{m+1}^- + e_m(t)\,N_{m+2}^+ N_{m+1}^+ N_m^+ + e_m^*(t)N_{m+1}^- N_{m+2}^- N_{m+3}^-], \tag{37}$$

gives the three-photon transitions $m \rightleftharpoons m+3$ induced by the last two terms. Further expansion of the series (34), which is convergent for $\omega_1 < \omega_q$, gives other multi-photon transitions.

4. Two-photon transitions: $s = 1$

For the case of spin 1 there are three nonequidistant energy-levels denoted as

$$E_1 = -\omega_0 + \tfrac{1}{3}Q, \quad E_0 = -(2/3)Q, \quad E_{-1} = \omega_0 - \tfrac{1}{3}Q \tag{38}$$

the first-order approximation Hamiltonian (36) is

$$F_1(t) = -\frac{\omega_1^2}{2}\,[f_0\hat{N}_{1,-1} + f_0^+\hat{N}_{-1,1} + (d_1 + d_{-1})(\hat{N}_1 - \hat{N}_{-1}) + (d_1 - d_{-1})(\hat{N}_1 + \hat{N}_0 + \hat{N}_{-1} - 3\hat{N}_0)], \tag{39}$$

where

$$f_0(t) = 2\left[\frac{2Q}{\Delta^2 - Q^2}\,g(2\Delta) - \frac{1}{\Delta - Q}\,g(\Delta + Q) + \frac{1}{\Delta + Q}\,g(\Delta - Q)\right],$$

$$d_1(t) = \frac{2}{\Delta + Q}\left[t - \frac{\sin(\Delta + Q)t}{\Delta + Q}\right], \quad d_{-1}(t) = \frac{2}{\Delta - Q}\left[t - \frac{\sin(\Delta - Q)t}{\Delta - Q}\right]$$

with $\Delta = \omega - \omega_0$, and $\hat{N}_m \equiv \hat{N}_{m,m}$.

By definition (3) the sum of operators $N_1 + N_0 + N_{-1}$ is proportional to the identity operator, while N_0 alone is not affected by the double quantum transitions between $|1\rangle$ and $|-1\rangle$ level. Therefore, as the last term of (39) commutes with the first three terms it will not be taken into further consideration.

By introducing the fictitious spin 1/2 angular momentum operators acting in two-level system $|1\rangle$ and $|-1\rangle$ as

$$\hat{S}_x^{(2)} = \tfrac{1}{2}(\hat{N}_{1,-1} + \hat{N}_{-1,1}), \quad \hat{S}_y^{(2)} = \frac{1}{2i}(\hat{N}_{1,-1} - \hat{N}_{-1,1}), \quad \hat{S}_z^{(2)} = \tfrac{1}{2}(\hat{N}_1 - \hat{N}_{-1}), \tag{40}$$

the remaining part of $F_1(t)$ can be rewritten as

$$F_1'(t) = -\omega_1^2 t\,[A(t)\hat{S}_x^{(2)} - B(t)\hat{S}_y^{(2)} + C(t)\hat{S}_z^{(2)}], \tag{41}$$

with

$$A(t) = \frac{2Q}{\Delta^2 - Q^2}\,\frac{\sin 2\Delta t}{2\Delta t} - \frac{1}{\Delta - Q}\,\frac{\sin(\Delta + Q)t}{(\Delta + Q)t} + \frac{1}{\Delta + Q}\,\frac{\sin(\Delta - Q)t}{(\Delta - Q)t},$$

$$B(t) = \frac{2Q}{\Delta^2 - Q^2}\,\frac{1 - \cos 2\Delta t}{2\Delta t} - \frac{1}{\Delta - Q}\,\frac{1 - \cos(\Delta + Q)t}{(\Delta + Q)t} + \frac{1}{\Delta + Q}\,\frac{1 - \cos(\Delta - Q)t}{(\Delta - Q)t},$$

and

$$C(t) = \frac{4}{\Delta + Q}\left[1 - \frac{\sin(\Delta + Q)t}{(\Delta + Q)t}\right] + \frac{4}{\Delta - Q}\left[1 - \frac{\sin(\Delta - Q)t}{(\Delta - Q)t}\right].$$

Time dependent coefficients A, B and C are functions of the rf frequency and of the quadrupole coupling Q. Fig. 1 shows the dependence of the frequency for the coefficient $A(t)$, $B(t)$ and $C(t)$ at time 50 μs and $Q = 10^6\ \mathrm{s}^{-1}$. It reveals that these coefficients which determine the role of the particular fictitious angular momentum component. in double-quantum spin dynamic, have singularities not only at the classical double-quantum transition, $\Delta = 0$, but also $\Delta = Q$ and $\Delta = -Q$. In terms of the effective Hamiltonian, it can be rewritten as

$$\mathcal{H}_{1\mathrm{rf}}(t) = -\tfrac{1}{2}\omega_1^2 [a(t) S_x^{(2)} - b(t) S_y^{(2)} + c(t) S_z^{(2)}], \quad (42)$$

with

$$a(t) = \frac{2Q}{\Delta^2 - Q^2}\cos 2\Delta t - \frac{\cos(\Delta + Q)t}{(\Delta - Q)} + \frac{\cos(\Delta - Q)t}{\Delta + Q},$$

$$b(t) = \frac{2Q}{\Delta^2 - Q^2}\sin 2\Delta t - \frac{\sin(\Delta + Q)t}{\Delta - Q} + \frac{\sin(\Delta - Q)t}{\Delta + Q},$$

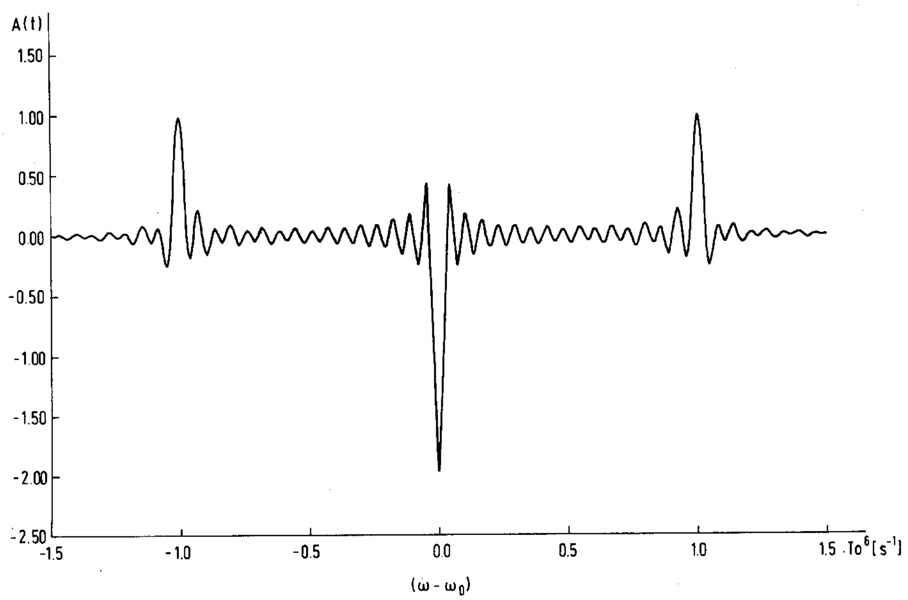
$$d(t) = \frac{4[1 - \cos(\Delta + Q)t]}{\Delta + Q} + \frac{4[1 - \cos(\Delta - Q)t]}{\Delta - Q}.$$

This Hamiltonian acts in the double-quantum space in a similar manner as the combination of three coherent rf fields simultaneously applied perpendicular to the static magnetic field. These fields have different frequencies and three resonances appear at $2\Delta = 0$, $\Delta + Q = 0$, and $\Delta - Q = 0$. In addition to this there is also the time dependent Bloch–Siegert shift expressed by the coefficient at $S_z^{(2)}$.

4.1. *Irradiation at* $\Delta = 0$

If the rf field frequency is equal to one-half of the energy separation of the levels $m = 1$ and $m = -1$

$$h\omega = \frac{E_1 - E_{-1}}{2} = h\omega_0, \quad (43)$$



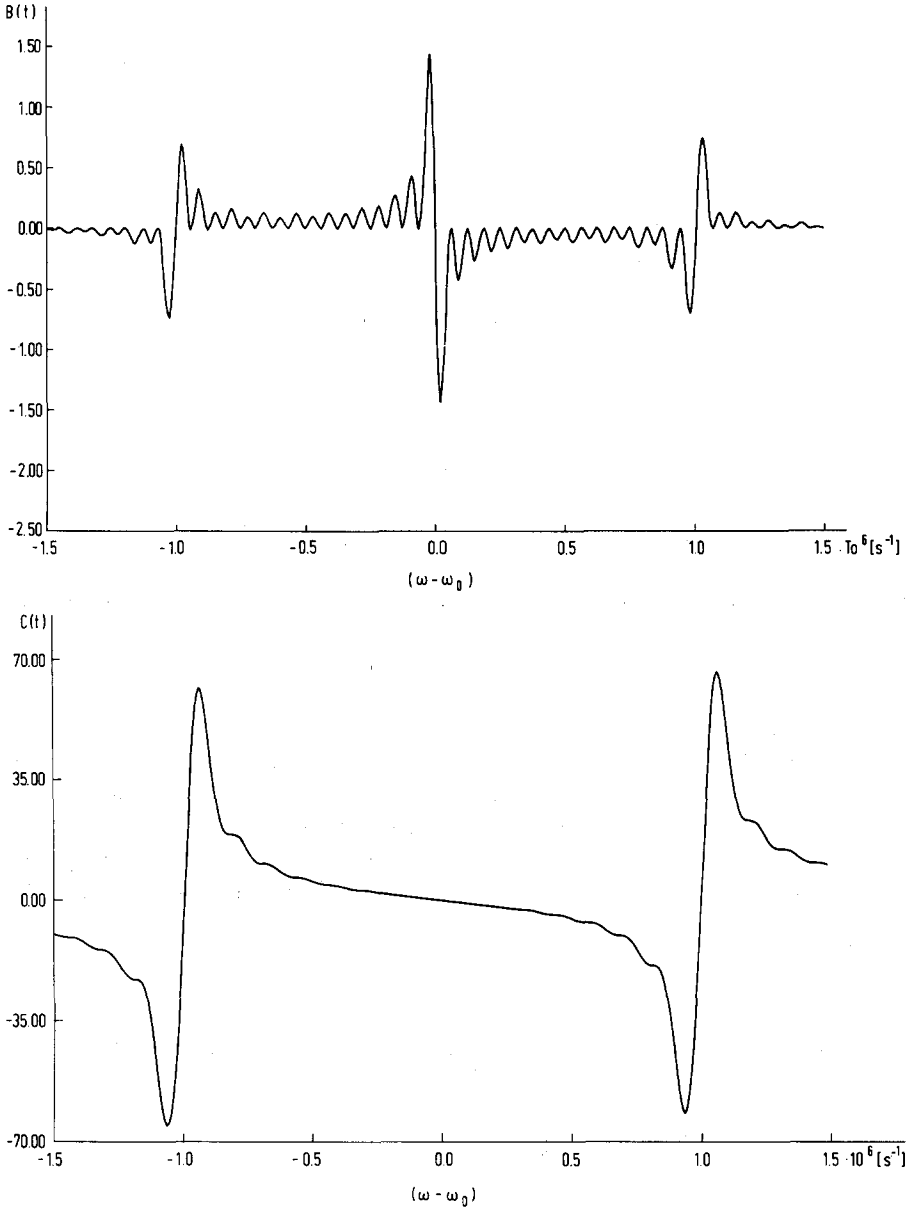


Fig. 1. The frequency dependence of the coefficients which determine the effect of the particular fictitions angular momentum component to the double quantum resonances for $S = 1$.

then the effective Hamiltonian (42) becomes

$$\mathscr{H}_{1\mathrm{rf}} = \frac{\omega_1^2}{Q}(1 - \cos Qt)\, S_x^{(2)} = H_{1\mathrm{rf}}^{(2)}(t)\, S_x^{(2)}. \tag{44}$$

Its time dependence differs from the time dependence of the magnitude of the applied rf field $H_1(t)$ (fig. 2).

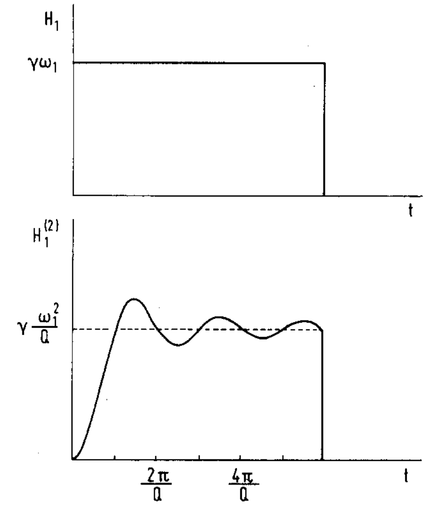


Fig. 2. The time dependence of the applied rf amplitude and the effective rf field acting in the double quantum space.

It does not follow the time dependence of H_1 but is delayed for the time proportional to the inverse quadrupole coupling constant,

$$\tau \approx 2\pi/Q.$$

$H_1^{(2)}$ vanishes when the energy levels become equidistant, i.e. when $Q \to 0$, what makes sense. The time dependence of the Hamiltonian (44) can be considered as being composed of three kinds of interactions: the static field along x-axis and two circular fields rotating with the frequency Q in the opposite sense.

In the further calculations we shall neglect all terms of the density matrix operators and $L(t)$ including the operator N_0, since it does not play a role at DQ transitions. Thus the time evolution operator to the first-order approximation is

$$L_1(t) = \exp(2\mathrm{i}\omega_0 S_z^{(2)} t) \cdot \exp(-\mathrm{i}\mathscr{H}_1^{(2)}(t) \cdot S_x^{(2)}). \tag{45}$$

By defining the initial equilibrium density matrix in the high temperature approximation as

$$\rho(0) = 1 - \frac{1}{kT}\sum_m \epsilon_m \hat{N}_m = 1 - \frac{1}{kT}[-2\omega_0 S_z^{(2)} - \tfrac{1}{3}N_0 Q] \tag{46}$$

the double-quantum rf pulse will induce the coherent transitions between $|1\rangle$ and $|-1\rangle$ state according to

$$\langle S_z^{(2)}\rangle = \mathrm{Tr}\, S_z^{(2)} L_1(t)\rho(0)L_1^+(t) = \frac{\epsilon_1 - \epsilon_{-1}}{2kT}\cos\left[\frac{\omega_1^2}{Q}\left(t - \frac{\sin Qt}{Q}\right).\right] \tag{47}$$

If the duration of the applied rf field is such that

$$\frac{\omega_1^2}{Q}\left(1 - \frac{\sin Qt_0}{Qt_0}\right) = \frac{\pi}{2}.$$

then the spin system is transformed from the initial thermal equilibrium state (46) into the state with angular momentum pointed along y-axis, $S_z^{(2)} \to S_y^{(2)}$, and $S_y^{(2)}$ is afterward precessing around the applied static field according to

$$\langle S_y^{(2)}(t)\rangle = \mathrm{Tr}\, S_y^{(2)} L_1(t)\, \rho_0 L_1^{+}(t) = \frac{2\omega_0}{kT} \mathrm{Tr}\, S_y^{(2)}\, \mathrm{e}^{i2\omega_0 S_z^{(2)}}\, S_y^{(2)}\, \mathrm{e}^{-2i\omega_0 S_z^{(2)} t} = \frac{2\omega_0}{kT} \mathrm{Tr}\, S_y^{(2)2} \cdot \cos 2\omega_0 t \qquad (48a)$$

The precession frequency of the transverse component of the fictitious spin 1/2 operator is $2\omega_0$. For the $S_x^{(2)}$ component we get

$$\langle S_y^{(2)}(t)\rangle = -\frac{2\omega_0}{kT} \mathrm{Tr}\, S_x^{(2)2} \sin 2\omega_0 t. \qquad (48b)$$

Let us examine the situation when the rf field phase is changed after the certain time t_0 for the angle φ. In this case the time evolution operator is:

$$L_1(t) = \exp(-\mathrm{i}\mathcal{H}_s t) \cdot T \exp\left(-\mathrm{i} \int_{t_0}^{t} \tilde{\mathcal{H}}_{\mathrm{rf}}(t')\, \mathrm{d}t'\right) \cdot T \exp\left(-\mathrm{i} \int_0^{t_0} \tilde{\mathcal{H}}_{\mathrm{rf}}(t')\, \mathrm{d}t'\right)$$

$$= \exp(2\mathrm{i}\omega_0 S_z t) \cdot \exp(-\mathrm{i}H_1^{(2)}(t-t_0))[S_x^{(2)} \cos 2\varphi + S_y^{(2)} \sin 2\varphi](t-t_0) \exp(-\mathrm{i}H_1^{(2)}(t)\, S_x^{(2)} t), \qquad (49)$$

with

$$H_1^{(2)}(t) = \left(1 - \frac{\sin Qt}{Qt}\right) \frac{\omega_1^2}{Q}.$$

This result shows that the phase change is delayed for $\tau \approx 2\pi/Q$ and is associated with the double phase shift in DQ space. It means that the phase shift of rf field for 45° becomes the phase shift of 90° in DQ space (fig. 3).

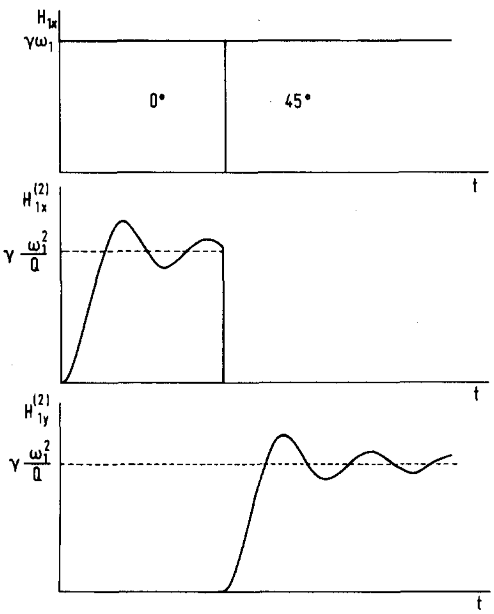


Fig. 3. The effect of the 45° phase shift of the applied rf field to the rf field phase shift in the double quantum space.

This is a well known result from the previous considerations of the DQ transitions [1] but the delay which appears at every sudden change of the magnetic field has not been considered previously.

5. Two-photon transitions: $s = 3/2$

This formalism can be employed considering the problems with higher spin number. Here we will show the treatment of the coherent double quantum transitions for the quadrupole perturbed spin system with $s = 3/2$. In this case there are four energy levels

$$E_{3/2} = -(3/2)\omega_0 + (1/2)q, \quad E_{1/2} = -(1/2)\omega_0 - (1/2)q, \quad E_{-1/2} = (1/2)\omega_0 - (1/2)q,$$
$$E_{-3/2} = (3/2)\omega_0 + (1/2)q, \tag{50}$$

therefore the following standard-basis operators should be introduced: $N_{2/3}, N_{1/2}, N_{-1/2}, N_{-3/2}, N_{3/2,\,1/2}, N_{1/2,\,3/2}, N_{1/2,\,-1/2}, N_{-1/2,\,-3/2}$, and $N_{-3/2,\,-1/2}$. By using the expression (31) the first-order correction in exponent of the time-evolution operators gives

$$F_1(t) = -\frac{\omega_1^2}{2}\,[f_{1/2}N_{3/2,\,-1/2} + f^{+}_{1/2}N_{-1/2,\,3/2} + f_{-1/2}N_{1/2,\,-3/2} + f^{+}_{-1/2}N_{-3/2,\,1/2}$$
$$+ (d_{3/2} - d_{-1/2})(N_{3/2} - N_{-1/2}) + (d_{1/2} - d_{-3/2})(N_{1/2} - N_{-3/2})$$
$$- (d_{1/2} + d_{-3/2})(N_{3/2} - N_{1/2} + N_{-1/2} - N_{-3/2})]\,. \tag{51}$$

From the Hamiltonian (7) it can be found out easily that the double quantum transitions can be induced only between levels $|3/2\rangle \rightleftharpoons |-1/2\rangle$ and $|1/2\rangle \rightleftharpoons |-3/2\rangle$ and, therefore, two fictious spin 1/2 operators should be defined: $S_1^{(2)}$ for $|3/2\rangle \rightleftharpoons |-1/2\rangle$ and $S_2^{(2)}$ for $|1/2\rangle \rightleftharpoons |-3/2\rangle$ transitions. By using the new notation the static part of the Hamiltonian can be written as

$$\sum_{m=-3/2}^{m=3/2} E_m N_m = -(2\omega_0 - q)S_{1z}^{(2)} - (2\omega_0 + q)S_{2z}^{(2)} - \omega_0(S_{1z}^{(1)} + S_{2z}^{(1)}), \tag{52}$$

with

$$S_{1z}^{(1)} = \tfrac{1}{2}(N_{3/2} - N_{1/2}), \quad S_{2z}^{(1)} = \tfrac{1}{2}(N_{-1/2} - N_{-3/2}).$$

The last term commutes with the rest and will not be considered in the following. The first-order approximation of Magnus expansion can be written as

$$\mathscr{H}_{1\mathrm{rf}}(t) = -\frac{\omega_1^2}{2q}\,[a_1(t)S_{x1}^{(2)} - b_1(t)S_{y1}^{(2)} + c_1(t)S_{z1}^{(2)}$$
$$+ a_2(t)S_{x2}^{(2)} - b_2(t)S_{y2}^{(2)} + c_2(t)S_{z2}^{(2)} - d(S_{z1}^{(1)} + S_{z2}^{(1)})]\,, \tag{53}$$

with

$$a_1(t) = 12q\left[\frac{q}{\Delta(\Delta+q)}\cos(2\Delta+q)t + \frac{\cos\Delta t}{\Delta+q} - \frac{\cos(\Delta+q)t}{\Delta}\right],$$

$$b_1(t) = 12q\left[\frac{q}{\Delta(\Delta-q)}\sin(2\Delta+q)t + \frac{\sin\Delta t}{\Delta+q} - \frac{\sin(\Delta+q)t}{\Delta}\right],$$

$$c_1(t) = \frac{9q}{\Delta-q}[1-\cos(\Delta-q)t] - \frac{9q}{\Delta+q}[1-\cos(\Delta+q)t] - \frac{16q}{\Delta}(1-\cos\Delta t),$$

$$a_2(t) = 12q\left[\frac{q}{\Delta(\Delta-q)}\cos(2\Delta-q)t - \frac{\cos\Delta t}{\Delta-q} + \frac{\cos(\Delta-q)t}{\Delta}\right],$$

$$b_2(t) = 12q\left[\frac{q}{\Delta(\Delta-q)}\sin(2\Delta-q)t - \frac{\sin\Delta t}{\Delta-q} + \frac{\sin(\Delta-q)t}{\Delta}\right],$$

$$c_2(t) = \frac{9q}{\Delta-q}[1-\cos(\Delta+q)t] - \frac{16q}{\Delta}(1-\cos\Delta t) - \frac{9q}{\Delta-q}[1-\cos(\Delta-q)t].$$

The last term of (23) commutes with the other terms describing the DQ transition and can be removed from further examination. It can be found that irradiation at the frequency

(a) $\omega = \omega_0 - q/2$ gives the DQ transitions between $|+3/2\rangle$ and $|-1/2\rangle$ levels with

$$a_1 = -48\left(1-\cos\frac{q}{2}t\right),\quad b_1 = 0,$$

$$c_1 = -6\left(1-\cos\frac{3}{2}qt\right) + \frac{14}{2}\left(1-\cos\frac{q}{2}t\right), \tag{54}$$

while the irradiation at $\omega = \omega_0 + q/2$ gives

$$a_2 = -48\left(1-\cos\frac{q}{2}t\right),\quad b_2 = 0,$$

$$c_2 = 6\left(1-\cos\frac{3}{2}qt\right) - \frac{14}{2}\left(1-\cos\frac{q}{2}t\right). \tag{55}$$

These expressions differ from the one for $s = 1$ since there are nonzero values of $S_z^{(2)}$ when $\omega = \omega_0 \pm q/2$. They represent the contribution to the static Hamiltonian and bring about the shift of the DQ resonance lines. The DQ resonance at $\omega = \omega_0 - q/2$ is shifted toward lower frequencies while the resonance line at $\omega = \omega_0 + q/2$ toward higher frequencies for $4\omega_1^2/q$. These are the so-called Bloch–Siegert shifts and are well-known from experiments [6]. These shifts mean that the DQ resonance conditions are fulfilled only if the rf field frequency is shifted for the same value. If we make the additional transformation of the effective Hamiltonian (53) into a frame rotating with the angular velocity $c = \pm 4\omega_1^2/q$ around z axis then this transformation gives for the DQ Hamiltonian (53) the transformed Hamiltonian

$$\mathcal{H}_{1\mathrm{rf}}^{(2)^T} = \sum_{i=1}^{2} [a_i(t) \cos c_i t + b_i(t) \sin c_i t] S_{xi}^{(2)} + [a_i(t) \sin c_i t - b_i(t) \cos c_i t] S_{yi}^{(2)}$$

$$= \sum_{i=1}^{2} [a_i(t, \Delta \pm c) S_{xi}^{(2)} - b_i(t, \Delta \pm c) S_y^{(2)} + c_i(t, \Delta \pm c) S_z^{(2)}]. \qquad (56)$$

Assuming that the oscillating terms can be averaged out at times $t > 2\pi/q$ then the irradiation at the shifted DQ resonance

$$\omega = \omega_0 - \tfrac{1}{2}\left(q + \frac{h\omega_1^2}{q}\right)$$

gives

$$a_1 = -\frac{48}{1 - (2\omega_1/q)^4}, \quad b_1 = 0, \quad c_1 = 0, \qquad (57)$$

while the irradiation at

$$\omega = \omega_0 + \tfrac{1}{2}\left(q + \frac{h\omega_1^2}{q}\right)$$

gives

$$a_2 = -\frac{48}{1 - (2\omega_1/q)^4}, \quad b_2 = 0, \quad c_2 = 0. \qquad (58)$$

It shows that the DQ resonance line is shifted for the values $\pm 4\omega_1^2/q$ and the magnitude of the DQ rf field is increased for a factor $[1 - (2\omega_1/q)^4]^{-1}$.

6. Conclusion

The employed formalism enables us to evaluate the effective Hamiltonians governing the DQ phenomena in the approximation $\omega_1/Q < 1$ for quadrupole perturbed spin system of any spin number. The obtained results differ to some extent from results of previous calculations [1] for $s = 1$ which was treated almost exactly. Namely, the effective DQ rf field vanishes for equidistant levels, i.e. when $Q = 0$, and there is the time delay between the applied rf field and the effective DQ rf field which is equal to $\tau \approx 2\pi/Q$. The Magnus expansion of the time evolution operator is not the usual perturbation approach which requires $\omega_1/Q \ll 1$ but can be applied to the magnitude of rf field ω_1/Q is of the order of 0.3 since the different terms of (5) play the dominant role at different rf frequencies. Thus, when irradiating at DQ transition only $\mathcal{H}_{1\mathrm{rf}}$ is constant while others are oscillating and can be averaging out.

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