A perturbation approach to dipolar coupling spin dynamics

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Abstract

A perturbation method is presented which can be applied to the description of a wide range of physical problems that deal with dynamics of dipolarly coupled spins in solids. The method is based on expansion $e^{A+B}$ in a perturbation series. As example of application the method, the multile-quantum coherence dynamics in three and four spin cluster are considered. The calculated 0Q- and 2Q intensities vs the duration of the preparation period give closed agreement with exact results and simulations data. The exact solutions for $J_{0Q}$ and $J_{2Q}$ coherences in four spin system are obtained.
Dipolar coupling spin dynamics represents a significant interest from both the point of view of the general problems of physics of many bodies, and from a position of the nuclear magnetic resonance (NMR) [1, 2]. In solids, the evolution of a spin system under the dipole-dipole interaction (DDI) involves many spins and leads to unsolvable problems. Even the analysis using the numerical calculation becomes difficult because the number of states $N = 2^n$ is growing exponentially with the increasing of $n$. So in existing theories, only macroscopic characteristics such as spin-spin relaxation times, the second and the fourth moments of resonance lines were taken into account [1]. This difficulties are very clearly displayed in multiple-quantum (MQ) spin dynamics. The MQ phenomena involves various multiple-spin transitions between the Zeeman energy levels and form MQ coherence at times $t > \omega_d^{-1}$, where $\omega_d$ is the characteristic frequency of DDI [3]. The problem in analytical description of MQ is that the different modes of coherence grow in at different times, with higher modes requiring longer excitation times than lower modes [4]. Hence, $\omega_d t > 1$ is not a small parameter, and, at first glance, perturbation theory methods cannot be used to study MQ dynamics. Indeed only simple exactly solvable models of spin system such as two and three dipolar coupling spin-1/2 [5, 6] or one-dimensional linear chains spin [7] system were analyzed theoretically. The last achievement in this direction is the model with identical DDI coupling constant for all spin pairs [8, 9]. Note, that the simplified calculations are essential for the case of indentical DDI coupling constant has been already mentioned [10]. Such approaches cannot describe MQ processes except for zeroth and second-order coherences. Thus, the development of method that can successfully represent important features of MQ dynamics with a larger then 0Q and 2Q coherences is needed.

Importance of the analytical description of the MQ processes in solids is that involving the excitation of collections of dipolar coupling spins, can provide important structural, as well as the spin dynamics informations. Moreover, during the past few years, the NMR is considered as the best candidate [11, 12, 13] for experimental realization quantum information processes. It was experimentally demonstrated the creating pseudopure spin states in large clusters of coupled spins by MQ method [14] and that dynamics of the quantum entanglement is uniquely determined by the time evolution of MQ coherences [6]. Thus, investigation of the quantum information processes with MQ methods are of current interest.

We present a perturbation approach to the problem of dipolar coupling spin dynamics in solids. DDI of all spins was divided into several groups that are characterized by the
identical DDI coupling constants. Since the magnitudes of the dipolar coupling constants vary inversely with the cube of internuclear distance, the coupling constants are different for these groups.

Our main idea is to take into account in MQ NMR dynamics influence of the groups with different degree of accuracy. Spin groups with smaller DDI coupling constants can be considered as perturbation (spins located far apart) while the nearest neighbours are taken into account exactly. As the result, we can develop a perturbation method that allows obtaining the description of the MQ with a large coherence evolution under DDI in an analytical form. The proposed approach will be a powerful method to describe wide ranges of physical problems that deal with dynamics of dipolar coupled spins in solid. On the one hand, this approach uses the advantages of exactly solvable models \([9, 15]\). On the other hand, it simplifies calculations by using a perturbation technique. Results will show that the perturbation method can be applied to solve complex spin-dynamics problem and to obtain the solution in an analytical form. The method is based on the differential method \([16, 17]\) expresses \(e^{A+B}\) as an infinite product of exponential operators \([17]\). In the case when the norm of operator \(B\) is small then one of operator \(A\), \(\|B\| < \|A\|\), we will try to obtain the perturbation series which takes into account up to second order terms in ratio \(\|B\| / \|A\|\). Then the problems in description the MQ dynamics will be significantly simplified.

Let us consider a spin system with Hamiltonian, \(\mathcal{H}\) which includes only two parts with different DDI constants \(\alpha\) and \(\beta\): \(\mathcal{H} = A + B\), where \(A = \alpha A\) and \(B = \beta B\), \(\alpha = \|A\|\) and \(\beta = \|B\|\) are the norms of operators \(A\) and \(B\), respectively (\(\alpha > \beta\) and \([A, B] \neq 0\)). The evolution of the spin system is governed by propagator

\[
e^{-it\mathcal{H}} = e^{-it(\alpha A + \beta B)}.
\] (1)

We seek to express (1) as a series in such that

\[
e^{-it(\alpha A + \beta B)} = e^{-it\beta B} \sigma(t),
\] (2)

where operator \(\sigma(t)\) obeys the differential equation \([17, 18]\)

\[
\frac{id\sigma(t)}{dt} = \alpha A^{(0)}(t) \sigma(t),
\] (3)

with initial condition

\[
\sigma(0) = 1
\] (4)
and \( A^{(0)} (t) = e^{-it\beta B} A e^{it\beta B} \). Assume that \( \alpha t \geq 1 \) and \( \beta t < 1 \). First, we will restrict ourself by keeping only first-order terms that are linearly proportion to \( \beta \). This leads to

\[
\frac{d\sigma^{(0)} (t)}{dt} = \alpha (A - it\beta [B, A]) \sigma^{(0)} (t). \tag{5}
\]

To solve Eq. (5) we will use the iterative method. We will search the solution of Eq. (5) as a series on parameter \((\alpha t)^n\):

\[
\sigma_A (t) = \sum_{n=0}^{\infty} \sigma_A^{(n)} (t) \tag{6}
\]

Taking into account that \( \sigma_A^{(0)} (t) = 1 \) the solution of Eq. (5) for \( n = 1 \) can be obtained:

\[
\sigma_A^{(1)} (t) = (-i\alpha t) A. \tag{7}
\]

For \( n = 2 \), one obtains

\[
\sigma_A^{(2)} (t) = \frac{(-i\alpha t)^2}{2} \left( A^2 + \frac{\beta}{\alpha} [B, A] \right) \tag{8}
\]

Keeping only linear in \( \frac{\beta}{\alpha} \) terms the following expression for operator \( \sigma_A^{(m)} (t) \) can be obtained

\[
\sigma_A^{(m)} (y) = \frac{(-i\alpha t)^m}{m!} \left( A^m - \frac{\beta}{\alpha} \left( (m-1)BA^{m-1} - \sum_{j=0}^{m-2} A^{m-1-j}BA^j \right) \right) \tag{9}
\]

Using Eq. (9) we obtain

\[
e^{-it(\alpha A + \beta B)} = \left( 1 - \beta \sum_{n=0}^{N} \frac{(it)^{n+1}}{(n+1)!} \sum_{j=0}^{n} \frac{(-1)^j (n)!}{j! (n-j)!} A^j B A^{n-j} \right) e^{-i\left( \alpha A + \frac{\beta}{\alpha} \left( \frac{(it)^{N+2}}{(N+2)!} \right) \right) [B, A]_{N+1}} \tag{10}
\]

where \([B, A]_{N+1}\) denotes the repeated commutators \([[[...[B, A], A]...A]_{N+1}\). After summation over \( j \) in Eq. (10) we have

\[
e^{-it(\alpha A + \beta B)} = \left( 1 - \beta \sum_{n=0}^{N} \frac{(it)^{n+1}}{(n+1)!} \{B, A^n\} \right) e^{-i\left( \alpha A + \frac{\beta}{\alpha} \left( \frac{(it)^{N+2}}{(N+2)!} \right) \right) (B, A^{N+1})} \tag{11}
\]

where

\[
\{B, A^0\} = B \quad \text{and} \quad \{B, A^{n+1}\} = \{[B, A^n], A\}. \tag{12}
\]

In the limit as the number of steps \( N \to \infty \) we obtain that \( \lim_{N \to \infty} \left( \frac{\beta (it)^{N+2}}{\alpha (N+2)!} \right) \) is 0. Consequently, the exponent in (11) can be presented in the limit as \( N \to \infty \) in the following
form: $\lim_{N \to \infty} e^{-i\left(\alpha A + \frac{\beta}{\alpha} (t\alpha)^{N+2} [B,A]_{N+1}\right)} = e^{-i\alpha t A}$, which does not include any terms with $B$, and the summing over $n$ up to indefinite, results in

$$e^{-i t (\alpha A + \beta B)} = \left(1 - i\frac{\beta}{\alpha} \int_0^{\alpha t} dx e^{-i x A} B e^{i x A}\right) e^{-i\alpha t A}, \quad (13)$$

which is a well known formula for expansion an exponential operator in a perturbation series [18]. To obtain expansion containing only linear to $\beta \alpha$ terms we have to require that $\frac{\beta}{\alpha} (t\alpha)^{N+2} \ll 1$. This requirement imposes restrictions also on time: $t \ll \frac{1}{\alpha} \left(\frac{\beta}{\alpha} (N + 2)!\right)^{\frac{1}{N+2}}$. So for the smallest of times $t \ll \frac{1}{\alpha} \left(\frac{\beta}{\alpha} (N + 2)!\right)^{\frac{1}{N+2}}$ or $t \ll \frac{1}{\beta}$, the Eq. (10) includes only terms linear in $\beta$. In an analog way, we obtain the expansion up to second order in the ratio $\frac{\beta}{\alpha}$:

$$e^{-i t (\alpha A + \beta B)} = \left\{1 - \frac{\beta}{\alpha} \sum_{m=0}^{\infty} \sum_{k=0}^{\infty} \frac{(-1)^m (ix)^k m! (k + m + 1)}{k! m! (k + m + 1)!} A^m B A^kight. \right.$$

$$+ \left. \left(\frac{\beta}{\alpha}\right)^2 \sum_{l=0}^{\infty} \sum_{p=0}^{\infty} \frac{(-1)^m p (ix)^k l! m! p! (l + m + p + 1)}{k! m! p! (k + l + m + p + 2)!} A^l B A^p B A^k\right\} e^{-i x A} \quad (14)$$

The series expansion (14) can be used not only for the small parameter $\frac{\beta}{\alpha} < 1$, but independently, for the parameter $x = \alpha t$. Formula (14) can be easily generalized for a case when the exponential operator contains arbitrary number of the non-commutative operators and can be extended to include various power of the operators. Eqs. (14) appears to be complex at glance, but in fact it is quite simple to use, as the following examples will illustrate.

Let us consider a cluster of three dipolar-coupled spin-$\frac{1}{2}$ nuclei. The MQ dynamics in the rotating frame is described by propagator (1), where the time-independent average Hamiltonian is given by

$$\mathcal{H} = -\frac{1}{2} \sum_{j<k} d_{jk} \left(I_j^+ I_k^+ + I_j^- I_k^-\right) \quad (15)$$

and $I_j^+$ and $I_j^-$ are the raising and lowering operators for spin $j$. The dipolar coupling constant, $d_{jk}$, for any pair of nuclei $j$ and $k$ in the cluster, is given by

$$d_{jk} = \frac{\gamma^2 \hbar}{2 r_{jk}^3} (1 - 3 \cos \theta_{jk}), \quad (16)$$

where $\gamma$ is the gyromagnetic ratio of the nuclei, $r_{jk}$ is the internuclear spacing, and $\theta_{jk}$ is the angle the vector $\vec{r}_{jk}$ makes with the external magnetic field. In the high-temperature
approximation the density matrix at the end of the preparation period is given by

\[ \rho(t) = e^{-iHt}\rho(0)e^{iHt} \]  

(17)

where \( \rho(0) \) is the initial density matrix in the high-temperature approximation

\[ \rho(0) = \sum_{j=1}^{3} I_j^z, \]  

(18)

\( I_j^z \) is the projection of the angular momentum operator on the direction of the external field for an spin \( j \). The average Hamiltonian (15) can be divided into the three parts according to the number of the different coupling constant \( d_{12} > d_{23} > d_{13} : \)

\[ H = H_{12} + H_{23} + H_{13}, \]  

(19)

where

\[ H_{jk} = -\frac{d_{jk}}{2} (I_j^+I_k^- + I_j^-I_k^+) \] with \( j \neq k \) and \( j, k = 1, 2, 3. \)  

(20)

The experimentally observed values are the intensities, \( J_{nQ}(t) \) of multiple-quantum coherences:

\[ J_{nQ}(t) = \frac{1}{Tr\rho^2(0)} \sum_{p,q} \rho_{pq}^2(t) \text{ for } n = m_{zp} - m_{zq}, \]  

(21)

where \( m_{zp} \) and \( m_{zq} \) are the eigenvalue of the initial density matrix (18). The perturbation method described above is used to calculate the time evolution of MQ coherences. Using expansion (14) with \( \alpha A = H_{12} \) and \( \beta B = H_{23} + H_{13} \) and keeping terms up to eighth order in \( x = \alpha t \), the normalized 0-quantum \((J_{0Q})\) and 2-quantum \((J_{2Q})\) intensities are given by

\[ J_{0Q} = 1 - \frac{8x^2}{3} + \frac{32x^4}{9} - \frac{256x^6}{125} + \frac{512x^8}{945} + \left(\frac{\beta}{\alpha}\right)^2 \left(\frac{8x^2}{3} + \frac{40x^4}{9} - \frac{176x^6}{45} + \frac{1544x^8}{945}\right) \]  

(22)

and

\[ J_{2Q} = -\frac{4x^2}{3} + \frac{16x^4}{9} - \frac{128x^6}{135} + \frac{256x^8}{945} - \left(\frac{\beta}{\alpha}\right)^2 \left(\frac{4x^2}{3} + \frac{32x^4}{9} - \frac{128x^6}{45} + \frac{1024x^8}{945}\right) \]  

(23)

where \( \left(\frac{\beta}{\alpha}\right)^2 = \left(\frac{d_{23}}{d_{12}}\right)^2 + \left(\frac{d_{13}}{d_{12}}\right)^2 \). Let us compare formulas (22) and (23) with results from Eq. (14) which the terms with \( x = \alpha t \) will be taken into account exactly. By summing over \( n \),
m, l, and k up to indefinitely in (14), we obtain the analytical expressions of the intensities of 0- quantum

\[ J_{0Q} = \frac{1}{3} \left\{ \cos 4x - 2 \left[ \left( \frac{\beta}{\alpha} \right)^2 - 1 \right] + 2 \left( \frac{\beta}{\alpha} \right)^2 \left( \cos x + \cos 3x - \cos 4x - x \sin 4x \right) \right\} \tag{24} \]

and of 2- quantum

\[ J_{2Q} = -\frac{\sin 2x}{3} \left\{ 2x \left( \frac{\beta}{\alpha} \right)^2 \cos 2x + 2 \left[ \left( \frac{\beta}{\alpha} \right)^2 - \left[ \left( \frac{\beta}{\alpha} \right)^2 - 1 \right] \cos x \right] \sin x \right\} \tag{25} \]

Now let us compare intensities (22) - (25) with the exact solution [5]. Figs. 1 and 2 show the evolution of the normalized 0Q and 2Q coherences for three spin cluster, where \( \frac{\beta}{\alpha} = 0.3 \) and at \( t = 0 \) the spin system is in thermal equilibrium (18). All approaches, perturbations (Eqs. (22) - (25)) and exact [5], give closed agreement up to \( x = 0.75 \) (in unit of \( \frac{1}{\alpha} \)), both for 0Q - and 2Q- coherences. The exact account of influence of the nearest neighbours gives a good agreements up to \( x = 2 \).

As a second example we consider is cluster consists of four spin arrange in corners of square in an external magnetic field perpendicular to the square plane. In this case the MQ spin dynamics is described by the average Hamiltonian

\[ H = H_1 + H_2, \tag{26} \]

with two different dipolar coupling constants \( D_1 \) and \( D_2 \), where \( D_1 \) and \( D_2 \) are the dipolar coupling constants between nearest neighbors and spins at opposite sites, respectively (\( \frac{D}{\alpha} = D_2 \frac{D_1}{D_1} = \frac{1}{2\sqrt{2}} \)) where

\[ H_1 = \left( -\frac{D_1}{2} \right) \sum_{j=1}^{4} (I_j^+ I_{j+1}^- + I_j^- I_{j+1}^+) = \alpha A \tag{27} \]

and

\[ H_2 = \left( -\frac{D_2}{2} \right) \sum_{j=1}^{2} (I_j^+ I_{j+2}^- + I_j^- I_{j+2}^+) = \beta B \tag{28} \]

Using the expansion (14) up to eighth order in \( x = \alpha t \), the normalized 0-quantum \( (J_{0Q}) \)

\[ J_{0Q} = 1 - 2x^2 + \frac{7}{4}x^4 - \frac{13}{18}x^6 + \frac{5}{28}x^8 - \left( \frac{\beta}{\alpha} \right)^2 \left( x^2 - \frac{13}{6}x^4 + \frac{121}{60}x^6 - \frac{599}{630}x^8 \right) \tag{29} \]

and 2-quantum \( (J_{2Q}) \)

\[ J_{2Q} = -\frac{x^2}{4} + \frac{x^4}{4} - \frac{1}{9}x^6 + \frac{1}{35}x^8 - \left( \frac{\beta}{\alpha} \right)^2 \left( \frac{x^2}{8} - \frac{x^4}{3} + \frac{11x^6}{30} - \frac{58x^8}{315} \right) \tag{30} \]
intensities can be determined. Formulas (29) and (30) will be compared with results from Eq.(14) in which the terms describing interaction of the neighbour spins will be taken into account exactly. By summation over \( n, m, l, \) and \( k \) up to indefinitely in Eq.(14) we obtain the analytical expressions of the intensities of \( 0Q \- \) quantum

\[
J_{0Q} = \frac{1}{4} \left( 1 + \sin^2 2x + 2 \sin^2 \sqrt{2}x \right) + \frac{x^2}{8} \left( \frac{\beta}{\alpha} \right)^2 \left( 2 \sin^2 2x - \frac{\sqrt{2}}{x} \sin 2\sqrt{2}x \right) \tag{31}
\]

and of \( 2Q \- \) quantum

\[
J_{2Q} = -\frac{1}{8} \left( \sin^2 2x + 2 \sin^2 \sqrt{2}x \right) + \frac{x^2}{16} \left( \frac{\beta}{\alpha} \right)^2 \left( 2 \sin^2 2x - \frac{\sqrt{2}}{x} \sin 2\sqrt{2}x \right) \tag{32}
\]

coherences.

To control the perturbation results (29) - (32) we obtained the exact solution for \( J_{0Q} \)

\[
J_{0Q} = \frac{9}{4} - \frac{1}{2} \cos \left( 2x \sqrt{2 + \left( \frac{\beta}{\alpha} \right)^2} \right) + \frac{1}{4} \cos 4x \cos \left( 2x \frac{\beta}{\alpha} \right) - \cos^2 \left( x \frac{\beta}{\alpha} \right) \tag{33}
\]

and for \( J_{2Q} \)

\[
J_{2Q} = -\frac{3}{4} + \frac{1}{4} \cos \left( 2x \sqrt{2 + \left( \frac{\beta}{\alpha} \right)^2} \right) + \frac{1}{4} \sin^2 2x \cos \left( 2x \frac{\beta}{\alpha} \right) + \frac{1}{2} \cos^2 \left( x \frac{\beta}{\alpha} \right) \tag{34}
\]

cohereces and fulfilled the numerical analysis of the MQ dynamics. The exact solutions (33) and (34) and computer simulation of the MQ coherences of four spins cluster have been obtained with a PC using the MATLAB package.

Figs. 3 and 4 show, that perturbation results (29) and (30) are in the agreement with (31) and (32) and the exact solutions (33) and (34) and with the simulation data one up to \( x = 1 \) (in unit of \( 1/\alpha \)). Calculations in which the interaction between the nearest neighbours is taken into account exactly (Eqs (31) and (32)) are in close agreement with the exact solutions (Eqs.(33) and (34)) and simulation data up to \( x = 3 \).

In conclusion, a perturbation method was developed which is based on the expansion of operator exponent in a perturbation series. Then the perturbation approach was applied to the description the MQ spin dynamics in solids. The analytical expressions for \( 0Q \) and \( 2Q \) dynamics in a three and four spin clusters in solids were obtained. In the four spin cluster the exact solution was obtained. The calculated \( 0Q \- \) and \( 2Q \) intensities vs the duration of
the preparation period agree well with exact solutions for three and for four spin clusters (Eqs.(33) and (34)).

The developed method can be extended to include various power of the operators with small norm and applied to the description widely range of physical problems deal with dynamics of dipolar coupling spins in solids. The results in an analytical form can be use to extract from experimental data the dipolar constants and the molecular structure information.

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Captions for figures.

Figure 1
Fig. 1 Time dependences (in units of $\frac{1}{\alpha}$) of the normalized intensities of $0Q$ coherence (solid-line is exact solution $[?]$, dot-line is the calculation using Eq.(22) and dash-line is the calculation using Eq.(24))

Figure 2
Fig. 2 Time dependences (in units of $\frac{1}{\alpha}$) of the normalized intensities of $2Q$ coherence (solid-line is exact solution $[?]$, dot--line is the calculation using Eq.(23) and dash-line is the calculation using Eq.(25))

Figure 3
Fig. 3 Time dependences (in units of $\frac{1}{\alpha}$) of the normalized intensities of $0Q$ coherence in four spin cluster. Solid-line is exact solution (Eq.(33), dot-line is the calculation using Eq.(29), dash-line is the calculation using Eq.(31), and open circle is computer simulations.

Figure 4
Fig. 4 Time dependences (in units of $\frac{1}{\alpha}$) of the normalized intensities of $2Q$ coherence in four spin cluster. Solid-line is exact solution (Eq.(34), dot-line is the calculation using Eq.(30), dash-line is the calculation using Eq.(32), and open circle is computer simulations.
The diagram illustrates the function $J_0(x)$ plotted against $x = \alpha t$, where $x$ is the independent variable and $t$ is the parameter. The graph shows the variation of $J_0(x)$ with $x$, highlighting the oscillatory behavior of this Bessel function of the first kind.
The graph shows the function $J_0(\alpha t)$ as a function of $x = \alpha t$. The x-axis represents $\alpha t$, ranging from 0.0 to 3.0, and the y-axis represents $J_0(\alpha t)$, ranging from 0.0 to 1.0. The graph includes a solid line and a dashed line, with data points marked by circles along the curve.
