Energy spectrum of the equal spin-spin interactions Hamiltonian

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Abstract

The energy spectrum of eigenvalues of the equal spin-spin interactions (ESSI) Hamiltonian has been found. The obtained spectrum is free from limitations imposed on number of spins and parameters of the ESSI Hamiltonian. This model can be used for consideration of spin dynamics of mesoscopic systems and molecules with large number of nuclei spins.

1 Introduction. Many-body problem of spin-spin interactions

Thorough attention of researches to the properties of the Hamiltonian of spin-spin interactions is kept during some decades. It is due to the fact that this Hamiltonian determines fine peculiarities of dynamics and kinetics of the electron and nuclei spins of paramagnet spin-systems. The Hamiltonian of a paramagnet (electronic and nuclear) has the following form [1]

\[ \mathcal{H} = \mathcal{H}_z + \mathcal{H}_d + \mathcal{H}_{dd}, \]

\[ \mathcal{H}_z = \hbar \omega_0 \sum_j S_j^z, \quad \mathcal{H}_d = \hbar \sum_{fj} A_{fj} S_j^z S_f^z, \quad \mathcal{H}_{dd} = \hbar \sum_{fj} B_{fj} (S_j^- S_f^+ + S_j^+ S_f^-), \]

\[ S^\pm = S^x \pm i S^y, \quad A_{fj} = A_{fj} + J_{fj}, \quad A_{fj} = (\hbar \gamma^2 / 2 R_{fj}^3)(1 - 3 \cos \theta_{fj}), \]

\[ B_{fj} = (-1/4)A_{fj} + (1/2)J_{fj}, \]

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where \( S^a_j \) is the \( a \)-th spin component of a spin \( S_j \) \((a = x, y, z)\), located in the point \( j \), \((R_{fj}, \theta_{fj}, \varphi_{fj})\) define the spherical coordinates of a vector connecting the points \( f \) and \( j \) in the laboratory frame which \( OZ \) axes is parallel to the applied constant magnetic field \( H_0 \), \( \gamma \) is a gyromagnetic ratio, \( \omega_0 = \gamma H_0 \) is Zeeman frequency, the value \( J_{fj} \) defines an exchange integral. Only the secular (diagonal) part of the dipole-dipole Hamiltonian is given by expression (1). This part determines the most essential contribution to dynamics and kinetics of spins in comparison with off-diagonal parts \([2, 3, 4]\). The Hamiltonian (1) represents a typical example of many-body interactions and so it is no needless to say about exact diagonalization of (1) if number of interacting spins \( n \geq 10 \). Even if the numerical calculation of the corresponding eigenvalues will be obtained, the analysis of this information 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 as spin-spin relaxation times, the second and the fourth moments of resonance lines were taken into account [1].

Recently in investigation of the NMR on protons in a nematic liquid crystal [5] a principal new NMR spectrum has been demonstrated. It consists of a set of well-resolved resonance lines instead of one usual unresolved resonance line broadened by spin-spin interactions. In recent time the authors brought the number of resonance lines up to the value 1024 [6]. This result opens new possibilities in studying of dynamics and kinetics of dipole-dipole connected spins in the mesoscopic systems and gives a new perspective physical medium for quantum information science.

In such a way, the theoretical description of quantum-statistical properties of dipole-dipole coupled spin-systems becomes a very interesting problem.

A liquid crystal where the spin-spin multiplet resolved spectrum with narrow lines was observed [5], includes partly oriented molecules, each molecule contains \( n = 19 \) interacting protons and intermolecular spin-spin interaction is negligible. It implies to find about a half-million of eigenvalues of the Hamiltonian (1) that is the useless problem for exact solution. We want to stress that at certain values of orientation angles \( \theta_{fj} \) the dipole-dipole interaction between close disposed spins can be less in comparison with remote spins. It is necessary to take also into account that orientation of spins in the space is not fixed precisely and true interaction constants are effectively replaced by their parts non-averaged by heat motion. This averaging of the spin-spin interaction of protons, located in the different part of the molecule is not equivalent: the effect of averaging is greater in the more mobile frag-
ments. So, the further progress is possible with using a simplified theoretical model, which keeps nevertheless the main features of the basic Hamiltonian \[^{1}\]. In our opinion such theoretical model can be presented by the *equal spin-spin interactions* (ESSI). The Hamiltonian of the ESSI has the form:

\[ H^* = H_z + H_d^* + H_{dd}^*, \]

where \( A \) and \( B \) defines the average values of parameters \( A_{fj} \) and \( B_{fj} \) for separate molecule. The Hamiltonian of such type was considered in paper related to multiple nonergodic quantum dynamics \[^{7}\]. It seems that the range of applicability of this Hamiltonian is much wider *viz.*, it can be applicable for consideration the sets of spins in mesoscopic magneto-active clusters.

The averaged constants \( A \) and \( B \) take into account the interaction of the chosen spin with all others, keeping the difference between the longitudinal (\( A \)) and transverse (\( B \)) spin components. These constants can be obtained from real interaction potential as

\[ \langle A \rangle = \frac{1}{n} \sum_{fj} A_{fj}, \quad \Delta A = \left[ \frac{1}{n} \sum_{fj} (A_{fj} - A)^2 \right]^{1/2}, \quad A = \langle A \rangle \pm \Delta A, \]

and the same for constant \( B \).

In the next section the energy spectrum of the Hamiltonian (2) will be found.

### 2 The matrix structure of the ESSI model

The operators \( H_z \) and \( H_d^* \) commute with each other and with a longitudinal component \( S_j^z \) of a separate spin. So the eigenvalues

\[ E_{np} = \hbar \omega_0 \frac{(2p - n)}{2} + \hbar A \left( 3p^2 - 3np + n^2 - n \right) / 4 \]

of the operator \( H_z + H_d^* \) are expressed by means of eigenvalues \((\pm 1/2)\) of the operator \( S_j^z \), where \( n \) defines the total number of spins and \( p \) is a number of
spins oriented positively along the applied magnetic field. Eigenfunctions of the operator $\mathcal{H}_z + \mathcal{H}_d^*$

$$|\chi_{\alpha=1}(n, p)\rangle =$$

$$= |m_1 = 1/2, m_2 = 1/2, \ldots, m_p = 1/2, m_{p+1} = -1/2, \ldots, m_{n-1} = -1/2, m_n = -1/2\rangle \equiv$$

$$\equiv |+, +, \ldots, +, -, \ldots, -, -\rangle \quad (4)$$

are also constructed as products of $n$ eigenfunctions $|m_j\rangle$ of operators $S_j^z$. The state (3) is degenerated $z(n, p) = C_n^p$ times at the given $n$ and $p$. All set of eigenfunctions $|\chi_{\alpha}(n, p)\rangle$, belonging to the given $E_{np}$ is obtained from the function $|\chi_{\alpha=1}(n, p)\rangle$ by permutation of its initial arguments running over all combinations from $n$ over $p$, i.e. $\alpha = 1, 2, \ldots, z(n, p)$.

Due to the structure of the operators $S_j^- S_j^+ + S_j^+ S_j^-$, the Hamiltonian $\mathcal{H}_{dd}^*$ does not have nonzero matrix elements between states with unequal number of positively oriented spins. So its matrix has blocked-diagonal form, where the sizes of blocks is determined as $C_n^p \times C_n^p$. Diagonal elements of the operator $\mathcal{H}_z + \mathcal{H}_d^*$ inside blocks are the same and determined by expression (3). In such a way the problem of diagonalization of the Hamiltonian (2) is reduced to the finding of eigenvalues of the operator $\mathcal{H}_{dd}^*$ in basis of states (4) with eigenvalues belonging to (3).

### 3 Eigenvalues of the operator $\mathcal{H}_{dd}^*$

For diagonalization of the operator $\mathcal{H}_{dd}^*$ a special numerical program was written. It helps to find the desired matrices in basis (4) inside $(n, p)$-blocks and includes subsequent calculation of eigenvalues and eigenfunctions of corresponding matrices. The spectrum of eigenvalues together with their degeneration multiplicity $g$ of the operator $\mathcal{H}_{dd}^*$ has been found for all $n$ and $p$ satisfying to condition $n \leq 8$. Analyzing these results we established that in each $(n, p)$-block:

1. the number of different eigenvalues is defined as
   \[ r(n, p) = r(n, n - p) = p + 1, \]  
   \[ (5) \]

2. the unequal eigenvalues of the operator $\mathcal{H}_{dd}^*$ are determined as
   \[ \hbar \varepsilon_k(n, p) = \hbar \varepsilon_k(n, n - p) = \hbar B[-p + k(n - 2p + 1) + k^2], \]  
   \[ (6) \]
3. the energy degeneration of the level $\varepsilon_k(n, p)$ is

$$g_k(n, p) = g_k(n, n - p) = C_n^{p-k} - C_n^{p-k-1}, \quad (7)$$

where $0 \leq p \leq p^*$, $0 \leq k \leq p$, $p^* = \lfloor n/2 \rfloor$ is the integer part of $n/2$ and $k$ numbers the operator $\mathcal{H}_{dd}^*$ unequal eigenvalues.

In further the correctness of these formulae was confirmed by direct numerical calculations for all possible values of $n$ and $p$ up to $n = 11, p = 4$. These calculations give us a ground to consider that formulae (3), (5) and (6) are exact expressions for the spectrum of the Hamiltonian (2) describing ESSI-model.

The eigenfunctions of the Hamiltonian $\mathcal{H}_{dd}^*$ were also calculated

$$|\Psi_\beta(n, p)\rangle = \sum_{\alpha=1}^{z} C_{\alpha\beta}(n, p) |\chi_\alpha(n, p)\rangle, \quad 1 \leq \beta \leq z(n, p), \quad (8)$$

by determination the sets of coefficients

$$(C_{1\beta}(n, p), C_{2\beta}(n, p), C_{3\beta}(n, p), \ldots, C_{z\beta}(n, p)).$$

Unfortunately, the compact expressions for coefficients $C_{\alpha\beta}(n, p)$ were not found. Expressions for $C_{\alpha\beta}(n, p)$ were obtained numerically for all cases, where the energy spectrum has been determined. These expressions are rather cumbersome and so, for example, in the Table 1 the coefficients $C_{\alpha\beta}(n, p)$ were given only for $n = 5$.

Taking into account the fact that the function $|\chi_\alpha(n, p)\rangle$ belongs to the same eigenvalue (3), one can conclude that any their linear combination, in particular combination (8), also belongs to this eigenvalue. Due to this property the eigenvalues of the ESSI Hamiltonian (2) can be presented in the form of simple sum of energies (3) and (6)

$$E_k(n, p) = E_{np} + h\varepsilon_k(n, p), \quad (9)$$

To each set of the three indices $n, p, k$ corresponds $g_k(n, p)$ eigenfunction (8).

In conclusion we would like to note that exact expressions (3), (5)–(7) found for the quantum model ESSI are not exact solution but has the anzatz status. The found solution was guessed and then checked on large number of cases including block ($n = 11, p = 4$), which consists of 330 states.
Table 1: The eigenvalues, degeneration multiplicity value and eigenfunctions of the Hamiltonian $H_{dd}^*$ for five spins

| $n$ | $p$ | $\varepsilon_k(n, p)$ | $g_k(n, p)$ | Coefficients $C_{\alpha\beta}(n, p)$ of the functions $|\Psi_\beta(n, p)\rangle$ | Basis functions $|\chi_\alpha(n, p)\rangle$ |
|-----|-----|-----------------|-------------|---------------------------------|-----------------|
| 5   | 0   | 0               | 1           | $(1, 0, 0, 0, 1)/\sqrt{2}$       | $|--, --, --, --|$ |
|     |     |                 |             | $(-1, 0, 0, 2, -1)/\sqrt{6}$     | $|--, +, --, --|$ |
|     |     |                 |             | $(-1, 0, 3, -1, -1)/2\sqrt{3}$   | $|--, --, +, --|$ |
|     |     |                 |             | $(-1, 4, -1, -1, -1)/2\sqrt{5}$  | $|--, --, --, +|$ |
| 1   | -1  | 4               |             | $(1, 1, 1, 1, 1)/\sqrt{6}$       | $|+,-,-,-, -|$ |
|     |     |                 |             | $(1, -1, 1, -1, -1, 0, 0, 0, 1)/\sqrt{10}$ | $|+,-,-,-, -|$ |
|     |     |                 |             | $(2, -2, -3, 3, -2, 0, 0, 5, -1, -2)/2\sqrt{15}$ | $|+,-,-,-, -|$ |
|     |     |                 |             | $(2, 2, 1, -1, -2, 0, 4, 1, -1, -2)/6$ | $|+,-,-,-, -|$ |
|     |     |                 |             | $(-1, 1, -1, 1, -1, 3, -1, -1, 1, -1)/3\sqrt{2}$ | $|--,-,+,--|$ |
| 2   | -2  | 5               |             | $(1, 1, -1, 0, 0, 0, 0, 0, 0, 0, 1)/\sqrt{10}$ | $|+,-,-,-, -|$ |
|     |     |                 |             | $(1, -1, -1, 0, 0, 0, 0, 0, 2, -1)/\sqrt{10}$ | $|+,-,-,-, -|$ |
|     |     |                 |             | $(2, 2, -3, 3, -2, 0, 0, 5, -1, -2)/2\sqrt{15}$ | $|+,-,-,-, -|$ |
|     |     |                 |             | $(2, 2, 1, -1, -2, 0, 4, 1, -1, -2)/6$ | $|+,-,-,-, -|$ |
|     |     |                 |             | $(-1, 1, -1, 1, -1, 3, -1, -1, 1, -1)/3\sqrt{2}$ | $|--,-,+,--|$ |
| 3   | -2  | 5               |             | $(1, 1, -1, 0, 0, 0, 0, 0, 0, 0, 1)/\sqrt{10}$ | $|+,-,-,-, -|$ |
|     |     |                 |             | $(1, -1, -1, 1, 0, 0, -1, 0, 2, -1)/\sqrt{10}$ | $|+,-,-,-, -|$ |
|     |     |                 |             | $(2, 2, -3, 3, -2, 0, 0, 5, -1, -2)/2\sqrt{15}$ | $|+,-,-,-, -|$ |
|     |     |                 |             | $(2, 2, 1, -1, -2, 0, 4, 1, -1, -2)/6$ | $|+,-,-,-, -|$ |
|     |     |                 |             | $(-1, 1, -1, 1, -1, 3, -1, -1, 1, -1)/3\sqrt{2}$ | $|--,-,+,--|$ |
| 4   | -1  | 4               |             | $(1, 1, -1, 0, 0, 0, 0, 0, 0, 0, 1)/\sqrt{10}$ | $|+,-,-,-, -|$ |
|     |     |                 |             | $(1, -1, -1, 0, 0, 0, 0, 0, 2, -1)/\sqrt{10}$ | $|+,-,-,-, -|$ |
|     |     |                 |             | $(2, 2, -3, 3, -2, 0, 0, 5, -1, -2)/2\sqrt{15}$ | $|+,-,-,-, -|$ |
|     |     |                 |             | $(2, 2, 1, -1, -2, 0, 4, 1, -1, -2)/6$ | $|+,-,-,-, -|$ |
|     |     |                 |             | $(-1, 1, -1, 1, -1, 3, -1, -1, 1, -1)/3\sqrt{2}$ | $|--,-,+,--|$ |
| 5   | 0   | 1               |             | $(1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1)/\sqrt{10}$ | $|+,-,-,-, -|$ |
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References

[1] A. Abragam, The Principles of Nuclear Magnetism, Oxford: Clarendon Press, 1961.

[2] V. A. Acarkin, Nuclear dynamic polarization in solid dielectrics, Moscow: Nauka, 1980.

[3] V. A. Acarkin, M. I. Rodak, Usp. Fiz. Nauk 107, 3 (1972).

[4] M. Goldman, Spin temperature and nuclear magnetic resonance in solids, Oxford: Clarendon Press, 1970.

[5] A. K. Khitrin, V. L. Ermakov, B. M. Fung, Chem. Phys. Lett. 350, 161 (2002).

[6] A. K. Khitrin, V. L. Ermakov, B. M. Fung, J. Chem. Phys. 117, 6903 (2002).

[7] M. G. Rudavec, E. B. Fel’dman, Pisma Zh. Eksp. Teor. Fiz. 75, 760 (2002).