# NMR Multiple Quantum Dynamics in Large Spin Networks

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## Contents



## I. Statistical Physics of Large Spin Networks

Excitation of NMR multiple quantum (MQ) transitions in a solid is possible due to the presence of an intricate dipolar couplings network amidst nuclear spins. In a magnetic field, a non-symmetric rigid N-spin 1/2 system, has

$$\binom{N}{2}$$

distinct dipolar coupling constants given by

$$D_{ij} = \gamma^2 \hbar^2 (3cos^2\theta_{ij} - 1)/(2{r_{ij}}^3) \qquad (1)$$

where the symbols represent the customary universal constants and lattice parameters. Radiative coupling among the $2^N$ Zeeman levels, which are further spread by dipolar interactions, leads to

$$\binom{2N}{N-n}$$

accessible MQ coherences of order n (n≠0), where n is the difference in the magnetic quantum numbers of the coupled levels. Such MQ transitions are detected indirectly through two-dimensional methods, some of which are specifically tailored for solids, e.g., time-reversal excitation (1).

In a solid, the local dipolar field at a nuclear site originates from all other magnetic moments in the sample. This mean field description is useful for understanding lineshapes and spin thermodynamics arguments in some NMR experiments (2). The retarded time for the propagation of a dipolar field at the speed of light on a length scale of a micron is about $10^{-15}$ s. Hence, it could be argued that all aspects of the many-body problem need to be considered in order to understand the dynamics of MQ coherences in experiments.

However, a considerable simplification occurs by examining the equation of motion of the density operator, $\rho(\tau)$, for the spin system. While exposed to a typical MQ rf irradiation scheme, the spin system evolves under some non-secular average dipolar Hamiltonian $\mathcal{H}$ according to ,

$$\rho(\tau) = \rho(0) + (i/\hbar)\tau[\rho(0), \mathcal{H}] + , \qquad (2)$$
$$(i/\hbar)^2(\tau^2/2!)[[\rho(0), \mathcal{H}], \mathcal{H}] + \ldots$$

From this equation, one notes the appearance of multiple spin coherences with increasing time. These coherences can only grow one spin at a time due to the bilinear nature of $\mathcal{H}$ within this commutator algebra. Amalgamation of clusters of correlated spins are forbidden under such selection rule. In addition, the multiple spin coherences are weighted by dipolar coupling constants in the commutators (for two-spin coherences) and by products of dipolar coupling constants arising from the nested commutators (for higher order spin coherences). Therefore, one can appreciate that while all spins are coupled to each other, the "propagation" of dipolar correlations depends on the values of the dipolar coupling constants and their products, in addition to the evolution time $\tau$.

Another feature underlying eqn. 2 is that it only describes the growth of multiple spin coherences. This is due to the nature of Schrödinger's equation from which it is derived. The loss of coherence in the spin system can only be dealt with by treating the lattice and its interactions quantum mechanically, thereby leading to decoherence. Alternatively, relaxation can be introduced phenomenologically within the spin system evolution.

Dipolar interactions are long-ranged due to the $r^{-3}$ dependence (see eqn. 1). However, as seen from the discussion of eqn. 2, the time-resolved nature of MQ NMR experiments effectively limits the range of dynamical coupling among spins. For finite time evolution, only the multiple spin coherences with the largest dipolar coupling constants and their products should contribute significantly to MQ spectra, i.e., $Tr[I_z \cdot \rho(t)]$. As a consequence, under such conditions, a macroscopic solid can then be viewed as an ensemble of loosely coupled subsystems. The dynamics in any MQ NMR experiments correspond to the average behavior over this ensemble.

A few subtle points about this ensemble approximation should be clear. The correlation length of any multiple spin coherences must be smaller than a subsystem size. Interaction energies between subsystems are assumed weak in comparison to interaction energies within subsystems. This amounts to saying that surface effects between subsystems are neglected for MQ dynamics during an experiment; however, in the end, they are necessary to achieve equilibrium among subsystems in the ensemble, e.g. a uniform spin temperature. Underlying this ensemble construction is the property of statistical homogeneity. On a subsystem scale, the statistical properties are stationary in space, i.e., a subsystem is statistically translationally invariant in space. A physical property of the macroscopic solid is equal to this property averaged over the subsystems, i.e., spatial ergodicity exists.

In a sense, this ensemble approach applied to the non-equilibrium rf-driven spin system permits the growth process of multiple spin coherences to be treated from a statistical mechanics perspective. For example, if all the possible coherences in an N-spin system are excited across such an ensemble of subsystems, and all coherences have the same weight, as would be the case for an infinite excitation period, then the intensities in a MQ spectrum could possibly exhibit a Gaussian profile, i.e.,

$$I(n) = \{4^N/(\pi N)^{1/2}\}\, exp[-n^2/N] \qquad (3)$$

Traditionally, this approximation has been used to interpret MQ NMR spectra of solids even for finite time excitation periods (1) when coherences cannot be treated equally (3). Averaging over products of dipolar coupling constants in the ensemble (at finite times) does not lead to Gaussian behavior (3,4). In addition, a thorough examination of the Gaussian approximation and its implications reveals several aspects of non-Gaussian behavior in $^1$H MQ NMR spectra of adamantane and hexamethylbenzene (5). Actually, it appears that exponential behavior is a more appropriate description of MQ NMR spectral intensity profiles and their interpretation (5).

The growth dynamics of individual coherences within a subsystem is dictated by eqn. 2. It is possible to map, in an isomorphic fashion, this equation of motion onto a graph model (3). In this graph theoretical method, the spins correspond to vertices. Colors of the vertices stand for the states of the spin operators, e.g., $I_x$, $I_y$, and $I_z$. Pairwise dipolar correlations are delineated by edges whose weights are proportional to the absolute values of dipolar coupling constants. The sign of the dipolar coupling constants appears as an irrelevant variable when one considers MQ NMR experiments with time-reversal excitation; the signal is proportional to the square of the modulus of the density operator (see eqn. 2). Hence, the analytical solution of eqn. 2 can be examined with a graph ensemble. As an N-spin correlation is characterized by a product of N spin operators with N-1 dipolar coupling constants (see eqn. 2), the only permissible graphs in the ensemble are trees, i.e., graphs without loops (N vertices connected with N-1 edges). A tree of N vertices has a weight proportional to the absolute value of the product of N-1 dipolar coupling constants (edges). This visualization approach provides insight into the

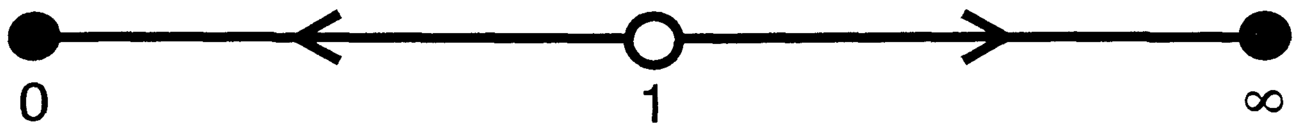


Figure 1: Flow diagram for products of the angular part [$|3\cos^2\theta - 1|$] of dipolar coupling constants in large multiple spin coherences. The stable fixed points (solid circle), 0 and $\infty$, and the unstable fixed point (empty circle), 1, are indicated for large products.

multiple spin growth processes as shown here with two aspects of the dynamics: anisotropy effects, and maximal spanning tree dynamics.

## II. Anisotropy of Growth of Multiple Spin Coherences

Consider a tree corresponding to an N-spin correlation. Its weight, the product of the N-1 dipolar coupling constants can be factored (see eqn. 1) into three groups: products of universal constants ($\gamma^2\hbar^2/2$), products of length scales ($r^{-3}$), and products of angular factors ($3\cos^2\theta - 1$). The product of the universal constants and the length scales converges to zero in the limit of large N. The product of the angular factors has three classes of behavior depending on the values of the angles in the products. When $35.3° < \theta < 144.7°$, the product converges to zero as N increases since $|3\cos^2\theta - 1| < 1$. With $\theta$ in the angular ranges, $0° \leq \theta \leq 35.3°$ or $144.7° \leq \theta \leq 180°$, $|3\cos^2\theta - 1| > 1$, hence, the product diverges to infinity with increasing N. Finally, if the angles in the product vary between these three angular ranges, the product will either converge to zero or diverge to infinity depending on the relative proportions of the different ranges and the values of $\theta$s in the product. One should note that for all three classes, the product of the angular factors with the universal constants and length scale factors always converges to zero in the limit of large N (3,4).

The behavior of the products of the angular factors can be summarized with a flow diagram (Figure 1) for the absolute value of the product. The dynamics of the products are determined by three fixed points as N increases in the product. The stable fixed point 0 corresponds to $35.3° < \theta < 144.7°$, while the other stable fixed point, $\infty$, attracts products within the angular ranges of $0° \leq \theta \leq 35.3°$ or $144.7° \leq \theta \leq 180°$. The unstable fixed point, 1, is satisfied only in products where $\theta = 35.3°$ or $144.7°$. The stable fixed point 0 can be arrived at directly if any of the angles in the products is equal to $54.7°$ or $125.3°$. On the other hand, the stable fixed point $\infty$ can only be reached asymptotically as N tends to infinity.

Therefore, anisotropy effects should influence the multiple spin growth processes. On the basis of the properties of products of angular factors, one would expect that the individual correlated clusters of spins or trees to show some anisotropy. Indeed, it would appear that in a magnetic field the growth of large correlated clusters should be dominated by correlations within the angular ranges of $0° \leq \theta \leq 35.3°$ or $144.7° \leq \theta \leq 180°$. This expectation is observed in tree growth simulation studies presented in the next section. In a MQ NMR experiment on a macroscopic solid, the signal should be the average over the subsystems. As the magnetic field imposes a direction for the growth processes, one would therefore expect anisotropy effects to "survive" at the macroscopic level the averaging process in single crystal MQ NMR studies. Such anisotropy effects have yet to be investigated experimentally.

## III. Maximal Spanning Tree Dynamics

Studies of the statistical properties of dipolar coupling constants and their products have revealed, in large spin networks, that their distributions range over several orders of magnitude (4). Due to the broadness of these distributions, it becomes important to distinguish between the most probable value and the average value characteristic of the distributions. Physical measurements, on such distributions, yield observables which depend on the sample

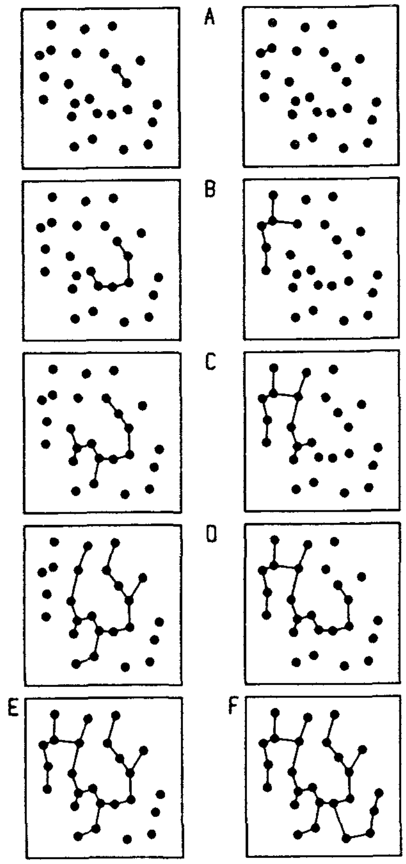


Figure 2: Schematic growth of multiple spin coherences according to a maximal spanning tree (MST) algorithm as described in the text. The vertices represent spins, while the edges correspond to established dipolar correlations according to eqn. 2. Two different initial conditions, on the same spin system, are shown on both sides. Time steps: A) 1, B) 5, C) 10, D) 15, E) 20, F) 24. Note that both realizations converge to an identical cluster of correlated spins (tree) at time steps E and F. The Zeeman field is oriented vertically and parallel to the plane.

size, the number of elements in the distribution, and the realization of these elements in the sample (3,4). In large networks, it turns out that the most probable value is dominated by the smallest and the most numerous dipolar coupling constants and their products. On the other hand, the average value is dominated by the largest and the least abundant nearest neighbor dipolar coupling constants and their products.

Thus, for any finite excitation time, it is expected that the dynamics of the multiple spin coherences will be dominated by nearest neighbor coupling constants for pairs of spins, and by the largest products of coupling constants for correlated clusters of three or more spins. An algorithm can therefore be constructed, such that a correlation or a tree can only grow by adding one spin at a time in the direction with the largest coupling constant. As a consequence, the weight of this tree is always the largest possible. This algorithm determines the maximal spanning tree (MST). The MST has the maximal weight and spans the entire spin network after some period of growth.

Figure 2 shows the growth of a MST starting from different initial conditions in a 25-spin network. The choice of a lattice with topological disorder is needed in order to prevent any degeneracy for the MST. The same generic growth behavior would be observed in a regular lattice, however, the degeneracy of the MST would obscure the present discussion. One should also appreciate that in this network, there is only one 25-quantum coherence possible (see eqn. 2). Yet, this coherence is weighted by a product of 24 dipolar coupling constants chosen among

$$\binom{25}{2} = 300;$$

hence, there are roughly $10^{32}$ possible such products in this network. The MST is the one with the largest product of coupling constants among all of these trees. That the MST is associated with the observable 25-quantum coherence in an experiment might seem surprising at first sight in view of the possible $10^{32}$ products. Nevertheless, as discussed above and elsewhere (3,4), the statistical properties of multiplicative processes are dominated by rare events in distributions. This consequence is necessary for a logically consistent interpretation of MQ NMR measurements over an ensemble of loosely coupled subsystems. In general, for an N-spin system coupled with N-1 dipolar coupling constants chosen among

$$\binom{N}{2},$$

there are $N^{N-2}$ distinct trees.

The multiple spin coherence growth depicted in the simulations of Figure 2 shows that different initial conditions lead to distinct clusters of correlated spins at intermediate time steps. The trees of this growth algorithm converge to a unique tree at later stages (time step 20, Figure 2E) before reaching the MST at the final time step. The MST is the fixed point attractor for the algorithm. Interestingly, this growth process, at intermediate time steps, can be viewed as a propagation of multiple spin correlations *directly* on the MST. An ensemble of subsystems, with the growth limited onto the MST, would show a distribution of products at intermediate steps before progressing towards a unique tree at later stages of growth. In a sense, while such an ensemble looks random at early and intermediate times, there is some definite underlying order present in the growth process. As there exists exactly a unique path between any two vertices on the MST, one could imagine simulating "spin diffusion" as a deterministic process on the MST of large spin networks.

Another appealing feature of the results in Figure 2 is the angular distribution of $\theta$s in the MST. Out of 24 polar angles ($\theta$), 8 are found in the range $35.3° < \theta < 144.7°$, while the rest are within $0° \leq \theta \leq 35.3°$ or $144.7° \leq \theta \leq 180°$. Qualitatively, in the MST, there is a predominance of angles in the product of angular factors whose absolute values are greater than 1. This demonstrates the relevance of anisotropy effects in the growth process of multiple spin coherences as discussed in section II.

## IV. Perspectives

MQ NMR experiments have been performed on solids and anisotropic fluid phases over more than a decade. A full understanding of the fundamental aspects of the growth of multiple spin coherences in large networks still remains a delicate problem as demonstrated here and elsewhere (3-5). While some interpretations of MQ NMR spectra have been suggested (1,5), it is clear that further work on the statistical physics of strongly dipolar coupled spin systems is needed if MQ NMR is going to succeed to probe materials on mesoscopic length scales.

## V. Acknowledgments

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