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Spins swing like pendulums do: an exact classical model for TOCSY transfer in systems of three isotropically coupled spins 1/2

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Abstract

An exact correspondence is found between the quantum dynamics of three isotropically coupled spins 1/2 and the dynamics of three coupled classical oscillators. This correspondence is demonstrated by experimentally simulating the polarization transfer functions of an isotropic mixing TOCSY experiment with a set of mechanically coupled pendulums. The extend to which the exact correspondence holds is analyzed and it is shown that it breaks down for systems consisting of more than three coupled spins.

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1. Introduction

Quantum phenomena are often highly counterintuitive and classical analogues are known only for a small number of simple quantum systems. A famous example is the Feynman–Vernon–Helwarth theorem which states that the behavior of any quantum mechanical two-level system can be modeled by classical torque equations, i.e., there is a one-to-one correspondence between the time evolution of the two-level system and the dynamics of a spinning top [1]. In the context of NMR, a single spin 1/2 in an external magnetic field is a prototype example, where the torque equations are reflected in the well-known Bloch equations [2]. The Feynman–Vernon–Helwarth theorem has also helped in the design and interpretation of experiments in other spectroscopic fields, such as laser spectroscopy [3]. Here, we present a classical model that quantitatively reflects the coherent evolution in an ensemble of up to three coupled spins 1/2 under isotropic mixing conditions with arbitrary coupling constants and coupling topology.

The TOCSY experiment based on isotropic mixing forms one of the most efficient methods to transfer

coherence or polarization between coupled homonuclear spins in high-resolution NMR [4,5]. Effective isotropic mixing conditions can also be created in heteronuclear spin systems by a number of well-known pulse sequences [5–7]. Simulating the transfer dynamics is important in practice because it enables spectroscopists to determine the optimal duration of isotropic mixing periods in NMR experiments [5,8,9].

In their seminal paper on isotropic mixing experiments, Braunschweiler and Ernst stated that for isotropically coupled spins “the situation is to some extent analogous to a network of coupled mechanical oscillators where normal modes also involve collective motions of several oscillators” [4]. However, so far it was not clear to what extend this analogy holds if coherence transfer under isotropic mixing and the transfer of energy in coupled mechanical oscillators are compared quantitatively. Here, we demonstrate that a system of three coupled mechanical oscillators is not only a qualitative analogy but in fact quantitatively reflects all aspects of polarization and coherence transfer for three isotropically coupled spins 1/2. Hence, a system of three coupled pendulums can faithfully simulate the quantum dynamics of TOCSY transfer. However, for more than three isotropically coupled spins the exact correspondence breaks down and in this case coupled mechanical oscillators form only a rather qualitative analogy of TOCSY transfer.

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2. Theory

We consider the evolution of an ensemble of three coupled spins 1/2 under an isotropic mixing Hamiltonian of the form

$$H_{\text{iso}} = \sum_{k < l} 2\pi J_{kl} \{I_{kx}I_{lx} + I_{ky}I_{ly} + I_{kz}I_{lz}\} \quad (1)$$

with the coupling constants J_{kl} between spins k and l . For three spins 1/2, there are only three distinct energy levels of which two have a twofold and one has a fourfold degeneracy [5,10].

Under the action of an isotropic mixing Hamiltonian, the initial polarization of a given spin is transferred throughout a coupling network in a coherent way [4,5]. For an initial spin density operator

$$\rho(0) = I_{kz} \quad (2)$$

the Liouville–von Neumann equation

$$\frac{d\rho}{dt} = -i[\mathcal{H}_{\text{iso}}, \rho] \quad (3)$$

leads to the following set of coupled differential equations for the expectation values of the nine orthogonal operators I_{1z} , I_{2z} , I_{3z} , $(I_{1y}I_{2x} - I_{1x}I_{2y})$, $(I_{1y}I_{3x} - I_{1x}I_{3y})$, $(I_{2y}I_{3x} - I_{2x}I_{3y})$, $2(I_{1x}I_{2x} + I_{1y}I_{2y})I_{3z}$, $2(I_{1x}I_{3x} + I_{1y}I_{3y})I_{2z}$, and $2(I_{2y}I_{3x} + I_{2x}I_{3y})I_{1z}$:

$$\dot{P}_k = 2\pi J_{kl}A_{kl} + 2\pi J_{km}A_{km}, \quad (4)$$

$$\dot{A}_{kl} = \pi J_{kl}(P_l - P_k) + \pi J_{km}(B_{kl} - B_{lm}) + \pi J_{lm}(B_{km} - B_{kl}), \quad (5)$$

$$\dot{B}_{kl} = \pi J_{lm}(A_{kl} - A_{km}) - \pi J_{km}(A_{kl} + A_{lm}), \quad (6)$$

with $\{k, l, m\} = \{1, 2, 3\}$ and cyclic permutations thereof. The terms

$$P_k = \langle I_{kz} \rangle \quad (7)$$

represent polarizations of the individual spins, the terms

$$A_{kl} = \langle I_{ky}I_{lx} - I_{kx}I_{ly} \rangle \quad (8)$$

are the expectation values of zero-quantum coherences and the terms

$$B_{kl} = \langle 2(I_{kx}I_{lx} + I_{ky}I_{ly})I_{mz} \rangle \quad (9)$$

reflect the expectation values of anti-phase zero-quantum terms. Analytical solutions for these expectation values are known for arbitrary coupling constants J_{12} , J_{13} , and J_{23} [10].

Now we consider the equation of motion for a classical system of three coupled mechanical oscillators with mass m and spring constants κ and c_{kl} (c.f. Fig. 1):

$$m\ddot{x}_k = -\kappa x_k + c_{kl}(x_l - x_k) + c_{km}(x_m - x_k). \quad (10)$$

The oscillation frequencies of the uncoupled oscillators are

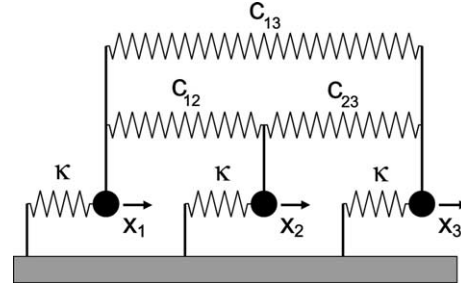


Fig. 1. Schematic representation of three coupled harmonic oscillators with spring constants κ and c_{kl} .

$$v' = \frac{1}{2\pi} \sqrt{\frac{\kappa}{m}} \quad (11)$$

and we define the mechanical coupling constants J'_{kl} in terms of the spring constants c_{kl} as

$$J'_{kl} = \frac{c_{kl}}{4\pi^2 m v'^2}. \quad (12)$$

In the case of only two coupled mechanical oscillators, the energy of oscillator k is transferred in a time $\tau'_{kl} = 1/(2J'_{kl})$ to oscillator l , in complete analogy to the time $\tau_{kl} = 1/(2J_{kl})$ required for the complete polarization transfer between two isotropically coupled spins 1/2 [4].

For given initial positions x_k and velocities \dot{x}_k of three coupled oscillators, the solution of the set of differential equations (Eq. (10)) is tedious but straight-forward [11]. In the mechanical weak coupling limit ($|J'_{kl}| \ll |v'|$) where the oscillation frequency v' is much larger than the coupling constants J'_{kl} , it can be shown [11] that the classical terms

$$P'_k = \frac{1}{2v'^2} \left(4\pi^2 v'^2 x_k^2 + \dot{x}_k^2 \right), \quad (13)$$

$$A'_{kl} = \frac{\pi}{v'} (\dot{x}_k x_l - x_k \dot{x}_l), \quad (14)$$

$$B'_{kl} = -\frac{1}{2v'^2} \left(4\pi^2 v'^2 x_k x_l + \dot{x}_k \dot{x}_l \right) \quad (15)$$

satisfy the same set of differential equations as the quantum mechanical expectation values P_k , A_{kl} , and B_{kl} (Eqs. (4)–(6)). Hence, in this limit the mechanical system exactly models all aspects of the three-spin system. The polarization P_k of the k th spin corresponds to the classical quantity P'_k , which is proportional to the sum of the kinetic and potential energy of the k th oscillator. The expectation values of the zero-quantum terms A_{kl} (cf. Eq. (8)) correspond to classical terms A'_{kl} and the anti-phase zero quantum terms B_{kl} (cf. Eq. (9)) correspond to the classical terms B'_{kl} .

3. Experiments

In order to demonstrate the striking correspondence between isotropic mixing and coupled mechanical

oscillators, we performed isotropic mixing experiments using the ^1H spin system vinyl magnesium bromide and also simulated the polarization transfer dynamics both numerically and experimentally using a set of three coupled pendulums.

Vinyl magnesium bromide was dissolved in tetrahydrofurane- D_8 and the NMR experiments were performed at a temperature of 298 K in a magnetic field of 14.09 T, corresponding to a ^1H NMR frequency of 600 MHz. The coupling constants are $J_{12} = 17.6$, $J_{13} = 7.7$, and $J_{23} = 22.8$ Hz. During the mixing period of the experiments, an MLEV-17 sequence [12] with a rf amplitude $\nu_{\text{rf}} = \gamma B_{\text{rf}} / (2\pi)$ of 8 kHz was applied to the spin system. This multiple-pulse sequence had a cycle time τ_{cyc} of 2 ms and in the rotating frame defined by the spin-lock field effective isotropic mixing conditions were created. In this frame of reference, the initial condition $\rho(0) = I_{1z}$ was prepared by starting at thermal equilibrium and applying a 90° pulse to the spin system after selective saturation of spins 2 and 3. NMR spectra were acquired after integer multiples of $2\tau_{\text{cyc}} = 4$ ms. The experimental polarization transfer function $P_k(t)$ is given by the integrated intensity of the detected resonance of spin k normalized by the integrated intensity of the resonance of the excited spin at an isotropic mixing period $t = 0$ ms. In Fig. 2 theoretical polarization transfer functions [10] are shown (thick curves) for this spin system.

In order to realize a corresponding set of three coupled mechanical oscillators experimentally, we built a set of three pendulums with stiff rods coupled by U-shaped steel springs (cf. Fig. 3) [13]. Each pendulum has a weight of about 6 kg. For small angles of deflection, pendulums represent good approximations for harmonic oscillators. The mechanical couplings between the pendulums were adjusted to yield mechanical coupling constants $J'_{kl} = sJ_{kl}$ with a scaling factor $s = 1/570$. Hence, the time evolution of the pendulum system was 570 times slower than the time evolution in the corresponding spin system. In Fig. 2, the total duration of the polarization transfer functions was 140 ms for the spin system, corresponding to 80 s for the system of coupled pendulums. The mechanical oscillation frequency of the uncoupled pendulums was $\nu' = 0.56$ Hz which is about 14 times larger than the largest coupling constant. As demonstrated by exact simulations of $P'_k(t)$ for three coupled mechanical oscillators (see thin curves in Fig. 2), this ratio between ν' and J'_{kl} is sufficiently large to closely approach the dynamics of the mechanical weak coupling limit.

Fig. 4 shows photographic traces of the oscillations of the three coupled pendulums after the first pendulum was selectively excited. The envelope of these traces is proportional to the square root of $P'_k(t)$ and hence proportional to the square root of the energy of the pendulums. The white circles represent the correspond-

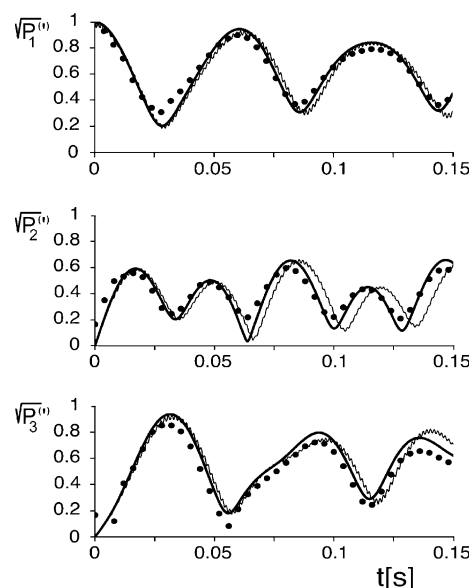


Fig. 2. This figure shows the square root of theoretical (thick curves) [10] and experimental (dots) isotropic mixing polarization transfer functions $P_k(t)$ for the spin system of vinyl magnesium bromide. The solid curves are identical to the square root of $P'_k(t)$ for a corresponding system of three coupled harmonic oscillators in the mechanical weak coupling limit $|J'_{kl}| \ll |\nu'|$ with $J'_{12} = J_{12} = 17.6$, $J'_{13} = J_{13} = 7.7$, and $J'_{23} = J_{23} = 22.8$ Hz. The thin curves correspond to the case where the oscillation frequency $\nu' = 300$ Hz is 14 times larger than the largest coupling constant, effectively approximating the mechanical weak coupling limit.



Fig. 3. Experimental pendulum system used to demonstrate the correspondence between TOCSY transfer in isotropic mixing experiments and the transfer of energy between coupled pendulums. Each pendulum has a weight of about 6 kg. The couplings between the pendulums are provided by U-shaped steel springs.

ing square root of the measured polarization of each nuclear spin as a function of time (cf. black dots in Fig. 2). In the NMR experiments, relaxation effects were negligible. However, the mechanical oscillations had a damping constant $T' = 51$ s. This was taken into account in Fig. 4 by multiplying the square root of the experimental polarization transfer amplitudes $P_k(t)$ by an exponential damping function $\exp\{-t/T\}$ with the damping constant $T = sT'$. A reasonable match is found between the dynamics of the coupled pendulums and the

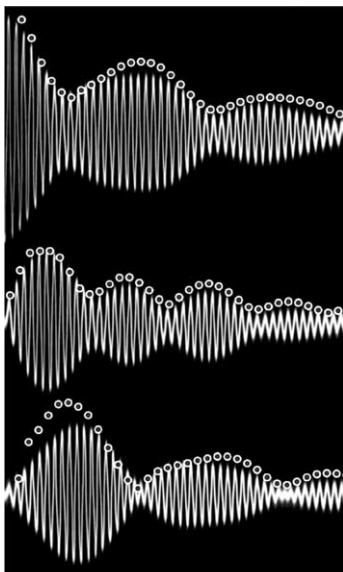


Fig. 4. Experimental comparison of the transfer dynamics of polarization in the spin system of vinyl magnesium bromide and the transfer of energy in a set of three coupled pendulums. The white curves are photographic traces of light emitting diodes attached to the pendulums. The envelope of each oscillation is proportional to the square root of the energy of the corresponding pendulum. The circles correspond to the square root of the experimental TOCSY transfer amplitudes shown in Fig. 2, which were damped to match the energy dissipation of the mechanical oscillation (see text for details).

isotropically coupled spins. The remaining discrepancies can be attributed to experimental imperfections and to the fact that in the mechanical system the weak coupling limit and the limit of small deflections from equilibrium was only approximately fulfilled.

4. Discussion

The exact match between TOCSY transfer in isotropic mixing experiments and the transfer of energy between coupled mechanical oscillators is not only of theoretical interest but also provides a direct and intuitive approach to understand the complex spin dynamics under isotropic mixing conditions. As indicated above, this exact analogy also holds for homonuclear spin-lock experiments with isotropic coupling terms if polarization along the spin-lock axis is considered.

The term P'_k represents the total (i.e., kinetic and potential) energy of pendulum k , scaled by mv^2 (cf. Eq. (13)). In the mechanical weak coupling limit, the potential energy stored in the couplings between the pendulums is negligible and the sum

$$P' = P'_1 + P'_2 + P'_3 \quad (16)$$

is constant. Hence in this analogy the well-known conservation of the total polarization $P = P_1 + P_2 + P_3$ under isotropic mixing conditions [4,5] corresponds to

the conservation of the total energy in the pendulum system. It is interesting to note that in the quantum system the conservation of the norm of the density operator under unitary evolution (3) results in the conservation of the term

$$C = \sum_{k=1}^3 P_k^2 + 2 \sum_{k<l} A_{kl}^2 + 2 \sum_{k<l} B_{kl}^2. \quad (17)$$

The corresponding quantity of the system of three coupled mechanical oscillators is also conserved in the mechanical weak coupling limit.

It is also interesting to ask whether the exact correspondence between the spin dynamics under isotropic mixing conditions and the dynamics of coupled mechanical oscillators also holds for larger spin systems. In systems consisting of more than four coupled spins, the polarization of individual spins can become negative in isotropic mixing experiments [8,14]. Hence, the exact correspondence cannot hold for more than four spins because the energy of a given pendulum cannot become less than zero. However, according to numerical simulations, the exact correspondence already breaks down for four coupled spins for which analytical isotropic mixing polarization transfer functions are known [15]. One of the reasons [13] is that for more than three spins distinct terms of the density operator such as $2(I_{kx}I_{lx} + I_{ky}I_{ly})I_{mz}$ and $2(I_{kx}I_{lx} + I_{ky}I_{ly})I_{nz}$ are created in the course of polarization transfer. In general, the expectation values of these operators have distinct time evolutions if $m \neq n$. However, according to Eqs. (9) and (15) the distinct quantum mechanical expectation values would both be represented by the same classical quantity $B'_{kl} = -(1/2v^2)(4\pi^2 v^2 x_k x_l + \dot{x}_k \dot{x}_l)$. Hence, for more than three spins, coupled mechanical oscillators only form a rather qualitative analogy of TOCSY transfer and cannot quantitatively simulate the dynamics under isotropic mixing.

For classical simulations of the dynamics of three coupled spins under isotropic mixing conditions, the construction of a corresponding system of coupled electrical oscillators [16] would be interesting because of its considerably increased flexibility compared to mechanical pendulum systems. This would make it more convenient to change coupling constants and to record the desired transfer function and would allow a more straight-forward realization of negative coupling constants. Furthermore, it is an open question whether classical analogies also exist for other effective spin–spin coupling tensors, such as in planar [17], dipolar [18] or cylindrical [19] mixing experiments, which in general have markedly different transfer dynamics [5,19,20]. Finally, it should be noted that in the physics literature, further analogies have been discussed between the dynamics of coupled pendulums and experiments involving quantum mechanical three-level systems, such as

spin filter experiments [21], the stimulated resonance Raman effect [22] and forces on three-level atoms due to electromagnetic driving fields [23].

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