Loschmidt echoes in Nuclear Magnetic Resonance: multiple quantum coherence excitations and decoherence

Claudia M. Sánchez,
L. Buljubasich, H. M. Pastawski, A. K. Chattah

FAMAF-UNC and IFEG-CONICET (ARGENTINA)

e-mail: claudia@famaf.unc.edu.ar

June, 2016

MOTIVATION

1. To understand the relationship between the system dynamics and decoherence.
2. Echoes in NMR: time reversal is unavoidably degraded by uncontrolled, internal or environmental, degrees of freedom.
3. *Central Hypothesis of Irreversibility:* decoherence is tied to T_2 (dipolar interactions).
4. *Complex many-body dynamics could rule an emergent mechanism of decoherence and irreversibility in the thermodynamic limit.*

IMPLEMENTATIONS

- Decoherence $\Longleftrightarrow$ Irreversibility $\Longleftrightarrow$ **Many-body quantum dynamics.**

- Nuclear Magnetic Resonance.

Loschmidt Echo: Signal attenuation after time reversal

$$M(t) = \left|\langle \Psi_0 \right| \exp\left\{ i(\mathcal{H}_0 + \Sigma)t \right\} \exp\left\{ -i\mathcal{H}_0 t \right\} \left| \Psi_0 \rangle \right|^2$$

REVERTING THE EVOLUTION

Forward

$$\mathcal{U}(\tau) = e^{-i\mathcal{H}_0\tau}$$

Backward

$$\mathcal{V}(\tau') = e^{i\phi I_z} e^{i\mathcal{H}_0\tau} e^{-i\phi I_z}$$

- In general, the elements ρ_{ij} are not detectable. It is only possible to detect magnetization.
- A series of signals is measured for different phases. The Fourier Transform separates different coherence orders:

$$S_\phi(\tau) = \sum_n e^{in\phi} S_n(\tau)$$

DENSITY MATRIX ELEMENTS

- Diagonal initial state, elements represent the populations of each state
- Evolution generates off diagonal elements

$$
\begin{array}{cc}
 & \begin{array}{cccccccc} |{+}{+}{+}\rangle & |{+}{+}{-}\rangle & |{+}{-}{+}\rangle & |{-}{+}{+}\rangle & |{+}{-}{-}\rangle & |{-}{+}{-}\rangle & |{-}{-}{+}\rangle & |{-}{-}{-}\rangle \end{array} \\
\begin{array}{c} \langle{+}{+}{+}| \\ \langle{+}{+}{-}| \\ \langle{+}{-}{+}| \\ \langle{-}{+}{+}| \\ \langle{+}{-}{-}| \\ \langle{-}{+}{-}| \\ \langle{-}{-}{+}| \\ \langle{-}{-}{-}| \end{array} &
\left[\begin{array}{cccccccc}
\rho_{11} & \rho_{12} & \rho_{13} & \rho_{14} & \rho_{15} & \rho_{16} & \rho_{17} & \rho_{18} \\
\rho_{21} & \rho_{22} & \rho_{23} & \rho_{24} & \rho_{25} & \rho_{26} & \rho_{27} & \rho_{28} \\
\rho_{31} & \rho_{32} & \rho_{33} & \rho_{34} & \rho_{35} & \rho_{36} & \rho_{37} & \rho_{38} \\
\rho_{41} & \rho_{42} & \rho_{43} & \rho_{44} & \rho_{45} & \rho_{46} & \rho_{47} & \rho_{48} \\
\rho_{51} & \rho_{52} & \rho_{53} & \rho_{54} & \rho_{55} & \rho_{56} & \rho_{57} & \rho_{58} \\
\rho_{61} & \rho_{62} & \rho_{63} & \rho_{64} & \rho_{65} & \rho_{66} & \rho_{67} & \rho_{68} \\
\rho_{71} & \rho_{72} & \rho_{73} & \rho_{74} & \rho_{75} & \rho_{76} & \rho_{77} & \rho_{78} \\
\rho_{81} & \rho_{82} & \rho_{83} & \rho_{84} & \rho_{85} & \rho_{86} & \rho_{87} & \rho_{88}
\end{array}\right]
\end{array}
$$

SPIN INTERACTIONS

- Protons (^{1}H, $I = 1/2$) in the presence of a strong magnetic field.

- Hamiltonian: $\mathcal{H} = \mathcal{H}^{\text{Zeeman}} + \mathcal{H}^{\text{Dipolar}}$

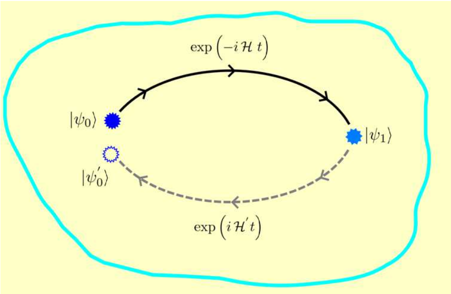
$$
\begin{aligned}
\mathcal{H} &= \omega_z \sum_i I_i^z + \sum_{i<j} d_{ij} \left[3 I_i^z I_j^z - \mathbf{I_i} \cdot \mathbf{I_j}\right] \\
&= \omega_z \sum_i I_i^z + \sum_{i<j} d_{ij} \left[2 I_i^z I_j^z - \frac{1}{2} \left(I_i^+ I_j^- + I_i^- I_j^+ \right)\right]
\end{aligned}
$$

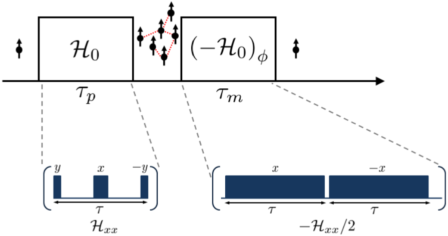
where $I_i^u = \sigma_u/2$ and $I_i^\pm = I_i^x \pm I_i^y$.

- Initial state: $\rho_0 \propto I^z = \sum_j I_j^z$

EXPERIMENTAL MEASUREMENTS OF THE LE

- Perfect reversion $\Longleftrightarrow$ $LE = 1$
- Degradation of the signal produces a decay in LE
- Magic Echo sequence for the evolution and its reversal





$$\mathcal{H}_{xx} = \sum_{i<j} d_{ij}\left(3I_i^x I_j^x - \mathbf{I_i}\cdot\mathbf{I_j}\right)$$

MULTIPLE-SPIN CORRELATIONS

Correlations development

$$\rho(\tau+\delta\tau) = e^{-i\delta\tau\mathcal{H}}\rho(\tau)e^{i\delta\tau\mathcal{H}} \sim \rho(\tau) - i\delta\tau[\mathcal{H},\rho]$$

Multi-spin operators of the form: $I_u^l \dots I_v^o I_w^p (u, v, w = x, y, z)$ describes modes in which K spins are interconected.

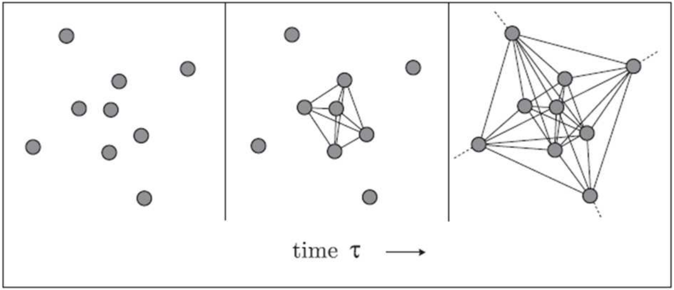
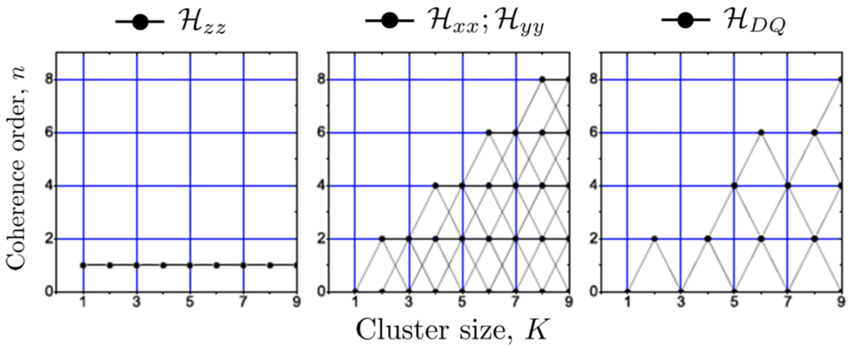


Figure from Baum, Munowitz, Garroway, Pines, J. Chem. Phys. 83 (5) 1985.

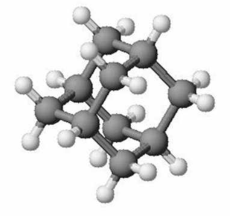
A WALK THROUGH LIOUVILLE SPACE

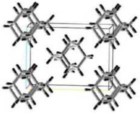
Routes in the Liouville space allowed for coherences

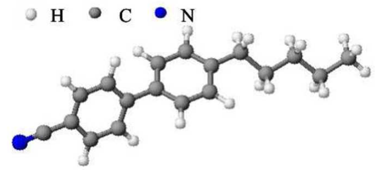
$\mathcal{H}_{zz}$	$\mathcal{H}_{xx}$; $\mathcal{H}_{yy}$	$\mathcal{H}_{DQ}$
$\Delta K = \pm 1; \Delta n = 0$	$\Delta K = \pm 1; \Delta n = 0, \pm 2$	$\Delta K = \pm 1; \Delta n = \pm 2$



SPIN SYSTEMS: GEOMETRIES AND DIMENSIONALITIES







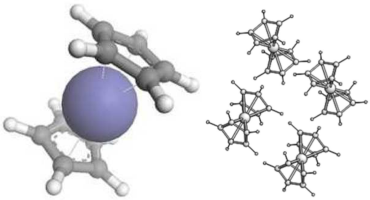
Adamantane ($C_{10}H_{16}$)

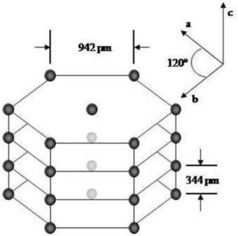
- FCC structure.
- Average out of intramolecular interactions.
- Each point with 16 spins.
- Intermolecular interactions.
- Infinite System.

Liquid crystal (5CB)

- Liquid crystals in nematic mesophase
- Intramolecular interactions in finite systems
- Less than 20 spins.

SPIN SYSTEMS: GEOMETRIES AND DIMENSIONALITIES





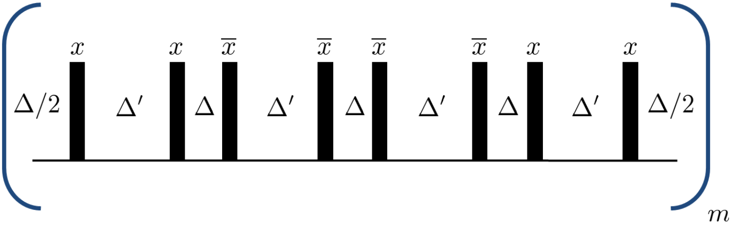
Ferrocene: $(C_5H_5)_2Fe$

- Two cyclopentadienyl rings separated by an Fe nucleus.
- Intra and intermolecular interactions.
- Infinite System.

HAp: $Ca_5(PO_4)_3OH$

- It can be considered as 1−dimensional spin chain with near-neighbor couplings.

OTHER PULSE SEQUENCES



Evolution with

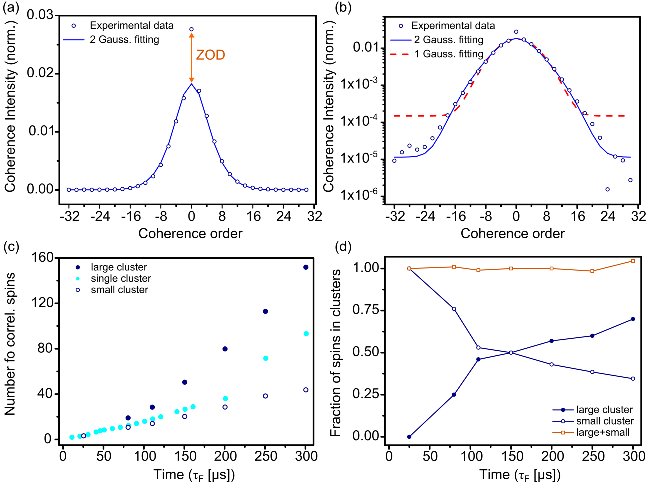
$$\mathcal{H}_{DQ} = -\frac{1}{2}\sum_{i<j} d_{ij}\left(I_i^+ I_j^+ + I_i^- I_j^-\right)$$

$$\Delta K = \pm 1, \; \Delta n = \pm 2$$

In the pulse sequence with $\mathcal{H}_{DQ}$ evolution, the reversion is produced by changing the phases of the pulses.

EXPERIMENTS IN FERROCENE

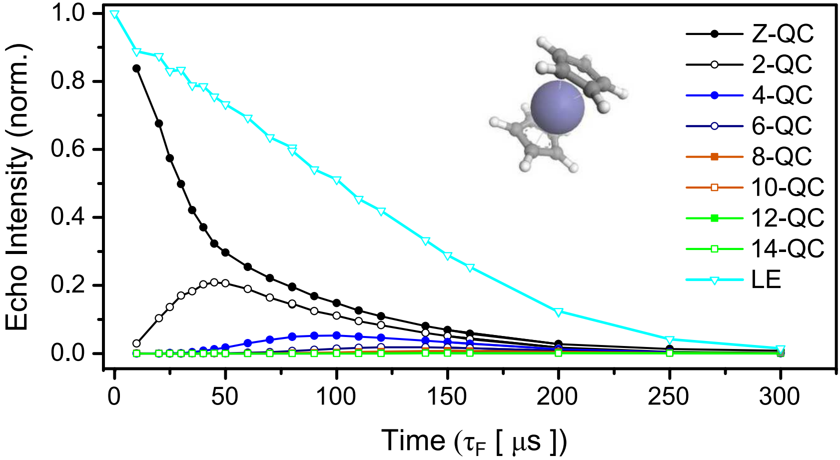
- Clusters and Decoherence.
- Data acquired with the Magic Echo pulse sequence



Sánchez CM, Acosta RH, Levstein PR, Pastawski HM, Chattah AK., Phys. Rev. A **90** 2014.

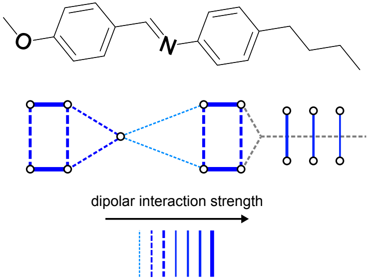
EXPERIMENTS IN FERROCENE

- Loschmidt Echo and Multiple Quantum Coherence curves

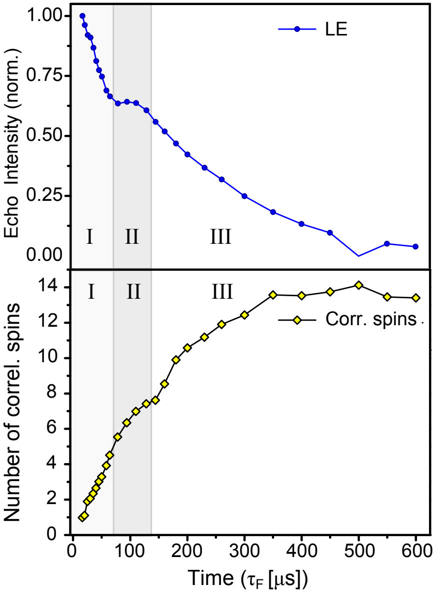


EXPERIMENTS IN A LIQUID CRYSTAL

Spin counting and **LE correlation**

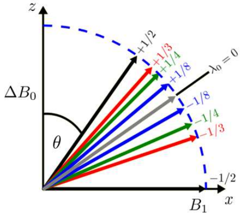


N−(4−**Metoxybenzylidene**) −
4−**butylaniline (MBBA)**



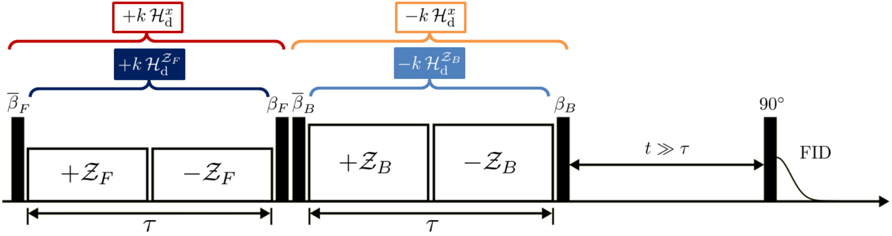
OUR NEW PULSE SEQUENCE: "PRL echo"

Scaling factor k: from -1/2 to 1



- **Hamiltonian**

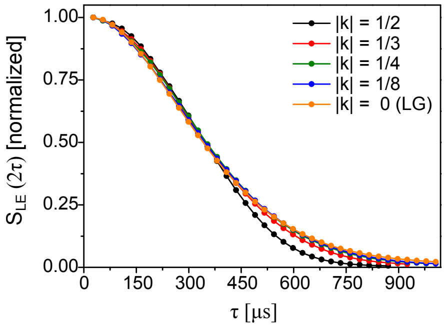
$$\mathcal{H} = -\gamma B_e I^{\mathcal{Z}} + \lambda_0(\theta) \sum_{i<j} d_{ij}(3 I_i^{\mathcal{Z}} I_j^{\mathcal{Z}} - \mathbf{I}_i \cdot \mathbf{I}_j)$$

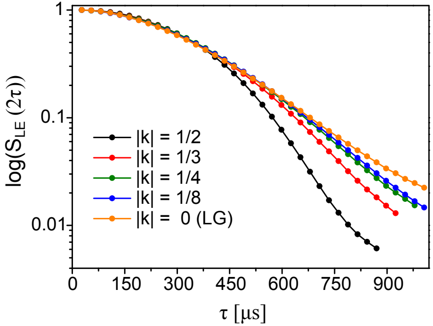


Buljubasich L, Sánchez CM, Dente AD, Levstein PR, Chattah AK, Pastawski HM, J. Chem. Phys., **143**, 2015.

EXPERIMENTS IN ADAMANTANE

- The **same initial decay rate** for all scaling factors.
- For $\tau > 450\,\mu s$, the curves are **ordered according $|\mathbf{k}|$.**





Buljubasich L, Sánchez CM, Dente AD, Levstein PR, Chattah AK, Pastawski HM, J. Chem. Phys., **143**, 2015.

CONCLUSIONS

1. Study of the connectivity of the system through MQC evolution.
2. Cluster size extracted by means of Gaussian curves fittings.
3. It was possible to observe correlations between the growth of the system and decoherence.
4. The difference in the coupling constants values separates the time evolution of the system by allowing a temporary stagnation in clusters size evidencing correspondence with decoherence.
5. There is a decoherence mechanism residing in the growth rate of the state of the system. It is beyond the size, or complexity of the state.

CONCLUSIONS

1. Study of the connectivity of the system through MQC evolution.
2. Cluster size extracted by means of Gaussian curves fittings.
3. It was possible to observe correlations between the growth of the system and decoherence.
4. The difference in the coupling constants values separates the time evolution of the system by allowing a temporary stagnation in clusters size evidencing correspondence with decoherence.
5. There is a decoherence mechanism residing in the growth rate of the state of the system. It is beyond the size, or complexity of the state.

THE END