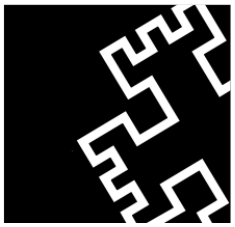
Spin dynamics simulation of electron spin relaxation in $Ni^{2+}(aq)$

Jyrki Rantaharju



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Introduction

- The ability to quantitatively predict and analyze the rate of electron spin relaxation of electronically open-shell systems is important for electron paramagnetic resonance and paramagnetic nuclear magnetic resonance spectroscopies.

- The Bloch-Redfield-Wangsness theory is rarely applicable to paramagnetic systems. Solving the stochastic Liouville equation has constituted a state-of-the-art method for electron spin relaxation.

- In principle it is possible to simulate nuclear and electron spin relaxation of any system for which the well-established MD and QC electronic structure methods are applicable.

- We demonstrate this using aqueous solution of Ni^{2+} ions as a model system.

- We sample a MD trajectory by quantum chemical (QC) calculations and, in turn, numerically solve the Liouville-von Neumann equation for the time evolution of the spin density matrix.

- We found only one attempt [1] of such simulation from literature. At present day we have better MD and QC. The relaxation times we extract from our simulation are in very good agreenment with the available experimental data.

[1] M. Odelius, C. Ribbing and J. Kowalewski, Spin dynamics under the Hamiltonian varying with time in discrete steps: Molecular Dynamics Based Simulation of Electron and Nuclear Spin Relaxation in Aqueous Nickel(II), Journal of Chemical Physics **104**, 3181 (1996).

Hamiltonian

- The two electrons of Ni^{2+} constitute an effective spin-1 system. To the spin Hamiltonian we include the g and ZFS tensors

$$\begin{aligned} \hat{H}(t) &= \mu_{\mathrm{B}} \hat{\mathbf{S}} \cdot \mathbf{g}(t) \cdot \mathbf{B} + \hat{\mathbf{S}} \cdot \mathbf{D}(t) \cdot \hat{\mathbf{S}} = \hat{H}_0 + \hat{H}_I(t) \\ \hat{H}_0 &= \mu_{\mathrm{B}} g B \hat{S}_z = \hbar \omega_0 \hat{S}_z \\ \hat{H}_I(t) &= \mu_{\mathrm{B}} \hat{\mathbf{S}} \cdot [\mathbf{g}(t) - g\mathbf{1}] \cdot \mathbf{B} + \hat{\mathbf{S}} \cdot \mathbf{D}(t) \cdot \hat{\mathbf{S}}, \end{aligned} \tag{1}$$

- QC calculations of MD snapshots produce a piecewise constant, time-ordered series of spin Hamiltonians $\hat{H}_1, \hat{H}_2, \hat{H}_3, \ldots, \hat{H}_{l-1}, \hat{H}_l$, with the time step τ.

- In this simulation the length of the used MD trajectory was 750 ps and it was sampled to a piecewise constant series of $l = 15625$ spin Hamiltonians $\{\hat{H}_i\}$ with the time step of 48 fs.

Superpropagators

- We transform the $\{\hat{H}_i\}$ to superpropagators $e^{\hat{\hat{L}}_1\tau}, e^{\hat{\hat{L}}_2\tau}, e^{\hat{\hat{L}}_3\tau}, \ldots, e^{\hat{\hat{L}}_{l-1}\tau}, e^{\hat{\hat{L}}_l\tau}$, where the $\hat{\hat{L}}_j$ are Liouvillians defined as $\hat{\hat{L}}_j = i[\cdot, \hat{H}_j]$

- The density operator is defined as

$$\hat{\rho}(t) = |\Psi(t)\rangle\langle\Psi(t)|, \tag{2}$$

where $|\Psi(t)\rangle$ is the state of the spin system. $\hat{\rho}$ is the solution of the Liouville-von Neumann equation,

$$\frac{d\hat{\rho}(t)}{dt} = \hat{\hat{L}}(t)\hat{\rho}(t), \tag{3}$$

- which means that we can express $\hat{\rho}(t)$, in rotating frame, at the time instant $t = n\tau$ as

$$\hat{\rho}^r(n\tau) = e^{-\hat{\hat{L}}_0 n\tau} e^{\hat{\hat{L}}_n \tau} e^{\hat{\hat{L}}_{n-1}\tau} \cdots e^{\hat{\hat{L}}_1 \tau} \hat{\rho}(0) \equiv \hat{\hat{\mathcal{L}}}\ (n)\hat{\rho}(0), \tag{4}$$

  where $\hat{\hat{L}}_0$ is the Liouvillian form of $\hat{H}_0$.

Ensemble

- Considering an ensemble of spin systems, with the assumption that all its members are initially in the same state, the ensemble average of $\hat{\rho}^r$ can be calculated as $\langle \hat{\rho}^r(n\tau) \rangle = \langle \hat{\hat{\mathcal{L}}}\ (n) \rangle \hat{\rho}(0)$.

- Assuming ergodicity and that the series $\{\hat{H}_i\}$ is long enough, the ensemble average of $\hat{\hat{\mathcal{L}}}\ (n)$ is obtained as

$$\langle \hat{\hat{\mathcal{L}}}\ (n) \rangle = \frac{1}{m(n)} e^{-\hat{\hat{L}}_0 n\tau} \sum_{i=1}^{m(n)} e^{\hat{\hat{L}}_{i+n}\tau} e^{\hat{\hat{L}}_{i+n-1}\tau} \cdots e^{\hat{\hat{L}}_i \tau}, \tag{5}$$

  where $m(n)$ is the number of the sub-series $\hat{H}_i, \ldots, \hat{H}_{i+n}$ that can be extracted from $\{\hat{H}_i\}$. $m(n)$ should be large enough to render $(1/m(n)) \sum_{i=1}^{m(n)} \hat{H}_i(n\tau)$ a good approximation of $\hat{\hat{H}}_0$.

Matrix representation

- $\hat{\rho}^r$ lives in a nine-dimensional space and its components can be expressed in the following orthonormal basis consisting of the shift operators and the z component of $\hat{\mathsf{S}}$:

$$\begin{aligned}\{\hat{B}_i\} \quad = \quad & \frac{\hat{S}_-\hat{S}_-}{2}, \frac{\hat{S}_-\hat{S}_z + \hat{S}_z\hat{S}_-}{2}, \frac{\hat{S}_-}{2}, \frac{\hat{S}_z}{\sqrt{2}}, \frac{3\hat{S}_z\hat{S}_z - 2\hat{1}}{\sqrt{6}}, \\ & \frac{\hat{1}}{\sqrt{3}}, \frac{\hat{S}_+\hat{S}_z + \hat{S}_z\hat{S}_+}{2}, \frac{\hat{S}_+}{2}, \frac{\hat{S}_+\hat{S}_+}{2}. \end{aligned} \tag{6}$$

- $\hat{\rho}$ can now be expressed as a ket vector and $\langle\hat{\hat{\mathcal{L}}}\,(n)\rangle$ as a matrix operator, in the nine-dimensional space:

$$|\hat{\rho}(0)) = \sum_{j=1}^{9} c_j |\hat{B}_j); \tag{7}$$

$$\langle\hat{\hat{\mathcal{L}}}\,(n)\rangle = \sum_{j,k=1}^{9} \mathcal{L}_{jk}(n) |\hat{B}_j)(\hat{B}_k|. \tag{8}$$

Relaxation experiment

- In thermal equilibrium the magnetization M is aligned with the Cartesian z axis. In a T_1 experiment, M is flipped by 180 with a π-pulse and the relaxation rate of the z component, M_z, is measured, as it decays back to equilibrium. In a T_2 experiment M is rotated by 90 with a $\pi/2$-pulse to the x axis, after which the relaxation rate of M_x is measured.

- In the present simulation method the feedback from the individual members of the spin ensemble to the surrounding lattice is neglected and, as a result, all components of M decay to zero instead of the nonvanishing equilibrium value of M_z in a real, interacting spin system. At high temperatures this model gives accurate results.

Correlation functions

- The elements $\mathcal{L}_{jk}(n) = (\hat{B}_j|\hat{B}_k(n\tau)) = (\hat{B}_j|\langle\hat{\hat{\mathcal{L}}}\ (n)\rangle|\hat{B}_k)$ are correlation functions of the members $\hat{B}_i$ of the shift and z operator basis. The inner product $(\hat{B}_j|\hat{B}_k(n\tau))$ is defined as $Tr[\hat{B}_j^\dagger \hat{B}_k(n\tau)]$.

- The expressions for the normalized Cartesian z component of $\mathbf{M}$ in a T_1 experiment, as well as the x component in a T_2 experiment (where $\mathbf{M}$ is initially aligned along the x axis) are, at time $n\tau$,

$$\frac{M_z^r(n\tau)}{M_z^r(0)} = \mathcal{L}_{44}(n)\ ;\ \frac{M_x^r(n\tau)}{M_x^r(0)} = \frac{\mathcal{L}_{33}(n) + \mathcal{L}_{88}(n)}{2}, \tag{9}$$

  respectively.

- The correlation functions of the normalized components of $\hat{\mathbf{S}}$ are defined as

$$C^r_{\mu\nu}(n\tau) = \frac{(\hat{S}_\mu|\hat{S}_\nu(n\tau))}{\sqrt{(\hat{S}_\mu|\hat{S}_\mu)(\hat{S}_\nu|\hat{S}_\nu)}}. \tag{10}$$

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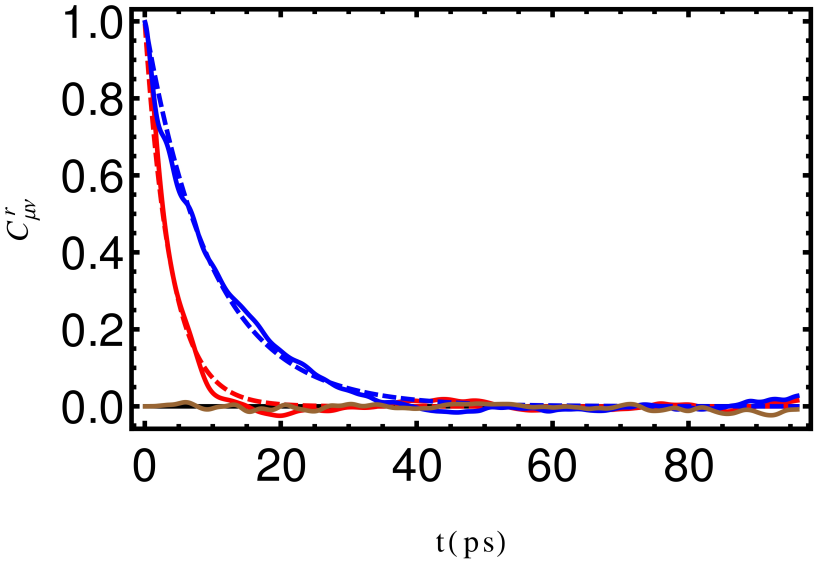
Simulation

- We calculate the Liouvillian form of the Hamiltonians $\{\hat{H}_i\}$ as well as the matrix representations of the Liouvillians with the help of the routines of SpinDynamica [1]. Furthermore, the matrix representations of the exponential propagators are obtained with the $MatrixExp$ routine of Mathematica. We implemented a Mathematica routine for computing the evolution of $\langle \hat{\hat{\mathcal{L}}}\ (n) \rangle$ from the list of matrix representations of the exponential propagators. The propagation of $\langle \hat{\hat{\mathcal{L}}}\ (n) \rangle$ is fast and memory efficient.

[1] SpinDynamica is a platform for spin dynamical simulations in Mathematica, programmed by Malcolm H. Levitt, with contributions by Jyrki Rantaharju, Andreas Brinkmann and Soumya Singha Roy (see www.SpinDynamica.soton.ac.uk).



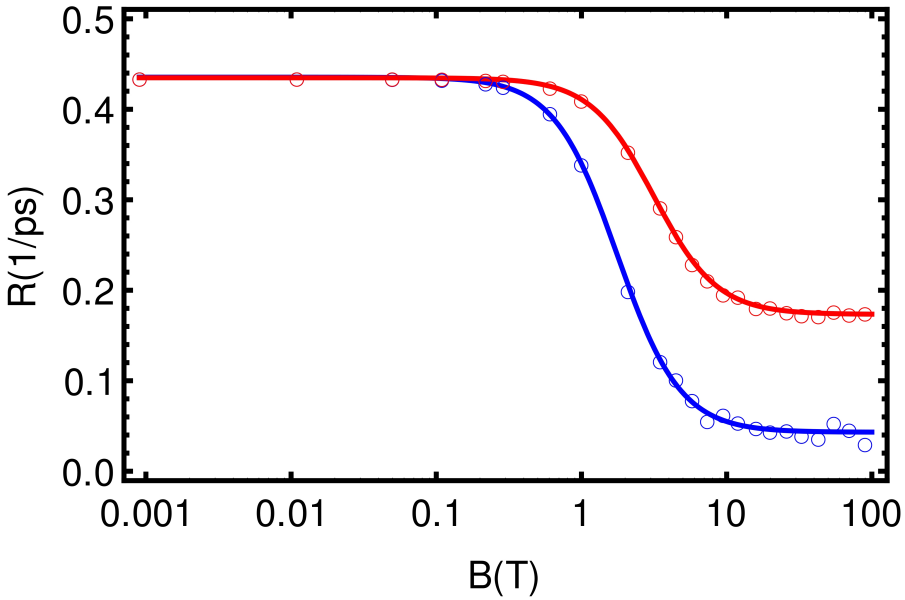
Electron spin magnetisation decay $M_z^r(t)/M_z^r(0)$ (blue), $M_x^r(t)/M_x^r(0)$ (red) in T_1 and T_2 relaxation simulations, respectively, for $Ni^{2+}(aq)$ at 300 K. Also shown are the respective single-exponential fits, plotted with dashed lines, as well as the cross-correlation function $C_{zx}^r(t)$ (brown) in a 4.5 T magnetic field along the z axis.

Relaxation rate

- Simulated R_1 (blue open circles), R_2 (red open circles) relaxation rates of electron spin in $Ni^{2+}(aq)$ at 300 K in the range from 0.001 T to 100 T. Also shown are their fits to Eq. (9) as blue and red solid lines, respectively. The data are presented as functions of the strength of the magnetic field.
- The rates follow the equation

$$R_{1,2}(B) = Y_{1,2} + \frac{A_{1,2}}{U_{1,2} + B^2}, \qquad (11)$$

where $Y_{1,2}, A_{1,2}$, and $U_{1,2}$ are fitted constants.



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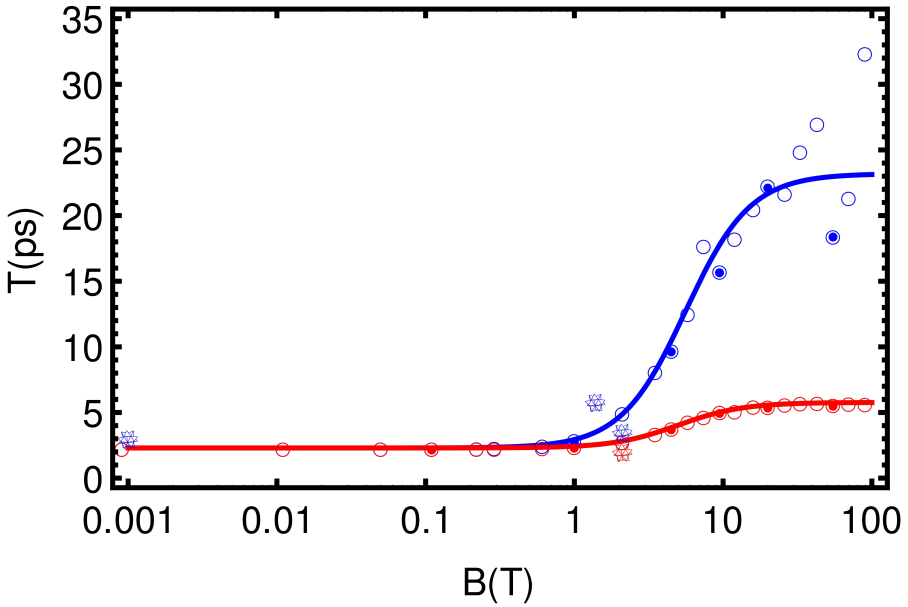
Relaxation time

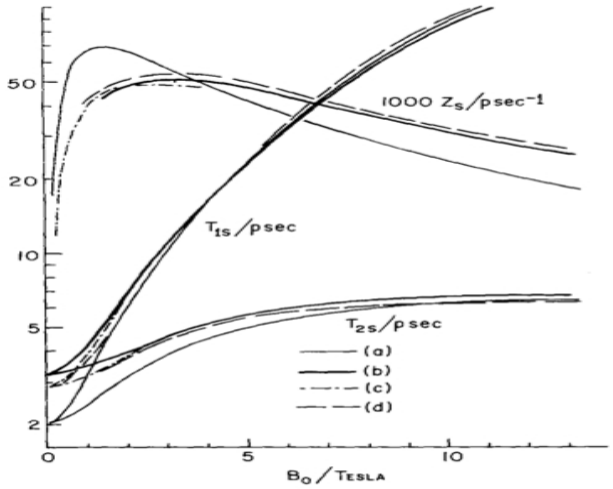
Simulated T_1 (blue) and T_2 (red) electron spin relaxation times in $Ni^{2+}(aq)$ at 300 K as a function of magnetic field. The open circles are the simulation results and the solid lines are fitted. The filled circles correspond to simulations done without the fluctuating part of the g tensor. The stars represent the available experimental results: $T_1 = T_2 = 2.9$ ps (blue) at $B = 0$ T [1], $T_1 = 5.7$ ps (blue) at 1.39 T at the temperature of 223 K [2], and $T_1 = 3.4$ ps (blue) (if $T_1 \gg T_2$) and $T_1 = 1.9$ ps (red) (if $T_1 = T_2$) at 2.11 T and 243 K [3].



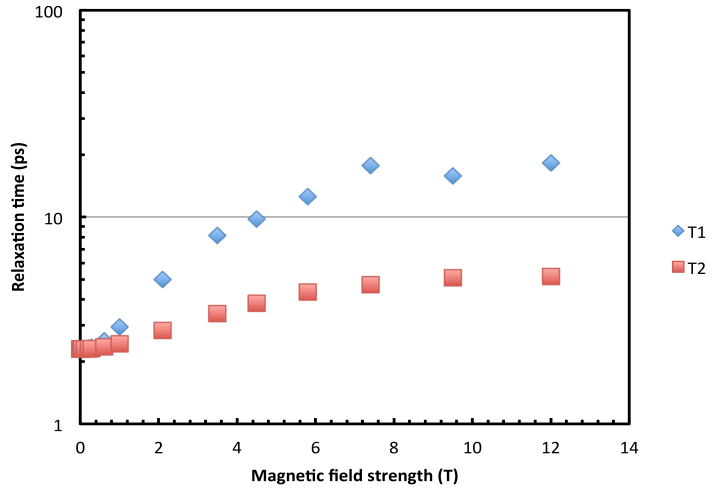
[1] H. L. Friedmann, M. Holz, H. G. Hertz, EPR Relaxations of Aqueous Ni^{2+} Ion, The Journal of Chemical Physics **70**, 3369 (1979).

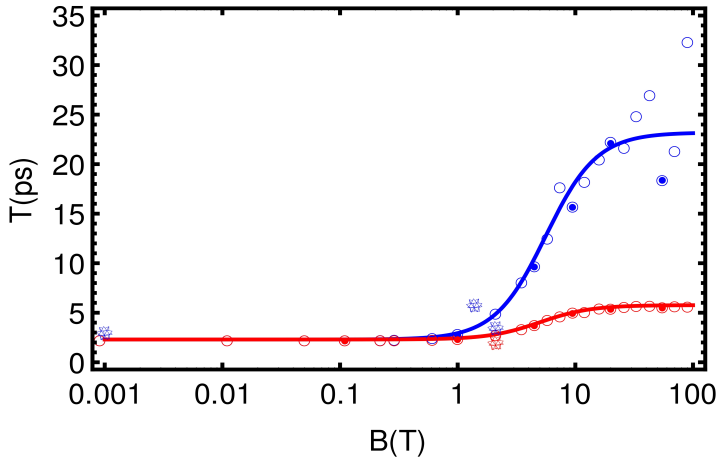
[2] D. Fiat, A. M. Chmelnick, Oxygen-17 Magnetic Resonance Studies of the Hydration of the Ferrous and Nickelous Ions, Journal of American Chemical Society **93**, 2875 (1971).

[3] J. Granot, A. M. Achlama, D. Fiat, Proton and Deuterium Magnetic Resonance Study of the Aqueous Nickelous Complex, The Journal of Chemical Physics **61**, 3043 (1974).



Screen capture from publication H. L. Friedmann, M. Holz, H. G. Hertz, EPR Relaxations of Aqueous Ni^{2+} Ion, The Journal of Chemical Physics **70**, 3369 (1979)..





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