

# LIQUID-STATE PARAMAGNETIC RELAXATION FROM FIRST PRINCIPLES

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Nuclear magnetic resonance relaxation of diamagnetic compounds in liquid state is typically well-described by the Redfield relaxation theory [1]. The Redfield theory is a good approximation in the regime where the magnitude of the interaction Hamiltonian is weak as compared to the average Zeeman interaction and the timescale of relaxation is much greater than the timescale of molecular fluctuations contributing significantly to the magnetization decay. However, in paramagnetic systems the former condition is usually not met, whereas – sometimes – the latter is. We simulate paramagnetic relaxation from first principles by sampling a molecular dynamics trajectory with quantum-chemical calculations, and producing a time series of the instantaneous parameters of the spin Hamiltonian, which is, in turn, used to numerically solve the Liouville-von Neumann equation for the time evolution of the spin density matrix. Taking advance of the generalized cumulant expansion method [2], the spin-lattice ( $T_1$ ) and spin-spin ( $T_2$ ) relaxation rates are extracted from the simulations of the time dependence of the longitudinal and transverse magnetization, respectively. We extend our earlier work [3] on electron spin relaxation and demonstrate the approach by simulating both the electron and nuclear spin relaxation in an aqueous solution of the  $\text{Ni}^{2+}$  ion. Good agreement with the available experimental data [4, 5, 6, 7, 8, 9] is obtained by the method. We used the SpinDynamica [10] code as a platform for our spin dynamics simulations.

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