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Liquid-state paramagnetic relaxation from first principles

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Quantitative understanding of the spin relaxation properties of paramagnetic systems is fundamentally important for paramagnetic nuclear magnetic resonance (pNMR) and electron spin/paramagnetic resonance (ESR/EPR) spectroscopies. The stochastic Liouville equation (SLE) is the state-of-the-art method to simulate spin relaxation in paramagnetic systems. The most frequently used approach to solve SLE assumes that microscopic dynamics can be approximated in operator form, such as using diffusion operators and in the form of the Fokker-Planck-SLE. Application of SLE and its special cases, such as Swedish slow-motion theory, typically require empirical parameters either for the magnetic interaction Hamiltonian or for models of molecular motion. Parameter-free computations of the paramagnetic systems have so far been largely absent. Modern computational resources allow such first-principles approaches to be used in many a areas of science, to justify empirical models and fix their parameters.

We take a non-empirical approach [1] to solve the SLE in the Langevin form and present first-principles computations in which the time evolution of the spin density matrix is governed by quantum-chemically calculated spin Hamiltonian. A time series of such Hamiltonians is sampled, in turn, from a molecular dynamics simulation trajectory. We demonstrate the approach by studying the aqueous solution of the Ni(2+) ion. Taking advantage of Kubo's theory, the spin-lattice (T1) and spin-spin (T2) relaxation rates are extracted from the simulations of the time dependence of the longitudinal and transverse magnetization, respectively. Good agreement with the available experimental data is obtained by the method.

[1] J. Rantaharju and J. Vaara, *Liquid-state paramagnetic relaxation from first principles*, Physical Review A **94,** 043413:1-10 (2016).