Understanding DNP Mechanism with Pulsed EPR

Krishnendu Kundu

National High Magnetic Field Laboratory, Florida, USA

I dedicated my first talk to the application of the EPR technique to Quantum Information Sciences. In first half of the present talk, I will focus on the role of the EPR to understand the Dynamic Nuclear Polarisation (DNP) technique that utilizes electrons to enhance the magnetic resonance signal of nuclei. Nuclei are approximately 3-4 orders of a weaker magnet than an electron, which results in an inherent poor sensitivity in the nuclear magnetic resonance (NMR) technique. DNP can boost NMR signal by several orders of magnitude and the technique becomes very successful and popular in the last two decades. DNP enhancements are often recorded with nitroxyl radical where the EPR line width meets the condition larger than the nuclear Larmor frequency. In such cases, the DNP process has been described as a multi-spin mechanism. A high concentration of radicals is generally used to facilitate the proximity of the radical and enhance the efficiency in the enhancement factor. Assuming a strong interaction among electron spins, researchers promoted a thermodynamic model to explain DNP experiments in such conditions that became known as thermal mixing (TM).

During my post-doctoral research at the Weizmann Institute of Science, Israel, I was interested to revisit the DNP mechanism with rigorous quantum mechanical simulation and EPR-DNP experiments. The key finding is that under DNP conditions, the steady-state electron polarisation profile along the EPR spectrum determines the nuclear polarisation. In practice, these polarisation profiles have been mapped by Electron-Electron Double Resonance (ELDOR) experiments and show substantial deviation from the shapes predicted by the Thermal Mixing (TM) model. The polarisation profiles were analyzed using a phenomenological model describing the electron spectral diffusion (the eSD model) that is based on a set of coupled rate equations for the polarizations composing the EPR line shapes. In order to substantiate the eSD model and relate it to basic principles, I performed exact spin dynamics computations on a small coupled-spin system taking into account the total spin Hamiltonian including dipolar flip-flop term, the microwave irradiation field and relaxation processes. The master equation in Liouville space for the diagonal matrix elements (the populations) in the eigenstate representation is solved and steady-state energy-population plots are presented. These plots together with their EPR spectra for different conditions demonstrate for which interaction and relaxation parameter these results correspond to the TM model and provide a possible reason for the disagreement with the TM model in experimental results with nitroxyl. Furthermore, it is shown that a zero-quantum electron cross-relaxation mechanism must be added to the calculations to obtain EPR profiles that resemble the experimental results that can be simulated using the eSD model. As will be shown, the addition of the cross-relaxation mechanism also enables us to reproduce with the help of the eSD model the concentration dependence of spectral diffusion observed experimentally.

In the last part of my talk, I shall present my research plan, which is mostly based on my day 1 talk on electron qubits. The problem with spins is that they can only be manipulated by magnetic fields and not (in general) by electric signals. This is unfortunate because magnetic fields, in contrast to electrical signals, are forbiddingly difficult to control both on small-length scales and at high speeds. My research plan is to exploit the electric-field sensitivity of spin qubits, with a special interest in clock transition qubits. Application of electric field will be further extended to design to gate operation on a pair of clock transition qubits. The proposal includes a building of a pulsed EPR spectrometer with key features of arbitrary waveform generation (AWG), Electric field capabilities and tunable broad microwave frequency range. Further, the spectrometer will be extended to DNP and ENDOR capabilities.