Time-domain Electron Decoupling

Strong EPR-NMR (hyperfine) dipolar couplings yield effective electron→nuclear polarization transfer. However, nuclear spins strongly coupled to electron spins suffer from very short relaxation times and broad NMR lineshapes. This paramagnetic relaxation effect (PRE) prevents high-resolution NMR and internuclear distance measurements close to EPR spins. Paramagnetic broadening is a major problem in DNP experiments.

Our laboratory has developed an innovative strategy to remove PREs by decoupling the electron spins using custom-built frequency-agile gyrotrons. Analogous to proton spin decoupling, electron spin decoupling increases NMR resonance intensity and narrows the linewidths. After DNP, the microwave frequency is quickly switched on-resonance with electron spins. Chirped microwave pulses through the EPR resonance decouple the hyperfine interaction. We have proven that time-domain frequency chirps are much more effective than CW irradiation. Both electron decoupling and time-domain DNP can be implemented with frequency chirps that invert longitudinal electron spin magnetization. Using chirped microwave pulses rather than square “hard pulses”, we have demonstrated that currently available gyrotron oscillators can be used for electron decoupling and time-domain DNP instead of the less accessible gyro-amplifiers.

Before we attempted to implement electron decoupling, we performed spin physics calculations to simulate electronic adiabatic inversions in MAS experiments. We also simulated the microwave field within MAS rotors to understand the effect of an inhomogeneous electron on adiabatic inversions and, therefore, electron decoupling. Our laboratory’s systematic spin physics and electromagnetic simulations published in 2015 (Hoff et al.), two years before we first implemented electron decoupling in practice, reflects how robust theoretical analysis underpins our instrumentation and method development.
**Connection:** The improved NMR resolution, longer spin relaxation, and higher-intensity signals available with electron decoupling will permit improved structural characterization of HIV latency reversal agents.

**Future Directions:** Higher electron Rabi frequencies will improve electron decoupling and provide the capability to perform direct transfers to nuclear spins very close to polarizing agents while retaining excellent spectral resolution. This innovation will be a “game-changer” for the DNP field, when some of the deleterious influences of electrons are manipulated by these methods. Such direct transfers and strong hyperfine couplings will be leveraged to perform DNP at room temperature and to repeat experiments limited by the electronic magnetization recovery time in the order of milliseconds.