学位論文の要約

題目　Dynamics of nuclear spins in unexplored arenas
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序論

Nuclear spin diffusion suppresses the local difference of polarization by transporting the polarization of one spin to more distant nuclear spins and obeys the general diffusion equation $\partial p/\partial t = D\Delta p$, where D is the diffusion coefficient and p is the nuclear polarization. D has been calculated in high-temperature approximation where $p \ll 1$. In the first part of this thesis, we propose a correction $1/\sqrt{1-\bar{p}^2}$ to the diffusion coefficient D as a result of extending the Lowe-Gade formula to low-temperature case. We will also show how this correction can be observed experimentally.

In the second part of this thesis, we study Cross Polarization (CP) proceeding in a different arena, which is realized through simultaneous nutations around a pair of orthogonal axes of the source spins at frequencies ω_{1I} and ω_{2I}. In DOuble NUTaion Cross Polarization (DONUT CP), frequency mixing is achieved through generating the sum and difference frequencies $\omega_{1I} \pm \omega_{2I}$, resulting different Hartmann-Hahn matching conditions. The experimental results also exhibit some interesting characteristics that can lead to further studies on this topic.

１．Speedup of nuclear spin diffusion in hyperpolarized solids

Dynamic Nuclear Polarization (DNP) is a powerful technique to enhance the NMR signal by transferring the electron spin polarization to the nearby nuclei, leading to an inhomogeneous profile of nuclear spin polarization. This local difference of polarization distribution is suppressed by spin diffusion that transports the polarization to more distant nuclear spins and obeys the general diffusion equation $\partial p/\partial t = D\Delta p$, where D is the diffusion coefficient and p is the nuclear polarization. The spin diffusion equation has been derived and the diffusion coefficient D has been calculated in high-temperature approximation, where the nuclear spin polarization $p \ll 1$. It is obvious that D obtained in this way may not be sufficient to describe the spin diffusion in a hyperpolarized system where p can be close to unity.

We propose a correction to the coefficient of nuclear spin diffusion by a factor $1/\sqrt{1-\bar{p}^2}$, where $\bar{p}$ is the average nuclear spin polarization. The correction, derived by extending the Lowe-Gade theory to low-temperature cases, implies that transportation of nuclear magnetization through nuclear spin diffusion accelerates when the system is hyperpolarized, whereas for low polarization the correction factor approaches unity and the diffusion coefficient coincides with the conventional diffusion coefficient valid in the high-temperature limit. The proposed scaling of the nuclear spin diffusion coefficient can lead to observable effects in the buildup of nuclear polarization by dynamic nuclear polarization.

２. Double nutation cross polarization between heteronuclear spins in solids

Cross Polarization (CP) is another widely-used tool to enhance the NMR signal of nuclei (^{13}C, ^{15}N...) with low gyromagnetic ratio, utilizing the polarization of abundant spin such as proton. So far, numerous variants of CP have been developed in order to improve its performance.

In this work, we study transfer of magnetization from one nuclear spin species to another in solid-state nuclear magnetic resonance by cross polarization (CP) employing the radiofrequency irradiation that causes simultaneous nutations around a pair of orthogonal axes. Under such DOuble NUTation (DONUT), polarization transfer undergoes in an unexplored arena of what we refer to as the nutation frame, which represents the interaction frame with respect to the Hamiltonian that drives nutation. The effect of DONUT is to develop either the zero-quantum or double-quantum secular component of the heteronuclear dipolar interaction, causing flip-flop or flop-flop exchange of the spin states. We demonstrate DONUT CP in polycrystalline adamantane, glycine, and histidine, also examining folding of the CP spectrum under magic angle spinning as well as the buildup behavior of the magnetization in comparison with the conventional CP scheme. In addition, we put forth a concept of spin relaxation in the nutation frame, which is a straightforward extension of the well-known concept of spin relaxation in the rotating frame.