DNP Solid Effect: rate equation for spin 1

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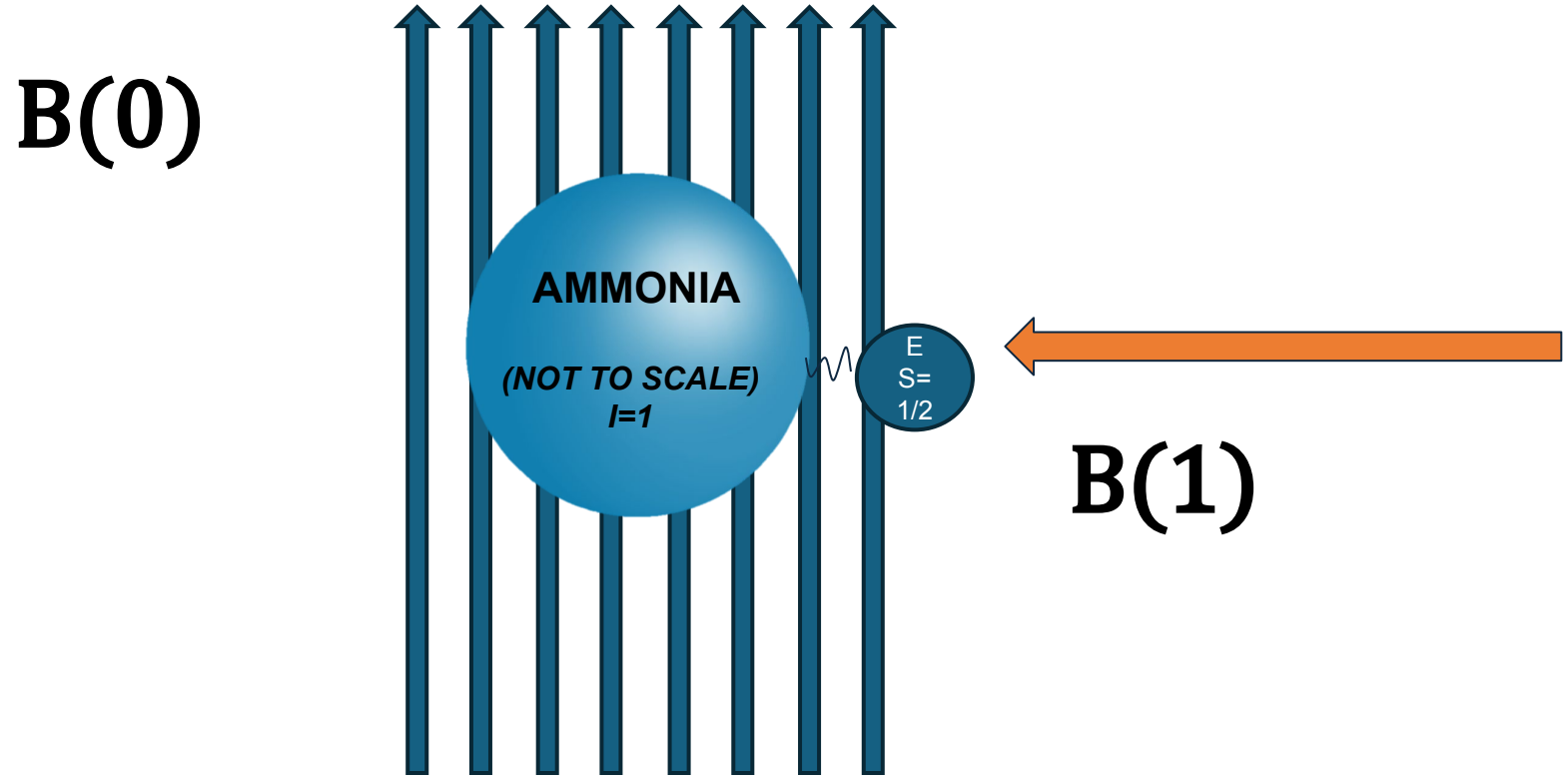
Outline

- DNP
- Solid Effect
- Polarization for spin I=1: P_I and spin S=½ :P_s
- Direction Transitions
- Rate equations
- Polarization form
- Key Points

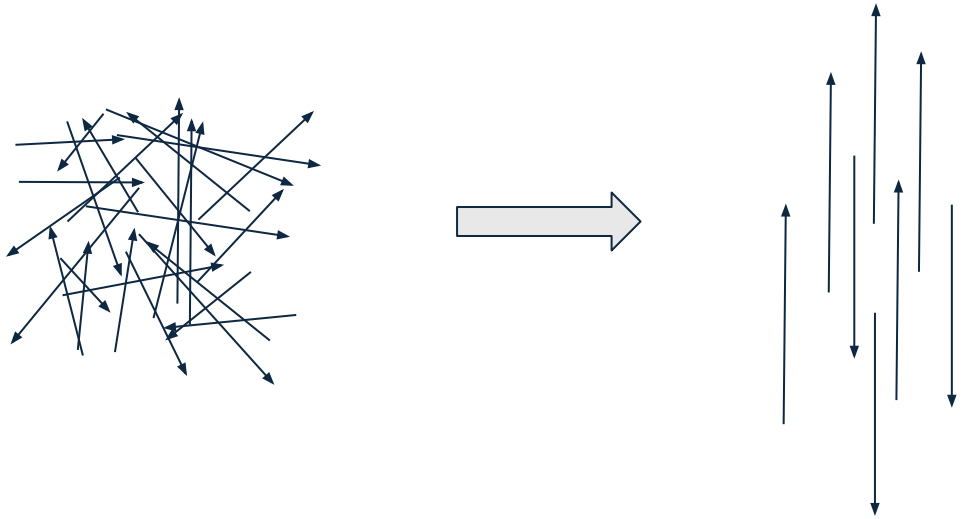
Dynamic Nuclear Polarization (DNP)



Spin Diffusion

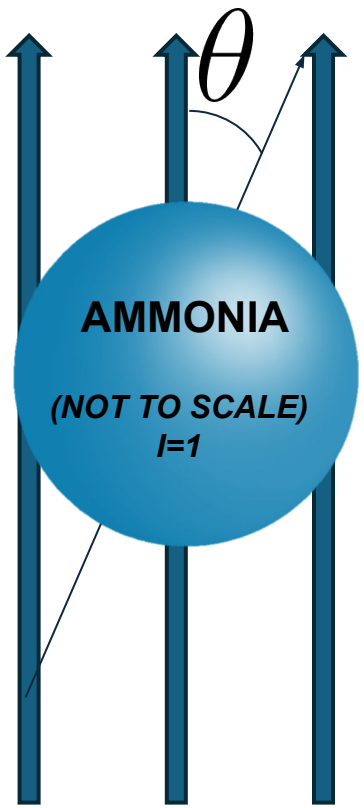
Process in which the polarization in the nuclear population spreads from the local cite of the radical

In the solid effect, the polarization transfer from the electron to the nucleus arises via the hyperfine interaction



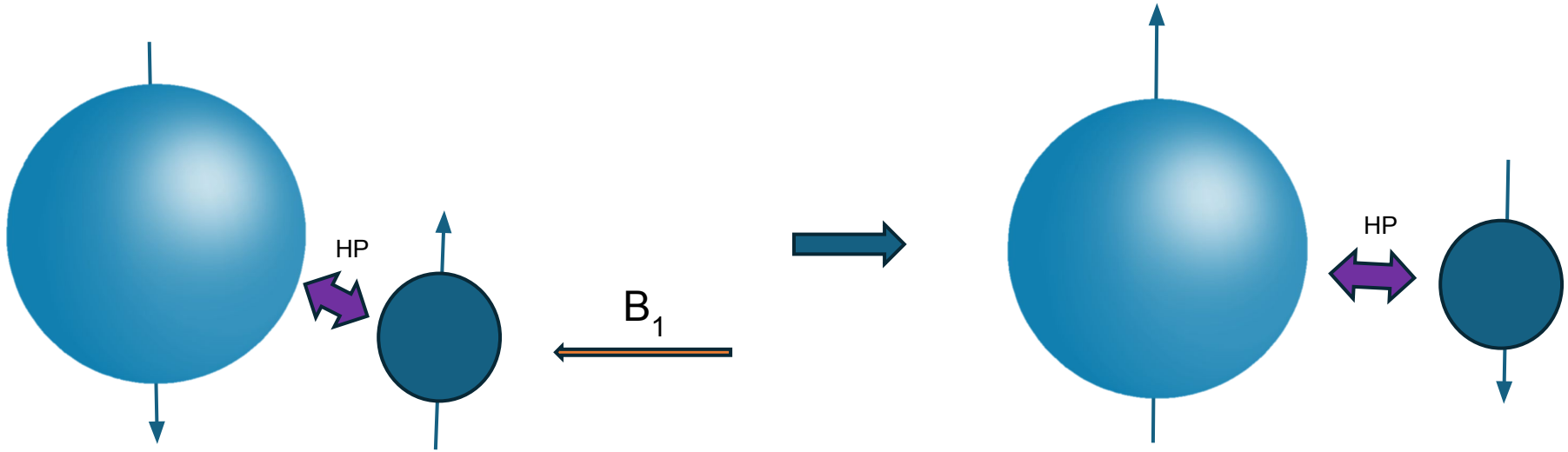
θ dependence

The angle dependence arises from the misalignment of the magnetic field and the principal axis the EFG due to the quadrupolar interaction



Solid Effect in DNP

- Hyperfine coupling mediates the interaction between the electron and nucleus
- Microwave field B1 drives electron transitions



Polarization equations for I=1 and S=½

Standard equation for polarization of nucleus

$$P_z = \frac{1}{Tr\{\rho\}} Tr\{\frac{\rho}{N_I I} \sum_{I=1}^{N_I} I_z^i\}$$

Where the ρ is the density matrix of the nucleus, N_I:the number of Nucleons of spin I, I=1 and and I^i_z is the spin along the z axis

For ND3 the density matrix ρ is given by $\begin{bmatrix} \rho_+ & 0 & 0 \\ 0 & \rho_0 & 0 \\ 0 & 0 & \rho_- \end{bmatrix}$ in the basis of the spinor S_z

$$P_1^I = \frac{\rho_+^I - \rho_-^I}{\rho_+^I + \rho_-^I + \rho_0^I}$$

$$P_{\frac{1}{2}}^S = \frac{\rho_+^S - \rho_-^S}{\rho_+^S + \rho_-^S}$$

Hamiltonian for Solid Effect

$$\hat{\mathcal{H}} = -\omega_{0I} I_z + \omega_{0S} S_z + 2\omega_{1I} cos(\omega t) S_x + S \cdot A \cdot I$$

Nuclear Zeeman

Electron Zeeman

Microwave Driving field

Hyperfine interaction

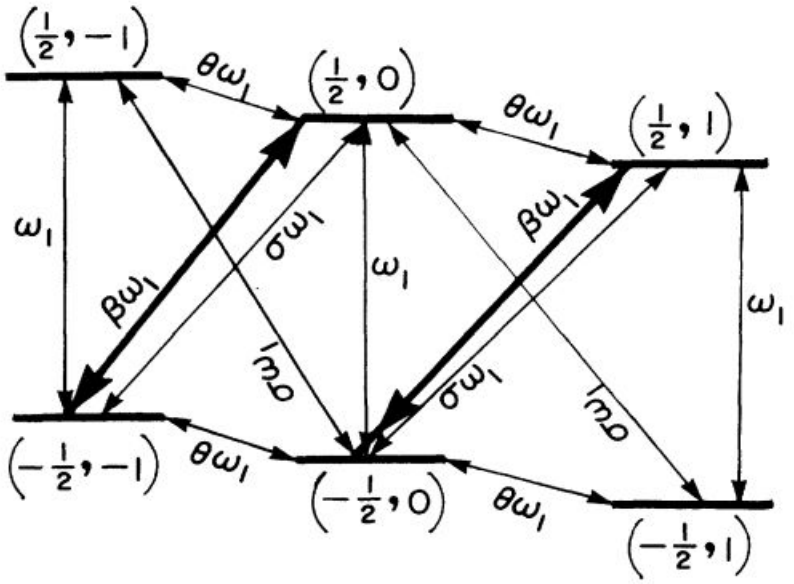
S: total spin operator
A: hyperfine tensor
I: nuclear spin operator
ω: microwave frequency
$\omega_{0I} = \gamma_I |B_0|$ is the resonance frequency
$\omega_{0S} = -\gamma_S |B_0|$
$\omega_{0S} = -\gamma_S |B1|$

We will treat this Hamiltonian using perturbation theory where we interpret the first two terms, the electron and nuclear Zeeman, as the unperturbed part of the Hamiltonian and the Microwave and Hyperfine as a perturbation.

The only terms that contribute to the solid effect, for the hyperfine tensor are: A_{zx} and A_{zy}

In ND3 we know that there is much more going on than the SE, but this is a good starting point.

Energy transitions



Energy level diagram for ND3, I=1 and S=½, in a magnetic field

https://doi.org/10.1103/PhysRevB.35.3088

2nd order perturbation Theory

First order perturbation theory only allows transition for a spin $\frac{1}{2}$ nucleon since they have a single transition, from a + to a - state.

Need 2nd order perturbation for spin 1 to allow transitions from - to 0 and from 0 to + spin states

Transition Rates

$$W^{+} = 2\pi\left(\frac{\omega_{1S}}{\omega_{0I}}\right)^{2}\left|\frac{\sqrt{2}}{4}A_{z+}\right|^{2}\delta(\omega_{0s}+\omega_{0I}-\omega)$$

Transition rate constant for polarization in the positive direction, going to I=+1

$$W^{-} = 2\pi(\frac{\omega_{1S}}{\omega_{0I}})^{2}|\frac{\sqrt{2}}{4}A_{Z-}|^{2}\delta(\omega_{0S}-\omega_{0I}-\omega)$$

Transition rate constant for polarization in the negative direction, going to I=-1

$$A_{z\pm} = A_{zx} \pm iA_{zy}$$

Quantifies how strongly the electron spin flips interacts with the nuclear spin changes

Rate equations

$$\frac{d}{dt}(\rho_+^S\rho_+^I) = \frac{d}{dt}(\rho_-^S\rho_-^I) = 0$$

$$\frac{d}{dt}(\rho_-^S\rho_+^I) = W^+(\rho_+^S\rho_0^I - \rho_-^S\rho_+^I)$$

$$\frac{d}{dt}(-\rho_+^S\rho_0^I) = W^+(\rho_+^S\rho_0^I - \rho_-^S\rho_+^I)$$

$$\frac{d}{dt}(\rho_-^S\rho_0^I) = W^-(\rho_+^S\rho_-^I - \rho_-^S\rho_0^I)$$

$$\frac{d}{dt}(-\rho_+^S\rho_-^I) = W^-(\rho_+^S\rho_-^I - \rho_-^S\rho_0^I)$$

Rate equations for the probability

No change in the populations of the electron and nucleons in the ± spin states due to the forbidden interactions of electrons and nucleons transitions in the same direction

These are the rates only for the solid effect, other effects will have a different transition equations

Polarization form

$$\frac{d}{dt}(P_1) = 2W^-(\rho^S_+\rho^I_- - \rho^S_-\rho^I_0) + 2W^+(\rho^S_+\rho^I_0 - \rho^S_-\rho^I_+)$$

$$\frac{d}{dt}(P_1) = (1 - P_S)(W^+(\rho^I_0 + \rho^I_+) + W^-(\rho^I_- + \rho^I_0))$$

The polarization direction is dependent on the microwave frequency.

In this case, as you polarize in the spin + direction, you have your microwave frequency set to $\omega = \omega_{0S} - \omega_{0I}$

ND3 Planned Investigation of the rate equations

- Compute rate equations for different types of SE.
- Compute rate equations for Thermal mixing.
- Compute rate equations for cross effect.
- Explore different source and sink parameterizations.

- Investigate which effects contribute significantly to ND3 polarization e.g. ISE, DSE, cross effect, TE,...

- Verifying validity of equation by coding the equations introducing comparing to data

- S-curve can help be used to disentangle the mechanisms

Putting Note together to share with details and comparisons to historic calculations.

Thank you for your time!