Effects Known to be Caused by Hyperfine Interactions

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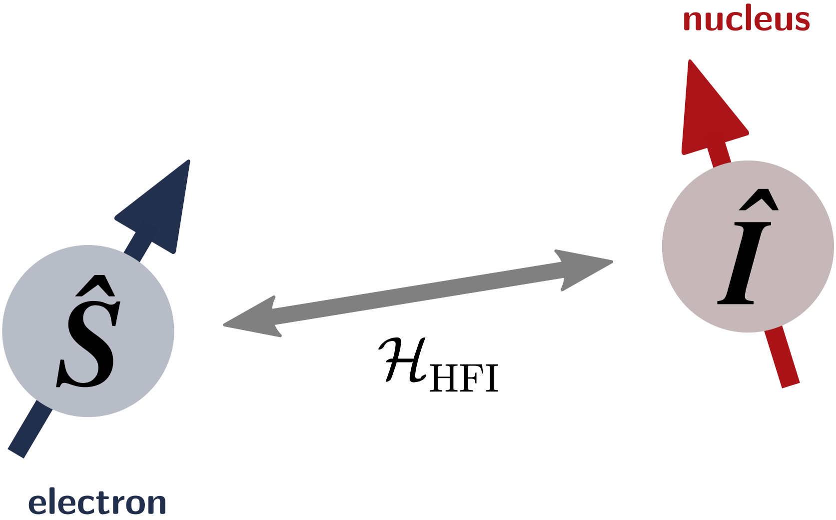
What is a Hyperfine Interaction?

A short introduction for our non-spectroscopic friends



Spin Hamilton operator of the hyperfine interaction (HFI)

$$\mathcal{H}_{\text{HFI}} = \mathcal{H}_{\text{isotropic}} + \mathcal{H}_{\text{dipolar}}$$

Fermi contact interaction

$$\mathcal{H}_{\text{isotropic}} = a\hat{\boldsymbol{S}}\hat{\boldsymbol{I}}$$

Interaction between magnetic dipoles of electron and nucleus

$$\mathcal{H}_{\text{dipolar}} = \hat{\boldsymbol{S}}\mathbf{A}\hat{\boldsymbol{I}}$$

☛ No dependence on the external magnetic field!

Prerequisites for hyperfine interactions

- electron spin
  - radicals
  - high-spin systems
- nuclear spin
  - magnetic isotopes

A few typical magnetic isotopes

- hydrogen: ^{1}H, ^{2}H
- carbon: ^{13}C
- nitrogen: ^{14}N, ^{15}N

Overview

Introduction: What is a Hyperfine Interaction?

Spin mixing

- Magnetic Field Effect (MFE)
- Magnetic Isotope Effect (MIE)
- Photo-CIDNP

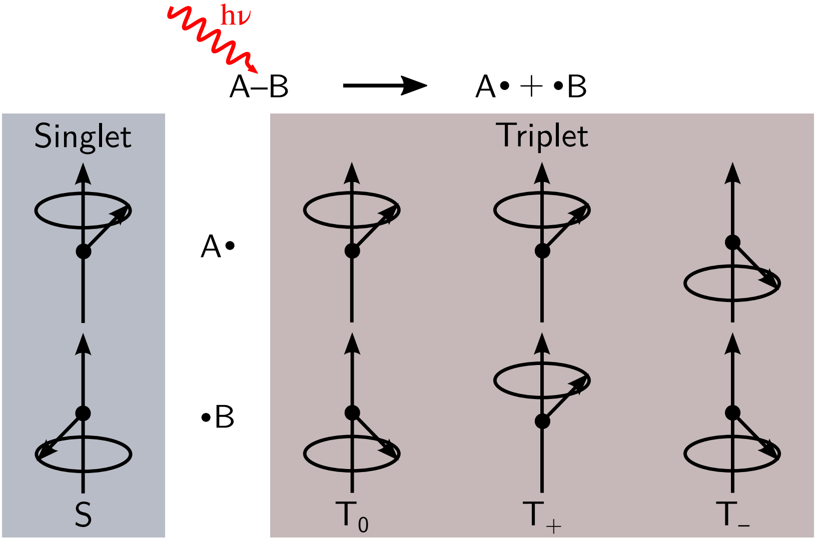
Spin relaxation/decoherence

- Electron spins
- Nuclear spins

Summary: Which effects can be caused by HFI?

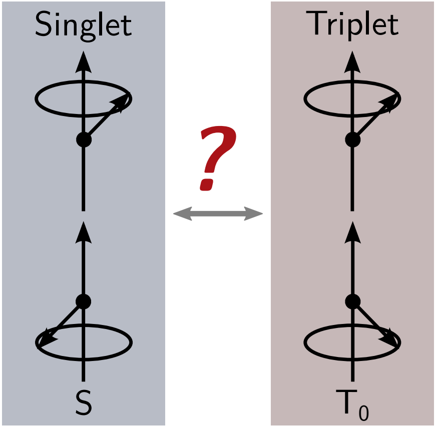
Spin Mixing

We need (at least) two correlated spins.



Spin Mixing

How to interconvert between S and T_0?



Prerequisite

- different Larmor precession frequencies for the spins

Two mechanisms

- hyperfine interactions
- Δg mechanism

What about S–T_+ and S–T_-?

- T_+ and T_- are typically energetically far separated from S.

- Magnetic field effect (MFE)
  - Effects of (very!) small magnetic fields on chemical reactions
  - Typically $|\boldsymbol{B}| \ll k_\mathrm{B}T$
- Magnetic isotope effect (MIE)
  - Effects of isotopes on chemical reactions
  - Separate from the *kinetic* isotope effect
- Chemically induced dynamic nuclear polarisation (photo-CIDNP)
  - Strong enhancement of NMR signals

Magnetic Field Effects

A famous quote by Peter Atkins

> *The study of the effect of magnetic fields on chemical reactions has long been a romping ground for charlatans. Contributions to the literature of the subject range over the span of scientific competence, from the benignly insane to whatever lies at the other extreme removed by a hair's breadth from the first.*
>
> – Peter Atkins, 1976

Peter Atkins: Magnetic field effects, *Chemistry in Britain* **12**:214–218, 1976

How to create a radical pair?

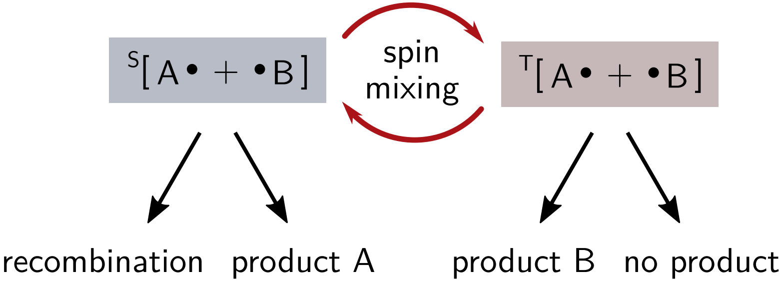
- Homolytic bond cleavage
- Electron transfer following light excitation
- (Re)encounter of two radicals

Characteristics of a radical pair

- Spins are magnetically coupled
  - Via distance-dependent dipolar and/or exchange interaction
  - Total spin $S = 0$ or $S = 1$
- Four energy levels: S, T_0, T_+, T_-
- Can undergo spin mixing between $S = 0$ and $S = 1$

Magnetic Field Effect

The radical-pair mechanism



- Singlet and triplet RP have different fates
- HFI modulates the frequency of spin mixing

☛ Energies $\ll k_{\mathrm{B}}T$ can influence chemical reactions!

Magnetic Isotope Effect

Difference in magnetic field effects due to different isotopes

Prerequisites

- Isotopes with different nuclear spin
- Radical pair to interact with

Mechanism

- Same as for the magnetic field effect
- Different strength depending on the nuclear spin multiplicity

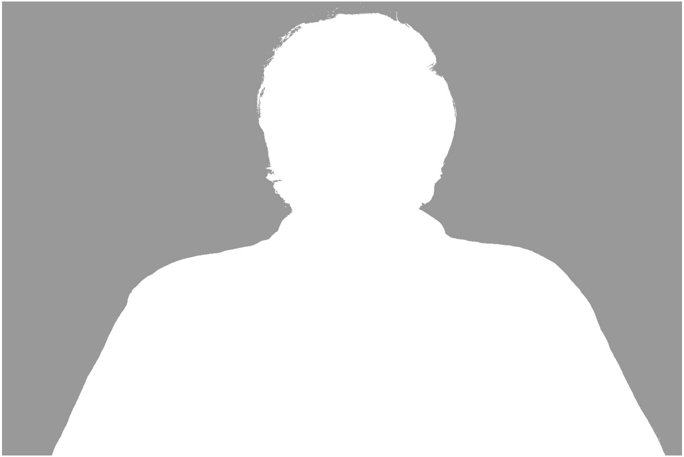
Difference to kinetic isotope effect

- Caused by nuclear spin, not by mass of the isotope
- Mechanism based on spin dynamics, not (directly) kinetics

☛ For $^{1}H/^{2}H$ exchange usually hard to distinguish MIE and KIE

photo-CIDNP

Overcoming the sensitivity problem of NMR – and much more



Ask the expert(s) for details!

I'm only an EPR spectroscopist . . .

Overview

Spin relaxation/decoherence

A very simple picture

Two basic mechanisms

- Spin–lattice relaxation (T_1)
  - Return of the longitudinal component of the magnetization to its equilibrium value
  - T_1 is sometimes called spin relaxation time
- Spin–spin relaxation (T_2)
  - Loss of phase-coherence of the spins
  - T_2 is sometimes called spin decoherence time

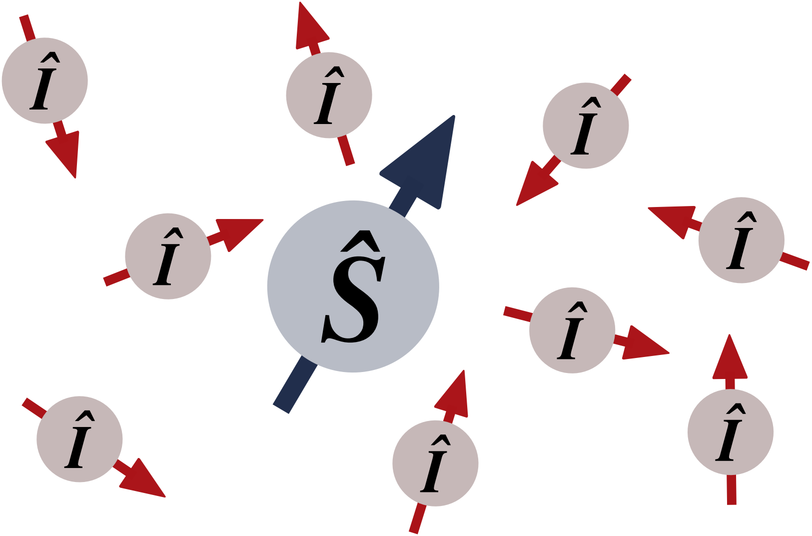
Role of the hyperfine interaction

- Spin relaxation due to electron–nuclear spin flip
- Dephasing by random precessions in the fluctuating hyperfine fields

☛ Two perspectives: electron spin and nuclear spin

Electron Spin Relaxation

„Hyperfine bath“ due to surrounding nuclei



Electron Spin Relaxation

What can we do about it?

Reminder: two mechanisms

- Spin relaxation due to electron–nuclear spin flip
- Dephasing by random precessions in the fluctuating hyperfine fields

A few comments

- Biological systems provide a well-ordered environment.
- Organic solids are usually „a mess“:
  noncrystalline, inhomogeneous (unordered), flexible.

How to prolong spin relaxation and decoherence rates?

- Reduce the strength of the HFI (*e.g.*, deuteration)
- Mismatch between e^- hopping rate and precession in the HFI field

Nuclear Spin Relaxation

Paramagnetic relaxation enhancement due to nearby electron spins

- Usually, paramagnetic species in the NMR are a bad idea . . .
  - Line width depends on lifetime
  - Fast relaxation broadens lines beyond the detection limit
- Paramagnetic relaxation enhancement
  - No NMR signals within a certain distance to the electron spin
  - Useful in MRI to enhance contrast or to speed up data acquisition

Again: Ask the experts for details . . .

I'm only an EPR spectroscopist

Summary

Effects known to be caused by hyperfine interactions

- Spin mixing (of electron spins)
  - MFE (RPM, TM)
  - MIE
  - photo-CIDNP (via RP, TSM)
- Spin relaxation/decoherence
  - electron spin: HFIs of the environment
  - nuclear spin: nearby paramagnetic centres (PRE)

☛ HFIs are not the only possible cause for these effects.
  - MFE: Δg mechanism
  - relaxation: dipolar and exchange interaction between like spins

Summary

A bit of literature

- Z. G. Yu, F. Ding, H. Wang: Hyperfine interaction and its effects on spin dynamics in organic solids, *Phys. Rev. B* **87**:205446, 2013
  - Theory-heavy, but detailed overview, focus on organic solids
- P. Atkins: Magnetic field effects, *Chem. Br.* **12**:214–218, 1976
  - Hard to come by, but excellent introduction
- M. P. de Jong: Recent progress in organic spintronics, *Open Phys.* **14**:337–353, 2016
  - Readable summary, highlights HFI contributions
- Geng *et al.*: A review on organic spintronic materials and devices: I. Magnetic field effect on organic light emitting diodes, *J. Sci. Adv. Mater. Devices* **1**:128–140, 2016
  - Somewhat convoluted, focus on MFE on organic LEDs
- U. E. Steiner, T. Ulrich: Magnetic field effects in chemical kinetics and related phenomena, *Chem. Rev.* **89**:51–147, 1989
  - Seminal contribution, predates the spintronics hype