Nuclear Magnetic Resonance Laboratory course
Assignment 7

Quadrupole Interaction II: Second order Quadrupole interaction

Dr. rer. nat. habil Thomas Meier, HPSTAR

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Abstract

Nuclear Magnetic Resonance (NMR) is a versatile tool for probing the atomic-scale environment of materials, especially when studying nuclei with a spin greater than $\frac{1}{2}$. In such cases, quadrupole interactions arise between the nuclear electric quadrupole moment and the surrounding electric field gradient. These interactions are often highly sensitive to the local electronic structure and symmetry, making them a valuable source of information. For elements like antimony (Sb), these interactions can produce broad and complex NMR line shapes due to significant second-order quadrupole effects.

This lab course will focus on reconstructing these broad line shapes using specialized wide-line excitation methods, which are tailored for capturing wide-ranging NMR signals that conventional techniques may miss. Antimony's broad spectral features, caused by strong second-order quadrupole interactions, pose unique challenges in both data acquisition and interpretation. By employing wideline techniques, we can effectively excite and detect the full breadth of the NMR signal, providing a more complete picture of the quadrupolar parameters, such as quadrupole coupling constants and asymmetry parameters, as well as the local structural and electronic environment surrounding Sb nuclei.

Throughout this lab course, you will be tasked with optimizing NMR experiments for antimony, applying wideline excitation to capture the entire spectral range, and reconstructing the broad line shapes that arise from quadrupole interactions. Careful analysis of these spectra will allow you to extract meaningful information about the material's local environment, helping to connect the observed quadrupolar features to the underlying atomic structure.

1 Theoretical background

For these experiments, you will need the following theoretical background. Please prepare necessary mathematical expressions and derivations:

- How does quadrupole interactions arise from the interaction between a nucleus' electric quadrupole moment and the electric field gradient (EFG) at the nuclear site. The distinction between first-order (linear) and second-order (non-linear) effects is crucial, as second-order effects often dominate in systems with low symmetry.
- The electric field gradient (EFG) reflects the spatial distribution of charges surrounding the nucleus. How does the magnitude and asymmetry of the EFG influence the quadrupole interaction and its effect on the NMR spectra, particularly for systems like antimony with non-cubic symmetry?
- The quadrupole coupling constant (C_Q) and the asymmetry parameter (η) are key parameters that characterize the quadrupolar interaction. How do these parameters affect the splitting, broadening, and overall shape of the NMR line, providing insights into the symmetry and electronic environment of the nucleus?

- Review techniques for wide-line NMR methods
- Students need to develop skills in correlating the observed NMR spectra with the underlying material structure, specifically how variations in quadrupole parameters can indicate changes in local symmetry, bonding, or coordination environments around the antimony nuclei.
- Material-specific properties of antimony (Sb) relevant to NMR. Understanding the nuclear properties of antimony, such as its nuclear spin (5/2 for ^{121}Sb), quadrupole moment, and natural abundance, is crucial for interpreting the NMR data. Additionally, students should be aware of how antimony's electronic environment and its role in different materials affect the NMR spectra.

2 Tasks

Please work on the tasks step-by-step and summarize your observations thoroughly and logically when you hand in the assignment. Please provide data plots and calculations to underline your conclusions. We recommend the use of ONMR running in Origin7 or later, for data analysis.

- **Preparation of the NMR Spectrometer for Wideline Excitation**: The NMR spectrometer is to be prepared for wideline detection using Variable Offset Cumulative Spectroscopy (VOCS). This includes selecting the appropriate frequency range, adjusting power levels, and optimizing pulse sequences to effectively capture the broad line shapes characteristic of antimony nuclei.
- **Detection of the Central Transitions for ^{121}Sb and ^{123}Sb**: The central transitions of the two naturally occurring isotopes of antimony, ^{121}Sb (spin 5/2) and ^{123}Sb (spin 7/2), are to be detected. Spectra will be acquired using the VOCS technique, with variable offset frequencies employed to span the broad spectral range necessary for these isotopes.
- **Optimization of VOCS Parameters**: VOCS acquisition parameters such as pulse width, offset increment, and acquisition time must be optimized to ensure high signal-to-noise ratios and comprehensive coverage of the entire spectral profile for both isotopes. Fine adjustments to offset increments will be required to fully cover the broad spectra.
- **Reconstruction of the Full Spectra**: After data acquisition, the full NMR spectra are to be reconstructed by combining individual spectra obtained at different offsets. This process will ensure a complete and continuous spectrum is obtained for both ^{121}Sb and ^{123}Sb isotopes.
- **Analysis of the Spectral Line Shapes**: The reconstructed spectra are to be analyzed to extract key quadrupole interaction parameters, including the quadrupole coupling constant (C_Q) and the asymmetry parameter (η). These parameters are to be derived primarily from the central transition regions, where the effects of quadrupolar broadening are minimized but still provide valuable quadrupolar interaction information.
- **Comparison with Known Quadrupole Parameters**: The experimentally derived quadrupole parameters for both ^{121}Sb and ^{123}Sb are to be compared with established values from the literature. Any discrepancies between the experimental and known values will be discussed in the context of material structure and potential sources of error in the VOCS approach.
- **Discussion of Structural and Electronic Insights**: The extracted quadrupole parameters will be interpreted to provide insights into the local structure and symmetry around the antimony nuclei. The results will be correlated with the material's electronic structure, bonding environments, and deviations from known structural models where applicable.

3 Literature

- Eiichi Fukushima, *Experimental pulse NMR - a nuts and bolts approach*

- Dustin Wheeler and Mark Conradi, *Practical Exercises for Learning to Construct NMR/MRI Probe Circuits*
- Noel Mispelter, *NMR probeheads for biophysical and Biomedical Experiments*
- Reyes, A. P., Ahrens, E. T., Heffner, R. H., Hammel, P. C., and Thompson, J. D. (1992). Cuprous oxide manometer for high-pressure magnetic resonance experiments. Review of Scientific Instruments, 63(5), 3120–3122. https://doi.org/10.1063/1.1142564
- Meier, T. (2016). High Sensitivity Nuclear Magnetic Resonance at Extreme Pressures [Leipzig University], $http : //www.qucosa.de/recherche/frontdoor/?tx_slubopus4frontend[id] = 20390$

4 Literature

- doi: 10.1103/PhysRev.80.580
- doi: 10.1021/ar400045t
- https://www.pascal-man.com/EACself.pdf