# Utilising First-Principles Calculations to Inform the Development and Application of Solid-State NMR Methodology

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Recent advances enabling accurate determination of NMR parameters in periodic systems have revolutionized the application of Density Functional Theory (DFT) calculations in solid-state NMR spectroscopy, particularly among experimentalists. Much of the information contained within solid-state NMR spectra lies unexploited owing to the difficulty of obtaining high-resolution spectra, and the challenges associated with assignment and interpretation. Determining the structure of ordered crystalline solids can be straightforward using Bragg diffraction. However, it is often the deviations from periodicity that produce the interesting physical properties of commercial interest. As NMR is sensitive to the atomic-scale environment, it provides a useful tool for studying disordered materials, and its combination with first-principles calculations offers a particularly attractive approach.

In order to compare experiment and calculation, a vital requirement is an initial structural model. This can be a problem for disordered materials, where diffraction only provides information on the average structure. In this project we will investigate new approaches to generating potential structural models for a range of disordered solids. Of particular interest will be the extension of the recent AIRSS (ab initio random structure searching) approach to materials with much larger numbers of atoms in the unit cell. This will be achieved by fixing the position of known structural features and groups, with other atoms randomly substituted, unlike most current work where all atomic positions are allowed to vary. Additional approaches will include the exploration of Monte Carlo methods (e.g., using GULP) and Molecular Dynamics to generate suitable model structures. Once candidate structures have been generated using this new suite of approaches, multinuclear NMR parameters can be calculated, using codes such as CASTEP, and compared to simple experimental spectra. The calculated parameters will then enable a range of new multinuclear multidimensional NMR experiments to be designed and optimized for specific systems of interest.

Areas of initial application include the hydration of high-pressure silicates, cation/anion disorder in wasteforms, and the disorder of guest molecules and charge-balancing anions in microporous catalysts.

The student would join an active research group (currently with 1 PDRA, 5 PhD students and 4 undergraduate project students), with strong collaborative links to computational and theory

groups. The student would also be a member of the St Andrews Centre for Magnetic Resonance (CMR), bringing together researchers in St Andrews and Dundee across Chemistry, Biology and Physics.

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The Centre for Doctoral Training in Integrated Magnetic Resonance is a collaboration between researchers at the Universities of Warwick, St Andrews, Dundee, Southampton, Aberdeen and Nottingham.