# APPENDIX

## Near-zero-field nuclear magnetic resonance

We investigate nuclear magnetic resonance (NMR) in near-zero-field, where the Zeeman interaction can be treated as a perturbation to the electron mediated scalar interaction ($J$-coupling). This is in stark contrast to the high field case, where heteronuclear $J$-couplings are normally treated as a small perturbation. We show that the presence of very small magnetic fields results in splitting of the zero-field NMR lines, imparting considerable additional information to the pure zero-field spectra. Experimental results are in good agreement with first-order perturbation theory and with full numerical simulation when perturbation theory breaks down. We present simple rules for understanding the splitting patterns in near-zero-field NMR, which can be applied to molecules with non-trivial spectra.

Nuclear magnetic resonance experiments are typically performed in high magnetic fields, on the order of 10 T in order to maximize chemical shifts and to achieve high nuclear spin polarization and efficient detection via inductive pickup. The advent of various pre- or hyperpolarization schemes, and alternative methods of detection based on superconducting quantum interference devices (SQUIDs) [1] or atomic [2, 3] magnetometers has enabled NMR experiments in very low (≈earth's field) and even zero magnetic field, generating significant experimental [4–16] and theoretical interest [12, 17, 18]. Low-field NMR carries the advantage of providing high absolute field homogeneity, yielding narrow resonance lines and accurate determination of coupling parameters [9, 14]. Further, elimination of cryogenically cooled superconducting magnets facilitates the development of portable devices for chemical analysis and imaging. In this regard, atomic magnetometers are an ideal tool because, in contrast to SQUIDs, they do not require cryogenic cooling. Recent work using atomic magnetometers to detect NMR was performed at zero field, in part, because of the need to match the resonance frequencies of the nuclear spins and the magnetometer's alkali spins, which have very different gyromagnetic ratios [14, 16]. It has been pointed out that zero-field NMR leaves some ambiguity in determination of chemical groups, and that this ambiguity can be removed by application of small magnetic fields [17].

Here, we examine, experimentally and theoretically, the effects of small magnetic fields in near-zero-field