

INTRODUCTION

Nuclear magnetic resonance (NMR) spectroscopy can provide detailed information about nuclei of almost any element. NMR allows one to determine the chemical environment and dynamics of molecules and ions that contain the observed nuclei. With modern NMR spectrometers, one can observe nuclei of several elements at once. Biological NMR, for example, often employs radio frequency pulses on ^1H , ^{13}C , and ^{15}N nuclei within a single experiment. Some of the most useful NMR experiments obtain information by using 20 or more radio frequency pulses applied to the different NMR nuclei at specific times. What makes these sophisticated experiments possible is the mathematical perfection of the quantum mechanics that underlies NMR.

Whether one looks at liquids, solids, or gases, the nuclei being observed are selected by their unique resonance (Larmor) frequencies in the radio frequency range of the electromagnetic spectrum. Choosing a nucleus for observation is analogous to choosing a radio station.

NMR requires a magnet, usually with a very homogeneous magnetic field except when pulsed magnetic field gradients are applied. The magnetic field splits the quantized nuclear spin angular momentum states, thereby allowing transitions between them that can be stimulated by radio frequency excitation. Only transitions between adjacent levels are allowed, and since the levels for a given nucleus are equally separated in energy, the transitions all occur at the same resonance (Larmor) frequency.¹ The resonance frequency of a given nucleus is proportional to the strength of the magnetic field and is generally in the radio frequency range of 10^6 to 10^9 sec^{-1} on superconducting magnets of 1–25 Tesla magnetic field strength. Several specific advantages of high magnetic fields are that they give stronger NMR signals, better resolution of chemical shifts, and better resolution for solid samples of odd-half-integer quadrupolar nuclei.

Magnetic resonance imaging is a special type of NMR that takes advantage of the linear relationship between the resonance frequency of a nucleus and the magnetic field. In the presence of a magnetic field gradient, the observed resonance frequency varies with position within the sample, allowing for direct correlation between frequency and position that can be used to create an image. Pulsed magnetic field gradients are also used to select desired NMR signals in nonimaging experiments.

¹But higher order transitions can be observed in some cases.

The quantum mechanics that is the basis of NMR spectroscopy has been covered beautifully in books by Abragam (1983), Spiess (1978), Mehring (1983), Ernst et al. (1987), Gerstein and Dybowski (1985), Levitt (2008), and Jacobsen (2007). In this book, the goal is to review the theoretical basis of NMR in a concise, cohesive manner and demonstrate the mathematics and physics *explicitly* with Mathematica notebooks. Readers are urged to go through all the Mathematica notebooks as they are presented and to use the notebooks as templates for homework problems and for real research problems. The notebooks are a “toolbox” for NMR calculations.

The primer is intended for graduate students and researchers who use NMR spectroscopy. The chapters are short but become longer and more involved as the primer progresses. The primer starts with chapters describing the NMR spectrometer and the NMR experiment and proceeds with the classical view of magnetism, the Bloch equation, and the vector model of NMR. Then it goes directly to quantum mechanics by introducing the density operator, whose evolution can be predicted by using either matrix representation of the spin angular momentum operators or commutation relations between them (product operator theory). It then transitions to coherence order pathways, phase cycles, pulsed magnetic field gradients, and the *design* of NMR pulse sequences. With the help of Mathematica notebooks, it presents the elegant mathematics of solid state NMR, including spherical tensors and Wigner rotations. Then the focus changes to the effects of atomic and molecular motions in solids and liquids on NMR spectra, including mathematical methods needed to understand slow, intermediate, and fast exchange. Finally, it finishes with the amazing and perfect connection between molecular-level reorientational dynamics and NMR relaxation.