Problems in MR that Need Quantum Mechanics: The Density Matrix Approach

Robert V. Mulkern, Jr, PhD

Departments of Radiology

Children's Hospital

Brigham and Women's Hospital

Harvard Medical School

Boston, MA

The nuclear magnetic moment or "spin" of the proton and some other nuclei upon whom we rely so heavily for our livelihoods is an inherently "quantum mechanical" concept (1,2). It has no real, or perhaps better stated, "classical" analogue despite the picture we so often see and use of a spinning sphere with an arrow through it. The nuclear spin was introduced within the nascent framework of quantum mechanics (QM) in order to explain experimentally observed phenomena such as the splitting of atomic, optical spectral lines (1). Later, of course, the concept was incorporated into our fundamental understanding of nuclear magnetic resonance (NMR) (2,3) and its younger sibling magnetic resonance imaging (MRI) (4). Since spin is a concept so inherently "quantum mechanical" one is left pondering why most of the physics in our Society's journals so rarely rely on QM to approach and/or solve problems that we may encounter in our field. The Bloch equations, which we do use so often, may be derived from the QM commutation relations of momentum and spatial coordinates (operators), though classical derivations are also available by considering loops of current and their magnetic moments within a larger magnetic field (5). First principle derivations using QM to describe T1 and T2 relaxation phenomena within few spin systems in terms of mutual, microscopic fluctuating magnetic fields, embodied within the so-called Bloembergen, Pound, Purcell (BPP) theory, were forwarded as early as 1948 (6) and offered insights into the field dependence of relaxation times as well as their dependence on translational and rotational molecular motions. In reality, however, we rarely use BPP theory and often forget, or fail to appreciate, that it too is based on several approximations and is strictly derivable for only small spin systems. Instead, within the context of tissue water, undeniably the bread and butter of our trade, we tend to simply add relaxation terms empirically to the Bloch equations and arrive at exponential type decays/recoveries, or in the case of multiple water compartments in slow to intermediate exchange, multi-exponential decays/recoveries to equilibrium for the transverse and longitudinal magnetizations, respectively. This classical approach is enormously useful in modeling complex biological tissue and offers reasonable descriptions of tissue contrast but, one is left wondering, where did all the QM go and also where, if ever, is it still needed? A complete QM description of all the interactions among the large number of water proton "spins" via their mutual, through-space dipolar interactions (inter- as well as intra-molecular interactions) within even the tiniest MRI voxel would be hopeless. This is why for the most part QM is not applied to such systems and macroscopic classical equations must suffice. In several instances, however, we are acquiring signals from molecules other than water, in which, unlike water, the neighboring protons are not in chemically

equivalent positions within the molecule. This gives rise to both a "chemical shift" effect due to fields generated by intra-molecular electronic currents, and a more indirect "J-coupling" interaction between neighboring spins as mediated through the bonding electron spin components (2,3). The "spin topology" comes into play in the final determination of the actual Hamiltonian of these small coupled spin systems and QM can then, in all its glory, be applied to calculate the spectral response of any sequences, e.g. PRESS, STEAM, LASER, etc, that we may apply to localize and measure these "metabolite" signals. The fundamental QM tool I use to perform such calculations is the so-called "Density Matrix" and, though generally not favored by chemists and others seeking quick but incomplete insights, it is by far the most comprehensive tool. Furthermore, its use really leaves very little to the imagination once applied in the "Shut Up and Calculate" manner ostensibly espoused by Richard Feynman in response to the many individuals overly concerned with the philosophical "meaning" of Quantum Mechanics. So…let's shut up and calculate!

1) Some Key Problems in Calculating Spectral Responses of Coupled Spin Systems to Localizing Pulse Sequences
   a) Weakly Coupled Systems (Lactate, ATP)
   b) Strongly Coupled Systems (Citrate, glutamate)
   c) Pulse-acquire, PRESS and STEAM
   d) RARE Imaging Acquisitions of 31P ATP
   e) High Field Voxel Subdivisions from Selective Pulses
   f) The Dipolar Hamiltonian (Water, magic angle effect)

2) How Key Problems are Solved: The Density Matrix Approach
   a) Rules of the Road for Angular Momentum Operators and Spin Topology
   b) Identifying the Hamiltonian
   c) Calculating the Eigenvalues and Eigenstates of the Hamiltonian
   d) Identifying the Density Matrix Operator for each Pulse Sequence
   e) QM Representations of RF Pulses
   f) Calculating the Trace of the Density Matrix for the Transverse Magnetization Operator (the "signal")
   g) Fourier Transform step for Spectrum

References:

1) Merzbacher E. "Quantum Mechanics", 3 rd Ed. 1998, John Wiley & Sons, Inc, NY, NY.
2) Abragam A. "The Principles of Nuclear Magnetism", 1961, Oxford University Press, London, UK.
3) Hennel JW, Klinowski J. "Fundamentals of Magnetic Resonance", 1993, Longman Group UK Limited.
4) Hashemi RH, Bradley WG, Lisanti CJ. "MRI: The Basics", 3 rd, Ed. 2010, Lippincott Williams & Wilkins, Philadelphia, PA.

5) Griffith DJ. "Introduction to Electrodynamics", 3 rd Ed. 1999, Prentice Hall, Upper Saddle River, NJ.
6) Bloembergen N, Purcell EM, Pound RV. Relaxation effects in nuclear magnetic resonance absorption. Phys Rev 1948;73:679-712.