Appendix A: Connections to Other Mechanical Detection Methods

The "ideal detection sphere" arguments leading up to the BOOMERANG detector of Figure 1.3 represent a significant break from the conceptual development of the several other force-detected magnetic resonance methods shown, with BOOMERANG, in Figure A.1. The more traditional line of thinking has

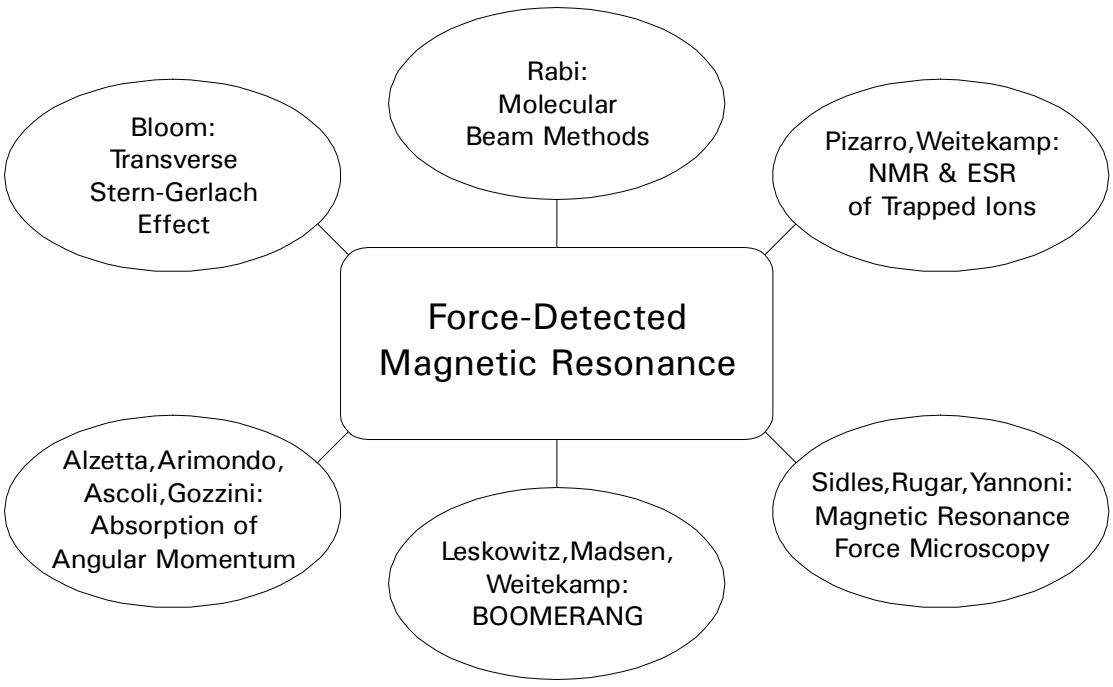

Figure A.1. Force-detected magnetic resonance methods.

been characterized by a "Stern-Gerlach" view, which has pervaded the field since the very first method of magnetic resonance, the Rabi molecular beam method[1] (which preceded by 8 years the observation of magnetic resonance in condensed phases using magnetic induction by Purcell[2] and Bloch[3]).

Rabi's method makes use of the Stern-Gerlach effect, the state-dependent force **F** on a spin-magnetic dipole $\boldsymbol{\mu}$ in an inhomogeneous static field:

$$\mathbf{F} = \boldsymbol{\mu} \cdot \mathbf{G} . \qquad (A.1)$$

Here, $\mathbf{G} = \partial \mathbf{B} / \partial \mathbf{r}$ is the gradient tensor of the static field **B** with respect to the spatial coordinates **r**. This force spatially separates populations of molecules in a beam by the eigenvalue of the projection of their spin angular momentum onto the static field direction. An applied rf field induces spin flips that reverse the initial deflections of the separate populations, modulating the intensity of the molecular beam at a detector in accordance with the spin-resonance condition. A Stern-Gerlach separation of eigenstates of precessing *transverse* angular momentum for magnetic resonance of molecular beams was later proposed[4] and demonstrated[5] by Bloom and coworkers.

Both the spectroscopic resolution and sensitivity of these methods is limited by the residence time of the spins in the field. A key improvement in force-detected magnetic resonance is to keep the spins in the field for a longer time by confining them to a harmonic motion, applying the forcing fields at the mechanical resonance frequency of that motion. This is a feature of proposals by Pizarro and Weitekamp to detect electron spin resonance (ESR) and NMR of electromagnetically trapped

ions by way of a resonance-induced change in the amplitude of their orbits using switched field gradients[6-8].

Spin-dependent mechanical resonance is also a feature of a torque-detection method for magnetic resonance of condensed phases in homogeneous fields, which was introduced in the 1960's by Gozzini and coworkers[9-14]. In those experiments, a spin-bearing solid sample (the solid free-radical diphenylpicrylhydrazyl, DPPH) suspended in a homogeneous magnetic field is made to absorb angular momentum from an rf field applied at the frequency of spin precession. The sample spins, which are bound to a torsional oscillator, transmit their acquired angular momentum via rapid thermalization with the lattice to the oscillator, which therefore experiences a torque. This absorption of angular momentum from the applied field is analogous to the absorption of power from the field attempted long ago by Gorter[15] and finally observed as a rise in temperature of the sample by Schmidt and Solomon[16]. While these methods may be used in a homogeneous field, the thermalization of angular momentum or of energy with the lattice, a necessary component of the methods, limits their use in the great majority of modern NMR pulse sequences, which rely on persistence of spin coherence through numerous rf pulses.

Mechanical detection was revived in the context of condensed phases by Sidles, who proposed a "folded Stern-Gerlach effect"[17] — the resonant driving of small oscillators, such as force-microscope cantilevers, with spin-dependent forces in accordance with Equation (A.1). The version of this proposal that has been implemented uses cyclic adiabatic rapid passage (ARP) or cyclic saturation to

modulate longitudinal magnetization at an audio frequency in the presence of a field gradient, driving the oscillator to which either the sample[18,19] or a small ferromagnetic particle[20], which provides the gradient, is attached. The ferromagnetic particle serves the dual purpose of providing a coupling force and varying the spin-resonance condition across the sample volume, which provides an imaging capability. The first experimental demonstration of this approach, which is now called magnetic resonance force microscopy (MRFM), was performed in Daniel Rugar's laboratory at IBM Almaden[18]. This first demonstration was an ESR experiment with solid DPPH bound to the cantilever. Subsequently, MRFM as been extended to proton[19], and fluorine[21] NMR and to ferromagnetic resonance in cobalt thin films[22].

The sensitive-slice imaging capability of MRFM bears resemblance to Damadian's magnetic resonance imaging method[23,24]. MRFM was also originally motivated by biological imaging — although at a dramatically reduced size scale. Rugar and Sidles have attempted to set the groundwork for a means of imaging biomolecules magnetically, angstrom-thick slice by angstrom-thick slice. A very challenging intermediate goal is detection of magnetic resonance from single electrons using MRFM, and to this end great strides have been made, particularly in Rugar's laboratory, such that as of this writing it is now possible to observe magnetic forces with sub-attonewton per root hertz sensitivity at cryogenic temperatures[25]. This is in principle sufficient to observe resonance from single electrons, but so far efforts have been unsuccessful[26].

In light of the history behind Equation (A.1), it is not surprising that authors describing molecular beam and MRFM-type force detection propose use of the highest gradients possible. The experimental trend in MRFM has been toward ever-increasing gradients, and as of this writing MRFM has been performed with gradients as large as 250 kT/m[27]. But, as we have seen in Chapter 1, no gradients are in fact needed to observe magnetic resonance with force detection, and there are very good reasons for avoiding their use. What is going on here?

The answer lies in the choice of a mathematical model for the sample. In Equation (A.1), the "sample" is a point dipole.

The geometric optimization described in Chapter 2 takes into account the shape and size of a *whole* sample and asks the question of what detector provides optimal signal-to-noise *for that sample*.[†] Our choice of a sphere with a specified R_{max} is based on computational simplicity and also on the fact that for powdered samples and fluids, one can arrange to pack the sample into a sphere. Often in solid-state magnetic resonance, even single crystals are shaped into spheres to mitigate susceptibility effects. In commercial (inductive) instruments for both solids and liquids, the effective sample volume is most often a cylinder with near-unit aspect

[†] Specifically, the uncertainty in the measurement of the *average* magnetization of the sample is the observable that is optimized. This is not the only one that might be considered. For example, the "local sensitivity" alluded to in Chapter 3 varies over the sample volume by more than an order of magnitude. It might be of interest to optimally assess anisotropies in some heterogeneous sample. The information-theoretic question of how best to generalize the optimization given arbitrary constraints is well worth serious consideration.

ratio, a close match to a sphere mathematically. A sphere is in any case a first approximation to *any* 3-D sample.

Which brings us back to the point dipole. This sample can be viewed as a sphere with vanishing R_{max}. The theory of Chapter 2 is applicable, and in this special case, a moving sensor magnet designed for optimal detection is as small as possible and as close as possible to the sample dipole. *In the absence of any compensation magnets* this leads to the conclusion that higher gradients mean better sensitivity, as the detector would impose the largest possible gradient at the position of the sample dipole[28].

The difficulty of constructing nanoscopic BOOMERANG magnet assemblies with narrow gap spacings, relative to single magnet particles on cantilevers, is apparent. If the goal is to observe magnetic resonance from a single, isolated, fixed spin (nuclear or electronic), then the BOOMERANG concept is probably more trouble than it is worth. If the (single) spin is not in a fixed location, but instead is diffusing in a target volume or on a surface, then the elimination of field gradients is again relevant. It is almost always the case that the real information sought from an experiment is hidden in a volume that is at least as large as a molecule. Even imperfect composite magnet assemblies that allow a larger sample region with many spins during detection can extract *information* at a greater rate than can be had one spin at a time.

Single-electron-spin sensitivity in MRFM may well be achieved in the very near future, and the very much more challenging observation of magnetic resonance from single nuclear spins may also be possible in theory. But the probable range of

superiority of force-detection over inductive detection (as regards sensitivity) is between 10^0 and 10^{12} or so spins in volumes of up to approximately 0.1 mm^3. Such samples possess enormous information content that may best be extracted by whole-sample BOOMERANG methods, and we have proceeded accordingly in our efforts.

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