What's missing from the traditional explanation of NMR experiments?

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The basic quantum mechanics of NMR

We consider a nucleus that possesses a magnetic moment $\boldsymbol{\mu}$ and an angular momentum $\hbar\,\boldsymbol{I}$. The two quantities are parallel, and we may write[1]

$$\boldsymbol{\mu} = \gamma\hbar\boldsymbol{I}; \tag{1}$$

where the gyromagnetic ratio γ is constant. By convention, $\mathbf{I}$ denotes the nuclear angular momentum in units of $\hbar$. The energy of interaction with the applied magnetic field is

$$U = -\boldsymbol{\mu}\cdot\mathrm{B}_a, \tag{2}$$

where $\mathbf{B}_a$ is the applied,external field. If $\mathbf{B}_a = B_o\hat{\mathbf{z}}$, then

$$U = -\mu B_o = -\gamma\hbar B_o I_z. \tag{3}$$

The allowed values of I_z are $m_I = I,\ I-1, ..., -I,$ and $U = -m_I\gamma\hbar B_o$. Thus, for the case in which $I = 1/2$, in an external magnetic field of B_o, **such a nucleus has two energy levels** corresponding to $m_I = \pm 1/2$, as in the figure below. If $\hbar\omega_o$ denotes the energy difference between the two levels, then $\hbar\omega_o = \gamma\hbar B_o$ or

$$\omega_o = \gamma B_o. \tag{4}$$

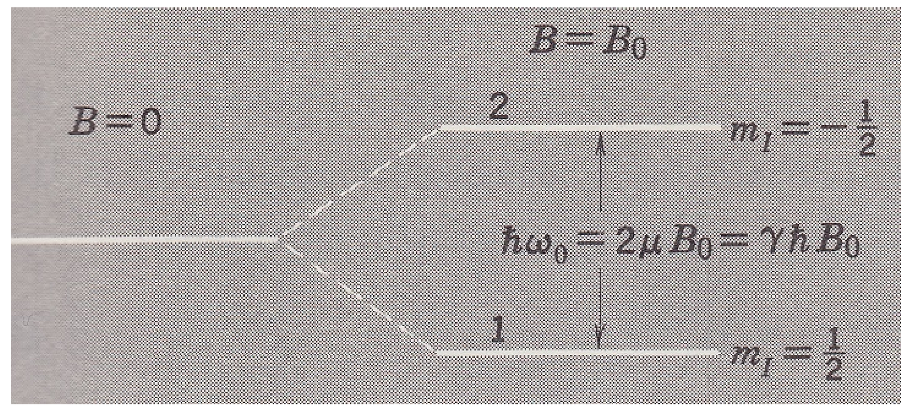

FIGURE 1: The usual two-level system considered for Hydrogen NMR

B_o can be scanned, resonance found, I or μ too, and so forth

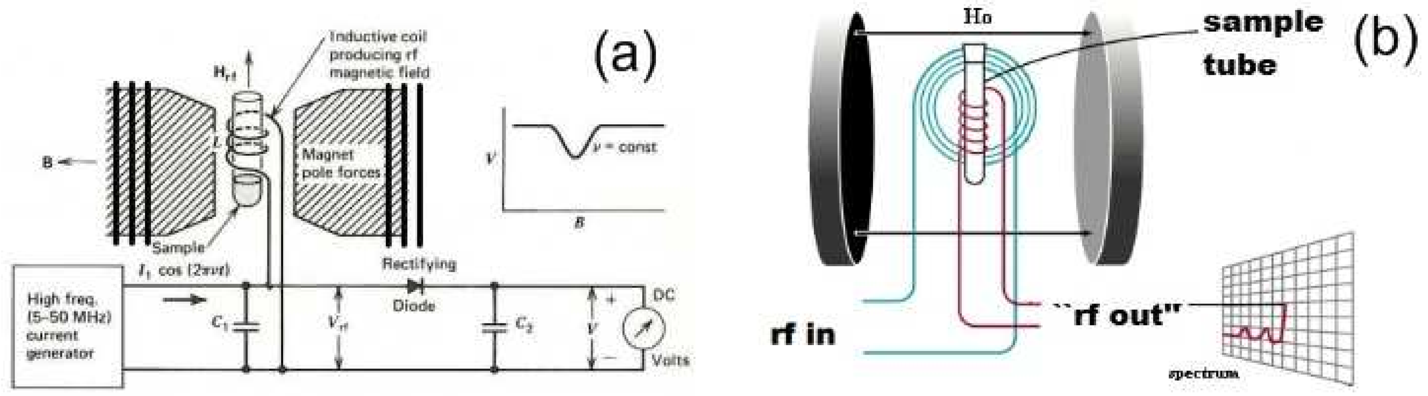

FIGURE 2: Typical NMR installations. The main variant to these are experiments in which the B-field is fixed and the rf spectrum is scanned. In either case, the resonance frequency can be found with good precision.

Where is the problem here?

Well, it's subtle. In most descriptions[2, 3], it is taken for granted that Hydrogen NMR is proton NMR, without discussion of why this is the case, or its implications. No mention is made of the magnetic moments of the two electrons that make up the covalent bond connecting the Hydrogen atom to the (most often) carbon backbone of the molecule in solution, or why or how they cancel their magnetic fields at the location of the Hydrogen nucleus. Fundamental notions in quantum mechanics could be brought in, but are left out...

Students ask, 'where does the Hyperfine structure of Hydrogen go, where does it come from in the first place, and how are the energy level gaps related?'

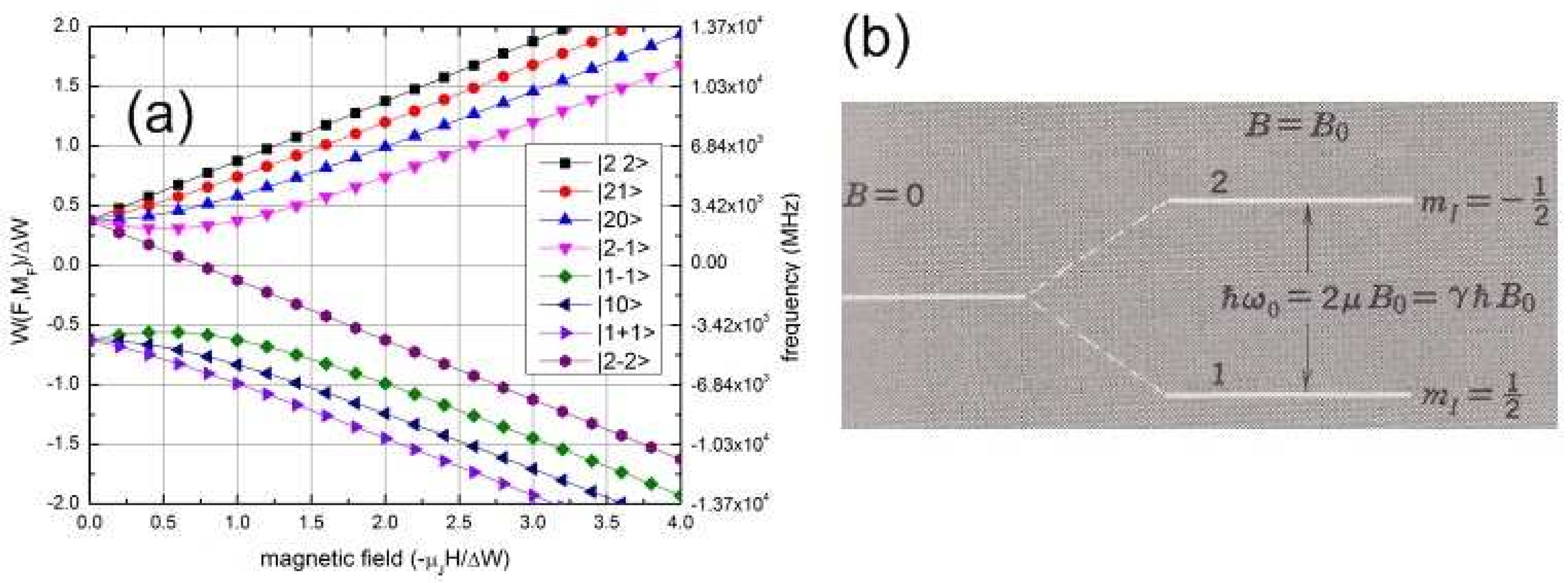

FIGURE 3: On the left (a), one has a Breit-Rabi diagram, such as can be acquired through optical pumping experiments, which shows the Energy level diagram demonstrating the Hyperfine Structure associated with the ground state of Rb, or H. On the right (b), one has the Energy level diagram assumed in NMR experiments for H. Of course they are radically different. In our advanced lab course, PHYS 480W[4], groups of students do these experiments in different orders. Students wonder if any of the gaps in (a) correspond to the one gap in (b), and where on abscissa in diagram (a) we'd be given the permanent magnet used in the NMR experiment, and so forth.

Implications for Advanced Lab goals

In our advanced lab course, we make opportunities for students to become proficient with modern experimental equipment and techniques, to interface equipment with computers using LabVIEW, and to prepare professional papers, and so forth. Beyond this, something of note is going on here,

- when two experiments attempt measurements with overlapping or similar objectives, students can study experimental design in more productive ways (how design serves desired outcomes, experimental 'logic', what is assumed and what is 'left out, because everyone knows that....', and so forth).
- look for opportunities to make explicit the connection between experimental and theoretical physics (e.g. this apparatus implements the following theoretical question....),
- look for connections between the substance of a given experiment and other experiments of current interest or which are at the head of current developments in physics, e.g. entanglement, in this case.....(this will require some explanation, but, Einstein's first concern with hidden variables and incompleteness has to do with single particle wavefunctions, which comes into this discussion).

Summary and Conclusions

We think a brief discussion of the implications of the Pauli Exclusion Principle in connection with the physics of covalent bonds would clarify the context in which NMR experiments with the hydrogens can be simply understood, especially with regard to the necessary disappearance of the hyperfine splitting of the ground state of Hydrogen.

Figure 5: Thanks to DOE (DE-FG02-97ER54437) and NSF (CBET-0903832 and CBET-0903783) for help with this work!

References

[1] This discussion is adapted from Kittel, "Solid State Physics", (Wiley, New York, 7th. Ed. 2005), Chap. 13

[2] A.C. Melissinos and J. Napolitano, "Experiments in Modern Physics", (Academic Press, San Diego, 2nd. Ed. 2003), Chap.7

[3] D.A. McQuarrie and J.D. Simon, "Physical Chemistry: A Molecular Approach", (University Science Books, Sausilito, CA, 1997) Chap.14. These are excellent texts which we use in our courses. We allege no errors in them about NMR experiments!

[4] See http://www.sandiego.edu/~severn/p480w, for class details