



# DYNAMIC NUCLEAR POLARIZATION [D.N.P.]: ELEMENTARY EXPOSURE TO THE PHENOMENON OF DNP

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**Abstract:** Within a single experimental specimen there could be several spin species ensembles present. In a strong externally (external to the specimen) applied magnetic field, every one of the spin ensemble would be in equilibrium with the lattice (non-spin quantized levels of various degrees of freedom) and attain thermal equilibrium populations governed by the Boltzmann distribution for the corresponding quantization of energy level differences. In a Nuclear Magnetic Resonance, of the several nuclear species, one of the species is selected to apply the RF radiation at frequency corresponding to energy level difference of one of the species namely electron, proton, carbon, nitrogen, phosphorus etc. As a variation, it is possible to saturate the levels of one spin species. That is, by a high power RF radiation the RF induced transition rates can be increased so that the populations almost equalize. This would be a non-thermal population difference. Since this is part of the lattice of some other spin species, its population distribution can be affected. Presence of such a non thermal population difference can cause non-thermal equilibrium in another spin ensemble in the specimen. When such non-thermal equilibria attain a steady state, then what is called Dynamic Spin Population exists. In general when it pertains to nuclear ensembles it is referred to as Dynamic Nuclear Polarization. The description of such Dynamic Nuclear Polarization, and the enumeration of a variety of experiments involving Dynamically Polarized nuclear states are the subject matter to be included in this contribution.

**Keywords:** multiple resonances; spectroscopy; dynamic population distribution; dynamic nuclear polarization; magnetic resonance; Overhauser effect; ENDOR

## 1. Introduction:

In an earlier article in this journal [1] the main purpose was to make available an elementary introduction to the Instrumentation aspects for detecting magnetic resonance of nuclei. Such of those nuclei that possess non-zero spin quantum numbers, are the species on which nuclear magnetic resonance experiments can be possible. Enough literature references were provided to acquaint with the Magnetic Resonance phenomenon, in particular the Nuclear Magnetic Resonance [N.M.R]. It was also mentioned therein that the advances in technology enables new features in instrumentation, so that in quick succession new experiments become possible. This unravels the fact that magnetic resonance is a versatile phenomenon, in particular, the NMR. The purpose of that article [1] required a historical perspective of the developments in NMR instrumentation, so that the advanced instrumental features are grasped and appreciated by beginners. This interest generated among many, in turn, can make possible the use of the full potential of the NMR experiments and devising various NMR applications. With this background provision, the present contribution intends to highlight the escalated potential of NMR experiments. From the domain of NMR of a nuclear species with a single RF frequency radiation (in a given external magnetic field) to the much advanced domain of Multiple Resonances, in which radiations at more than one RF frequency are applied at a given strength of external magnetic field.

The main consideration in this multiple resonance experiments is how the polarization gets established for each of the spin ensembles involved, which are to be irradiated and detected. In a resonance (single radiation) experiment the spin distribution is allowed to be established in a steady, homogenous external magnetic field. This is accomplished by allowing equilibrium between spin degrees of freedom and, almost infinitude of, non-spin degrees of freedom (the lattice). And the equilibrium population distributions are governed by the Boltzmann distribution function at the specified ambient (laboratory) temperature, which is the lattice temperature of the specimen under study. This is referred to as the Thermal Equilibrium Population.

In the context of multiple resonances, beginning is made with the thermal equilibrium of each of the spin species

independently obeying the Boltzmann distribution criterion. Then, a situation is experimentally created (by appropriate resonance frequency radiation) in the spin systems that any one of the spin system may be in a **non-thermal equilibrium** population. The remaining spin species then would equilibrate in presence of such a non-thermal population of one of the spin species. The result is a dynamic process among the spin species and lattice. Eventually a *steady-state population distributions* of spin species levels is attained. This steady-state with dynamic processes between the spin species is characterized by non-thermal equilibrium polarization of *spin species ensembles*. Finally such spin populations are attributed to have been caused by coupled relaxation mechanisms. A steady state (time independent distribution) is referred to as the dynamic nuclear polarization (**D.N.P** or **DNP**) as referred to in title of this contributory article. The instrumental requirements obviously would require more than one spectrometer to monitor experiments with a single specimen, but containing several spin species. An enumeration of experiments with established dynamic nuclear polarization among several spin species ensembles would be the content of this article.

To consider the coupled relaxation mechanisms for a better perspective, let us suppose there are two different spin species in a specimen (by the word specimen, we should mean an experimental sample). Each one of the spin systems would have distinctly different Zeeman splitting. However, when the Zeeman splitting are comparable, the exchange of energy between these two spin systems would be significant. When the two Zeeman splitting are far different then mutually coupled relaxations can be less significant. But there can be efficient lattice couplings that can render the later processes also much significant. For a familiarity of terms related to coupled spin transitions the illustration in Figure-1 would be helpful. After this much of introduction to the principles governing the DNP experiments, a beginning can be made with consolidating the relaxation aspects with a two level spin system. SCHEME-1 below summarizes the necessary relaxation process. A few schemes for illustrating the technique and a description for observing such double resonance phenomenon (consequent upon the established DNP under the specified experimental conditions) are given in the following pages. Under SCHEME-2 the situation for two different spin ensembles (spin system 1 and spin system 2) under a steady intense external magnetic field is depicted. This could also be simultaneous existence of electron-spin Zeeman splitting and Proton-spin Zeeman splitting SCHEME-3.

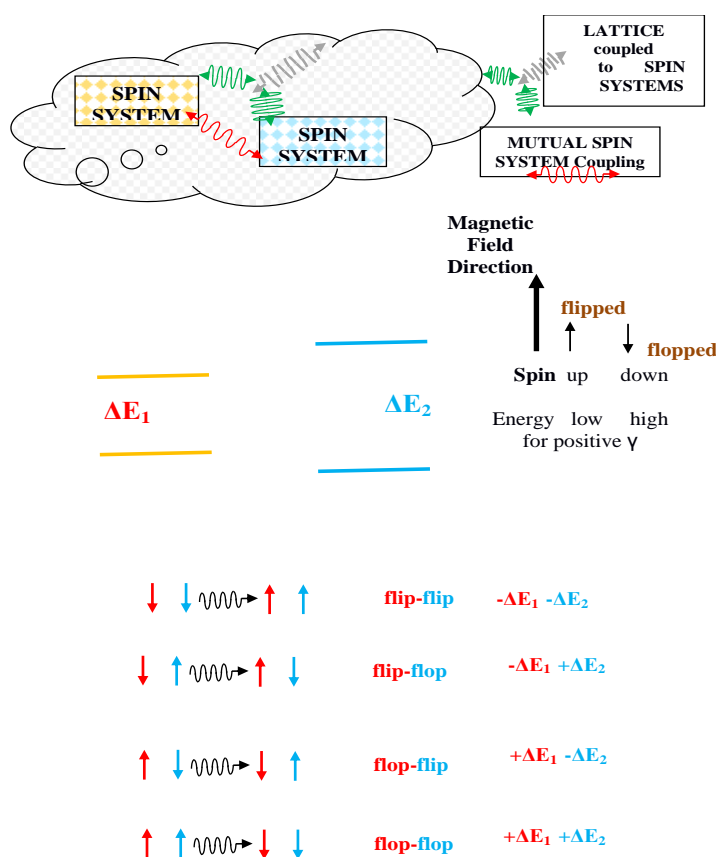
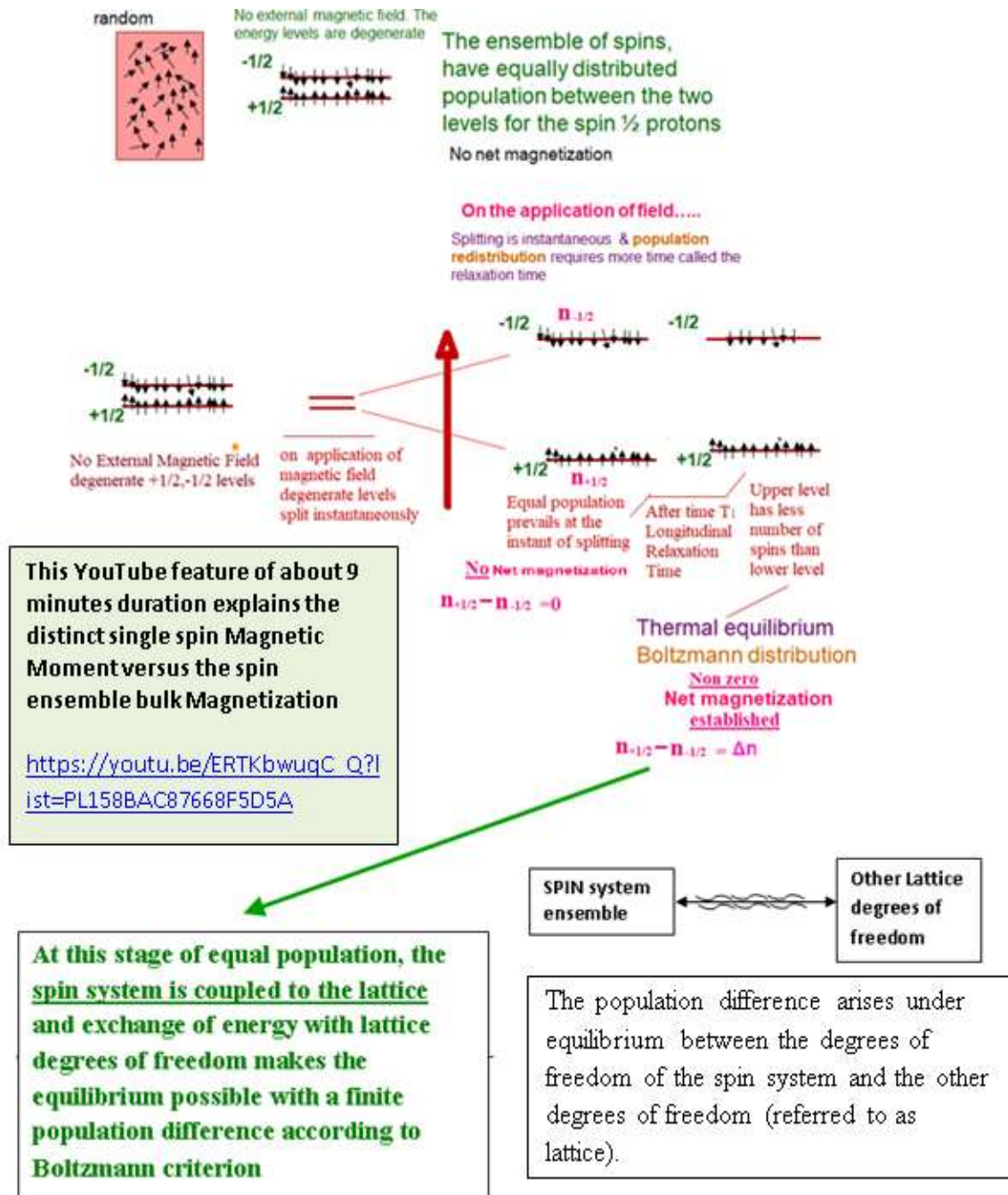
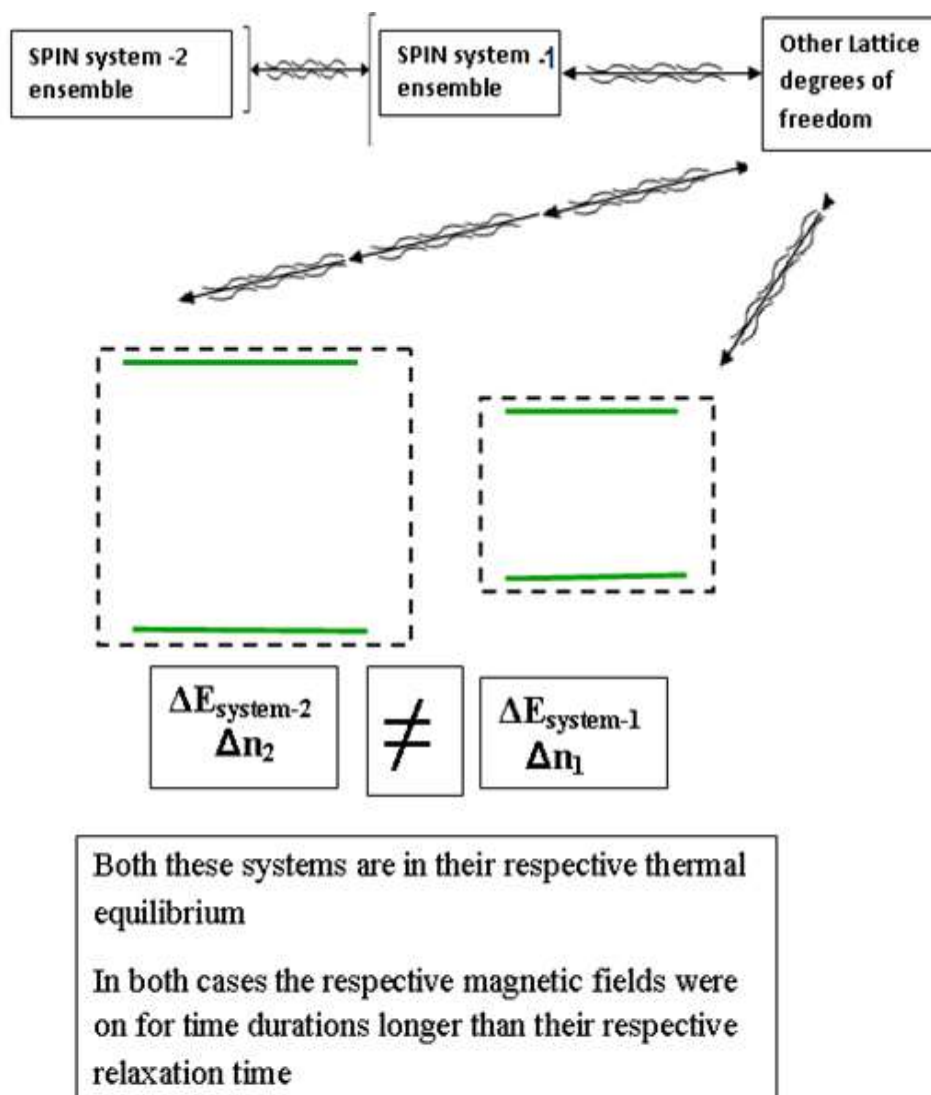


Figure 1: Simultaneous two spin orientations change coupled spin transition caused by coupled relaxation mechanism.

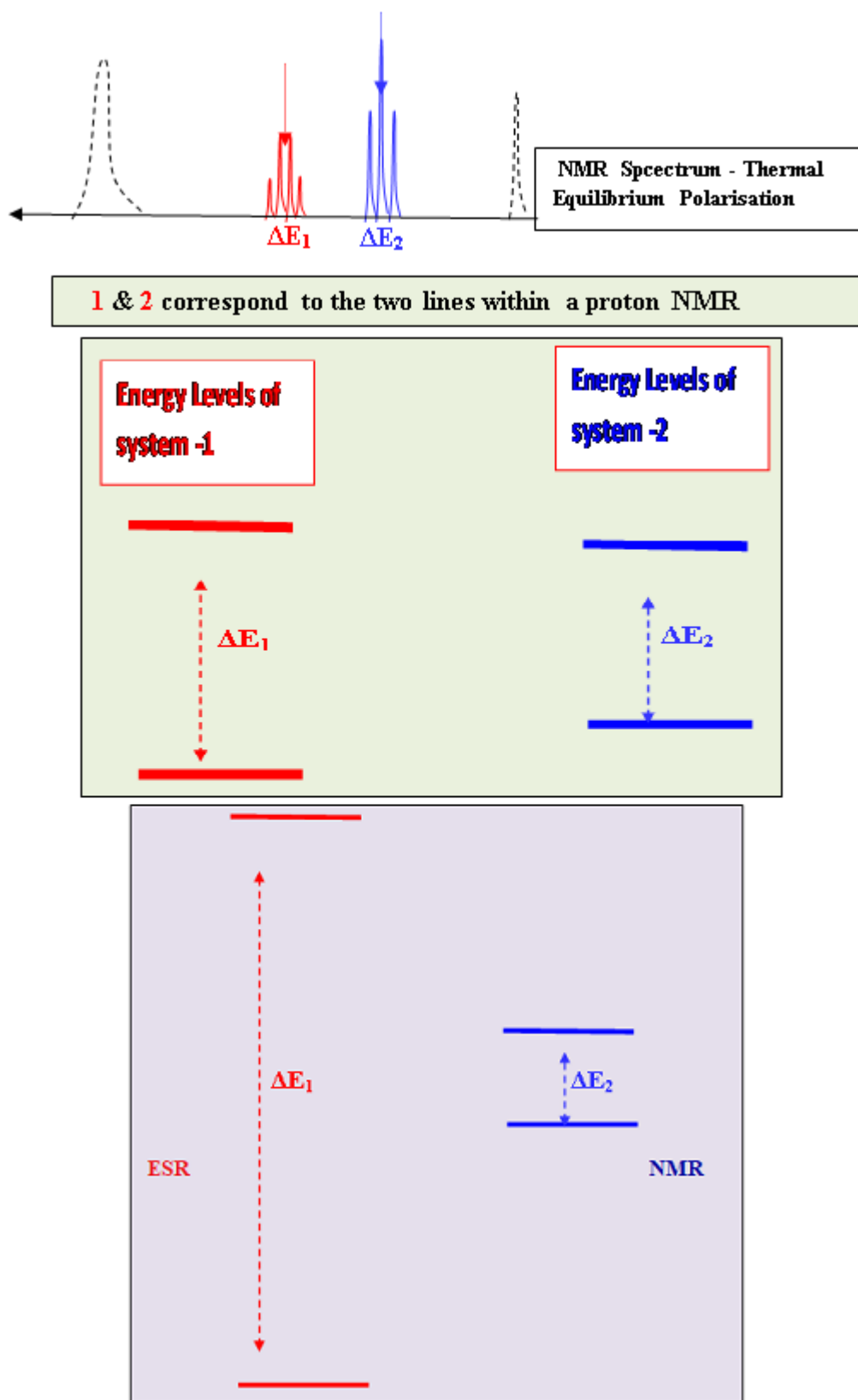


Scheme 1: Spin system thermal equilibrium explained: Steady temperature under thermal equilibrium (spin system and lattice); time independent population difference.

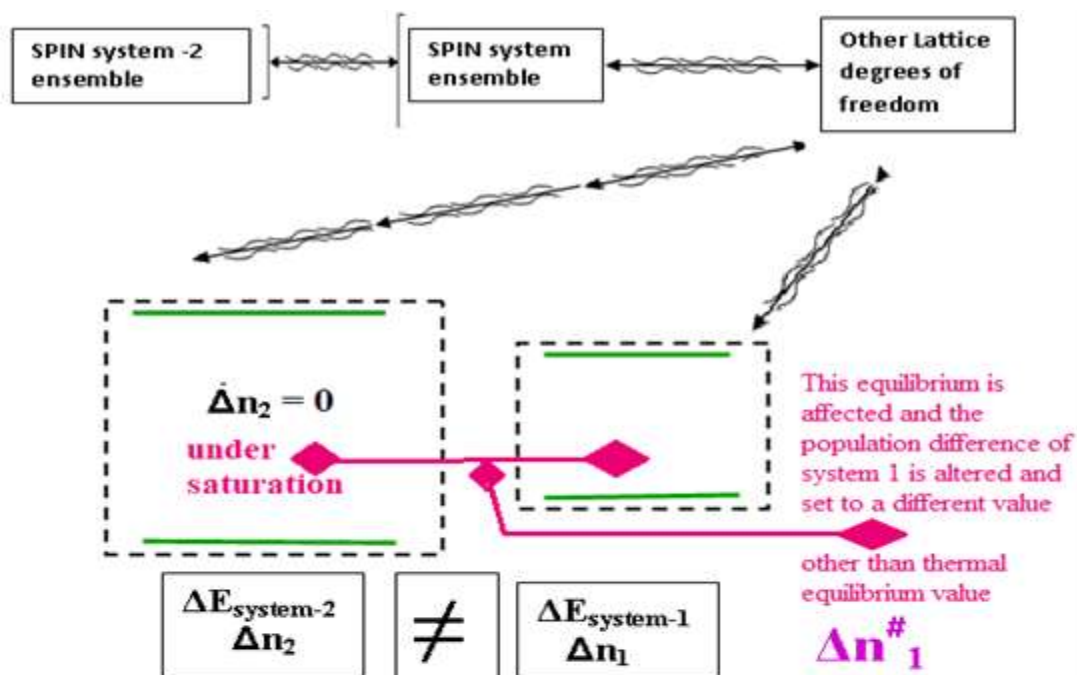


The two spin systems interacting as above could be such that both the system belong to same resonating nuclear species in a single spectrum: for example in a proton NMR spectrum of a molecule, two lines in the spectrum would have different chemical shifts; the two lines are corresponding to two different resonance frequencies; each resonance corresponds to a pair of energy levels of distinctly different energy level separations. **Since both lines are from within a single spectrum, the difference of transition energies would not be widely different as represented in the top two levels of SCHEME-3**

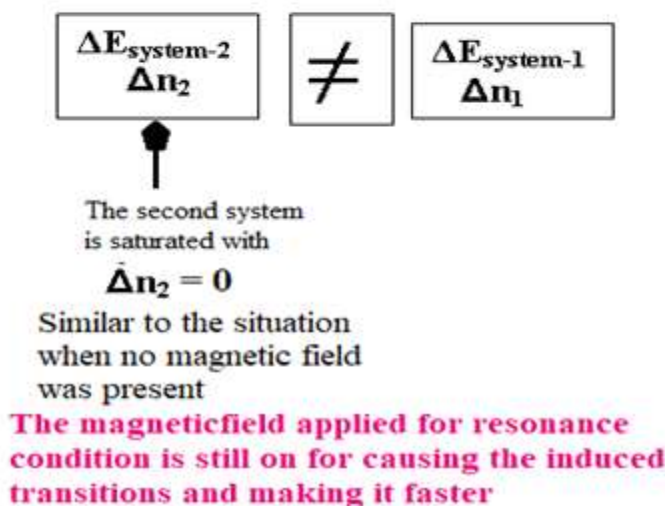
Scheme 2: TWO DISTINCT SPIN SYSTEMS: - Mutual equilibrium; both in equilibrium with lattice. Both the spin systems are under thermal equilibrium at the lattice temperature (a “stable” thermal equilibrium).



Scheme 3: NMR spectrum.



If in the second system a high power electromagnetic radiation causes much faster induced transitions, then the induced transition rates will increase the number upward transitions. EM induced transitions are of equal rates upward and downward, and by thermal equilibrium the population of lower level was larger, hence number of upward transitions is increased with increase in the rate of transition rates. The downward transitions will be less. This tends to increase the upper level population and decrease the lower level population. Eventually a saturation results where the two populations are equal and remain in an equilibrium in presence of high power radiation at the same high level.



Scheme 4: D.N.P.

The gyro magnetic ratio of electron spin is about 660 times larger than the proton spins. Hence in principle the energy level splitting for (1/2 and -1/2) electron spins would be 660 times larger than that for the proton spin energy levels. At a value of of 3.3 Kilo Gauss external magnetic field strength, the electron spin splitting would be nearly 9.5 GHz ( $9.5 \times 10^9$  Hz) while that of protons would be around 14.5 MHz ( $14.5 \times 10^6$  Hz). And, to be capable of doing a double resonance experiment with electron spins and nuclear spins, the sample containing these two spin systems must be kept inside the same magnet. The two spin systems must be experiencing the

same magnetic field strength. 3.3 Kilo Gauss is a typical magnetic field provided in a commercial EPR spectrometer, and the 9.5 GHz frequency is in the microwave range of the electromagnetic radiation spectrum, while the 14.5 MHz is in the radio frequency (RF) range.

It must be remarked at this stage that since the two frequencies fall in such distinctly different frequency ranges, the EPR detection technique and the PMR detection technique can be much different. On the other hand, for a double resonance experiment the sample containing Electron spins and the Proton spins must be the same and the double resonance has to be on this one and the same sample kept within the same magnet. Thus around a magnet capable of providing homogeneous stable magnetic field of 3.3 Kilo Gauss, an EPR spectrometer part and the PMR spectrometer part have to be built and available for simultaneous observation of EPR and NMR of the sample.

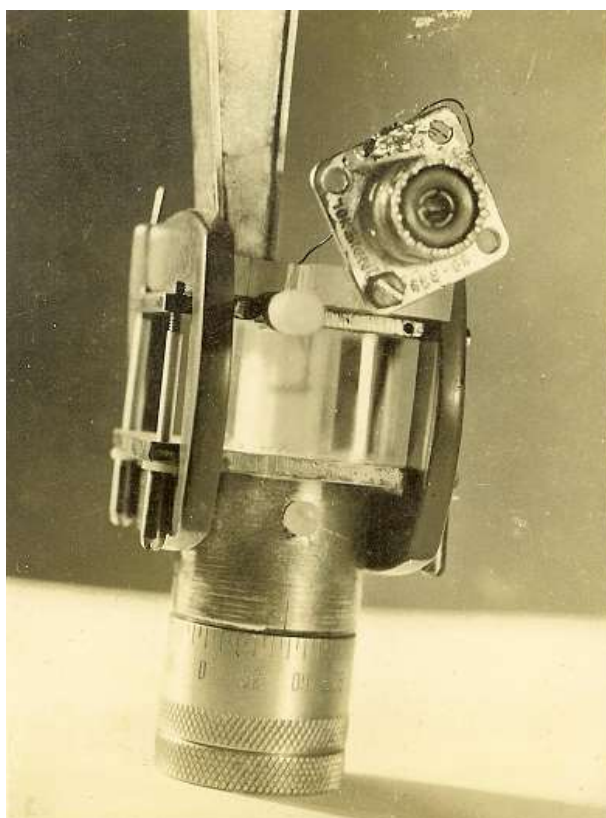


Figure 2: Coil in the cavity.

The 9.5 GHz frequency EPR part requires a **microwave cavity based** probe to hold the sample and the PMR part at 14.5 MHz requires **a RF Coil based** resonance [1] circuit. Thus for this magnetic field a **Coil-in-the-Cavity** [3] arrangement is used for the double resonance probe construction. Such an arrangement is displayed in Figure-2 below: The microwave cavity is a quartz cavity and hence the cavity is partly transparent within which it is possible to see a four turn thin wire coil (enameled wire) and its two ends are connected to the UHF connector mounted on top of the cavity and this female connector is for the corresponding connector from NMR transmitter detector circuit. The tapering metallic rectangular part is part of the X-band microwave travelling wave guide which is the usual microwave analogue of the RF cable. This assembly of coil in the cavity constitutes the probe part of the electron-nuclear double resonance spectrometer. The wave guide part would be connected to an X-band EPR spectrometer, and the Coil part would be connected to the RF transmitter-detector unit corresponding to the NMR resonance frequency. To be specific a solution of a stable free radical in a Proton can be the sample on which a double resonance can be observed.

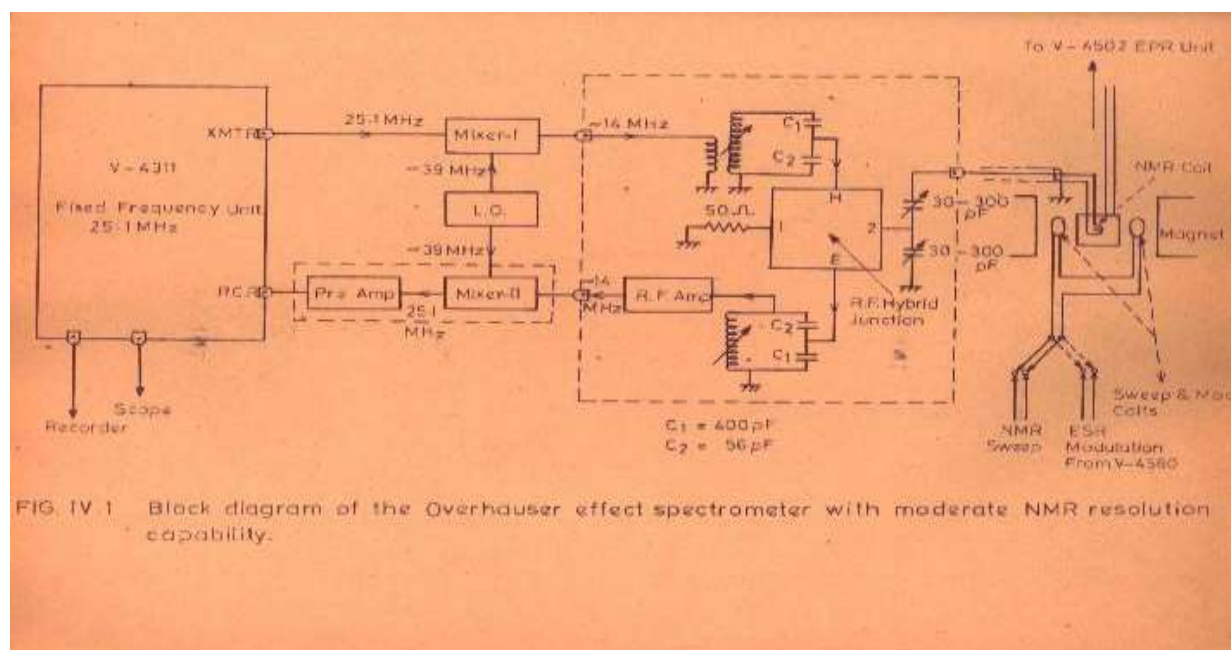


Figure-3: Block diagram of a typical home-built (assembled) overhauser effect spectrometer.

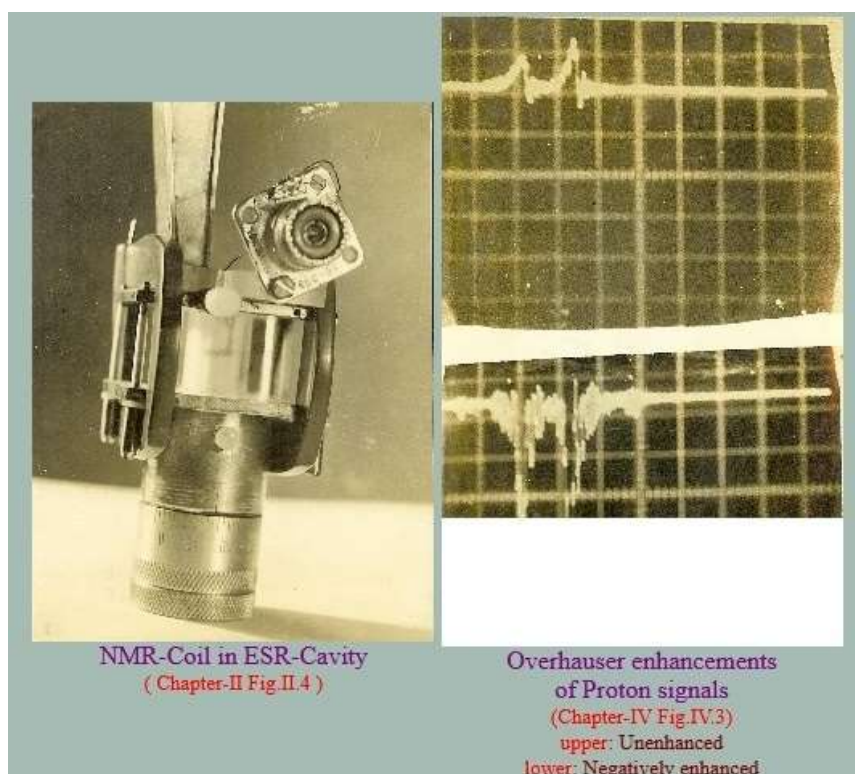


Figure 4: Overhauser effect enhancement of the solvent protons (inverted).

The Double Resonance Effect observed by saturating the EPR levels of the solute Free Radical, while monitoring PMR levels of the solvent protons is the electron-nuclear Overhauser effect.

References:

[1] Review Of The Elements Of Nuclear Magnetic Resonance Instrumentation, S. Aravamudhan, JAFS, (ISSN 2395-5554 (Print) |ISSN 2395-5562 (Online)) Vol. 2(2)| November 2016, page-108.





[2] <https://www.youtube.com/watch?v=TJyfRsOVKqw&list=PL158BAC87668F5D5A> NMR videos at this you tube link can be helpful.

[3] [http://www.angelfire.com/art3/saravamudhan/thesis\\_sa.html](http://www.angelfire.com/art3/saravamudhan/thesis_sa.html) This web page consists of the Abstract of a Ph.D., thesis on DNP. And the web page also includes a copy of the full text (in e-book form) of the Ph.D., thesis and the Chapter I of this thesis is a review of the DNP phenomenon. The references to this Chapter include exhaustive list of publications available on DNP, appropriately cited in the main text of the Chapter content. However, for convenience of readers some of the references are listed as follows; I. Solomon, Phys. Rev. 99, 559, (1955); A.W. Overhauser, Phys. Rev. 92, 411 (1953); K.H. Hausser and D. Stehlik, Advances in Magnetic Resonance, Ed., J.S. Waugh, Academic Press, 3, 79-139, (1968).