Advanced Quantum Mechanics with Applications
Prof. Saurabh Basu
Department of Physics
Indian Institute of Technology, Guwahati

Lecture - 13
Nuclear Magnetic Resonance

So, let us look at the magnetic resonance phenomenon in quantum mechanics and in particular we are going to talk about Nuclear Magnetic Resonance. However, we can sort of the same formalism would go through for other resonance phenomenon which will I just briefly mention.

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Introduction:

If a sample is placed in a magnetic field and is subjected to radiofrequency (RF) radiation, at appropriate frequencies, nuclei in the sample can absorb the radiation.

The frequency of radiation necessary for absorption of energy depends on 3 things:

(i) the type of the nucleus, e.g. ^{1}H or ^{13}C.

(ii) the chemical environment of the nucleus

(iii) the spatial location of the sample in the magnetic field (principle used in MRI)

So, as an introduction it to NMR or Nuclear Magnetic Resonance can be said that if a sample is placed in a magnetic field and then it is subjected to a radio frequency radiation. So, at appropriate values of the frequencies the nuclear in the sample can absorb radiation. And of course, one knows that nuclei do not exist alone or individually, in a sample they are always surrounded by electrons as we know of an atomic structure. And as so, basically that will give information about the environment of the nuclei, but here we are particularly talking about the response of the nuclei and not of the electrons to that external radio frequency of radiation that is mentioned here.

So, the frequency of radiation necessary for absorption of energy or the radiation that depends on 3 factors that is the type of the nucleus. So, whether you have hydrogen or

you have carbon; so, it will the absorption frequency or the emission frequency would be different. And, then the chemical environment of the nucleus and this is what we were trying to talk about that the environment is important and if a particular nucleus is chemically different than another nucleus. So, this frequency will change is valid in that case.

And, the special location of the sample especially if you, have an inhomogeneous magnetic field and this is the principle that is used in MRI. So, these are the 3 factors that the frequency of radiation that will depend on.

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Nuclei have positive charges. Usually nuclei behave as if they are spinning.

Classical electromagnetics says that anything that is charged and moving has a magnetic moment and hence produces a magnetic field.

Therefore a tiny magnet is called as nuclear spin. If we put this tiny magnet in presence of a large magnetic field, the nuclear spin will assume two orientations corresponding to spin-1/2 ($I = \frac{1}{2}$):

(a) parallel to the field ;   (b) antiparallel to the field.

For a large number of nuclei have $I = \frac{1}{2}$, such as ^{15}N, ^{19}F and ^{31}P, such two state description is relevant.

So, going ahead with the discussion nuclei have positive charges. Usually the nuclei's behave as if they are spinning, a spinning about a certain axis and if there is a magnetic field external magnetic field precise around that in a conical fashion. So, since they have charges and they are spinning or other moving then the classical electromagnetic says that electromagnetic theory says that anything that is charged and moving has should have a magnetic moment and hence, produces a magnetic field. This tiny magnet or this magnetic field that is produced by the nucleus is called as the nuclear spin. If you put this tiny magnet in presence of a large magnetic spin, then the nuclear spin will assume two orientations and we have particular talking about spin half for the nucleus. So, that is a nuclear spin equal to half.

So, there are possibilities that this nucleus spins will align in the direction of the field which is parallel to the field or they could align antiparallel to the field and one of course, has lower energy than the other will see that in details. So, for a large number of nuclei the spin is actually half. The most common examples are we have given to already, that is carbon and hydrogen.

Addition to that the nitrogen and then there are fluorine and phosphorus and the for these nuclei thus, two state description is particularly relevant. So, what is this NMR and how do we understand it? And, the simplest form we also know about infrared spectroscopy, which is the simplest form or rather example of transitions being induced by the oscillating electric field of light or photons.

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As IR spectroscopy is the simplest example of transitions being induced by the light's oscillating electric field, NMR is likewise the simplest example of transitions induced by the oscillating magnetic field.

But because the strength of the matter magnetic field interactions are typically two orders of magnitude smaller than the electric field counterpart, NMR is much more delicate proble of structure and properties.

Magnetic resonance phenomena denote absorption or emission of EM radiation by atomic nuclei or even the electrons in presence of external magnetic field.

So, NMR likewise is the simplest example of transitions induced by the oscillating magnetic field and we have already talked about the oscillating the frequency is in the radio frequency regime. But, because the strength of the matter magnetic field interactions so, this is are typically quite low. In fact, two orders of magnitude lower than the corresponding electric field counterpart, NMR is actually a much more delicate probe of structure and properties of materials. And so, magnetic resonance phenomenon denote absorption or emission of electromagnetic radiation by the atomic nuclei or even the electrons in presence of external magnetic field.

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Generically, resonance phenomena include:

(i) Nuclear magnetic resonance (NMR)

(ii) Electron spin resonance (ESR)

In particular we shall talk about NMR, however the formalism for resonance is

valid for ESR as well.

NMR was discovered by E. Purcell and F. Bloch in 1946. It has important

applications in:
(i) determination of molecular structure
(ii) Dynamical measurements both in the liquid and the solid state
(iii) Magnetic resonance imaging (MRI)

So, the resonance of phenomena the other resonance phenomena that we are aware of includes ESR, the Electron Spin Resonance and of course, the one that is under focus is the nuclear magnetic resonance. So, in particular we talking will shall talk about NMR. However, the formalism is for resonance is valid for ESR as well. Now, NMR was discovered by E. Purcell and F. Bloch in 1946. And, it has important applications in a determination of the molecular structure, the dynamical measurements in the liquid and the solid state and the MRI that we are familiar with which is used for as a very important diagnostic tool for several kinds of diseases. So, let us try to understand the mechanism of NMR.
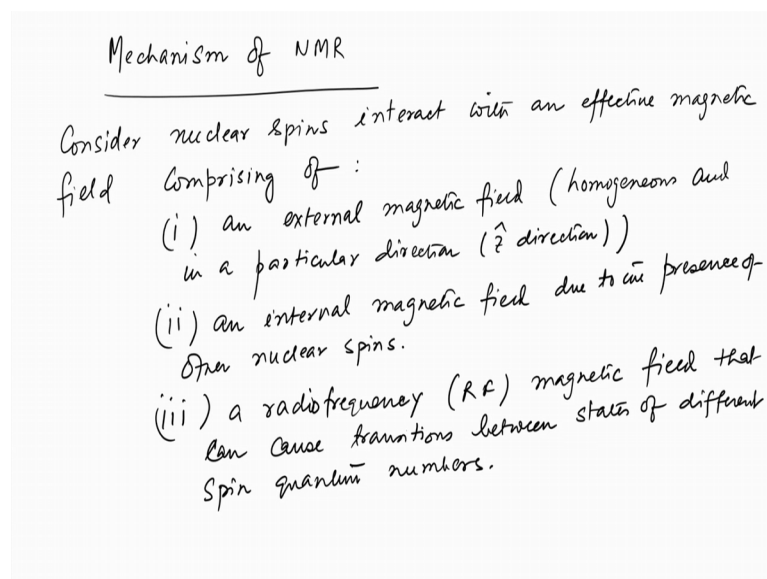
So, consider nuclear spins interact with an effective magnetic field comprising of two parts. So, one is or rather three let us see an external magnetic field which is which is homogeneous and in a particular direction and of course, the preferred direction is most of the times is say z direction. Number 2, that is an internal magnetic field due to the presence of other nuclear spins ok.

And, third and importantly a radio frequency RF magnetic field that can cause transitions between states of different quantum numbers or rather spin quantum numbers, magnetic quantum numbers alright. So, let us see that how these three factors affect or rather how we can write down the minimal Hamiltonian for all these three kinds of interaction.

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So, we all know that the Zeeman-Hamiltonian written for a single spin in presence of what we said as a constant H 0 in the z direction and 2 an RF in the x direction. So, this is like H 1 cosine omega t x cap where omega is the frequency of this RF field. And, then the Hamiltonian H is written as minus mu dot H of t; remember we are writing the curly H for the Hamiltonian and a straight H as we the in block letters or bold letters for the magnetic field.

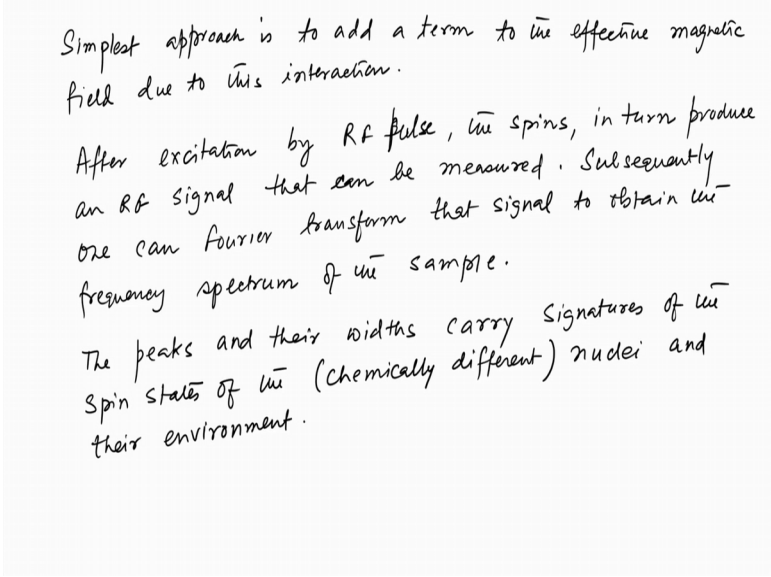So, this is equal to so, H of t equal to H 0 z plus H 1 cosine omega t x cap. Now, it is important to sort of also know that which not very relevant for us in terms of computation. But, this is replaced by a circularly polarized field of the form say H 1 cos omega t x cap plus a sin omega t y cap for diagnostics such as MRI etcetera ok. But, here for our case it is simply in the x direction with the cosine variation.

Now, we have another term which we had forgotten or rather not taken into account so far. In fact, this one if you see it is number 3 and let us talk about the number 2, which is interaction between the spins. Now, this is one can assume a spin dipolar interaction between the spins having a form and its I am this regarding the dimensions that is putting the interaction dimensions simply this is like this which is S i dot S j r ij square and divided by r ij to the power so 5.

So, this is a generic dipole-dipole interaction that is familiar in the context of classical electromagnetism and that can be taken as the interaction between the spins. However, it

is often a what is done is that this term is neglected and this term is in some sense included in the H 0.

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Simplest approach is to add a term to the effective magnetic field due to this interaction.

After excitation by RF pulse, the spins, in turn produce an RF signal that can be measured. Subsequently one can Fourier transform that signal to obtain the frequency spectrum of the sample.

The peaks and their widths carry signatures of the spin states of the (chemically different) nuclei and their environment.

So, let us write down the simplest approach is to add a term to the effective magnetic field due to this interaction. And, the reason for under playing the contribution of the spin-spin interaction is that, that in many systems such as a particularly in liquids you have we are talking about spin liquids your r ij's change so fast; r ij's are the distance between the spin at site i S i and S j the spin at site j. These change so fast that the averaging over configuration would yield a 0. However, it is not always true.

In fact, in presence of an RF field which actually measures the time interval over which this change takes place that is this r ij's change because, in a spin liquid will be no fixed rijs at all instance of time. So, if one takes an average then it gives a very small contribution. However, it is still a contribution which can be neglected or as it is written here it could be added to the effective magnetic field. So, this interaction can be actually included indirectly into the changing the external magnetic field, the constant magnetic field by a small value.

So, what happens is that after excitation by RF pulse, the spins in turn produce RF signal that can be measured. Subsequently one can Fourier transform that signal to obtain the frequency spectrum of the sample. So, importantly the peaks in the frequency spectrum and their widths carry signatures of the spin states of the let us write it as a chemically

different nuclei and their environment. So, these are the signatures that carries the NMR spectroscopy signatures for the all the information that one wants to get about the structure, the magnetic structure of a system by NMR spectroscopy.