

How NMR Works ----- Section I

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During the NMR course I use classic energy levels and vector model to explain simple NMR pulse sequences and spectra. It is limited, however, until to understand how NMR experiments work. Here I am going to introduce Quantum Mechanics for NMR only. If you can follow the section by section, you will understand how NMR works in general. These terms seem very tedious, but they are very simple and they have been presented this way. The quantum mechanical description of NMR is straightforward and it is possible to use it to analysis most of NMR experiments without using super computer or super brain. Here I just organize the ideas and present them in a simple way in order to let those chemists who has no quantum mechanics background understand the NMR with an “inside” view of their NMR experiments.

Concepts: ----- We are going to use these terms all the time. Just remember them.

1. **Wavefunctions:** ----It is mathematical function that contains a complete description of the system. If we know the wavefunction we can calculate the properties of the system. For example: a mathematical function of object in XY plane: $y = x^2 + 3$ or $f(x) = x^2 + 3$, from the function we can know the position of the object by given x value. A much better sample of a wavefunction is: $\Psi(r) = \exp(-ar)$. That is used to describe an electron in a hydrogen atom. Where r is the distance of the electron from the nucleus. Where a is a constant. This wavefunction contains all the information about the system ----one electron in a hydrogen atom. To extract the information held by this wavefunction, we have to use a tool ----an Operator to get it.
2. **Operators** :----- It acts on a function to produce a new function. For example: differentiate with respect to the variable x ; mathematically we write it as d/dx . This Operator can act on a function of $f(x)$ to produce a new function $f(x)'$: By using above sample $f(x) = x^2 + 3$, $d/dx f(x)$ will be $f(x)' = 2x$. This is a new function of x , but it tells us something new about the system. In NMR, we don't care about the function itself, but we really want to know the Operators (These operators are related to NMR pulses that manipulate spins in the magnet) ---we call them Observable. An Operator can help us to find the value or result.

To use operator on a function, there are few rules we have to follow.

- a. The **order** of operators and functions CANNOT be changed. $d/dx f(x)$ is not same as $f(x)d/dx$.
- b. Operators A, B, C act on function $f(x)$: $ABCf(x)$. Operate C $f(x)$ first, then B operate on the result of $Cf(x)$. So on so for. Again Cannot change the order.
- c. If the order changed, but the result is same, then the operator are said to **commute**. If the

result is not the same, then they are said not to commute.

3. Eigenfunctions and Eigenvalues of Operators

Some WaveFunctions, when a particular Operator acts on them, the WaveFunctions themselves are not changed (remain as the same function), but multiplication by a constant. For example:

$d/dx \exp(aX) = a \exp(aX)$ ----- a is a constant. The function is the same before and after the operation. In this case, we call the constant EigenValue, and the function is called EigenFunction of Operator d/dx . This kind of equation is called EigenValue Equation. Some operators may have many EigenFunctions.

Note: In NMR, we are interested in Energy levels that corresponding to the wavefunctions. Operators are important tools for us to find these values as the EigenValue. To find these EigenValues and Eigenfunctions, we have to find the Operators ---- Energy Operator ----It has a special name---- **Hamiltonian (Labeled with H)**. -----Find a right Hamiltonian to get a right EigenValue is kind of art. Here we just use those that others have provided to us.

4. Hamiltonian and Angular Momentum of Nucleus

A nucleus --- called nuclear spin (quantum number I is none zero) ---- in a magnetic field B_0 . Someone has constructed a Hamiltonian for us:

$H = -\gamma \hbar I_z B_0$ -----Gama is the constant ($s^{-1} \cdot T^{-1}$), called gyromagnetic ratio that is a property of a nucleus. B_0 (T) is the strength of the magnet and I_z is the Operator ----- Represents nuclear spin angular momentum---along the z axis with the same direction of the B_0 field. The angular momentum is a property of the nucleus along with its mass and charges.

Operator I_z ----- is very important in NMR. Operator I_z has $(2I + 1)$ EigenFunctions with associated EigenValues. Where I is called quantum number, or long name nuclear spin angular momentum quantum number or spin quantum number, it is a property of the nucleus. For example, ^{13}C , 1H , ^{31}P ($I=1/2$), 2H ($I=1$) and ^{12}C , ^{16}O ($I=0$, no NMR).

Let's make a simple case first, let $I=1/2$: The Operator I_z will have $(2 * 1/2 + 1) = 2$ EigenFunctions (We just name them as $\psi(1/2)$ and $\psi(-1/2)$, in fact you can name them anyway you want. Also I_z has two EigenValues ($+1/2$, $-1/2$) associate with the EigenFunction.

So the EigenEquation would be:

$$I_z \Psi = m \hbar \Psi$$

Where the m is a part of the EigenValue --it is a constant but also it is another

quantum number. It takes value of -I and +I in integer steps. In this case -1/2 and +1/2.

$$I_z \Psi_{\frac{1}{2}} = \frac{1}{2} \hbar \Psi_{\frac{1}{2}}$$

$$I_z \Psi_{-\frac{1}{2}} = -\frac{1}{2} \hbar \Psi_{-\frac{1}{2}}$$

Note: I_z is the Operator, represents the z component of nuclear spin angular momentum. (Also I_x and I_y , represents x component and y component respectively. We will use them later on). At this point, we don't know the WaveFunction, and we don't have to know the WaveFunction to get the EigenValue.

Now let's back to the Energy Operator ---- Hamiltonian:

If we only consider only one spin, and its spin quantum number is $I=1/2$. The Hamiltonian can be written as:

$$\hat{H}_{one\ spin} = -\gamma B_0 \hat{I}_z$$

The two EigenFunctions are $\psi_{+1/2}$ and $\psi_{-1/2}$, again we don't have to know what is it and how they are constructed now. By using these two functions, we can use $\hat{H}_{one\ spin}$ to get an EigenValue -- observable ---Energy Level.

$$\hat{H}_{one\ spin} \Psi = E \Psi$$

It is called Schrödinger Equation. If the EigenFunction is $\Psi(x,t)$, then it is called time dependent Schrödinger Equation. In NMR, we deal with the time dependent Eigenfunction. Where E is the EigenValue, i.e. Energy. First, let's calculate the Energy with time independent EigenFunctions. By using above introduction, we can re-write the equation by inserting the defined terms.

$$\hat{H}_{one\ spin} \psi_{+\frac{1}{2}} = -\gamma B_0 \hat{I}_z \psi_{+\frac{1}{2}}$$

Note: The Hamiltonian is constructed for one spin. If there is a two spin system, then there are some differences. Let's work on the simplest first. The Operator \hat{I}_z acts on the EigenFunction $\psi_{+1/2}$ or $\psi_{-1/2}$:

$$\hat{H}_{one\ spin} \psi_{+\frac{1}{2}} = -\gamma B_0 \hat{I}_z \psi_{+\frac{1}{2}}$$

Then we already have: $\hat{I}_z \psi_{+\frac{1}{2}} = \frac{1}{2} \hbar \psi_{+\frac{1}{2}}$

By plugging it into above equation:

$$\hat{H}_{one\ spin}\psi_{+\frac{1}{2}} = -\gamma B_0 \frac{1}{2} \hbar \psi_{+\frac{1}{2}} = -\frac{1}{2} \hbar \gamma B_0 \psi_{+\frac{1}{2}}$$

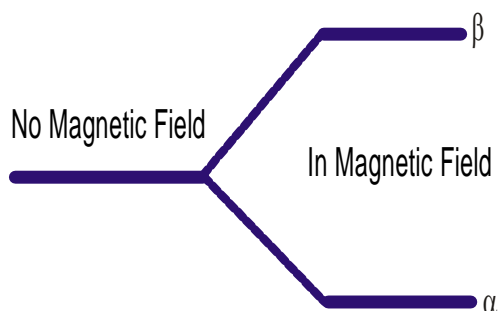
Comparing with the Schrödinger Equation, the Energy term is:

$$E = -\frac{1}{2} \hbar \gamma B_0$$

By using the other EigenFunction $\psi_{-1/2}$ We will get:

$$E = +\frac{1}{2} \hbar \gamma B_0$$

Note: Above results tell us, if we place a nucleus (one spin with $I=1/2$) in the magnet field of B_0 , There will be two energy levels. One is $E = -\frac{1}{2} \hbar \gamma B_0$ we called it α state, One is $E = +\frac{1}{2} \hbar \gamma B_0$, we call it β state.



The Energy of the allowed transition from α state to β state:

$$\Delta E = +\frac{1}{2} \hbar \gamma B_0 - (-\frac{1}{2} \hbar \gamma B_0) = \hbar \gamma B_0$$

Note: in NMR, we would like to use frequency in Hz as energy. $\hbar = \frac{h}{2\pi}$; $\Delta E = h\nu$ or $\nu = \Delta E/h$ in frequency unit.

The frequency (Energy) between α state and β state is:

$$\nu = \frac{\gamma B_0}{2\pi} \text{ (in Hz)} \quad \text{----- Larmor Frequency}$$

For example: If we place one proton nucleus into a 14.09197 Tesla magnet field. The Larmor frequency is: (The γ is a constant, for proton is $2.67522 \times 10^8 \text{ rad}\cdot\text{S}^{-1} \text{ T}^{-1}$.)

$$\nu = \frac{2.67522 \times 10^8 \times 14.09197}{2\pi} = 600,000,129.5 \text{ Hz or } 600 \text{ MHz.}$$

Note: In NMR, we directly write it as $\omega_0 = \gamma B_0$ in Hz. By applying the γ constant of each nucleus, we just make a table for all the Larmor frequencies at different magnet field available. In

general, we just use the proton frequency to describe the strength of magnetic field. It is impossible to make two exactly same strength magnetic field, so nucleus has different Larmor frequencies in different NMR instrument.