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| How NMR Works ------- Section Iby Shaoxiong Wu 02-20-2010  |
| 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: http://www.emory.edu/NMR/mysite06/My%20Stuff/How_NMR_Works/introduction-a_clip_image002.gif. 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 ***Bo***. Someone has constructed a Hamiltonian for us: http://www.emory.edu/NMR/mysite06/My%20Stuff/How_NMR_Works/introduction-a_clip_image002_0000.gif-------Gama is the constant (s-1·T -1), called gyromagnetic ratio that is a property of a nucleus. Bo (T) is the strength of the magnet and **Iz** is the Operator ----- Represents nuclear spin angular momentum---along the z axis with the same direction of the Bo field. The angular momentum is a property of the nucleus along with its mess and charges.Operator **Iz -----** is very important in NMR. Operator **Iz** 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 nuclus. For example, 13C, 1H, 31P (I=1/2), 2H (I=1) and 12C, 16O (I=0, no NMR). Let's make a simple case first, let I=1/2: The Operator **Iz** will have (2 \*1/2 +1)=2 EigenFunctions (We just name them as http://www.emory.edu/NMR/mysite06/My%20Stuff/How_NMR_Works/introduction-a_clip_image002_0001.gifand http://www.emory.edu/NMR/mysite06/My%20Stuff/How_NMR_Works/introduction-a_clip_image002_0002.gif, in fact you can name them anyway you want. Also **Iz** has two EigenValues (+1/2 , -1/2 ) associate with the EigenFunction. So the EigenEquation would be:$$I\_{z}Ψ=mℏΨ$$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. $$I\_{z}Ψ\_{\frac{1}{2}}=\frac{1}{2}ℏΨ\_{\frac{1}{2}}$$$$I\_{z}Ψ\_{-\frac{1}{2}}=-\frac{1}{2}ℏΨ\_{-\frac{1}{2}}$$Note: **Iz** is the Operator, represents the z component of nuclear spin angular momentum. (Also **Ix** and **Iy**, represents x component and y component respectively. We will use them late 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:$$\hat{H}\_{one spin}=-γB\_{0}\hat{I}\_{z}$$ |  |

The two EigenFunctions are ψ+1/2 and ψ-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}Ψ=EΨ$

It is called Shrödinger Equation. If the EigenFunction is Ψ(x,t), then it is called time dependent Shrödinger Equation. In NMR, we deal with the time dependent Eignefuction. 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.

$\hat{H}\_{one spin}ψ\_{+\frac{1}{2}}=-γB\_{0}\hat{I}\_{z}ψ\_{+\frac{1}{2}}$

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 Îz acts on the EigenFunction ψ+1/2 or ψ-1/2 :

$\hat{H}\_{one spin}ψ\_{+\frac{1}{2}}=-γB\_{0}\hat{I}\_{z}ψ\_{+\frac{1}{2}}$

Then we already have: $\hat{I}\_{z}ψ\_{+\frac{1}{2}}=\frac{1}{2} ħψ\_{+\frac{1}{2}}$

By plugging it into above equation:

$\hat{H}\_{one spin}ψ\_{+\frac{1}{2}}=-γB\_{0}\frac{1}{2} ħψ\_{+\frac{1}{2}}=-\frac{1}{2} ħγB\_{0}ψ\_{+\frac{1}{2}}$

Comparing with the Shrödinger Equation, the Energy term is:

E=$-\frac{1}{2} ħγB\_{0}$

By using the other EigenFunction ψ-1/2 We will get:

E=$+\frac{1}{2} ħγB\_{0}$

Note: Above results tell us, if we place a nucleus (one spin with I=1/2) in the magnet field of B0, There will be two energy levels. One is E=$-\frac{1}{2} ħγB\_{0}$ we called it α state, One is E=$+\frac{1}{2} ħγB\_{0}$, we call it β state.

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

ΔE=$+\frac{1}{2} ħγB\_{0}-(-\frac{1}{2} ħγB\_{0})$=$ ħγB\_{0}$

Note: in NMR, we would like to use frequency in Hz as energy. $ħ=\frac{h}{2π}$; ΔE=hυ or υ=ΔE/h in frequency unit.

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

υ=$ \frac{γB\_{0}}{2π}$ (in Hz) --------- 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 x 108 rad.S-1 T-1 . )

$$υ=\frac{2.67522 ×10^{8}×14.09197}{2π}=600,000,129.5Hz or 600MHz.$$

Note: In NMR, we directly write it as ω0=γB0 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.