

How NMR Works ----- Section IV

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Now let's get a work on something called Expectation Value.

From basic quantum theory, the value of an observable quantity A that could be represented by an operator \hat{A} , can be found for any state i as the expectation value, $\langle A \rangle^i$. In other word, a value (size, how much, how big, how fast, where ?) of something (here is A), can be calculated by using its operator, i.e. the \hat{A} act on a function or state function. For example:

$$\Psi^i = \sum_{k=1} C_k \phi_k \Rightarrow \quad \text{If } N=1 \text{ (one spin } l=1/2, \text{ then } k \text{ can be 1 and 2) then it is much clear to us:}$$

$$\Psi^1 = C_1^1 |\alpha\rangle + C_2^1 |\beta\rangle \quad \text{or as before.}$$

More general term to use these functions for an Expectation Value :Z-component of angular momentum Iz:

$$\begin{aligned} \langle I_z \rangle^{(1)} &= \langle \Psi^{*(1)} | I_z | \Psi^{(1)} \rangle \Rightarrow \langle [C_1^{*(1)} |\alpha\rangle + C_2^{*(1)} |\beta\rangle] | I_z | [C_1^1 |\alpha\rangle + C_2^1 |\beta\rangle] \rangle \\ &\Rightarrow C_1^{*(1)} C_1^1 \langle \alpha | I_z | \alpha \rangle + C_1^{*(1)} C_2^1 \langle \alpha | I_z | \beta \rangle + C_2^{*(1)} C_1^1 \langle \beta | I_z | \alpha \rangle + C_2^{*(1)} C_2^1 \langle \beta | I_z | \beta \rangle \\ &\Rightarrow \frac{1}{2} (C_1^{*(1)} C_1^1 - C_2^{*(1)} C_2^1) \end{aligned}$$

Omitted few steps from line two to line three, check previous section.

For Spin 2:

$$\begin{aligned} \langle I_z \rangle^{(2)} &= \langle \Psi^{*(2)} | I_z | \Psi^{(2)} \rangle \Rightarrow \langle [C_1^{*(2)} |\alpha\rangle + C_2^{*(2)} |\beta\rangle] | I_z | [C_1^{(2)} |\alpha\rangle + C_2^{(2)} |\beta\rangle] \rangle \\ &\Rightarrow C_1^{*(2)} C_1^{(2)} \langle \alpha | I_z | \alpha \rangle + C_1^{*(2)} C_2^{(2)} \langle \alpha | I_z | \beta \rangle + C_2^{*(2)} C_1^{(2)} \langle \beta | I_z | \alpha \rangle + C_2^{*(2)} C_2^{(2)} \langle \beta | I_z | \beta \rangle \\ &\Rightarrow \frac{1}{2} (C_1^{*(2)} C_1^{(2)} - C_2^{*(2)} C_2^{(2)}) \end{aligned}$$

More general term to use these functions for an Expectation Value **A**:

$$\begin{aligned} \langle A \rangle^{(i)} &= \langle \Psi^{*(i)} | A | \Psi^{(i)} \rangle \Rightarrow \langle [C_1^* \phi_1 + C_2^* \phi_2] | A | [C_1 \phi_1 + C_2 \phi_2] \rangle \\ &\Rightarrow C_1^* C_1 \langle \phi_1 | A | \phi_1 \rangle + C_1^* C_2 \langle \phi_1 | A | \phi_2 \rangle + C_2^* C_1 \langle \phi_2 | A | \phi_1 \rangle + C_2^* C_2 \langle \phi_2 | A | \phi_2 \rangle \\ &\Rightarrow \sum_{m,n} C_m^{*(i)} C_n^{(i)} A_{mn} \end{aligned}$$

Note: i, m and n are integers. The particular function of $\Psi^{(i)}$ occur in an ensemble, the probability is $P^{(i)}$

If we can measure $\langle A \rangle$ many times, the probability:

$$\sum_i p^i = 1$$

The overall expectation value will be :

$$\langle A \rangle = \sum_i P^i \langle A \rangle^{(i)} = \sum_{i=1} \sum_{m,n=1} P^i C_m^{*(i)} C_n^{(i)} A_{mn}$$

We want to know the value of A, we can calculate it from above equation. It tells us the average of value of many measurements, rather than the value of each measurement or a particular measurement. This value we called it --- **Expectation Value** --- **In NMR we are more interested in $\langle I_z \rangle, \langle I_x \rangle, \langle I_y \rangle$ etc.**

The following few steps may be too fast, I will use a real sample to explain it in more detail.

$$\text{From: } \langle A \rangle = \sum_i P^i \langle A \rangle^{(i)} = \sum_{i=1} \sum_{m,n=1} P^i C_m^{*(i)} C_n^{(i)} A_{mn}$$

$$\text{Let } \sigma_{mn} = \sum_i P^i C_m^{*(i)} C_n^{(i)} \quad \text{----- Take the probability and coefficients of each measurement.}$$

$$\text{Then: } \langle A \rangle = \sum_{m=1}^{2^N} \sum_{n=1}^{2^N} \sigma_{mn} A_{mn} \text{ or } \sum_{m,n} \sigma_{mn} A_{mn} \quad \text{----- N is the spin number. One spin, N=1.}$$

$$\langle A \rangle = \sum_{n=1}^{2^N} [\sigma A]_{n,n} = \text{Tr}[\sigma A]$$

Tr means trace, we take the trace of matrix and add them together as the result----- Expectation Value A.

Where the σ is called the density operator, it has by definition a $(2I+1)$ by $(2I+1)$ dimensional matrix representation. For example, a spin $I=1/2$, the density operator has a two by two matrix. The average of observable is taking the trace of the product of \mathbf{A} with σ . ($\text{Tr}[\sigma A]$ or $\text{Tr}[A\sigma]$).

Now let's work on a real sample:

Note:

If one spin and $I=1/2$, the probabilities of occurrence, P^1 and P^2 , are equilibrium, simply the populations of the states as determined by the Boltzmann distribution.

$$\frac{N_\beta}{N_\alpha} = e^{-\Delta E/kT} = e^{-\hbar B_0/kT} = e^{-\epsilon} \approx 1 - \epsilon$$

if we assume $\epsilon = \Delta E/kT$, and $\epsilon \ll 1$. Thus, $P^1 = \frac{1}{2}(1 + \epsilon/2)$ and $P^2 = \frac{1}{2}(1 - \epsilon/2)$. More correctly, the probability of spin stay in α state is $P^1 = \frac{1}{2}(1 + \epsilon/2)$; and the probability of spin stay in β state is $P^2 = \frac{1}{2}(1 - \epsilon/2)$.

If we use above result:

$$|\Psi^1\rangle = |\alpha\rangle \quad P^1 = \frac{1}{2}(1 + \epsilon/2)$$

$$|\Psi^2\rangle = |\beta\rangle \quad P^2 = \frac{1}{2}(1 - \epsilon/2)$$

$$\sigma_{mn} = \sum_i P^i C_m^{*i} C_n^i$$

$$\sigma_{\alpha\alpha} = p^1 C_\alpha^{*(1)} C_\alpha^1 + p^2 C_\alpha^{*(2)} C_\alpha^2 = \frac{1}{2} \left(1 + \frac{\epsilon}{2}\right) C_\alpha^{*(1)} C_\alpha^1 + 0$$

$$\Rightarrow \frac{1}{2} \left(1 + \frac{\epsilon}{2}\right)$$

$$\sigma_{\alpha\beta} = p^1 C_\alpha^{*(1)} C_\beta^1 + p^2 C_\alpha^{*(2)} C_\beta^2 = 0$$

$$\sigma_{\beta\alpha} = p^1 C_\beta^{*(1)} C_\alpha^1 + p^2 C_\beta^{*(2)} C_\alpha^2 = 0$$

$$\sigma_{\beta\beta} = p^1 C_\beta^{*(1)} C_\beta^1 + p^2 C_\beta^{*(2)} C_\beta^2 = 0 + \frac{1}{2} \left(1 - \frac{\epsilon}{2}\right) C_\beta^{*(2)} C_\beta^2$$

$$\Rightarrow \frac{1}{2} \left(1 - \frac{\epsilon}{2} \right)$$

So σ can be written:

(the detail matrix representation will be discussed in the next section):

$$\sigma = \begin{bmatrix} \sigma_{\alpha\alpha} & \sigma_{\alpha\beta} \\ \sigma_{\beta\alpha} & \sigma_{\beta\beta} \end{bmatrix} \quad \text{or}$$

$$\text{At equilibrium: } \sigma = \frac{1}{2} \begin{vmatrix} \left(1 + \frac{\epsilon}{2} \right) & 0 \\ 0 & 1 - \frac{\epsilon}{2} \end{vmatrix} = \frac{1}{2} \begin{vmatrix} 1 & 0 \\ 0 & 1 \end{vmatrix} + \frac{\epsilon}{4} \begin{vmatrix} 1 & 0 \\ 0 & -1 \end{vmatrix} \quad \rightarrow \frac{1}{2} \mathbf{1} + \sigma$$

Where $\mathbf{1}$ is called the identity matrix or unit matrix of appropriate dimensions, here is 2x2. It does not vary with time and contributes to the measurement. The second term is important. At equilibrium, the density matrix can be written:

Note:

$$\sigma_{\alpha\alpha} = 1/2[1 + (\epsilon/2)] + 0$$

$$\sigma_{\alpha\beta} = 0 + 0$$

$$\sigma_{\beta\beta} = 0 + 1/2[1 - (\epsilon/2)]$$

$$\sigma_{\beta\alpha} = 0 + 0$$

$$\sigma = \frac{\epsilon}{4} \begin{vmatrix} 1 & 0 \\ 0 & -1 \end{vmatrix}$$

We can use this result to recalculate the Z-component of Angular momentum:

$$\langle M_z \rangle = \text{Tr}(M_z \sigma)$$

We want to use this density matrix (for $l=1/2$ and one spin) to calculate the magnetization of Z-component:

$$\langle M_z \rangle = \text{Tr}(M_z \sigma) = N\gamma\hbar \text{Tr}(I_z \sigma) = (N\gamma\hbar) \frac{\epsilon}{4} = \frac{N\gamma^2 \hbar^2 B_0}{4kT}$$

$$I_z \sigma = I_z \cdot \frac{\epsilon}{4} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad \text{or} \quad \sigma = \left(\frac{\epsilon}{2} \right) I_z$$

Where $M_z = \sum_i N_i \mu_i$ is the bulk magnetization that is the total of magnetic dipole moment μ .

The dipole moment $\mu = \gamma\hbar I$ and $\epsilon = \frac{\gamma\hbar B_0}{kT}$. (See any NMR book).

$$\text{Tr}(I_z \sigma) = \text{Tr} \left\{ \frac{1}{2} \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \frac{\epsilon}{2} \times \frac{1}{2} \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \right\} = \frac{\epsilon}{8} \text{Tr} \left\{ \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \right\} = \frac{\epsilon}{8} \times 2 = \frac{\epsilon}{4}$$

Where $I_z = \frac{1}{2} \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$ and $\sigma = \left(\frac{\epsilon}{2}\right) I_z = \frac{\epsilon}{4} \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$

The Tr means add the diagonal number together. The final result is:

$$\langle M_z \rangle = \frac{N \gamma^2 \hbar^2 B_0}{4kT}$$

It tells us: The bulk magnetization of spin in the magnetic field B_0 is directly proportional to N , the total number of spins in the system, and γ^2 magnetogyric ratio, the strength of the magnetic field.

Note:

Matrix Operation:

$$\begin{bmatrix} a & b \\ c & d \end{bmatrix} \begin{bmatrix} e & f \\ g & h \end{bmatrix} = \begin{pmatrix} ae + ag & bf + bh \\ ce + cg & df + dh \end{pmatrix}$$

$$\begin{bmatrix} a & b & c & d \\ e & f & g & h \\ i & j & k & l \\ m & n & o & p \end{bmatrix} \begin{bmatrix} A & B & C & D \\ E & F & G & H \\ I & J & K & L \\ M & N & O & P \end{bmatrix} = \begin{bmatrix} aA + aE + aI + aM & b & c & d \\ eA + eE + eI + eM & f & g & h \\ i & j & k & l \\ m & n & o & p \end{bmatrix}$$
