Spin relaxometry method

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1 General framework of spin relaxometry

In the experiment, in order to detect the spectrum function, we usually couple the system with a probe. The property of the system, such as correlation function, will affect the dissipate of the probe. And this relation is usually called fluctuation-dissipation theorem. Here, we develop the general framework of using spin probe, such as NV center, to detect magnetic field fluctuation.

Here, we consider the spin probe Hamiltonian as

$$H = \frac{\omega}{2}\sigma_z - g\mu_B \sigma \cdot B(r,t). \tag{1}$$

where B(r,t) represents the magnetic field generated by the sample at spin probe location. We assume the effect of spin probe on the sample can be neglected. We assume the material is in thermal equilibrium at temperature T. Then the state of the material is describe by density matrix, $\rho = \sum_n p_n |n\rangle\langle n|$, with $p_n = e^{-\beta\omega_n}/\mathcal{Z}$. Then the state of total system is the tensor product of those two: $|n,\sigma\rangle = |n\rangle \otimes |\sigma\rangle$. The relaxation time T_1 of the spin probe is defined as

$$\frac{1}{T_1} = \frac{1}{2}(\frac{1}{T_{ab}} + \frac{1}{T_{em}}) \tag{2}$$

where $1/T_{ab}$ and $1/T_{em}$ can also be called as absorption rate and relaxation rate respectively. We can use the Fermi golden rule to write down

$$R_{em} = 2\pi \sum_{n,m} \frac{e^{-\beta\omega_n}}{\mathcal{Z}} |\langle m,-|g\mu_B \sigma \cdot B|n,+\rangle|^2 \delta(\omega + \omega_n - \omega_m) \tag{3}$$

$$= 2\pi (g\mu_B)^2 \sum_{n,m} \frac{e^{\beta\omega_n}}{\mathcal{Z}} (B^x_{nm}B^x_{mn} + B^y_{nm}B^y_{mn} + iB^y_{nm}B^x_{mn} - iB^x_{nm}B^y_{mn})\delta\omega + \omega_{nm} \tag{4}$$

$$= 2\pi (g\mu_B)^2 \sum_{n,m} \frac{e^{-\beta\omega_n}}{\mathcal{Z}} B^-_{nm}B^+_{mn}\delta(\omega + \omega_{nm}) \tag{5}$$

where $B^i_{mn} = \langle n|B^i|m\rangle$. We notice the spin energy gap is ω, therefore the only model of the magnetic field B oscillate at frequency ω will couple to the spin probe. In other word, we assume the response is linear.

Similarly, we can work out the absorption rate using Fermi golden rule,

$$R_{ab} = 2\pi (g\mu_B)^2 \sum_{n,m} \frac{e^{-\beta\omega_n}}{\mathcal{Z}} B^+_{nm}B^-_{mn}\delta(\omega - \omega_{nm}) \tag{6}$$

The relaxation rate can be conveniently expressed in terms of the noise tensor $N_{ij}(\omega)$, defined as

$$N_{ij}(\omega) = \frac{1}{2}\int_{-\infty}^{\infty} dt \langle \{B^i(t), B^j(0)\}\rangle e^{i\omega t} \tag{7}$$

$$= \sum_{n,m} \frac{e^{-\beta\omega_n}}{\mathcal{Z}}[B^i_{nm}B^j_{mn}\delta(\omega+\omega_{nm}) + B^j_{nm}B^i_{mn}\delta(\omega-\omega_{nm})]. \tag{8}$$

such that

$$\frac{1}{T_1} = \mu_B^2 N_{-+}(\omega) \tag{9}$$

Notice the noise tensor is the correlation. Or in some literatures, it is called fluctuation. It can be related to dissipation, the imagery part of retarded Green function, through fluctuation-dissipation theorem. We will derive the relation below.

The retarded green function is defined as

$$\chi^R_{ij}(t) = -i\theta(t)\langle [B^i(t), B^j(0)]\rangle \tag{10}$$

It is closed related to the linear response $B^i(t)$ of system if you apply the driving force $f(t)B^j$. Details is listed in the appendix. The retarded Green function can be expressed using its real ($\chi'_{ij}(t)$) and imagery part ($\chi''_{ij}(t)$). We omit the letter R later. The imagery part of $\chi_{ij}(t)$ can be written as

$$\chi''_{ij}(t) = -\frac{i}{2}[\chi_{ij}(t) - \chi_{ji}(-t)]. \tag{11}$$

This can be proved using

$$\chi''_{ij}(\omega) = -\frac{i}{2}(\chi_{ij}(\omega) - \chi^*_{ji}(\omega)) \tag{12}$$

which tells that the dissipative response comes from the anti-Hermitian part of $\chi_{ij}(\omega)$ matrix. By Fourier transformation, we can prove the real time relation.

Plug Eq.(9) to Eq.(11), we have

$$\chi''_{ij}(t) = -\frac{i}{2}[-i\theta(t)\langle B^i(t)B^j(0)\rangle + i\theta(t)\langle B^j(0)B^i(t)\rangle \tag{13}$$

$$+i\theta(-t)\langle B^j(-t)B^i(0)\rangle - i\theta(-t)\langle B^i(0)B^j(-t)\rangle\ ] \tag{14}$$

$$= \frac{1}{2}\langle B^j(0)B^i(t)\rangle - \frac{1}{2}\langle B^i(t)B^j(0)\rangle \tag{15}$$

Notice

$$\langle B^j(0)B^i(t)\rangle = \langle B^j(-t)B^i(0)\rangle = \mathrm{Tr}\left(e^{-\beta H}B^j(-t)B^i(0)\right) \tag{16}$$

$$= \mathrm{Tr}\left(e^{-\beta H}B^j(-t)e^{\beta H}e^{-\beta H}B^i(0)\right) \tag{17}$$

$$= \mathrm{Tr}\left(e^{-\beta H}B^i(0)B^j(-t+i\beta)\right) = \langle B^i(t-i\beta)B^j(0)\rangle \tag{18}$$

Therefore,

$$\chi''_{ij}(t) = -\frac{1}{2}\left[\langle B_i(t)B_j(0)\rangle - \langle B_i(t-i\beta)B_j(0)\rangle\right] \tag{19}$$

If we define $C_{ij}(\omega) = \int dt e^{i\omega t}\langle B_i(t)B_j(0)\rangle$, we have

$$\chi''_{ij}(\omega) = -\frac{1}{2}(1-e^{-\beta\omega})C_{ij}(\omega) \tag{20}$$

From

$$\chi''_{ij}(t) = \frac{1}{2}\langle B^j(0)B^i(t)\rangle - \frac{1}{2}\langle B^i(t)B^j(0)\rangle \tag{21}$$

we can also change the second term,

$$\langle B^i(t)B^j(0)\rangle = \mathrm{Tr}\left(B^j(0)e^{-\beta H}B^i(t)\right) \tag{22}$$

$$= \mathrm{Tr}\left(e^{-\beta H}B^j(0)e^{-\beta H}B^i(t)e^{\beta H}\right) \tag{23}$$

$$= \mathrm{Tr}\left(e^{-\beta H}B^j(0)B^i(t+i\beta)\right) \tag{24}$$

$$= \langle B^j(0)B^i(t+i\beta)\rangle. \tag{25}$$

If we define $\widetilde{C}_{ij}(\omega) = \int dt e^{i\omega t}\langle B^j(0)B^i(t)\rangle$, then

$$\chi''_{ij}(\omega) = \frac{1}{2}\left(1-e^{\beta\omega}\right)\widetilde{C}_{ij}(\omega) \tag{26}$$

To summarize, we have

$$\frac{2\chi''_{ij}(\omega)}{1-e^{\beta\omega}} = \widetilde{C}_{ij}(\omega) \tag{27}$$

$$\frac{-2\chi''_{ij}(\omega)}{1-e^{-\beta\omega}} = C_{ij}(\omega) \tag{28}$$

We notice the noise tensor is $N_{ij}(\omega) = \frac{1}{2}C_{ij}(\omega) + \frac{1}{2}\widetilde{C}_{ij}(\omega)$. Therefore, we arrive the essence of the fluctuation-dissipation relation,

$$N_{ij}(\omega) = -\coth(\frac{\beta\omega}{2})\chi''_{ij}(\omega), \tag{29}$$

where the left hand side tells the fluctuation of the system at thermal equilibrium, and the right hand side tells you the dissipative response of the system.

To summary, we have

$$\frac{1}{T_1} = -\mu_B^2\coth(\frac{\beta\omega}{2})\chi''_{-+}(\omega) \tag{30}$$

In the following, we will see this relation tells us how to measure the magnetic order, spin dynamics and etc. of the materials by measuring the relaxation rate the spin probe.

2 Sample induced magnetic fluctuations

In this section, we use dipole approximation to calculate the magnetic field fluctuations at the spin probe, caused by the thermal spin fluctuation in the sample.
Recall the Maxwell equation is

$$(-\frac{1}{c^2}\frac{\partial^2}{\partial t^2}+\nabla^2)A^\mu = -(0,\mu_0\vec{J}) = -\mu_0(0,\nabla\times\vec{m}), \tag{31}$$

where $\vec{m} = g_\sigma\mu_B\vec{S}(\rho,t)\delta(z)$, and ρ is the x-y plane coordinate. Here we follow the definition in ref.[1], where $\vec{m} = -g_\sigma\mu_B\vec{S}(\rho,t)\delta(z)$, so the Maxwell equation reads

$$(-\frac{1}{c^2}\frac{\partial^2}{\partial t^2}+\nabla^2)A^\mu = \mu_0(0,\nabla\times\vec{m}), \tag{32}$$

We use the Green function method to solve the Maxwell equation by defining

$$A^\mu(r,t) = \mu_0\int dt'dr'G_i^\mu(r-r',t-t')m_i(r',t') \tag{33}$$

where the Green function or the magnetic kernel needs to satisfy the following equation:

$$(-\frac{1}{c^2}\frac{\partial^2}{\partial t^2}+\nabla^2)G_i^\mu(r-r',t-t') = \delta(t-t')[0,\nabla\times(\delta(\rho-\rho')\delta(z-z')\widehat{e}_i)] \tag{34}$$

We assume the material has size L^2. By defining the discrete Fourier transformation,

$$G_\mu^i(\vec{r},t) = \frac{1}{L^2}\sum_{\vec{q}}\int\frac{d\omega}{2\pi}G_\mu^i(z,\vec{q},\omega)e^{i\vec{q}\cdot\vec{\rho}-\omega t} \tag{35}$$

then the Green function equation becomes

$$\left(\frac{\omega^2}{c^2}-q_x^2-q_y^2+\partial_z^2\right)G_i^\mu(z,\vec{q},\omega) = [0,(iq_x,iq_y,\partial_z)\times(\delta(z-z')\widehat{e}_i)]^\mu \tag{36}$$

The solution can be found as

$$G_x^\mu(z,\vec{q},\omega) = \frac{e^{-\lambda|z|}}{2}\begin{pmatrix} 0 \\ 0 \\ sign(z) \\ \frac{iq_y}{\lambda} \end{pmatrix}^\mu \tag{37}$$

$$G_y^\mu(z,\vec{q},\omega) = \frac{e^{-\lambda|z|}}{2}\begin{pmatrix} 0 \\ -sign(z) \\ 0 \\ -\frac{iq_x}{\lambda} \end{pmatrix}^\mu \tag{38}$$

$$G_z^\mu(z,\vec{q},\omega) = \frac{e^{-\lambda|z|}}{2}\begin{pmatrix} 0 \\ -\frac{iq_y}{\lambda} \\ \frac{iq_x}{\lambda} \\ 0 \end{pmatrix}^\mu \tag{39}$$

where $\lambda = \sqrt{\vec{q}^2 - \frac{\omega^2}{c^2}}$. By defining Fourier transformation as

$$A^\mu(\vec{r},t) = \frac{1}{\sqrt{L^2}}\sum_{\vec{q}}\int\frac{d\omega}{2\pi}A^\mu(z,\vec{q},\omega)e^{i(\vec{q}\cdot\vec{\rho}-\omega t)} \tag{40}$$

$$m_i(\vec{r},t) = \frac{1}{\sqrt{L^2}}\sum_{\vec{q}}\int\frac{d\omega}{2\pi}m_i(\vec{q},\omega)e^{i(\vec{q}\cdot\vec{\rho}-\omega t)}\delta(z), \tag{41}$$

we can verify that

$$A^\mu(z,\vec{q},\omega) = \mu_0 G_i^\mu(z,\vec{q},\omega)m_i(\vec{q},\omega). \tag{42}$$

And we can express $B(\vec{r},t)$ as

$$\vec{B}(\vec{r},t) = \frac{\mu_0}{\sqrt{L^2}}\int\frac{d\omega}{2\pi}\sum_{\vec{q}}\left[(iq_x,iq_y,\partial_z)\times G_i^\mu(z,\vec{q},\omega)\right]m_i(\vec{q},\omega)e^{i(\vec{q}\cdot\vec{\rho}-\omega t)} \tag{43}$$

$$= \frac{\mu_0}{\sqrt{L^2}}\sum_{\vec{q}}\int\frac{d\omega}{2\pi}\vec{H}_i(z,\vec{q},\omega)m_i(\vec{q},\omega)e^{i(\vec{q}\cdot\vec{\rho}-\omega t)}, \tag{44}$$

where $\vec{H}_i(z,\vec{q},\omega) = (iq_x,iq_y,\partial_z)\times\vec{G}_i(z,\vec{q},\omega)$.

From Eq.21, the important relation is

$$-\chi_{ij}^{''}(t) = \frac{1}{2}\langle[B^i(t),B^j(0)]\rangle \tag{45}$$

or in Fourier space

$$-\chi_{ij}''(\omega) = \int dte^{i\omega t}\frac{1}{2}\langle[B^i(t), B^j(0)]\rangle \tag{46}$$

We are going to use these relation to derive relaxation time as a function of spin-spin retarded green function. In the following, we define

$$S_{ij}(\omega) = \int dte^{i\omega t}\frac{1}{2}\langle[B^i(t), B^j(0)]\rangle \tag{47}$$

3 Appendix

Proof: $\langle m_\alpha(\vec{q}_1, \omega_1) m_\beta(\vec{q}_2, \omega_2)\rangle = \delta(\omega_1 + \omega_2)\delta(\vec{q}_1 + \vec{q}_2)\langle m_\alpha(\vec{q}_1, \omega_1) m_\beta(-\vec{q}_1, -\omega_1)\rangle$.
Because

$$\langle m_\alpha(t_1, \rho_1) m_\beta(t_2, \rho_2)\rangle = \langle m_\alpha(t_1 - t_2, \rho_1 - \rho_2) m_\beta(0, 0)\rangle \tag{48}$$

$$\sum_{\vec{q}_1,\vec{q}_2} \int \frac{d\omega_1}{2\pi} \int \frac{d\omega_2}{2\pi} e^{-i\omega_1 t_1 - i\omega_2 t_2 + iq_1\rho_1 + iq_2\rho_2} \langle m_\alpha(\omega_1, q_1) m_\beta(\omega_2, q_2)\rangle \tag{49}$$

$$= \sum_{\vec{q}_1,\vec{q}_2} \int \frac{d\omega_1}{2\pi} \int \frac{d\omega_2}{2\pi} e^{-i\omega_1(t_1 - t_2)} e^{iq_1(\rho_1 - \rho_2)} \langle m_\alpha(\omega_1, \vec{q}_1) m_\beta(\omega_2, \vec{q}_2)\rangle \tag{50}$$

Therefore, $\omega_1 = -\omega_2, \vec{q}_1 = -\vec{q}_2$.