Spin correlation from nuclear magnetic resonance

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There is a hyperfine interaction between the nuclear magnetic moment and electron magnetic moment. The magnetic moments (or electron spins) are magnetically ordered below a critical temperatures, forming the ordered phase (ferromagnets, antiferromagnets, and so on). The spin dynamics can be detected through the magnetic resonance of nuclear magnetic moment through the hyperfine interaction. The nuclear magnetic resonance (NMR) has several advantages
(i) The atomic sites can be specifically selected for the observation of the resonance.
(ii) The spin dynamics can be observed through the measurement of the characteristic relaxation times (T_1 and T_2). The NMR as well as the magnetic neutron scattering provides tools for the direct observation of the Fourier transform of the time-dependent spin-spin correlation function.

1. Longitudinal relaxation time

We assume that the operator of the hyperfine interaction is expressed by

$$H'_{\perp} = -\gamma\hbar \boldsymbol{I}\cdot\boldsymbol{H}_{hf} = -\frac{\gamma\hbar}{2}(I^{+}H_{hf}{}^{-} + I^{-}H_{hf}{}^{+})$$

The characteristic time T_1 (longitudinal relaxation time) given by

$$\begin{aligned}
\frac{1}{T_1} &= \frac{2\pi}{\hbar}\left(\frac{\gamma\hbar}{2}\right)^2 \sum_{n,m}\frac{e^{-\beta\varepsilon_n}}{Z}[\left|\langle m|H_{hf}{}^{+}|n\rangle\right|^2\delta(\varepsilon_m-\varepsilon_n+\hbar\omega_0)+\left|\langle m|H_{hf}{}^{-}|n\rangle\right|^2\delta(\varepsilon_m-\varepsilon_n-\hbar\omega_0)] \\
&= \frac{2\pi}{\hbar^2}\left(\frac{\gamma\hbar}{2}\right)^2 \sum_{n,m}\frac{e^{-\beta\varepsilon_n}}{Z}[\left|\langle m|H_{hf}{}^{+}|n\rangle\right|^2\delta(\frac{\varepsilon_m-\varepsilon_n+\hbar\omega_0}{\hbar})+\left|\langle m|H_{hf}{}^{-}|n\rangle\right|^2\delta(\frac{\varepsilon_m-\varepsilon_n-\hbar\omega_0}{\hbar})] \\
&= \frac{2\pi\gamma^2}{4}\sum_{n,m}\frac{e^{-\beta\varepsilon_n}}{Z}[\left|\langle m|H_{hf}{}^{+}|n\rangle\right|^2\frac{1}{2\pi}\int_{-\infty}^{\infty}dt\exp\{i(\frac{\varepsilon_m-\varepsilon_n+\hbar\omega_0}{\hbar})t\} \\
&\quad +\left|\langle m|H_{hf}{}^{-}|n\rangle\right|^2\frac{1}{2\pi}\int_{-\infty}^{\infty}dt\exp\{i(\frac{-\varepsilon_m+\varepsilon_n+\hbar\omega_0}{\hbar})t\}] \\
&= \frac{\gamma^2}{4}\sum_{n,m}\frac{e^{-\beta\varepsilon_n}}{Z}\int_{-\infty}^{\infty}dte^{i\omega_0 t}[\langle m|H_{hf}{}^{+}|n\rangle\langle n|H_{hf}{}^{-}|m\rangle\exp\{i(\frac{\varepsilon_m-\varepsilon_n}{\hbar})t\}+ \\
&\quad +\langle m|H_{hf}{}^{-}|n\rangle\langle n|H_{hf}{}^{+}|m\rangle\exp\{i(\frac{-\varepsilon_m+\varepsilon_n}{\hbar})t\}]
\end{aligned}$$

or

$$\frac{1}{T_1}=\frac{\gamma^2}{4}\sum_{n,m}\frac{e^{-\beta\varepsilon_n}}{Z}\int_{-\infty}^{\infty}dte^{i\omega_0 t}[\langle n|H_{hf}{}^{-}|m\rangle\langle m|e^{\frac{iHt}{\hbar}}H_{hf}{}^{+}e^{-\frac{iHt}{\hbar}}|n\rangle\}+\langle n|e^{\frac{iHt}{\hbar}}H_{hf}{}^{+}e^{-\frac{iHt}{\hbar}}|m\rangle\langle m|H_{hf}{}^{-}|n\rangle]$$

$$=\frac{\gamma^2}{4}\sum_{n,m}\frac{e^{-\beta\varepsilon_n}}{Z}\int_{-\infty}^{\infty}dte^{i\omega_0 t}[\langle n|H_{hf}{}^{-}|m\rangle\langle m|H_{hf}{}^{+}(t)|n\rangle\}+\langle n|H_{hf}{}^{+}(t)|m\rangle\langle m|H_{hf}{}^{-}|n\rangle]$$

$$=\frac{\gamma^2}{4}\sum_{n}\frac{e^{-\beta\varepsilon_n}}{Z}\int_{-\infty}^{\infty}dte^{i\omega_0 t}[\langle n|H_{hf}{}^{-}H_{hf}{}^{+}(t)|n\rangle\}+\langle n|H_{hf}{}^{+}(t)H_{hf}{}^{-}|n\rangle]$$

$$=\frac{\gamma^2}{2}\int_{-\infty}^{\infty}dte^{i\omega_0 t}\left\langle\{H_{hf}{}^{-}(0),H_{hf}{}^{+}(t)\}\right\rangle$$

where Z is the partition function, and ω_0 is the resonance frequency,

$$\{H_{hf}{}^{-},H_{hf}{}^{+}(t)\}=\frac{1}{2}(H_{hf}{}^{-}H_{hf}{}^{+}(t)+H_{hf}{}^{+}(t)H_{hf}{}^{-})$$

$$H_{hf}{}^{+}(t)=e^{\frac{iHt}{\hbar}}H_{hf}{}^{+}e^{-\frac{iHt}{\hbar}}\qquad\text{(Heisenberg representation)}$$

$$H_{hf}{}^{\pm}=H_{hf}{}^{x}\pm iH_{hf}{}^{y}$$

$$I^{\pm}=I_v\pm iI_y$$

Using the fluctuation-dissipation theorem, we have

$$\frac{1}{T_1}=\frac{\gamma^2}{2}\int_{-\infty}^{\infty}dte^{i\omega_0 t}\left\langle\{H_{hf}{}^{-}(0),H_{hf}{}^{+}(t)\}\right\rangle$$

$$=\frac{\gamma^2}{2}\hbar\coth(\frac{\hbar\omega_0}{2k_BT})\frac{\omega_0}{2}\int_{-\infty}^{\infty}dte^{i\omega_0 t}\left\langle H_{hf}{}^{-}(0)H_{hf}{}^{+}(t)\right\rangle$$

$$=\frac{\gamma^2}{2}\hbar\coth(\frac{\hbar\omega_0}{2k_BT})\,\mathrm{Im}\,\chi_{loc}^{+-}(\omega_0)$$

$$\approx\gamma^2k_BT\frac{\mathrm{Im}\,\chi_{loc}^{+-}(\omega_0)}{\omega_0}$$

Note that

$$\int_{-\infty}^{\infty} dt e^{i\omega_0 t}\left\langle \{H_{hf}^{-}(0), H_{hf}^{+}(t)\}\right\rangle = \frac{\hbar\omega_0}{2}\coth(\frac{\hbar\omega_0}{2k_B T})\int_{-\infty}^{\infty} dt e^{i\omega_0 t}\left\langle H_{hf}^{-}(0)H_{hf}^{+}(t)\right\rangle$$

(Moriya)

2. Fluctuation of local field: frequency spectrum

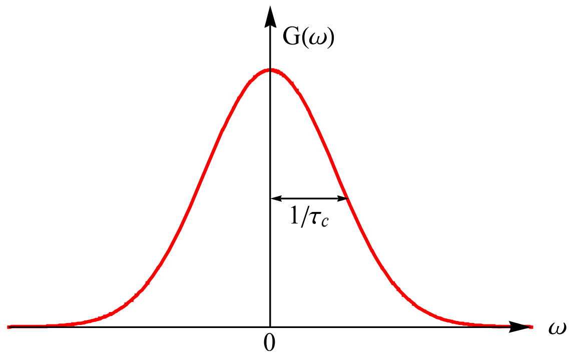

Fig. Fluctuation of the local magnetic field and the relaxation time τ_c.

$$G(\omega) = \frac{1}{2}\int_{-\infty}^{\infty} dt e^{i\omega t}\left\langle \{H_{hf}^{-}(0), H_{hf}^{+}(t)\}\right\rangle$$

$$\begin{aligned}
\int_{-\infty}^{\infty} d\omega G(\omega) &= \frac{1}{2}2\pi\int_{-\infty}^{\infty} dt\delta(t)\left\langle \{H_{hf}^{-}(0), H_{hf}^{+}(t)\}\right\rangle \\
&= \frac{1}{2}2\pi\left\langle \{H_{hf}^{-}(0), H_{hf}^{+}(0)\}\right\rangle \\
&= 2\pi\left\langle \left(H_{hf}^{x}(0)\right)^2 + \left(H_{hf}^{y}(0)\right)^2\right\rangle \\
&= 2\pi\left\langle \left(\boldsymbol{H}_{hf}(0)\right)^2\right\rangle \\
&\approx \frac{2G(\omega=0)}{\tau_c}
\end{aligned}$$

where $\left\langle \left(\boldsymbol{H}_{hf}(0)\right)^2\right\rangle = H_{loc}^2$, γH_{loc} is an instantraneous Larmor frequency for the nuclear spin, τ_c is the correlation time of the fluctuation. Note that $\omega_0 << 1/\tau_c$. So we can assume that $\omega_0 = 0$. Then we get

$$\frac{1}{T_1} = \gamma^2 G(\omega_0) \approx \gamma^2 G(\omega = 0) \approx \pi\gamma^2\left\langle \left(\boldsymbol{H}_{hf}\right)^2\right\rangle \tau_c = \pi\gamma^2\left\langle H_{loc}^2\right\rangle \tau_c$$

As τ_c becomes shorter, $1/T_1$ becomes small (motional narrowing).

4. Physical meaning for motional narrowing (Brownian motion)

4.1 One dimensional model of Brown motion (MacDonald)

We consider a simple model of Brownian movement, or so called random walk model, in one dimension. Consider a particle starting at $x = 0$ at $t = 0$, which suffers impacts at a steady rate per second. Each impact causes the particle to jump a small distance l, of constant magnitude, either in the positive or negative direction of x, and we assume that these steps of $+l$ or $-l$ are uncorrelated with one another.

Let us denote the n-th step by ln ($l_n = \pm$l), and consequently the total displacement x after N steps will be given by

$$x = \sum_{n=1}^{N} l_n \ .$$

It is obvious that if each and every l_n is equally likely to be either positive or negative, then on the average we have

$$\langle x \rangle = \sum_{n=1}^{N} \langle l_n \rangle = \langle l_1 + l_2 + \cdots + l_N \rangle = \langle l_1 \rangle + \langle l_2 \rangle + \cdots + \langle l_N \rangle = 0 \ .$$

The brackets < > signify an average taken over a large group of many similar observations of the displacement x.

We consider next the behavior of x^2,

$$\langle x^2 \rangle = \langle (l_1 + l_2 + \cdots + l_N)(l_1 + l_2 + \cdots + l_N) \rangle = \sum_{n=1}^{N} \langle l_n^{\ 2} \rangle + \sum_{n \neq m}^{N} \langle l_n l_m \rangle \ .$$

We note that

$$l_n^{\ 2} = l^2 \ .$$

On the other hand, in the second summation for cases are possible for each product, namely,

$$(+l,+l) = l^2 \ ; \qquad (+l,-l) = -l^2 \ ; \qquad (-l,+l) = -l^2 \ ; \qquad (-l,-l) = l^2 \ ;$$

If these products are supposed to occur with equal probability – and this corresponds to a complete lack of correlation between individual steps- then evidently the average of this type of term will be zero; $\langle l_n l_m \rangle$. Thus for a random walk with no correlation between successive steps,

$$\langle x^2 \rangle = Nl^2 ,$$

or

$$\sqrt{\langle x^2 \rangle} = \sqrt{N} l .$$

4.2 Line-width

T_2 is a measure of the time in which an individual spin becomes dephased by one radian because of a local perturbation in the magnetic field intensity. Let γh_n denote the local frequency deviation due to a perturbation h_n. Suppose that the local field has either a positive value h or a negative value $-h$ for an average time t or $-h$. In the time τ the spin will process by an extra phase angle

$$\delta\varphi = \pm\gamma h \tau$$

relative to the phase angle of the steady precession in the applied field H0,

$$\varphi_0 = \gamma H_0$$

After the N intervals of duration τ, the mean square dephasing angle in the field H_0 will be

$$\langle \varphi^2 \rangle = N(\delta\varphi)^2 = N\gamma^2 h^2 \tau$$

by analogy with a random walk process. The average number of steps necessary to depahe a spin by one radian is

$$\sqrt{\langle \varphi^2 \rangle} = \sqrt{N\gamma^2 h^2 \tau^2} = 1$$

or

$$N = \frac{1}{\gamma^2 h^2 \tau^2}$$

(spins dephased by much more than one radian do not contribute to the absorption signal). The number of steps takes place in a time T_2,

$$T_2 = N\tau = \frac{1}{\gamma^2 h^2 \tau}$$

or

$$\frac{1}{T_2} = \tau(\gamma h)^2$$

This means that the shorter is τ (rapid motion), the narrower is the resonance line width $1/T_2$.

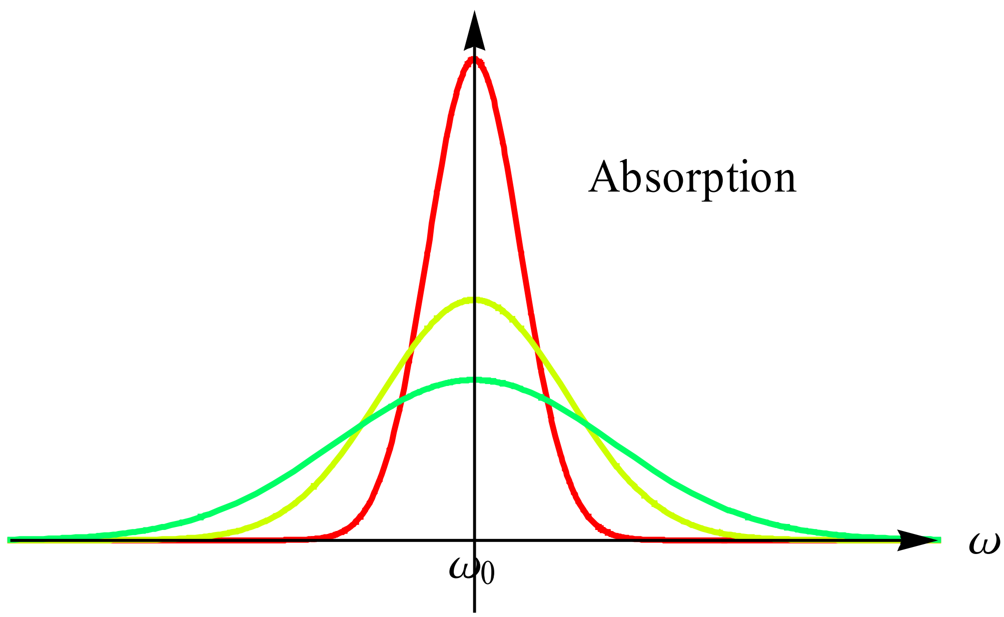

Fig. Motional narrowing effect

5. $1/T_1$ and Spin correlation

Here we show that $1/T_1$ can be closely related to the Fourier transform of the spin-spin correlation function. We start with the expression given by

$$\frac{1}{T_1} = \frac{\gamma^2}{2} \int_{-\infty}^{\infty} dt e^{i\omega_0 t} \left\langle \{H_{hf}^{-}(0), H_{hf}^{+}(t)\} \right\rangle$$

Here we assume that the hyperfine field can be expressed by

$$\boldsymbol{H}_{hf}(t) = \sum_{q} \boldsymbol{A}_q \cdot \boldsymbol{S}_q$$

where $\boldsymbol{A}_q$ is the tensor. We use the Fourier transform

$$\boldsymbol{S}_{\boldsymbol{q}} = \frac{1}{\sqrt{N}} \sum_{j} \boldsymbol{S}_j e^{i\boldsymbol{q}\cdot\boldsymbol{r}_j} , \qquad \boldsymbol{S}_j = \frac{1}{\sqrt{N}} \sum_{\boldsymbol{q}} \boldsymbol{S}_{\boldsymbol{q}} e^{-i\boldsymbol{q}\cdot\boldsymbol{r}_j}$$

$$\boldsymbol{A}_{\boldsymbol{q}} = \frac{1}{\sqrt{N}} \sum_{j} \boldsymbol{A}_j e^{-i\boldsymbol{q}\cdot\boldsymbol{r}_j} , \qquad \boldsymbol{A}_{\boldsymbol{q}}^{*} = \frac{1}{\sqrt{N}} \sum_{j} \boldsymbol{A}_j e^{i\boldsymbol{q}\cdot\boldsymbol{r}_j} = \boldsymbol{A}_{-q}$$

$$\begin{aligned}
\sum_{\boldsymbol{q}} \boldsymbol{A}_{\boldsymbol{q}} \cdot \boldsymbol{S}_{\boldsymbol{q}} &= \frac{1}{N} \sum_{\boldsymbol{q}} \sum_{j,k} \boldsymbol{A}_j \cdot \boldsymbol{S}_k e^{i\boldsymbol{q}\cdot(\boldsymbol{r}_k - \boldsymbol{r}_j)} \\
&= \frac{1}{N} \sum_{j,k} \boldsymbol{A}_j \cdot \boldsymbol{S}_k \sum_{\boldsymbol{q}} e^{i\boldsymbol{q}\cdot(\boldsymbol{r}_k - \boldsymbol{r}_j)} \\
&= \sum_{j,k} \boldsymbol{A}_j \cdot \boldsymbol{S}_k \delta_{j,k} = \sum_{j} \boldsymbol{A}_j \cdot \boldsymbol{S}_j
\end{aligned}$$

For simplicity we assume that the anisotropy of tensor $\boldsymbol{A}_{\boldsymbol{q}}$ is neglected.

$$H_{hf}^{\ -}(0) = \sum_{\boldsymbol{q}} A_{\boldsymbol{q}} S_{\boldsymbol{q}}^{\ -}(0), \qquad H_{hf}^{\ +}(t) = \sum_{\boldsymbol{q}'} A_{\boldsymbol{q}'} S_{\boldsymbol{q}'}^{\ +}(t)$$

and

$$\begin{aligned}
\left\langle \{H_{hf}^{\ -}(0), H_{hf}^{\ +}(t)\} \right\rangle &= \left\langle \{\sum_{\boldsymbol{q}} A_{\boldsymbol{q}} S_{\boldsymbol{q}}^{\ -}(0), \sum_{\boldsymbol{q}'} A_{\boldsymbol{q}'} S_{\boldsymbol{q}'}^{\ +}(t)\} \right\rangle \\
&= \sum_{\boldsymbol{q},\boldsymbol{q}'} A_{\boldsymbol{q}} A_{\boldsymbol{q}'} \left\langle \{S_{\boldsymbol{q}}^{\ -}(0), S_{\boldsymbol{q}'}^{\ +}(t)\} \right\rangle
\end{aligned}$$

Note that

$$\left\langle \{S_{\boldsymbol{q}}^{\ -}(0), S_{\boldsymbol{q}'}^{\ +}(t)\} \right\rangle = \left\langle \{S_{\boldsymbol{q}}^{\ -}(0), S_{-\boldsymbol{q}}^{\ +}(t)\} \right\rangle \delta(\boldsymbol{q} + \boldsymbol{q}')$$

we get

$$\left\langle\{H_{hf}^{-}(0),H_{hf}^{+}(t)\}\right\rangle=\sum_{\boldsymbol{q},\boldsymbol{q}'}A_{\boldsymbol{q}}A_{\boldsymbol{q}'}\left\langle\{S_{\boldsymbol{q}}^{-}(0),S_{-\boldsymbol{q}}^{+}(t)\}\right\rangle\delta(\boldsymbol{q}+\boldsymbol{q}')$$
$$=\sum_{\boldsymbol{q}}A_{\boldsymbol{q}}A_{-\boldsymbol{q}}\left\langle\{S_{\boldsymbol{q}}^{-}(0),S_{-\boldsymbol{q}}^{+}(t)\}\right\rangle$$
$$=\sum_{\boldsymbol{q}}\left|A_{\boldsymbol{q}}\right|^{2}\left\langle\{S_{\boldsymbol{q}}^{-}(0),S_{-\boldsymbol{q}}^{+}(t)\}\right\rangle$$

Using the fluctuation-dissipation theorem, we get

$$\frac{1}{T_1}=\frac{\gamma^2}{2}\sum_{\boldsymbol{q}}\left|A_{\boldsymbol{q}}\right|^{2}\int_{-\infty}^{\infty}dte^{i\omega_0 t}\left\langle\{S_{\boldsymbol{q}}^{-}(0),S_{-\boldsymbol{q}}^{+}(t)\}\right\rangle=\gamma^2 k_B T\sum_{\boldsymbol{q}}\left|A_{\boldsymbol{q}}\right|^{2}\frac{\operatorname{Im}\chi(\boldsymbol{q},\omega)}{\omega_0}$$

where $\operatorname{Im}\chi(\boldsymbol{q},\omega)=\chi''(\boldsymbol{q},\omega)$ is the imaginary part of the dynamics susceptibility. From the measurement of $1/T_2$, we may get the information of the dynamics susceptibility in the limit of low frequency. Here we note that

$$\frac{\operatorname{Im}\chi(\boldsymbol{q},\omega)}{\omega_0}=\chi(\boldsymbol{q},0)f_q(\omega)\,,$$

with the Lorentz distribution

$$f_q(\omega)=\frac{\pi\Gamma_{\boldsymbol{q}}}{\omega^2+\Gamma_{\boldsymbol{q}}^{2}}\,,$$

where $\chi(\boldsymbol{q},0)$ is the wave-vector dependent susceptibility and $\Gamma_{\boldsymbol{q}}$ is the characteristic relaxation rate. We assume that $f_{\boldsymbol{q}}(\omega)=f_{\boldsymbol{q}}(\omega=0)=\dfrac{\pi}{\Gamma_{\boldsymbol{q}}}$. Then we have

$$\frac{1}{T_1}=\gamma^2 k_B T\sum_{\boldsymbol{q}}\left|A_{\boldsymbol{q}}\right|^{2}\frac{\pi\chi(\boldsymbol{q}=0)}{\Gamma_{\boldsymbol{q}}}\approx\gamma^2 k_B T\left|A\right|^{2}\sum_{\boldsymbol{q}}\frac{\pi\chi(\boldsymbol{q}=0)}{\Gamma_{\boldsymbol{q}}}$$

5. The expression of T_2

$$\frac{1}{T_2}=\frac{1}{2T_1}+\int_{-\infty}^{\infty}\left\langle\left\{H_{hf}^{z}(0),H_{hf}^{z}(t)\right\}\right\rangle dt$$

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