Problem set for Solid-state NMR (SSNMR) Winter School 2008

Solid-state NMR of paramagnetic systems

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(1) Explain the thermal averaging mechanism of pseudo contact shift. What are the requirements for the electron spin system when pseudo contact shifts are observed in SSNMR?

(2) Explain the mechanism of contact shift. What are the requirements for the orbital for an unpaired electron when one can observe contact shift for a certain nucleus in SSNMR?

(3) What is the relationship between the spin-orbit coupling and g-tensor in general?

(4) What is the reason why pseudo contact shift is observed as anisotropic shift for systems with isotropic g-tensor?

(5) What is the definition of "susceptibility tensor"? What is the relationship between g-tensor and susceptibility tensor?

(6) Give a proof for the following equation

$$\sum_{\xi}\sum_{jkl}\boldsymbol{e}_j g_e B_0 < \xi \mid S_j S_Z \mid \xi > \mu_B /\{(kT)Tr(1)\} = g_e \boldsymbol{B}_0 \{S(S+1)\}\mu_B /(3kT)$$

(7) Assume that an isolated electron spin $\boldsymbol{S}_1$ (S_1 =1/2) is localized at the Cu(II) metal center, which is separated from ^{13}C by the distance *R*. How much anisotropic ^{13}C hyperfine shift is expected for the ^{13}C system? Answer the largest principal component of the pseudo contact tensor.

(8) Assume that electron spins $\boldsymbol{S}_1$ and $\boldsymbol{S}_2$ in two Cu(II) ions are separated from ^{13}C by *R* and $(1/2)^{1/3}R$. What is the range of the largest principal component of the pseudo contact tensor for the ^{13}C system?

(9) T_1 relaxation rate of a nuclear spin *I* in solids for paramagnetic systems due to dipolar contribution is given by

$$R_1^{SL} = \frac{2S(S+1)}{15}\left(\frac{\mu_0\hbar\gamma_I\gamma_S}{4\pi R^3}\right)^2\left\{\frac{\tau_C}{1+(\omega_I-\omega_S)^2\tau_C{}^2}+\frac{3\tau_C}{1+\omega_I{}^2\tau_C{}^2}+\frac{6\tau_C}{1+(\omega_I+\omega_S)^2\tau_C{}^2}\right\}$$

ω_I and ω_S denote nuclear and electron resonance frequency (angular frequency), respectively. What does τ_C donote in this equation? Which term is most dominant for solids? Why?