University of Washington
Department of Chemistry
Chemistry 553
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Lecture 28: The Redfield Equation and Its Applications

A. Dynamics of Nuclear Magnetization in an External Field

- A system composed of spin ½ nuclei is placed in a static magnetic field B_0., assumed parallel to the z axis of the laboratory frame. The equilibrium Hamiltonian (i.e. the Zeeman interaction) is

$$H_0 = -\mu_z B_0 = -\hbar\gamma B_0 I_z = -\hbar\omega_0 I_z \tag{28.1}$$

- The perturbation Hamiltonian is defined as

$$H_1(t) = -\sum_{q=x,y,z} \mu_q E_q(t) = -\hbar\gamma \sum_{q=x,y,z} I_q E_q(t) \tag{28.2}$$

- In the laboratory frame the equation of motion for the density operator is:

$$\begin{gathered}\frac{\partial \sigma^*_{\alpha\alpha'}}{\partial t} = \frac{\partial}{\partial t}\left(e^{iH_0t/\hbar}\sigma e^{-iH_0t/\hbar}\right)_{\alpha\alpha'} = \left(e^{iH_0t/\hbar}\frac{\partial\sigma}{\partial t}e^{-iH_0t/\hbar}\right)_{\alpha\alpha'} + \frac{i}{\hbar}\left(e^{iH_0t/\hbar}\left[H_0,\sigma\right]e^{-iH_0t/\hbar}\right)_{\alpha\alpha'} \\ \therefore \frac{\partial\sigma_{\alpha\alpha'}}{\partial t} = -\frac{i}{\hbar}\left[H_0,\sigma\right]_{\alpha\alpha'} + \sum_{\beta\beta'} R_{\alpha\alpha'\beta\beta'}\left(\sigma-\sigma_{eq}\right)_{\beta\beta'}\end{gathered} \tag{28.3}$$

- An ensemble property is always the trace of the property operator with the density matrix. So for the r (=x,y,or z) component of the magnetization:

$$\left\langle M_r(t)\right\rangle = Tr\left(\sigma(t)\mu_r\right) = \hbar\gamma\sum_{\alpha}\left\langle\alpha\right|\sigma(t)I_r\left|\alpha\right\rangle = \hbar\gamma\sum_{\alpha\alpha'}\sigma_{\alpha\alpha'}(t)\left(I_r\right)_{\alpha'\alpha} \tag{28.4}$$

- And the time derivative is

$$\frac{d}{dt}\left\langle M_r(t)\right\rangle = \hbar\gamma\sum_{\alpha\alpha'}\left(I_r\right)_{\alpha'\alpha}\frac{d\sigma_{\alpha\alpha'}(t)}{dt} \tag{28.5}$$

- Equation (27.21) is combined with the Redfield equation (27.19)

$$\begin{aligned}\frac{d}{dt}\left\langle M_r(t)\right\rangle &= \hbar\gamma\sum_{\alpha\alpha'}\left(I_r\right)_{\alpha'\alpha}\frac{d\sigma_{\alpha\alpha'}(t)}{dt} \\ &= \hbar\gamma\sum_{\alpha\alpha'}\left(-\frac{i}{\hbar}\left[H_0,\sigma\right]_{\alpha\alpha'} + \sum_{\beta\beta'}R_{\alpha\alpha'\beta\beta'}\left(\sigma-\sigma_{eq}\right)_{\beta\beta'}\right)\left(I_r\right)_{\alpha'\alpha}\end{aligned} \tag{28.6}$$

B. Nuclear Spin Precession

- The first term on the right of (28.6) is easy to evaluate and interpret;
- $$\begin{aligned}&\sum_{\alpha\alpha'} -\frac{i}{\hbar}\left[H_0,\sigma\right]_{\alpha\alpha'}\left(I_r\right)_{\alpha'\alpha} = -\frac{i}{\hbar}\sum_{\alpha}\left(\left[H_0,\sigma\right]I_r\right)_{\alpha\alpha} = -\frac{i}{\hbar}Tr\left(\left[H_0,\sigma\right]I_r\right) \\ &= -\frac{i}{\hbar}Tr\left(\left[I_r,H_0\right]\sigma\right) = \hbar\gamma B_0\frac{i}{\hbar}Tr\left(\left[I_r,I_z\right]\sigma\right) = -i\gamma B_0 Tr\left(\left[I_z,I_r\right]\sigma\right)\end{aligned} \tag{28.7}$$
- The commutator follows the rule of the commutation of Pauli spin matrices.

$$\left[I_i,I_j\right] = iI_k \quad i,j,k = x,y,z \tag{28.8}$$

- The result $-i\gamma B_0 Tr\left(\left[I_z, I_r\right]\sigma\right)$ depends upon the value of r. If we examine the longitudinal magnetization, z=r and the commutator is zero. If r=x then

$$-i\gamma B_0 Tr\left(\left[I_z, I_x\right]\sigma\right) = -i\gamma B_0 Tr\left(iI_y\sigma\right) = \gamma B_0 Tr\left(I_y\sigma\right) \qquad (28.9)$$

- The first term in on the rhs of (28.11) is the torque exerted by the magnetic field on the magnetic moment. If r=z there is no torque because the moment is parallel to the field. This torque term effect a precession of the magnetic moment about the field direction. The torque equation is also called the Bloch equation.

  - In (28.11) the second term effects relaxation:

$$\frac{d\langle M_r\rangle}{dt} = \hbar\gamma\sum_{\alpha\alpha'}\left(-\frac{i}{\hbar}\left[H_0, \sigma\right]_{\alpha\alpha'} + \sum_{\beta\beta'} R_{\alpha\alpha'\beta\beta'}\left(\sigma - \sigma_{eq}\right)_{\beta\beta'}\right)\left(I_r\right)_{\alpha'\alpha} \qquad (28.10)$$

- In the next lecture we will deal with with

$$\hbar\gamma\sum_{\alpha\alpha'\beta\beta'} R_{\alpha\alpha'\beta\beta'}\left(\sigma - \sigma_{eq}\right)_{\beta\beta'}\left(I_r\right)_{\alpha\alpha'} \qquad (28.11)$$

C. Relaxation of Longitudinal Nuclear Magnetization

- The relaxation operator is composed of a number of spectral densities evaluated at the ‘natural” frequencies of the system according to

$$R_{\alpha\alpha'\beta\beta'} = -\frac{1}{2\hbar^2}\left[\left(J_{\alpha\beta\alpha'\beta'}\left(\omega_\alpha - \omega_\beta\right) + J_{\alpha\beta\alpha'\beta'}\left(\omega_{\alpha'} - \omega_{\beta'}\right)\right) - \delta_{\beta'\alpha'}\sum_\gamma J_{\gamma\beta\gamma\alpha}\left(\omega_\gamma - \omega_\beta\right) - \delta_{\alpha\beta}\sum_\gamma J_{\gamma\alpha'\gamma\beta'}\left(\omega_\gamma - \omega_{\beta'}\right)\right]$$

(28.12)

- The meaning of this term is that relaxation is effected by fluctuations originating within the lattice that couple to the spin system at “natural” frequencies. As an example, consider the first term

$$\begin{aligned}
&-\frac{1}{2\hbar^2}\sum_{\alpha\alpha'\beta\beta'} J_{\alpha\beta\alpha'\beta'}\left(\omega_\alpha - \omega_\beta\right)\left(\sigma - \sigma_{eq}\right)_{\beta\beta'}\left(I_r\right)_{\alpha\alpha'} \\
&= -\frac{1}{2\hbar^2}\sum_{\alpha\alpha'\beta\beta'}\int_{-\infty}^{+\infty} d\tau G_{\alpha\beta\alpha'\beta'}(\tau) e^{-i\left(\omega_\alpha - \omega_\beta\right)\tau}\left(\sigma - \sigma_{eq}\right)_{\beta\beta'}\left(I_r\right)_{\alpha'\alpha} \\
&= -\frac{1}{2\hbar^2}\sum_{\alpha\alpha'\beta\beta' n}\int_{-\infty}^{+\infty} d\tau \left\langle \left(H_1(t)_{\alpha\beta}\right)\left(H_1(t-\tau)_{\beta'\alpha'}\right)\right\rangle e^{-i\left(\omega_\alpha - \omega_\beta\right)\tau}\left(\sigma - \sigma_{eq}\right)_{\beta\beta'}\left(I_r\right)_{\alpha'\alpha} \\
&= -\frac{\hbar^2\gamma^2}{2\hbar^2}\sum_{\alpha\alpha'\beta\beta' n}\int_{-\infty}^{+\infty} d\tau \left\langle E_n(t) E_n(t-\tau)\right\rangle e^{-i\left(\omega_\alpha - \omega_\beta\right)\tau}\left(\Delta\sigma\right)_{\beta\beta'}\left(I_n\right)_{\beta'\alpha'}\left(I_r\right)_{\alpha'\alpha}\left(I_n\right)_{\alpha\beta} \qquad (28.13) \\
&= -\frac{\gamma^2}{2}\sum_{\alpha\alpha'\beta\beta' n}\int_{-\infty}^{+\infty} d\tau \left\langle E_n(t) E_n(t-\tau)\right\rangle e^{-i\left(\omega_\alpha - \omega_\beta\right)\tau}\left(\Delta\sigma\right)_{\beta\beta'}\left(I_n\right)_{\beta'\alpha'}\left(I_r\right)_{\alpha'\alpha}\left(I_n\right)_{\alpha\beta} \\
&= -\frac{\gamma^2}{2}\sum_{\alpha\beta n}\int_{-\infty}^{+\infty} d\tau \left\langle E_n(t) E_n(t-\tau)\right\rangle e^{-i\left(\omega_\alpha - \omega_\beta\right)\tau}\left(\Delta\sigma I_n I_r\right)_{\beta\alpha}\left(I_n\right)_{\alpha\beta}
\end{aligned}$$

- Applying this analysis to each of the four terms in (28.13) yields:

$$\sum_{\alpha\alpha'\beta\beta'} R_{\alpha\beta\alpha'\beta'}\Delta\sigma_{\beta\beta'}\left(I_r\right)_{\alpha'\alpha} = \frac{\gamma^2}{2}\sum_{\alpha\beta n}\left(I_n\right)_{\beta\alpha}\left(\left[\left[I_r, I_n\right], \Delta\sigma\right]\right)_{\alpha\beta}\int_{-\infty}^{+\infty} d\tau e^{-it\left(\omega_\beta - \omega_\alpha\right)}\left\langle E_n(t)E_n(t-\tau)\right\rangle$$

$$= \frac{\gamma^2}{2}\sum_{\alpha\beta n}\left(I_n\right)_{\beta\alpha}\left(\left[\left[I_r, I_n\right], \Delta\sigma\right]\right)_{\alpha\beta} J_{nn}\left(\omega_{\beta\alpha}\right)$$

where $J_{nn}\left(\omega_{\beta\alpha}\right) = \int_{-\infty}^{+\infty} d\tau e^{-it\left(\omega_\beta - \omega_\alpha\right)}\left\langle E_n(t)E_n(t-\tau)\right\rangle$

(28.14)

- For the relaxation of z magnetization we let r=z. then

$$\sum_{\alpha\alpha'\beta\beta'} R_{\alpha\beta\alpha'\beta'}\Delta\sigma_{\beta\beta'}\left(I_z\right)_{\alpha'\alpha} = \frac{\gamma^2}{2}\sum_{\alpha\beta n}\left(I_n\right)_{\beta\alpha}\left(\left[\left[I_z, I_n\right], \Delta\sigma\right]\right)_{\alpha\beta} J_{nn}\left(\omega_{\beta\alpha}\right)$$

$$= \frac{\gamma^2}{2}\sum_{\alpha\beta}\left\{\left(I_x\right)_{\beta\alpha}\left(\left[\left[I_z, I_x\right], \Delta\sigma\right]\right)_{\alpha\beta} J_{xx}\left(\omega_{\beta\alpha}\right) + \left(I_y\right)_{\beta\alpha}\left(\left[\left[I_z, I_y\right], \Delta\sigma\right]\right)_{\alpha\beta} J_{yy}\left(\omega_{\beta\alpha}\right)\right\}$$

$$= \frac{\gamma^2}{2}\sum_{\alpha\beta}\left\{\left(I_x\right)_{\beta\alpha}\left(\left[iI_y, \Delta\sigma\right]\right)_{\alpha\beta} J_{xx}\left(\omega_{\beta\alpha}\right) + \left(I_y\right)_{\beta\alpha}\left(\left[-iI_x, \Delta\sigma\right]\right)_{\alpha\beta} J_{yy}\left(\omega_{\beta\alpha}\right)\right\}$$

(28.15)

- The remaining summations can be collapsed into traces. This requires setting the frequency difference in the argument of the spectral density. Matrix elements of I_x and I_y involve α and β states with spin quantum numbers that differ by ±1. Therefore the frequency difference is $\omega_0 = \omega_\beta - \omega_\alpha$ where ω_0 is called the Larmor frequency:

$$\sum_{\alpha\alpha'\beta\beta'} R_{\alpha\beta\alpha'\beta'}\Delta\sigma_{\beta\beta'}\left(I_z\right)_{\alpha'\alpha} = \frac{\gamma^2}{2} Tr\left\{I_x\left[iI_y, \Delta\sigma\right]\right\} J_{xx}\left(\omega_0\right) + \frac{\gamma^2}{2} Tr\left\{I_y\left[-iI_x, \Delta\sigma\right]\right\} J_{yy}\left(\omega_0\right)\Big\}$$

$$= \gamma^2 Tr\left\{i\left[I_x, I_y\right]\Delta\sigma\right\} J_{xx}\left(\omega_0\right) + \gamma^2 Tr\left\{-i\left[I_y, I_x\right]\Delta\sigma\right\} J_{yy}\left(\omega_0\right)$$

$$= -\gamma^2 Tr\left\{I_z\Delta\sigma\right\} J_{xx}\left(\omega_0\right) - \gamma^2 Tr\left\{I_z\Delta\sigma\right\} J_{yy}\left(\omega_0\right) = -\gamma^2\left(J_{xx}\left(\omega_0\right) + J_{yy}\left(\omega_0\right)\right)\left(\left\langle I_z\right\rangle - \left\langle I_z\right\rangle_{eq}\right)$$

(28.16)

- The Redfield Equation for the relaxation of the z component of the nuclear magnetization is

$$\frac{d\left\langle M_z\right\rangle}{dt} = \sum_{\alpha\alpha'}\left(-\frac{i}{\hbar}\left[H_0, \sigma\right]_{\alpha\alpha'} + \sum_{\beta\beta'} R_{\alpha\alpha'\beta\beta'}\left(\sigma - \sigma_{eq}\right)_{\beta\beta'}\right)\left(I_z\right)_{\alpha'\alpha}$$

$$= -\gamma^2\left(J_{xx}\left(\omega_0\right) + J_{yy}\left(\omega_0\right)\right)\left(\left\langle I_z\right\rangle - \left\langle I_z\right\rangle_{eq}\right) = -\frac{1}{T_1}\left(\left\langle I_z\right\rangle - \left\langle I_z\right\rangle_{eq}\right) \quad (28.17)$$

- Equation (28.17) means that z magnetization relaxes to its equilibrium value of $\left\langle I_z\right\rangle_{eq}$ as a result of random fields polarized in the x and y directions and which fluctuate at rates near the Larmor frequency ω_0, which is the resonance frequency of the nuclear spins. T_1 is called the spin-lattice relaxation time.

D. Relaxation of Transverse Nuclear Magnetism

- We can calculate the relaxation of M_x and M_y by setting r=x and r=y in equation (28.14). We obtain two equations:

$$\frac{d\left\langle M_x\right\rangle}{dt}=\omega_0\left\langle M_y\right\rangle-\frac{\left\langle M_x\right\rangle}{T_{2x}} \text{ and } \frac{d\left\langle M_y\right\rangle}{dt}=-\omega_0\left\langle M_x\right\rangle-\frac{\left\langle M_y\right\rangle}{T_{2y}} \qquad (28.18)$$

where

$$\frac{1}{T_{2x}}=\gamma^2\left(J_{yy}\left(\omega_0\right)+J_{zz}\left(0\right)\right) \text{ and } \frac{1}{T_{2y}}=\gamma^2\left(J_{xx}\left(\omega_0\right)+J_{zz}\left(0\right)\right) \qquad (28.19)$$

- Experimentally, only the transverse magnetization $M_\perp=M_x+iM_y$ is observed

  Because the rate of transverse relaxation in the x and y directions are much slower than the rate precession at the Larmor frequency, the average rate of relaxation of a period of precession is

$$\frac{1}{T_2}=\frac{1}{2}\left(\frac{1}{T_{2x}}+\frac{1}{T_{2y}}\right) \qquad (28.20)$$