University of Washington
Department of Chemistry
Chemistry 553
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Lecture 27: Redfield Theory: Relaxation in Random Fields
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A. General Theory of Redfield

- Here we dispense with the simplifying assumptions of the last lecture. We consider arbitrary initial conditions and the relaxation of off-diagonal elements of the density matrix.
- Again we assume the Hamiltonian has the form

$$H = H_0 + H_1(t) \tag{27.1}$$

- We can go into an interaction frame

$$H_1^*(t) = e^{iH_0t/\hbar} H_1(t) e^{-iH_0t/\hbar} \text{ and } \rho^*(t) = e^{iH_0t/\hbar} \rho(t) e^{-iH_0t/\hbar} \tag{27.2}$$

- As before we obtain to second order…

$$\frac{d\rho^*}{dt} = -\frac{i}{\hbar}\left[H_1^*(t), \rho^*(0)\right] - \frac{1}{\hbar^2}\int_0^t ds\left[H_1^*(t),\left[H_1^*(s), \rho^*(s)\right]\right] \tag{27.3}$$

(27.4)

- We now consider the $\alpha\alpha'$ matrix element

$$\frac{\partial}{\partial t}\overline{\langle\alpha|\rho^*|\alpha'\rangle} = \frac{\partial\overline{\rho^*_{\alpha\alpha'}}}{\partial t} = \frac{i^2}{\hbar^2}\int_0^t ds\overline{\left[H_1^*(t),\left[H_1^*(s), \rho^*(0)\right]\right]}_{\alpha\alpha'} \tag{27.5}$$

where 27.5 was obtained by ensemble averaging and subsequrntly zeroing out the commutator elements. This is possible to do IF we assume the density matrix and the Hamiltonian average independently. This means we obtain terms like:

$$\overline{\left(H_1^*(t)\rho^*(0)\right)}_{\alpha\alpha'} = \sum_\beta \overline{\left(H_1^*(t)\right)}_{\alpha\beta} \times \overline{\left(\rho^*(0)\right)}_{\beta\alpha'} = 0 \tag{27.6}$$

Because by definition $\overline{\left(H_1^*(t)\right)}_{\alpha\beta} = 0$

- We now expand the nested commutator on the rhs of (27.5). we perform the usual change of variable $\tau = t - s$ and transform back out of the interaction frame. We get:

$$\begin{aligned}
\frac{d\sigma^*_{\alpha\alpha'}}{dt} = -\frac{1}{\hbar^2}\sum_{\beta\beta'}\int_0^t d\tau\Big(& e^{it(\omega_{\alpha\beta}+\omega_{\beta\beta'})}e^{-i\omega_{\beta\beta'}\tau}\overline{\langle\alpha|H_1(t)|\beta\rangle\langle\beta|H_1(t-\tau)|\beta'\rangle}\sigma^*_{\beta'\alpha'}(0) \\
&+ e^{it(\omega_{\beta\beta'}+\omega_{\beta'\alpha'})}e^{-i\omega_{\beta\beta'}\tau}\overline{\langle\beta|H_1(t)|\beta'\rangle\langle\beta'|H_1(t-\tau)|\alpha'\rangle}\sigma^*_{\alpha\beta}(0) \\
&- e^{it(\omega_{\alpha\beta}+\omega_{\beta'\alpha'})}e^{-i\omega_{\beta'\alpha'}\tau}\overline{\langle\alpha|H_1(t)|\beta\rangle\langle\beta'|H_1(t-\tau)|\alpha'\rangle}\sigma^*_{\beta\beta'}(0) \\
& e^{it(\omega_{\beta\beta'}+\omega_{\beta'\alpha'})}e^{-i\omega_{\alpha\beta}\tau}\overline{\langle\alpha|H_1(t)|\beta\rangle\langle\beta'|H_1(t-\tau)|\alpha'\rangle}\sigma^*_{\beta\beta'}(0)\Big)
\end{aligned} \tag{27.7}$$

where $\sigma^*(t)=\overline{\rho^*(t)}$

- We now assume a form for the perturbation Hamiltonian:

$$H_1(t)=\sum_{q=x,y,z}A_qE_q(t) \tag{27.8}$$

- In 27.8 A_q is a system operator that does not commute with H_0 and $E_q(t)$ is a stationary random function of time. We use (27.8) in (27.7):

$$\begin{aligned}\frac{d\sigma^*_{\alpha\alpha'}}{dt}=-\frac{1}{\hbar^2}\sum_{q\beta\beta'}\int_0^t d\tau\Big(&e^{it(\omega_{\alpha\beta}+\omega_{\beta\beta'})}e^{-i\omega_{\beta\beta'}\tau}\left\langle\alpha\middle|A_q\middle|\beta\right\rangle\left\langle\beta\middle|A_q\middle|\beta'\right\rangle\overline{E_q(t)E_q(t-\tau)}\sigma^*_{\beta'\alpha'}(0)\\
&+e^{it(\omega_{\beta\beta'}+\omega_{\beta'\alpha'})}e^{-i\omega_{\beta\beta'}\tau}\left\langle\beta\middle|A_q\middle|\beta'\right\rangle\left\langle\beta'\middle|A_q\middle|\alpha'\right\rangle\overline{E_q(t)E_q(t-\tau)}\sigma^*_{\alpha\beta}(0)\\
&-e^{it(\omega_{\alpha\beta}+\omega_{\beta'\alpha'})}e^{-i\omega_{\beta'\alpha'}\tau}\left\langle\alpha\middle|A_q\middle|\beta\right\rangle\left\langle\beta'\middle|A_q\middle|\alpha'\right\rangle\overline{E_q(t)E_q(t-\tau)}\sigma^*_{\beta\beta'}(0)\\
&e^{it(\omega_{\beta\beta'}+\omega_{\beta'\alpha'})}e^{-i\omega_{\alpha\beta}\tau}\left\langle\alpha\middle|A_q\middle|\beta\right\rangle\left\langle\beta'\middle|A_q\middle|\alpha'\right\rangle\overline{E_q(t)E_q(t-\tau)}\sigma^*_{\beta\beta'}(0)\Big)\end{aligned} \tag{27.9}$$

where 27.9 is obtained by assuming the x, y, and z components of E(t) are not correlated: $\left\langle E_q(t)E_{q'}(t-\tau)\right\rangle=0$ if $q\neq q'$.

- We now define the generalized correlation function:

$$G_{\alpha\beta\beta'\alpha'}(\tau)=\sum_q\left\langle\alpha\middle|A_q\middle|\beta\right\rangle\left\langle\beta'\middle|A_q\middle|\alpha'\right\rangle\overline{E_q(t)E_q(t-\tau)} \tag{27.10}$$

and (27.9) changes to:

$$\begin{aligned}\frac{d\sigma^*_{\alpha\alpha'}}{dt}=-\frac{1}{\hbar^2}\sum_{\beta\beta'}\int_0^t d\tau\Big(&e^{it(\omega_{\alpha\beta}+\omega_{\beta\beta'})}e^{-i\omega_{\beta\beta'}\tau}G_{\alpha\beta\beta\beta'}(\tau)\sigma^*_{\beta'\alpha'}(0)+e^{it(\omega_{\beta\beta'}+\omega_{\beta'\alpha'})}e^{-i\omega_{\beta\beta'}\tau}G_{\beta\beta'\beta'\alpha'}(\tau)\sigma^*_{\alpha\beta}(0)\\
&-e^{it(\omega_{\alpha\beta}+\omega_{\beta'\alpha'})}e^{-i\omega_{\beta'\alpha'}\tau}G_{\alpha\beta\beta'\alpha'}(\tau)\sigma^*_{\beta\beta'}(0)-e^{it(\omega_{\beta\beta'}+\omega_{\beta'\alpha'})}e^{-i\omega_{\alpha\beta}\tau}G_{\alpha\beta\beta'\alpha'}(\tau)\sigma^*_{\beta\beta'}(0)\Big)\end{aligned}$$

(27.11)

- The finishing touch is to define the spectral density

$$J_{\alpha\beta\beta'\alpha'}(\omega)=\int_{-\infty}^{+\infty}G_{\alpha\beta\beta'\alpha'}(\tau)e^{-i\omega\tau}d\tau \tag{27.12}$$

$$\begin{aligned}\frac{d\sigma^*_{\alpha\alpha'}}{dt}=-\frac{1}{\hbar^2}\sum_{\beta\beta'}\Big(&e^{it(\omega_{\alpha\beta}+\omega_{\beta\beta'})}J_{\alpha\beta\beta\beta'}(\omega_{\beta\beta'})\sigma^*_{\beta'\alpha'}(0)+e^{it(\omega_{\beta\beta'}+\omega_{\beta'\alpha'})}J_{\beta\beta'\beta'\alpha'}(\omega_{\beta\beta'})\sigma^*_{\alpha\beta}(0)\\
&-e^{it(\omega_{\alpha\beta}+\omega_{\beta'\alpha'})}J_{\alpha\beta\beta'\alpha'}(\omega_{\beta'\alpha'})\sigma^*_{\beta\beta'}(0)-e^{it(\omega_{\beta\beta'}+\omega_{\beta'\alpha'})}J_{\alpha\beta\beta'\alpha'}(\omega_{\alpha\beta})\sigma^*_{\beta\beta'}(0)\Big)\end{aligned} \tag{27.13}$$

- A short-hand form for the Redfield equation is:

$$\frac{\partial\sigma^*_{\alpha\alpha'}}{\partial t}=\sum_{\beta\beta'}R_{\alpha\alpha'\beta\beta'}e^{it(\omega_\alpha-\omega_{\alpha'}-\omega_\beta+\omega_{\beta'})}\Delta\sigma^*_{\beta\beta'} \tag{27.14}$$

where

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

- Note master equations like the Redfield equation will relax to an infinite temperature where all populations are equal to 1/A, where A is the number of degrees of freedom. To account for contact with a lattice, the master equation is adjusted to reflect relaxation toward the equilibrium value

$$\sigma_{eq} = \frac{e^{-H_0/k_B T}}{Q} \tag{27.15}$$

so in equation (27.14)

$$\Delta\sigma(t) = \sigma(0) - \sigma_{eq} \approx \sigma(t) - \sigma_{eq} \tag{27.16}$$

Note replacing $\sigma(0)$ with $\sigma(t)$ is valid in the perturbation limit where t is small.