University of Washington
Department of Chemistry
Chemistry 553
Spring Quarter 2011

Lecture 26: Redfield Theory: Simple Example

5/27/11

A. Relaxation in Random Fields

- Here we consider the form of the master equation when we apply an alternating field with a frequency close to the "natural" frequencies of the system. Such a field can induce transitions and thus is said to be resonant with the system.
- For such a case we assume the Hamiltonian has the form

$$H = H_0 + H_1(t) \tag{26.1}$$

- We can go into an interaction frame

$$H_1^*(t) = e^{iH_0 t/\hbar} H_1(t) e^{-iH_0 t/\hbar} \text{ and } \rho^*(t) = e^{iH_0 t/\hbar} \rho(t) e^{-iH_0 t/\hbar} \tag{26.2}$$

  - In this interaction frame the equation of motion is:

$$\frac{\partial \rho^*(t)}{\partial t} = -\frac{i}{\hbar}\left[H_1^*(t), \rho^*(t)\right] \tag{26.3}$$

  - We now formally integrate both sides of (26.3)

-
$$\rho^*(t) = \rho^*(0) - \frac{i}{\hbar}\int_0^t ds \left[H_1^*(s), \rho^*(s)\right] \tag{26.4}$$

  - Then substitute (26.4) back into(26.3). We obtain

$$\frac{d\rho^*}{dt} = -\frac{i}{\hbar}\left[H_1^*(t), \rho^*(0)\right] - \frac{1}{\hbar^2}\int_0^t ds \left[H_1^*(t), \left[H_1^*(s), \rho^*(s)\right]\right] \tag{26.5}$$

- We can simplify the problem by assuming a particular form for the initial state. We assume

$$\langle m|\rho*(0)|n\rangle \begin{cases} =1 \text{ for } m=n=k \\ =0 \qquad \text{otherwise} \end{cases} \tag{26.6}$$

- Note in (26.6) the assumption is that only a single element, the kk element of the density matrix is non-zero.
- We now take matrix elements of both sides of 26.5 in an eigenbasis of H_0:

$$\begin{aligned} \langle m|\frac{d\rho^*}{dt}|m\rangle &= \frac{\partial}{\partial t}\langle m|\rho^*(t)|m\rangle \\ &= -\frac{i}{\hbar}\langle m|\left[H_1^*(t), \rho^*(0)\right]|m\rangle - \frac{1}{\hbar^2}\int_0^t ds \langle m|\left[H_1^*(t), \left[H_1^*(s), \rho^*(0)\right]\right]|m\rangle \end{aligned} \tag{26.7}$$

- Given the initial conditions in 26.6, the commutator matrix elements are zero. Then 26.7 reduces to

$$\begin{aligned}
&\frac{\partial}{\partial t}\langle m|\rho^*|m\rangle = \frac{\partial \rho^*_{mm}}{\partial t} = \frac{\partial \rho_{mm}}{\partial t}\\
&= \frac{i^2}{\hbar^2}\int_0^t ds\left(\langle m|H_1^*(t)|k\rangle\langle k|H_1^*(s)|m\rangle + \langle m|H_1^*(s)|k\rangle\langle k|H_1^*(t)|m\rangle\right) \qquad (26.8)\\
&= \frac{i^2}{\hbar^2}\int_0^t ds\left(e^{i\omega_{mk}(t-s)}\langle m|H_1(t)|k\rangle\langle k|H_1(s)|m\rangle + e^{-i\omega_{mk}(t-s)}\langle m|H_1(s)|k\rangle\langle k|H_1(t)|m\rangle\right)
\end{aligned}$$

where 26.8 was obtained using the interaction frame definition 26.2 and the initial condition 26.6. Note $\omega_{mk} = \omega_m - \omega_k$ and note also that there is no summation over k as the t=0 density matrix only has a single element that is non-zero, i.e. the kk element.

- We now assume a form for the perturbation Hamiltonian:

$$H_1(t) = \sum_{q=x,y,z} A_q E_q(t) \qquad (26.9)$$

- In 26.9 A_q is a system operator that does not commute with H_0 and $E_q(t)$ is a stationary random function of time.
- Because the perturbation is a random field we have to account for its effect by averaging over the ensemble, which we indicate with $\langle\ \rangle$.
- $\frac{d\langle\rho_{mm}\rangle}{dt} = \frac{1}{\hbar^2}\left\langle\left\{\sum_q \langle m|A_q|k\rangle\langle k|A_q|m\rangle\int_0^t d\tau\left\langle E_q(t)E_q(t-\tau)\right\rangle\cos\omega_{mk}\tau\right\}\right\rangle$ (26.10)

  where 26.10 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 $q \neq q'$.
- Note that in 26.10 we assume that $E_q(t)E_q(t-\tau)$ drops off very rapidly as t departs from 0. Together with the stationary character of the random perturbation we obtain

$$\begin{aligned}
&\frac{d\langle\rho_{mm}\rangle}{dt} \approx \frac{2}{\hbar^2}\sum_q \langle m|A_q|k\rangle\langle k|A_q|m\rangle\int_0^\infty d\tau\left\langle E_q(t-\tau)E_q(t)\right\rangle\cos\omega_{mk}\tau\\
&= \frac{2}{\hbar^2}\sum_q \langle m|A_q|k\rangle\langle k|A_q|m\rangle\int_0^\infty d\tau\left\langle E_q(t+\tau)E_q(t)\right\rangle\cos\omega_{mk}\tau \qquad (26.11)\\
&= \frac{2}{\hbar^2}\sum_q \langle m|A_q|k\rangle\langle k|A_q|m\rangle\int_0^\infty d\tau\left\langle E_q(\tau)E_q(0)\right\rangle\cos\omega_{mk}\tau = \frac{1}{\hbar^2}\sum_q J_q(\omega_{mk}) \equiv W_{k\to m}
\end{aligned}$$

where in 26.11 $J_q(\omega_{mk})$ is a spectral density, defined as the cosine Fourier transform of the correlation function $C_q(\tau) = \left\langle E_q(\tau)E_q(0)\right\rangle$ and $W_{k\to m}$ is the probability per unit time for the transition from k to m. Note we can interpret $\frac{1}{\hbar^2}\sum_q J_q(\omega_{mk})$ in this way because we only have a single original state: k.

- We assume a common form for the correlation function:

$$C_q\left(\tau\right) = E_q^2 e^{-|\tau|/\tau_0} \tag{26.12}$$

- Substitute 26.12 into 26.11

$$\frac{d\left\langle \rho_{mm} \right\rangle}{dt} = \frac{2}{\hbar^2}\sum_q \left\langle m \left| A_q \right| k \right\rangle \left\langle k \left| A_q \right| m \right\rangle E_q^2 \int_0^\infty d\tau e^{-|\tau|/\tau_0} \cos\omega_{mk}\tau = \frac{2}{\hbar^2}\sum_q \left|A_q\right|_{mk}^2 E_q^2 \left(\frac{\tau_0}{\omega_{mk}^2\tau_0^2 + 1}\right)$$

(26.13)

- For a 2-level system where the quantity $\omega_{mk} = \omega_0$ we have

$$\frac{1}{T_1} = \frac{2}{\hbar^2}\sum_q \left|A_q\right|_{mk}^2 E_q^2 \left(\frac{\tau_0}{\omega_0^2\tau_0^2 + 1}\right) \tag{26.14}$$

  Where T_1 quantifies the time scale of relaxation of the populations.