University of Washington
Department of Chemistry
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Lecture 21: Survey of Quantum Statistics
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A. Summary of Linear Response Theory

- In the last few lectures we established several key relationships. This includes the displacement of a property B of a system from equilibrium by the application of a weak field

$$\Delta B(t) = \langle B(t)\rangle - \langle B\rangle_0 = \int_{-\infty}^{t} ds F(s)\phi_{BA}(t-s) \tag{21.1}$$

where the linear response or after-effect function is

$$\phi_{BA}(t) = \int dX f_0 \{B(t), A(0)\} = \langle\{B(t), A(0)\}\rangle = -\frac{1}{k_B T}\langle \dot{B}(t) A(0)\rangle \tag{21.2}$$

- If the field is time dependent i.e. $F(t) = F_\omega \cos\omega t$ then

$$\begin{aligned}\Delta B(t) &= \int_{-\infty}^{t} ds F(s)\phi_{BA}(t-s) = F_\omega \operatorname{Re}\left[e^{i\omega t}\int_0^\infty e^{-i\omega\tau}\phi_{BA}(\tau)d\tau\right] \\ &= F_\omega \operatorname{Re}\left[e^{i\omega t}\chi_{BA}(\omega)\right] = F_\omega\left(\chi'(\omega)\cos\omega t + \chi''(\omega)\sin\omega t\right)\end{aligned} \tag{21.3}$$

- In equation (21.3) $\chi(\omega) = \chi'(\omega) - i\chi''(\omega)$ is the one-sided Fourier transform of the response function and is called the complex susceptibility. The real part is related to the cycle-averaged reversible work done by the field on the system $\bar{U}_\omega$ and the imaginary part is related to the dissipation of energy from the field by the system $\bar{D}_\omega$.

$$\bar{U}_\omega = \frac{|F_\omega|^2}{2}\cdot\chi'_{BA}(\omega) \text{ and } \bar{D}_\omega = \frac{\omega|F_\omega|^2}{2}\chi''_{BA}(\omega) \tag{21.4}$$

- A fundamental relationship between the imaginary part of the susceptibility and the correlation function is the fluctuation-dissipation theorem:

$$\chi''_{BA}(\omega) = \frac{\omega}{kT}\int_0^\infty dt\langle A(0)B(t)\rangle\cos\omega t \tag{21.5}$$

- Finally, as a result of the causality of the linear response function ($\phi_{BA}(t)=0$ if t<0) the real and imaginary parts of the complex susceptibility are related by the Kramers-Kronig relations:

$$\begin{aligned}\chi'(\omega) &= \frac{2}{\pi}\wp\int_0^{+\infty}\frac{y\chi''(y)}{y^2-\omega^2}dy \\ \chi''(\omega) &= -\frac{2\omega}{\pi}\wp\int_0^{+\infty}\frac{\chi'(y)}{y^2-\omega^2}dy\end{aligned} \tag{21.6}$$

- The physical meaning of the real and imaginary parts of the complex susceptibility can be given further meaning by way of example. Suppose a static field $\vec{E}_0$ is applied to a polarizeable material. The polarization $\vec{P}$ comprises the induced dipole moments and aligned permanent dipoles of the system. The polarization opposes the static field so the average field in the material is:

$$\vec{E} = \vec{E}_0 - \frac{\vec{P}}{\varepsilon_0} \tag{21.7}$$

  where ε_0 is the free space dielectric constant or the free space permittivity.

- The polarization is proportional to the average field

$$\vec{P} = \varepsilon_0(\varepsilon_r - 1)\vec{E} = \varepsilon_0\chi_e\vec{E} \tag{21.8}$$

  where the relative permittivity (also called the dielectric constant) is $\varepsilon_r = \frac{\varepsilon}{\varepsilon_0}$, ε is the permittivity of the material, and $\chi_e = \varepsilon_r - 1$ is th electric susceptibility.

- If the field is time dependent

$$\begin{aligned}P(t) &= \varepsilon_0\int_{-\infty}^{t}E(t')\phi(t-t')dt' = \varepsilon_0E_0\,\mathrm{Re}\left[\int_{-\infty}^{t}e^{i\omega t'}\phi(t-t')dt'\right] \\ &= \varepsilon_0E_0\,\mathrm{Re}\left[e^{i\omega t}\int_0^{\infty}e^{-i\omega\tau}\phi(\tau)d\tau\right] = \varepsilon_0E_0\,\mathrm{Re}\left[e^{i\omega t}\chi_e(\omega)\right] \\ &= \varepsilon_0E_0\,\mathrm{Re}\left[e^{i\omega t}\chi_e(\omega)\right]\end{aligned} \tag{21.9}$$

  where now $\chi_e(\omega) = \varepsilon_r(\omega) - 1$, $\varepsilon_r(\omega) = \varepsilon_r'(\omega) + i\varepsilon_r''(\omega)$

  and where the real and imaginary parts of $\varepsilon_r(\omega)$ satisfy KK relations.

  - Note: The convention for the permittivity has it origins in the definition of the electric displacement D:

$$\begin{aligned}\vec{P} &= \varepsilon_0E_0\,\mathrm{Re}\left[e^{i\omega t}\chi_e(\omega)\right] = \varepsilon_0E_0\,\mathrm{Re}\left[e^{i\omega t}(\varepsilon_r(\omega)-1)\right] \\ &= \varepsilon_0\vec{E}(t)(\varepsilon_r(\omega)-1) \\ \therefore\ \vec{D}(t) &= \vec{P}(t) + \varepsilon_0\vec{E}(t) = \varepsilon_r(\omega)\varepsilon_0\vec{E}(t) = \varepsilon(\omega)\vec{E}(t)\end{aligned} \tag{21.10}$$

- Now the refractive index is related to the dielectric permittivity by

  $n^2(\omega) = \varepsilon_r(\omega)$ so if the permittivity is complex so is the refractive index:

$$\begin{aligned} &n(\omega) = n'(\omega) + in''(\omega) \\ &\therefore \varepsilon_r'(\omega) = \left[n'(\omega)\right]^2 - \left[n''(\omega)\right]^2 \; and \; \varepsilon_r''(\omega) = 2n'(\omega)n''(\omega) \end{aligned} \tag{21.11}$$

- Consider an electromagnetic plane wave propagating through a medium with electric field

$$\vec{E}(t) = \text{Re}\left[\vec{E}_0 \exp\left[i(kx - \omega t)\right]\right] \tag{21.12}$$

and the wave number is $k = \frac{2\pi n(\omega)}{\lambda} = \frac{2\pi}{\lambda}\left(n'(\omega) + in''(\omega)\right)$. This puts (21.11) into the form

$$\begin{aligned} \vec{E}(t) &= \text{Re}\left[\vec{E}_0 \exp\left[i\left(\frac{2\pi x}{\lambda}\left(n'(\omega) + in''(\omega)\right) - \omega t\right)\right]\right] \\ &= \text{Re}\left[\vec{E}_0 \exp\left[i\left(\frac{2\pi x n'(\omega)}{\lambda} - \omega t\right)\right]\right] \exp\left(-\frac{2\pi x n''(\omega)}{\lambda}\right) \end{aligned} \tag{21.13}$$

  - According to (21.12) $n'(\omega)$, which is commonly referred to as the refractive index, changes the wavelength of the wave as it propagates through the medium while the dispersive term $n''(\omega)$ attenuates the amplitude of the wave.
  - Now consider now the wave intensity:

$$I \propto |E|^2 = I_0 \exp\left[\frac{-4\pi n''(\omega)}{\lambda} x\right] = I_0 \exp\left[\frac{-\omega \varepsilon_r''(\omega)}{n'(\omega)c} x\right] = I_0 e^{-\gamma x} \tag{21.14}$$

where γ is the coefficient of absorption given in the Lambert-Beer Law as

$$\gamma = \varepsilon_M C \tag{21.15}$$

C is the concentration in molar units and ε_M is the molar absorptivity.

B. Quantum Systems: Introduction

- To further apply linear response theory to spectroscopic problems we need to extend the formalism to quantum systems.
- We will first define the quantum Liouville operator, the density operator, and the and the essential features of quantum mechanical linear response theory…which leads to Kubo's theorem and the quantum mechanical fluctuation dissipation theorem.
- We will find the Classical/Quantum Correspondences useful.
  - The classical distribution function f(X,t) corresponds to the quantum density matrix *ρ(t)*. The equilibrium density operator is defined as

$$\rho_{eq} = \rho_0 = \frac{e^{-\beta H_0}}{Q} \ldots where \; Q = Tr\left(e^{-\beta H_0}\right) \tag{21.16}$$

Which corresponds to the classical distribution function:

$$f_{eq} = f_0 = f\left(X,0\right) = \frac{e^{-\beta H(p,q)}}{Q} \; where \ldots Q = \frac{1}{h^{3N}} \int dp_1 \ldots dp_N \int dq_1 \ldots dq_N e^{-\beta H(p,q)}$$

(21.17)

- The equation of motion of the density operator is

$$\frac{\partial \rho}{\partial t} = -\frac{i}{\hbar}\left[H,\rho\right] = -L\rho \qquad (21.18)$$
$$\text{where}\left[H,\rho\right] = H\rho - \rho H$$

- Classically:

$$\frac{\partial f}{\partial t} = -\left\{H, f\right\} = -Lf \qquad (21.19)$$
$$\text{where } \left\{H, f\right\} = \frac{\partial H}{\partial p}\frac{\partial f}{\partial q} - \frac{\partial H}{\partial q}\frac{\partial f}{\partial p}$$

- There is also correspondence between the classical ensemble average and the quantum mechanical average

$$\left\langle A(t)\right\rangle_{classical} = \int dX \; A\left(X,t\right) f\left(X,t\right) \Leftrightarrow \left\langle A(t)\right\rangle_{quantum} = Tr\left(A(t)\,\rho(t)\right) \qquad (21.20)$$

- Finally the quantum correlation function is

$$g_{BA}\left(t\right) = Tr\left\{\rho_0 \left(\frac{B(t)A(0) + A(0)B(t)}{2}\right)\right\} = Tr\left\{\frac{\rho_0}{2}\left[B(t)A(0)\right]_+\right\} \qquad (21.21)$$

- The quantum/classical correspondence is

$$g_{BA}\left(t\right) = Tr\left\{\frac{\rho_0}{2}\left[B(t)A(0)\right]_+\right\} \Leftrightarrow C_{BA}\left(t\right) = \int dXf_0 B(t)A(0) \qquad (21.22)$$

- With (20.1)-(20.7) we can obtain the quantum fluctuation dissipation theorem…which is our first step toward a theory of spectroscopic line shapes.

$$\frac{\partial \rho}{\partial t} = -\frac{i}{\hbar}\left[H,\rho\right] = -\frac{i}{\hbar}\left[H_0 - AF\left(t\right),\rho\right] = -\frac{i}{\hbar}\left[H_0,\rho\right] + \frac{i}{\hbar}\left[A,\rho\right]F\left(t\right) = -L_0\rho + \frac{i}{\hbar}\left[A,\rho\right]F\left(t\right)$$
$$\therefore \rho(t) = \rho_0 + \frac{i}{\hbar}\int_{-\infty}^{t} e^{-L_0(t-s)}\left[A,\rho\right]F\left(s\right)ds$$

(21.23)

- The displacement of the operator B is therefore:

$$\Delta B(t) = Tr\left(B\rho\right) - Tr\left(B\rho_0\right) \approx \frac{i}{\hbar}Tr\left(B\int_{-\infty}^{t} e^{-L_0(t-s)}\left[A,\rho\right]F\left(s\right)ds\right)$$
$$= \frac{i}{\hbar}\int_{-\infty}^{t} dsF\left(s\right)Tr\left(Be^{-L_0(t-s)}\left[A,\rho\right]\right) = \frac{i}{\hbar}\int_{-\infty}^{t} dsF\left(s\right)Tr\left(B(t-s)\left[A,\rho\right]\right) \qquad (21.24)$$
$$\frac{i}{\hbar}\int_{-\infty}^{t} dsF\left(s\right)Tr\left(B(t-s)\left[A,\rho\right]\right) = \frac{i}{\hbar}\int_{-\infty}^{t} dsF\left(s\right)\phi_{BA}\left(t-s\right)$$
$$\phi_{BA}\left(t\right) = Tr\left(B(t)\left[A,\rho\right]\right) \approx Tr\left(B(t)\left[A,\rho_0\right]\right)$$

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