Statistics and Spectroscopy

$$C_{\mu\mu}(t) = < \mu(t)\mu(0) >$$

Through correlation function we are looking at one single oscillator!

The average is done on the n states of the oscillator at thermal equilibrium

What if do we want to extend that statistics over all oscillators present in a condensed phase?

How to take care about their interactions?

Introduction to the density matrix operator $\hat{\rho}$

Pure state

$$\psi(q,t)$$

The wavefunction is a complex function that completely describes in terms of position *q* and time *t* the electrons of a molecular system.

$$\psi^*\psi = <\psi|\psi> = \psi^2 \quad \text{scalar}$$

ψ^2 is real and defines the probability of finding an electron with coordinates (q,t) in a dV of the space.

$$\frac{1}{V}\int_V \psi^*\psi = 1 \qquad \text{normalization}$$

$$\int \psi_1\psi_2 = 0$$

Orthogonal waves in a same system

The ensemble

$$\rho = |\psi><\psi|$$

$<\psi| = bra$ Row vector (c.c.part)*

$|\psi> = ket$ Column vector

$$\begin{pmatrix} a \\ b \end{pmatrix} \cdot \begin{pmatrix} a & b \end{pmatrix} = \begin{pmatrix} a^2 & ab \\ ba & b^2 \end{pmatrix} \quad \text{matrix}$$

All pure states along the diagonal and all possible interactions term out of the diagonal.

$\rho =$"*density*" of quantic states

Properties of density operator:

- ρ is Hermitian: $\rho_{mn} = \rho^*_{nm}$
- $\rho_{nn} \geq 0$ is the probability of the pure state n
- $Tr\{\rho\} = 1$ normalization
- $Tr\{\rho^2\} \leq 1$; it is 1 only for a pure state
- $Tr\{\rho A\} =< A >$ value of expectation (average on n states of ψ) on N molecules

Pure state

resulting from a superposition of two states

$$\rho = \begin{pmatrix} 1/2 & 1/2 \\ 1/2 & 1/2 \end{pmatrix}$$

$$Tr\{\rho^2\} = 1$$

Before measure

Statistic average

of two possible states in an ensemble

$$\rho = \begin{pmatrix} 1/2 & 0 \\ 0 & 1/2 \end{pmatrix}$$

$$Tr\{\rho^2\} = 1/2$$

After measure

Free evolution of $\hat{\rho}\,(t)$

$$\left.\begin{aligned}\frac{\partial|\psi>}{\partial t}&=-\frac{i}{\hbar}\hat{H}|\psi>\\ \frac{\partial<\psi|}{\partial t}&=\frac{i}{\hbar}<\psi|\hat{H}\end{aligned}\right\}\qquad \frac{\partial\rho}{\partial t}=\frac{\partial}{\partial t}(|\psi><\psi|)=-\frac{i}{\hbar}\hat{H}|\psi><\psi|+\frac{i}{\hbar}|\psi><\psi|\hat{H}$$

$$\frac{\partial\hat{\rho}}{\partial t}=-\frac{i}{\hbar}[\hat{H},\hat{\rho}]$$ Liouville - Von Neumann eq.

For a two-level system:

$$\frac{\partial}{\partial t}\begin{pmatrix}\rho_{11} & \rho_{12}\\ \rho_{21} & \rho_{22}\end{pmatrix}=-\frac{i}{\hbar}\left[\begin{pmatrix}E_1 & 0\\ 0 & E_2\end{pmatrix}\begin{pmatrix}\rho_{11} & \rho_{12}\\ \rho_{21} & \rho_{22}\end{pmatrix}-\begin{pmatrix}\rho_{11} & \rho_{12}\\ \rho_{21} & \rho_{22}\end{pmatrix}\begin{pmatrix}E_1 & 0\\ 0 & E_2\end{pmatrix}\right]=$$

$$\left[\begin{pmatrix}E_1\rho_{11} & E_1\rho_{12}\\ E_2\rho_{21} & E_2\rho_{22}\end{pmatrix}-\begin{pmatrix}\rho_{11}E_1 & \rho_{12}E_2\\ \rho_{21}E_1 & \rho_{22}E_2\end{pmatrix}\right]$$

$$\frac{\partial}{\partial t}\begin{pmatrix}\rho_{11} & \rho_{12}\\ \rho_{21} & \rho_{22}\end{pmatrix} = -\frac{i}{\hbar}\begin{pmatrix}0 & \rho_{12}(E_1-E_2)\\ \rho_{21}(E_2-E_1) & 0\end{pmatrix}$$

$$\left.\begin{aligned}\rho'_{11} &= 0\\ \rho'_{22} &= 0\end{aligned}\right\}$$ Populations are constant

Out-of-diagonal terms = COHERENCES

$$\begin{cases}\rho'_{12} = -\frac{i}{\hbar}\rho_{12}(E_1-E_2) \Rightarrow \rho_{12}(t) = \rho_{12}(0)e^{-i\omega_{12}t}\\ \rho'_{21} = -\frac{i}{\hbar}\rho_{21}(E_2-E_1) \Rightarrow \rho_{21}(t) = \rho_{21}(0)e^{+i\omega_{12}t}\end{cases}$$

Coherences oscillate at constant frequency ω_{12} in antiphase!

At resonance, you start rotating at twice the frequency with one component and at zero frequency with the other: *ROTATING WAVE APPROXIMATION*

The Liouville super-operator $\widehat{L}$

matrix

$$\frac{\partial\hat{\rho}}{\partial t} = -\frac{i}{\hbar}[\widehat{H},\hat{\rho}]$$

column vector

$$\frac{\partial}{\partial t}\begin{pmatrix}\rho_{12}\\ \rho_{21}\\ \rho_{11}\\ \rho_{22}\end{pmatrix} = -\frac{i}{\hbar}\begin{pmatrix}E_1-E_2 & & \cdots & \\ & E_2-E_1 & & \\ & & 0 & \\ & \cdots & & 0\end{pmatrix}\begin{pmatrix}\rho_{12}\\ \rho_{21}\\ \rho_{11}\\ \rho_{22}\end{pmatrix}$$

$$\frac{\partial\hat{\rho}}{\partial t} = -\frac{i}{\hbar}\widehat{L}\hat{\rho}$$

Super-operator operates on another operator!!

The super-operator representation allows for the introduction of …

DEPHASING FACTOR

$$\frac{\partial \hat{\rho}}{\partial t} = -\frac{i}{\hbar}\hat{L}\hat{\rho} - \hat{\Gamma}\hat{\rho}$$

empirical

$$\rho_{12}(t) = \rho_{12}(0)e^{-i\omega_{12}t}e^{-\Gamma t}$$

$$\rho_{21}(t) = \rho_{21}(0)e^{i\omega_{12}t}e^{-\Gamma t}$$

$$\rho_{11}(t) = e^{-\Gamma t}$$

$$\rho_{22}(t) = e^{-\Gamma t}$$

Γ rises from collisions in an ensemble so it has no meaning on a pure state ψ

collisions

- Elastic: oscillators change their phase
- Anelastic: there is exchange of energy! It is a channel for non-radiative relaxation

Hierarchy of representations:

Shroedinger $\longrightarrow$ $\psi(t)$ Evolution of a pure state:

$$\frac{\partial|\psi>}{\partial t} = -\frac{i}{\hbar}\widehat{H}|\psi>$$

Liouville – Von Neumann $\longrightarrow$ $[H, \rho]$ Evolution of a statistic ensemble:

$$\frac{\partial\hat{\rho}}{\partial t} = -\frac{i}{\hbar}[\widehat{H}, \hat{\rho}]$$

Liouville $\longrightarrow$ $L\,,\Gamma$ Evolution including damping:

$$\frac{\partial\hat{\rho}}{\partial t} = -\frac{i}{\hbar}\hat{L}\hat{\rho} - \hat{\Gamma}\hat{\rho}$$