Linear Response

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Previously on CHM676...

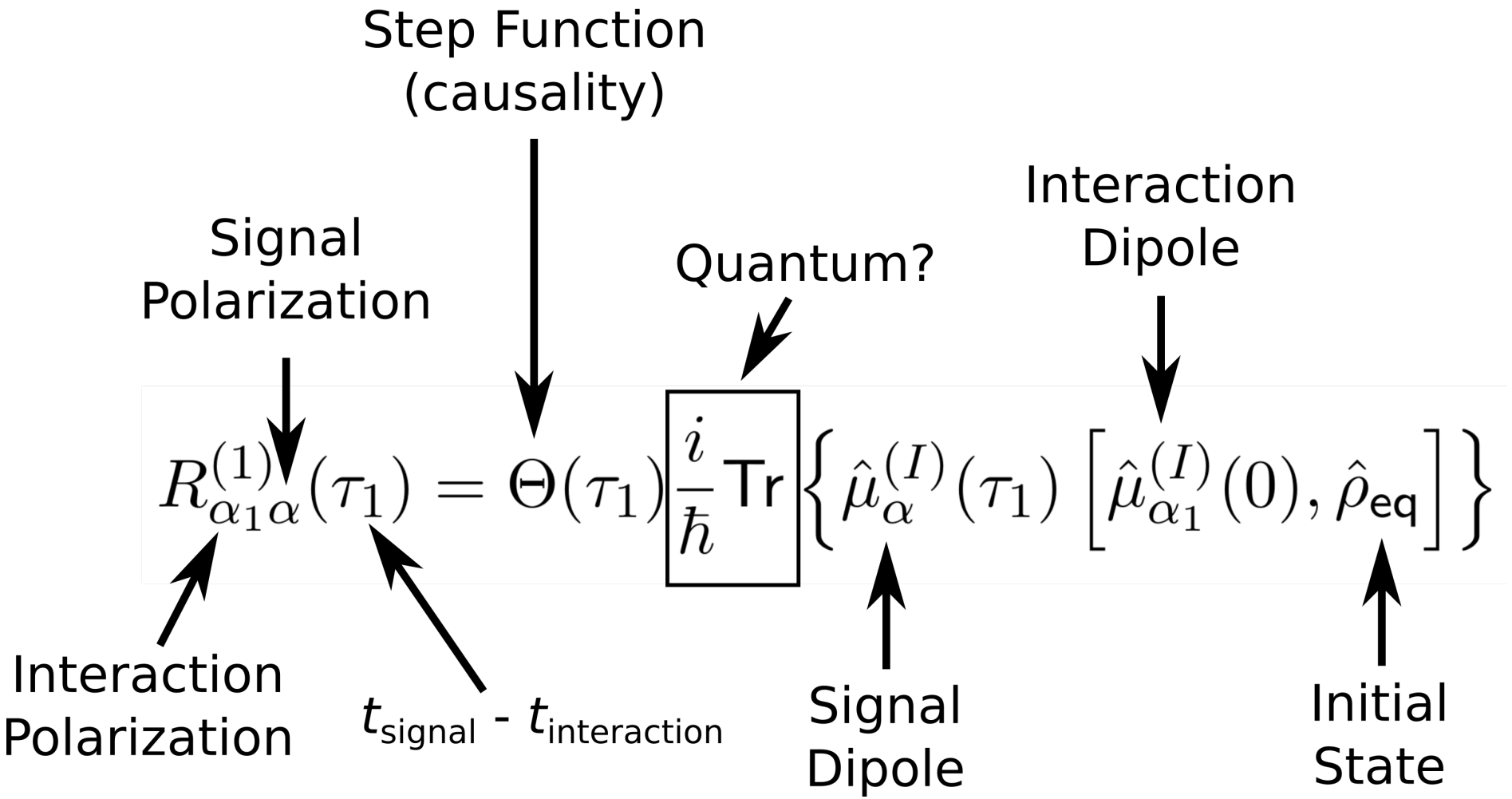
We derived a **microscopic** response expansion:

$$R^{(n)}_{\alpha_1 ... \alpha_n \alpha}(\tau_1, ..., \tau_n) = \Theta(\tau_1)\Theta(\tau_2)...\Theta(\tau_n)\left(\frac{i}{\hbar}\right)^n$$
$$\times \mathsf{Tr}\left\{\hat{\mu}^{(I)}_{\alpha}(\tau_1 + ... + \tau_n)\left[\hat{\mu}^{(I)}_{\alpha_n}(\tau_1 + ... + \tau_{n-1}), ...\left[\hat{\mu}^{(I)}_{\alpha_1}(0), \hat{\rho}_{\mathsf{eq}}\right]\right]\right\}$$

Today: Linear response.

Linear Response Tensor

Taking the $n = 1$ case:



Rearranging

$$
\begin{aligned}
R^{(1)}_{\alpha_1\alpha}(\tau_1) &= \Theta(\tau_1)\frac{i}{\hbar}\mathsf{Tr}\left\{\hat{\mu}^{(I)}_{\alpha}(\tau_1)\left[\hat{\mu}^{(I)}_{\alpha_1}(0),\hat{\rho}_{\mathsf{eq}}\right]\right\} \\
&= \Theta(\tau_1)\frac{i}{\hbar}\mathsf{Tr}\left\{\hat{\mu}^{(I)}_{\alpha}(\tau_1)\left(\hat{\mu}^{(I)}_{\alpha_1}(0)\hat{\rho}_{\mathsf{eq}}-\hat{\rho}_{\mathsf{eq}}\hat{\mu}^{(I)}_{\alpha_1}(0)\right)\right\} \\
&= \Theta(\tau_1)\frac{i}{\hbar}\mathsf{Tr}\left\{\hat{\mu}^{(I)}_{\alpha}(\tau_1)\hat{\mu}^{(I)}_{\alpha_1}(0)\hat{\rho}_{\mathsf{eq}}-\hat{\rho}_{\mathsf{eq}}\hat{\mu}^{(I)}_{\alpha_1}(0)\hat{\mu}^{(I)}_{\alpha}(\tau_1)\right\} \\
&= \Theta(\tau_1)\frac{i}{\hbar}\left[\left\langle\mu^{(I)}_{\alpha}(\tau_1)\mu^{(I)}_{\alpha_1}(0)\right\rangle_{\mathsf{eq}}-\left\langle\mu^{(I)}_{\alpha_1}(0)\mu^{(I)}_{\alpha}(\tau_1)\right\rangle_{\mathsf{eq}}\right] \\
&= \Theta(\tau_1)\frac{2}{\hbar}\mathsf{Im}\left\langle\mu^{(I)}_{\alpha_1}(0)\mu^{(I)}_{\alpha}(\tau_1)\right\rangle_{\mathsf{eq}}
\end{aligned}
$$

The linear response tensor is the **imaginary part** of the dipole-dipole **auto-correlation function**.

Autocorrelation Functions

An **autocorrelation function** indicates the degree of correlation between the value of a **single quantity** at **two different times**:

$$A_{\mu\mu}(\tau) = \langle \mu(\tau)\mu(0) \rangle \, .$$

Fluctuation-Dissipation Theorems

Our linear response expression is a specific example of the **fluctuation-dissipation theorem**:

> *A system's* **response** *to an external perturbation is directly related to the* **fluctuations** *of the relevant quantities at equilibrium.*

A Langevin dynamics example:

$$\langle \xi(t_2)\xi(t_1)\rangle = 2\gamma k_B T \delta(t_2 - t_1)$$

Key Point: *Equilibrium* correlation functions encode *non-equilibrium* response.

"Low-Temperature" Absorption

When $k_B T = 1/\beta$ is small relative to splitting between the ground and first excited states:

$$\hat{\rho}_{\text{eq}} \equiv \frac{e^{-\beta \hat{H}}}{\text{Tr}\{e^{-\beta \hat{H}}\}} \approx |0\rangle \langle 0| .$$

The equilibrium state is just the ground state! Then

$$\begin{aligned}
\left\langle \hat{\mu}_{\alpha_1}^{(I)}(0) \hat{\mu}_{\alpha}^{(I)}(\tau_1) \right\rangle_{\text{eq}} &= \sum_n \left\langle n \left| \mu_{\alpha_1}^{(I)}(0) \mu_{\alpha}^{(I)}(\tau_1) \hat{\rho}_{\text{eq}} \right| n \right\rangle \\
&= \left\langle 0 \left| \mu_{\alpha_1}^{(I)}(0) \mu_{\alpha}^{(I)}(\tau_1) \right| 0 \right\rangle \\
&= \left\langle 0 \left| \mu_{\alpha_1} e^{\frac{i}{\hbar} \hat{H} \tau_1} \mu_{\alpha} \right| 0 \right\rangle .
\end{aligned}$$

Absorption Line Shapes

Expanding in the Hamiltonian eigenbasis:

$$\begin{aligned}\left\langle \hat{\mu}_{\alpha_1}^{(I)}(0)\hat{\mu}_{\alpha}^{(I)}(\tau_1)\right\rangle_{\text{eq}} &= \left\langle 0\left|\mu_{\alpha_1}e^{\frac{i}{\hbar}\hat{H}\tau_1}\mu_{\alpha}\right|0\right\rangle \\ &= \sum_n \langle 0|\mu_{\alpha_1}|n\rangle\left\langle n\left|e^{\frac{i}{\hbar}\hat{H}\tau_1}\mu_{\alpha}\right|0\right\rangle \\ &= \sum_n e^{i\omega_{n0}\tau_1}\langle 0|\mu_{\alpha_1}|n\rangle\langle n|\mu_{\alpha}|0\rangle\end{aligned}$$

In isotropic media:

$$R^{(1)}(\tau_1) = \frac{2}{3\hbar\pi^2}\Theta(\tau_1)\sum_n \|\mu_{n0}\|^2\sin(\omega_{n0}\tau_1)$$

Key Point: The linear response function is a sum of **sin waves** at the **ground/excited-state frequency gaps** and weighted by **transition dipole** matrix elements.

Harmonic Oscillator

As a specific example:

$$\hat{H} = \frac{1}{2}\left(M\omega^2\hat{x}^2 + \frac{\hat{p}^2}{2M}\right)$$
$$\hat{\mu} = \mu^{(1)}\hat{x}$$

or in the energy eigenbasis:

$$\hat{H} = \begin{bmatrix} \frac{\hbar\omega}{2} & 0 & 0 & \dots \\ 0 & \frac{3\hbar\omega}{2} & 0 & \dots \\ 0 & 0 & \frac{5\hbar\omega}{2} & \\ \vdots & \vdots & & \ddots \end{bmatrix} \qquad \hat{x} = \begin{bmatrix} 0 & \sqrt{\frac{\hbar}{2M\omega}} & 0 & \dots \\ \sqrt{\frac{\hbar}{2M\omega}} & 0 & \sqrt{\frac{\hbar}{M\omega}} & \\ 0 & \sqrt{\frac{\hbar}{M\omega}} & 0 & \ddots \\ \vdots & & \ddots & \ddots \end{bmatrix}$$

Exercise 7: Harmonic Oscillator Absorption

1. Calculate the (squared) matrix elements $\|\mu_{n0}\|^2$ between the harmonic-oscillator ground state and the first two excited states (i.e., n = 1 and 2).
2. Calculate the frequency difference ω_{n0} between the ground state (n=0) and the first two excited states (i.e., n=1 and 2).
3. Write down an explicit expression for $R^{(1)}(\tau_1)$ for the harmonic oscillator, considering only the first three states (n=0, 1, and 2). (You can ignore polarization indices, assuming an isotropic distribution of dipole orientations.)
4. Given this result, what will the absorption spectrum for a harmonic oscillator look like? (You can either describe it in words or give a mathematical expression.)
5. Does your expression depend on $\hbar$? What does this suggest about the "quantumness" of the result?

Exercise 7: Extra Credit

In our calculation, we made a "low-temperature" assumption, that the population of excited states was negligible. A more complete expression is

$$R^{(1)}(\tau_1) = \frac{2}{3\hbar\pi^2}\Theta(\tau_1)\sum_{m,n}\rho_{mm}\|\mu_{nm}\|^2\sin(\omega_{nm}\tau_1),$$

where the index m runs over the *initial state* of the system (before excitation), and the index n runs over the *final* state (after excitation). The density matrix elements ρ_{mm} are given (at equilibrium) by

$$\rho_{mm} = \frac{e^{-\beta H_{mm}}}{\sum_k e^{-\beta H_{kk}}},$$

where the index k runs over all system states.

Assignment: For the harmonic oscillator, write down an explicit expression for ρ_{mm} that depends only on ω and m. (Include only the *first three* states in the sum over k.) Calculate numerical values for ρ_{11} with T = 300 K and both $\omega/(2\pi c) = 100$ cm^{-1} and $\omega/(2\pi c) = 1600$ cm^{-1}. In each case, how good is the "low-temperature" approximation?