

Linear Response

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We derived a **microscopic** response expansion:

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

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Today: Linear response.

Linear Response Tensor

Taking the $n = 1$ case:

$$R_{\alpha_1 \alpha}^{(1)}(\tau_1) = \Theta(\tau_1) \frac{i}{\hbar} \text{Tr} \left\{ \hat{\mu}_{\alpha}^{(I)}(\tau_1) \left[\hat{\mu}_{\alpha_1}^{(I)}(0), \hat{\rho}_{\text{eq}} \right] \right\}$$

Linear Response Tensor

Taking the $n = 1$ case:

Diagram illustrating the Linear Response Tensor for the $n = 1$ case, showing the relationship between various physical quantities and the response function $R_{\alpha_1\alpha}^{(1)}(\tau_1)$.

The equation is:

$$R_{\alpha_1\alpha}^{(1)}(\tau_1) = \Theta(\tau_1) \left[\frac{i}{\hbar} \text{Tr} \left\{ \hat{\mu}_{\alpha}^{(I)}(\tau_1) \left[\hat{\mu}_{\alpha_1}^{(I)}(0), \hat{\rho}_{\text{eq}} \right] \right\} \right]$$

Annotations and arrows indicate the physical meaning of the terms:

- Signal Polarization** points to $R_{\alpha_1\alpha}^{(1)}(\tau_1)$.
- Step Function (causality)** points to $\Theta(\tau_1)$.
- Quantum?** points to the $\frac{i}{\hbar}$ term.
- Interaction Dipole** points to $\hat{\mu}_{\alpha_1}^{(I)}(0)$.
- Initial State** points to $\hat{\rho}_{\text{eq}}$.
- Signal Dipole** points to $\hat{\mu}_{\alpha}^{(I)}(\tau_1)$.
- Interaction Polarization** points to α_1 .
- $t_{\text{signal}} - t_{\text{interaction}}$** points to τ_1 .

$$R_{\alpha_1\alpha}^{(1)}(\tau_1) = \Theta(\tau_1) \frac{i}{\hbar} \text{Tr} \left\{ \hat{\mu}_{\alpha}^{(I)}(\tau_1) \left[\hat{\mu}_{\alpha_1}^{(I)}(0), \hat{\rho}_{\text{eq}} \right] \right\}$$

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

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.*

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A Langevin dynamics example:

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

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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

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

Absorption Line Shapes

Expanding in the Hamiltonian eigenbasis:

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

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In isotropic media:

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

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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:

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

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 $\omega/(2\pi c) = 100 \text{ cm}^{-1}$ and $\omega/(2\pi c) = 1600 \text{ cm}^{-1}$. In each case, how good is the “low-temperature” approximation?