Diagrammatic Expansions

Mike Reppert

October 30, 2020

Previously on CHM676...

We developed a *microscopic expression* for the n^{th}-order response function:

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

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I.e., how to calculate nonlinear response functions without losing your mind.

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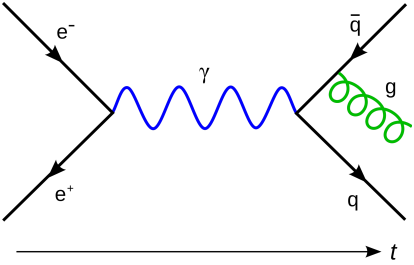
A: A one-to-one mapping between a particular set of mathematical expressions and symbolic diagrams



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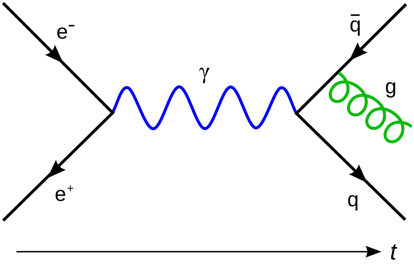

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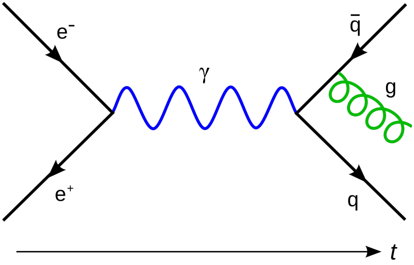

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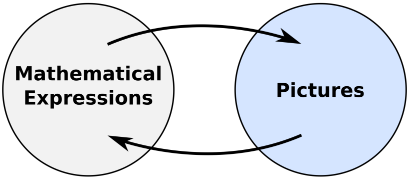

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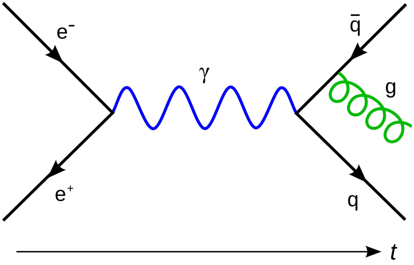

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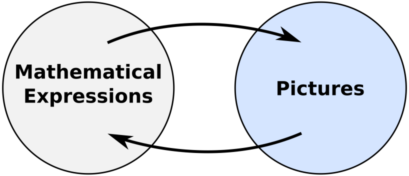

Our Target: A diagrammatic expansion for response theory

Diagrams for Nested Commutators

Nested Commutators

Let's start with some explicit examples of the *mathematical expressions* needed for response theory.

Single Commutator:

$$\left[\hat{\mu}^{(I)}_{\alpha_1}(0), \hat{\rho}_{\text{eq}}\right] = \hat{\mu}^{(I)}_{\alpha_1}(0)\hat{\rho}_{\text{eq}} - \hat{\rho}_{\text{eq}}\hat{\mu}^{(I)}_{\alpha_1}(0)$$

Double Commutator:

$$\begin{aligned}\left[\hat{\mu}^{(I)}_{\alpha_2}(\tau_1), \left[\hat{\mu}^{(I)}_{\alpha_1}(0), \hat{\rho}_{\text{eq}}\right]\right] &= \hat{\mu}^{(I)}_{\alpha_2}(\tau_1)\hat{\mu}^{(I)}_{\alpha_1}(0)\hat{\rho}_{\text{eq}} \\ &- \hat{\mu}^{(I)}_{\alpha_2}(\tau_1)\hat{\rho}_{\text{eq}}\hat{\mu}^{(I)}_{\alpha_1}(0) \\ &- \hat{\mu}^{(I)}_{\alpha_1}(0)\hat{\rho}_{\text{eq}}\hat{\mu}^{(I)}_{\alpha_2}(\tau_1) \\ &+ \hat{\rho}_{\text{eq}}\hat{\mu}^{(I)}_{\alpha_1}(0)\hat{\mu}^{(I)}_{\alpha_2}(\tau_1)\end{aligned}$$

Examples

Triple Commutator:

$$\left[\hat{\mu}^{(I)}_{\alpha_3}(\tau_1+\tau_2), \left[\hat{\mu}^{(I)}_{\alpha_2}(\tau_1), \left[\hat{\mu}^{(I)}_{\alpha_1}(0), \hat{\rho}_{\text{eq}}\right]\right]\right]$$

$$\begin{aligned}
&= \hat{\mu}^{(I)}_{\alpha_3}(\tau_1+\tau_2)\hat{\mu}^{(I)}_{\alpha_2}(\tau_1)\hat{\mu}^{(I)}_{\alpha_1}(0)\hat{\rho}_{\text{eq}} \\
&- \hat{\mu}^{(I)}_{\alpha_3}(\tau_1+\tau_2)\hat{\mu}^{(I)}_{\alpha_2}(\tau_1)\hat{\rho}_{\text{eq}}\hat{\mu}^{(I)}_{\alpha_1}(0) \\
&- \hat{\mu}^{(I)}_{\alpha_3}(\tau_1+\tau_2)\hat{\mu}^{(I)}_{\alpha_1}(0)\hat{\rho}_{\text{eq}}\hat{\mu}^{(I)}_{\alpha_2}(\tau_1) \\
&+ \hat{\mu}^{(I)}_{\alpha_3}(\tau_1+\tau_2)\hat{\rho}_{\text{eq}}\hat{\mu}^{(I)}_{\alpha_1}(0)\hat{\mu}^{(I)}_{\alpha_2}(\tau_1) \\
&- \hat{\mu}^{(I)}_{\alpha_2}(\tau_1)\hat{\mu}^{(I)}_{\alpha_1}(0)\hat{\rho}_{\text{eq}}\hat{\mu}^{(I)}_{\alpha_3}(\tau_1+\tau_2) \\
&+ \hat{\mu}^{(I)}_{\alpha_2}(\tau_1)\hat{\rho}_{\text{eq}}\hat{\mu}^{(I)}_{\alpha_1}(0)\hat{\mu}^{(I)}_{\alpha_3}(\tau_1+\tau_2) \\
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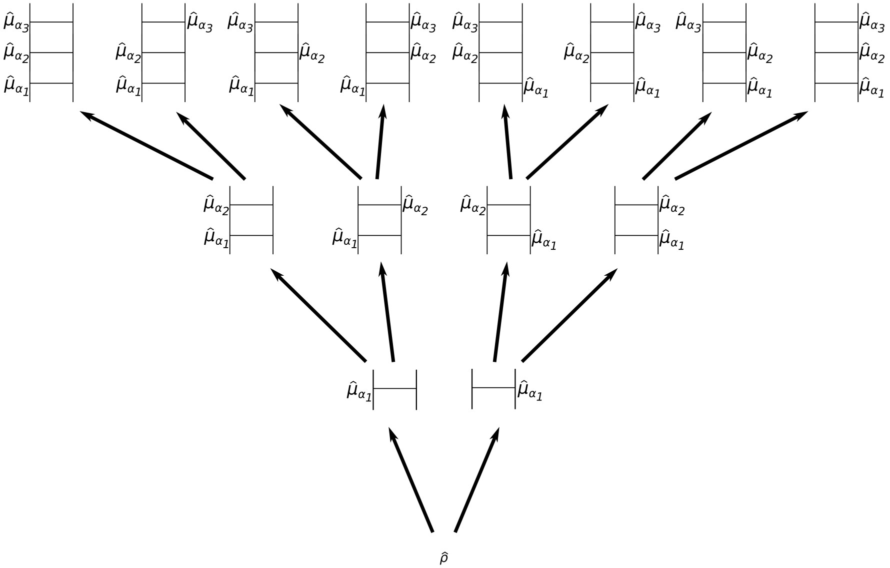
&- \hat{\rho}_{\text{eq}}\hat{\mu}^{(I)}_{\alpha_1}(0)\hat{\mu}^{(I)}_{\alpha_2}(\tau_1)\hat{\mu}^{(I)}_{\alpha_3}(\tau_1+\tau_2)
\end{aligned}$$

Notice:

- Each $\hat{\mu}^{(I)}_{\alpha_n}(\tau_1 + \ldots + \tau_{n-1})$ appears once
- Index n increases with distance from $\hat{\rho}_{\text{eq}}$
- Even # of terms to right of $\hat{\rho}_{\text{eq}} \Rightarrow$ positive sign
- Odd # of terms to right of $\hat{\rho}_{\text{eq}} \Rightarrow$ negative sign

Diagrammatic Representation



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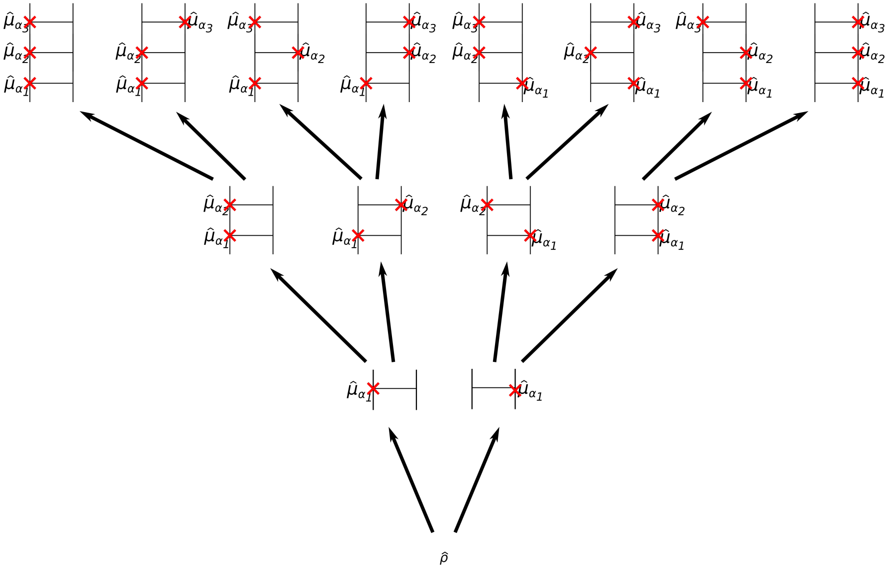

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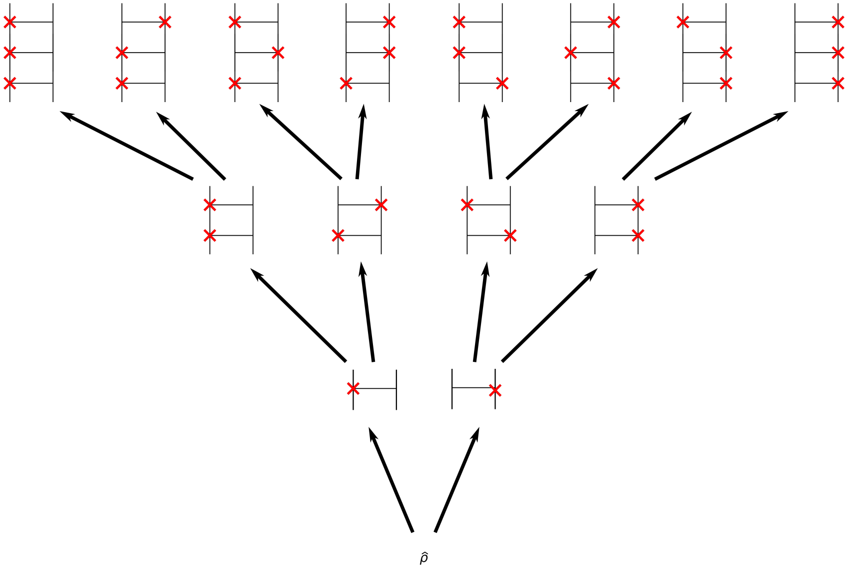

Commutator Diagram Rules

To generate the n^{th}-order commutator:

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  - Add a "$+$" to terms with an *even* number of right-side interactions
  - Add a "$-$" to terms with an *odd* number of right-side interactions

Diagrams for Eigenstate Expansions

Eigenstate Expansion

To interpret response functions microscopically, we need to expand in the system eigenstates.

Let the indices $a, b, c, d, \ldots$ represent eigenstates of the *molecular* Hamiltonian:

- Noting that $\hat{\rho}_{\text{eq}}$ is diagonal, substitute $\hat{\rho}_{\text{eq}} = \sum_a |a\rangle \, \rho_{aa}^{(\text{eq})} \, \langle a|$

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- Repeat until reaching the last $\hat{\mu}_{\alpha_n}^{(I)}$.

Third Order: Eigenstate Expansion

Step 1: Insert $\sum_a |a\rangle\, \rho_{aa}^{(\text{eq})}\, \langle a|$ in place of $\hat{\rho}_{\text{eq}}$

$$
\begin{aligned}
&\left[\hat{\mu}_{\alpha_3}^{(I)}(\tau_1+\tau_2), \left[\hat{\mu}_{\alpha_2}^{(I)}(\tau_1), \left[\hat{\mu}_{\alpha_1}^{(I)}(0), \hat{\rho}_{\text{eq}}\right]\right]\right] \\
&= \sum_a \Big\{ \hat{\mu}_{\alpha_3}^{(I)}(\tau_1+\tau_2)\hat{\mu}_{\alpha_2}^{(I)}(\tau_1)\hat{\mu}_{\alpha_1}^{(I)}(0)\, |a\rangle\, \rho_{aa}^{(\text{eq})}\, \langle a| \\
&\quad -\hat{\mu}_{\alpha_3}^{(I)}(\tau_1+\tau_2)\hat{\mu}_{\alpha_2}^{(I)}(\tau_1)\, |a\rangle\, \rho_{aa}^{(\text{eq})}\, \langle a|\, \hat{\mu}_{\alpha_1}^{(I)}(0) \\
&\quad -\hat{\mu}_{\alpha_3}^{(I)}(\tau_1+\tau_2)\hat{\mu}_{\alpha_1}^{(I)}(0)\, |a\rangle\, \rho_{aa}^{(\text{eq})}\, \langle a|\, \hat{\mu}_{\alpha_2}^{(I)}(\tau_1) \\
&\quad +\hat{\mu}_{\alpha_3}^{(I)}(\tau_1+\tau_2)\, |a\rangle\, \rho_{aa}^{(\text{eq})}\, \langle a|\, \hat{\mu}_{\alpha_1}^{(I)}(0)\hat{\mu}_{\alpha_2}^{(I)}(\tau_1) \\
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&\quad -\, |a\rangle\, \rho_{aa}^{(\text{eq})}\, \langle a|\, \hat{\mu}_{\alpha_1}^{(I)}(0)\hat{\mu}_{\alpha_2}^{(I)}(\tau_1)\hat{\mu}_{\alpha_3}^{(I)}(\tau_1+\tau_2) \Big\}
\end{aligned}
$$

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Step 2: Insert $\hat{1} = \sum_b |b\rangle\langle b|$ on the side of $\hat{\mu}^{(I)}_{\alpha_1}$ *away* from $\hat{\rho}_{\text{eq}}$.

$$\left[\hat{\mu}^{(I)}_{\alpha_3}(\tau_1+\tau_2), \left[\hat{\mu}^{(I)}_{\alpha_2}(\tau_1), \left[\hat{\mu}^{(I)}_{\alpha_1}(0), \hat{\rho}_{\text{eq}}\right]\right]\right]$$

$$\begin{aligned}
= \sum_{ab} \Big\{ & \hat{\mu}^{(I)}_{\alpha_3}(\tau_1+\tau_2)\hat{\mu}^{(I)}_{\alpha_2}(\tau_1)|b\rangle\langle b|\hat{\mu}^{(I)}_{\alpha_1}(0)|a\rangle\rho^{(\text{eq})}_{aa}\langle a| \\
& -\hat{\mu}^{(I)}_{\alpha_3}(\tau_1+\tau_2)\hat{\mu}^{(I)}_{\alpha_2}(\tau_1)|a\rangle\rho^{(\text{eq})}_{aa}\langle a|\hat{\mu}^{(I)}_{\alpha_1}(0)|b\rangle\langle b| \\
& -\hat{\mu}^{(I)}_{\alpha_3}(\tau_1+\tau_2)|b\rangle\langle b|\hat{\mu}^{(I)}_{\alpha_1}(0)|a\rangle\rho^{(\text{eq})}_{aa}\langle a|\hat{\mu}^{(I)}_{\alpha_2}(\tau_1) \\
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& +|b\rangle\langle b|\hat{\mu}^{(I)}_{\alpha_1}(0)|a\rangle\rho^{(\text{eq})}_{aa}\langle a|\hat{\mu}^{(I)}_{\alpha_2}(\tau_1)\hat{\mu}^{(I)}_{\alpha_3}(\tau_1+\tau_2) \\
& -|a\rangle\rho^{(\text{eq})}_{aa}\langle a|\hat{\mu}^{(I)}_{\alpha_1}(0)|b\rangle\langle b|\hat{\mu}^{(I)}_{\alpha_2}(\tau_1)\hat{\mu}^{(I)}_{\alpha_3}(\tau_1+\tau_2)\Big\}
\end{aligned}$$

Third Order: Eigenstate Expansion

Step 3: Insert $\hat{1} = \sum_c |c\rangle\langle c|$ on the side of $\hat{\mu}^{(I)}_{\alpha_2}$ *away* from $\hat{\rho}_{\text{eq}}$.

$$
\begin{aligned}
&\left[\hat{\mu}^{(I)}_{\alpha_3}(\tau_1+\tau_2), \left[\hat{\mu}^{(I)}_{\alpha_2}(\tau_1), \left[\hat{\mu}^{(I)}_{\alpha_1}(0), \hat{\rho}_{\text{eq}}\right]\right]\right] \\
&= \sum_{abc} \Big\{ \hat{\mu}^{(I)}_{\alpha_3}(\tau_1+\tau_2)|c\rangle\langle c|\hat{\mu}^{(I)}_{\alpha_2}(\tau_1)|b\rangle\langle b|\hat{\mu}^{(I)}_{\alpha_1}(0)|a\rangle\rho^{(\text{eq})}_{aa}\langle a| \\
&\quad -\hat{\mu}^{(I)}_{\alpha_3}(\tau_1+\tau_2)|c\rangle\langle c|\hat{\mu}^{(I)}_{\alpha_2}(\tau_1)|a\rangle\rho^{(\text{eq})}_{aa}\langle a|\hat{\mu}^{(I)}_{\alpha_1}(0)|b\rangle\langle b| \\
&\quad -\hat{\mu}^{(I)}_{\alpha_3}(\tau_1+\tau_2)|b\rangle\langle b|\hat{\mu}^{(I)}_{\alpha_1}(0)|a\rangle\rho^{(\text{eq})}_{aa}\langle a|\hat{\mu}^{(I)}_{\alpha_2}(\tau_1)|c\rangle\langle c| \\
&\quad +\hat{\mu}^{(I)}_{\alpha_3}(\tau_1+\tau_2)|a\rangle\rho^{(\text{eq})}_{aa}\langle a|\hat{\mu}^{(I)}_{\alpha_1}(0)|b\rangle\langle b|\hat{\mu}^{(I)}_{\alpha_2}(\tau_1)|c\rangle\langle c| \\
&\quad -|c\rangle\langle c|\hat{\mu}^{(I)}_{\alpha_2}(\tau_1)|b\rangle\langle b|\hat{\mu}^{(I)}_{\alpha_1}(0)|a\rangle\rho^{(\text{eq})}_{aa}\langle a|\hat{\mu}^{(I)}_{\alpha_3}(\tau_1+\tau_2) \\
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\end{aligned}
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Step 4: Insert $\hat{1} = \sum_d |d\rangle\langle d|$ on the side of $\hat{\mu}^{(I)}_{\alpha_3}$ *away* from $\hat{\rho}_{\text{eq}}$.

$$
\begin{aligned}
&\left[\hat{\mu}^{(I)}_{\alpha_3}(\tau_1+\tau_2), \left[\hat{\mu}^{(I)}_{\alpha_2}(\tau_1), \left[\hat{\mu}^{(I)}_{\alpha_1}(0), \hat{\rho}_{\text{eq}}\right]\right]\right] \\
&= \sum_{abcd} \Big\{ |d\rangle\langle d|\hat{\mu}^{(I)}_{\alpha_3}(\tau_1+\tau_2)|c\rangle\langle c|\hat{\mu}^{(I)}_{\alpha_2}(\tau_1)|b\rangle\langle b|\hat{\mu}^{(I)}_{\alpha_1}(0)|a\rangle\rho^{(\text{eq})}_{aa}\langle a| \\
&\quad -|d\rangle\langle d|\hat{\mu}^{(I)}_{\alpha_3}(\tau_1+\tau_2)|c\rangle\langle c|\hat{\mu}^{(I)}_{\alpha_2}(\tau_1)|a\rangle\rho^{(\text{eq})}_{aa}\langle a|\hat{\mu}^{(I)}_{\alpha_1}(0)|b\rangle\langle b| \\
&\quad -|d\rangle\langle d|\hat{\mu}^{(I)}_{\alpha_3}(\tau_1+\tau_2)|b\rangle\langle b|\hat{\mu}^{(I)}_{\alpha_1}(0)|a\rangle\rho^{(\text{eq})}_{aa}\langle a|\hat{\mu}^{(I)}_{\alpha_2}(\tau_1)|c\rangle\langle c| \\
&\quad +|d\rangle\langle d|\hat{\mu}^{(I)}_{\alpha_3}(\tau_1+\tau_2)|a\rangle\rho^{(\text{eq})}_{aa}\langle a|\hat{\mu}^{(I)}_{\alpha_1}(0)|b\rangle\langle b|\hat{\mu}^{(I)}_{\alpha_2}(\tau_1)|c\rangle\langle c| \\
&\quad -|c\rangle\langle c|\hat{\mu}^{(I)}_{\alpha_2}(\tau_1)|b\rangle\langle b|\hat{\mu}^{(I)}_{\alpha_1}(0)|a\rangle\rho^{(\text{eq})}_{aa}\langle a|\hat{\mu}^{(I)}_{\alpha_3}(\tau_1+\tau_2)|d\rangle\langle d| \\
&\quad +|c\rangle\langle c|\hat{\mu}^{(I)}_{\alpha_2}(\tau_1)|a\rangle\rho^{(\text{eq})}_{aa}\langle a|\hat{\mu}^{(I)}_{\alpha_1}(0)|b\rangle\langle b|\hat{\mu}^{(I)}_{\alpha_3}(\tau_1+\tau_2)|d\rangle\langle d| \\
&\quad +|b\rangle\langle b|\hat{\mu}^{(I)}_{\alpha_1}(0)|a\rangle\rho^{(\text{eq})}_{aa}\langle a|\hat{\mu}^{(I)}_{\alpha_2}(\tau_1)|c\rangle\langle c|\hat{\mu}^{(I)}_{\alpha_3}(\tau_1+\tau_2)|d\rangle\langle d| \\
&\quad -|a\rangle\rho^{(\text{eq})}_{aa}\langle a|\hat{\mu}^{(I)}_{\alpha_1}(0)|b\rangle\langle b|\hat{\mu}^{(I)}_{\alpha_2}(\tau_1)|c\rangle\langle c|\hat{\mu}^{(I)}_{\alpha_3}(\tau_1+\tau_2)|d\rangle\langle d| \Big\}
\end{aligned}
$$

Third Order: Eigenstate Interpretation

System begins in state $|a\rangle\langle a|$

$$\left[\hat{\mu}^{(I)}_{\alpha_3}(\tau_1+\tau_2),\left[\hat{\mu}^{(I)}_{\alpha_2}(\tau_1),\left[\hat{\mu}^{(I)}_{\alpha_1}(0),\hat{\rho}_{\text{eq}}\right]\right]\right]$$

$$\begin{aligned}
= \sum_{abcd}\Big\{ & |d\rangle\langle d|\hat{\mu}^{(I)}_{\alpha_3}(\tau_1+\tau_2)|c\rangle\langle c|\hat{\mu}^{(I)}_{\alpha_2}(\tau_1)|b\rangle\langle b|\hat{\mu}^{(I)}_{\alpha_1}(0)|a\rangle\rho^{(\text{eq})}_{aa}\langle a| \\
& -|d\rangle\langle d|\hat{\mu}^{(I)}_{\alpha_3}(\tau_1+\tau_2)|c\rangle\langle c|\hat{\mu}^{(I)}_{\alpha_2}(\tau_1)|a\rangle\rho^{(\text{eq})}_{aa}\langle a|\hat{\mu}^{(I)}_{\alpha_1}(0)|b\rangle\langle b| \\
& -|d\rangle\langle d|\hat{\mu}^{(I)}_{\alpha_3}(\tau_1+\tau_2)|b\rangle\langle b|\hat{\mu}^{(I)}_{\alpha_1}(0)|a\rangle\rho^{(\text{eq})}_{aa}\langle a|\hat{\mu}^{(I)}_{\alpha_2}(\tau_1)|c\rangle\langle c| \\
& +|d\rangle\langle d|\hat{\mu}^{(I)}_{\alpha_3}(\tau_1+\tau_2)|a\rangle\rho^{(\text{eq})}_{aa}\langle a|\hat{\mu}^{(I)}_{\alpha_1}(0)|b\rangle\langle b|\hat{\mu}^{(I)}_{\alpha_2}(\tau_1)|c\rangle\langle c| \\
& -|c\rangle\langle c|\hat{\mu}^{(I)}_{\alpha_2}(\tau_1)|b\rangle\langle b|\hat{\mu}^{(I)}_{\alpha_1}(0)|a\rangle\rho^{(\text{eq})}_{aa}\langle a|\hat{\mu}^{(I)}_{\alpha_3}(\tau_1+\tau_2)|d\rangle\langle d| \\
& +|c\rangle\langle c|\hat{\mu}^{(I)}_{\alpha_2}(\tau_1)|a\rangle\rho^{(\text{eq})}_{aa}\langle a|\hat{\mu}^{(I)}_{\alpha_1}(0)|b\rangle\langle b|\hat{\mu}^{(I)}_{\alpha_3}(\tau_1+\tau_2)|d\rangle\langle d| \\
& +|b\rangle\langle b|\hat{\mu}^{(I)}_{\alpha_1}(0)|a\rangle\rho^{(\text{eq})}_{aa}\langle a|\hat{\mu}^{(I)}_{\alpha_2}(\tau_1)|c\rangle\langle c|\hat{\mu}^{(I)}_{\alpha_3}(\tau_1+\tau_2)|d\rangle\langle d| \\
& -|a\rangle\rho^{(\text{eq})}_{aa}\langle a|\hat{\mu}^{(I)}_{\alpha_1}(0)|b\rangle\langle b|\hat{\mu}^{(I)}_{\alpha_2}(\tau_1)|c\rangle\langle c|\hat{\mu}^{(I)}_{\alpha_3}(\tau_1+\tau_2)|d\rangle\langle d|\Big\}
\end{aligned}$$

Third Order: Eigenstate Expansion

$\hat{\mu}^{(I)}_{\alpha_1}$ induces a transition to state b at $t = 0$

$$\left[\hat{\mu}^{(I)}_{\alpha_3}(\tau_1+\tau_2), \left[\hat{\mu}^{(I)}_{\alpha_2}(\tau_1), \left[\hat{\mu}^{(I)}_{\alpha_1}(0), \hat{\rho}_{\text{eq}}\right]\right]\right]$$

$$\begin{aligned} = \sum_{abcd} \Big\{ & |d\rangle\langle d|\,\hat{\mu}^{(I)}_{\alpha_3}(\tau_1+\tau_2)|c\rangle\langle c|\,\hat{\mu}^{(I)}_{\alpha_2}(\tau_1)|b\rangle\langle b|\,\hat{\mu}^{(I)}_{\alpha_1}(0)\,|a\rangle\,\rho^{(\text{eq})}_{aa}\,\langle a| \\ & -|d\rangle\langle d|\,\hat{\mu}^{(I)}_{\alpha_3}(\tau_1+\tau_2)|c\rangle\langle c|\,\hat{\mu}^{(I)}_{\alpha_2}(\tau_1)\,|a\rangle\,\rho^{(\text{eq})}_{aa}\,\langle a|\,\hat{\mu}^{(I)}_{\alpha_1}(0)\,|b\rangle\langle b| \\ & -|d\rangle\langle d|\,\hat{\mu}^{(I)}_{\alpha_3}(\tau_1+\tau_2)|b\rangle\langle b|\,\hat{\mu}^{(I)}_{\alpha_1}(0)\,|a\rangle\,\rho^{(\text{eq})}_{aa}\,\langle a|\,\hat{\mu}^{(I)}_{\alpha_2}(\tau_1)\,|c\rangle\langle c| \\ & +|d\rangle\langle d|\,\hat{\mu}^{(I)}_{\alpha_3}(\tau_1+\tau_2)\,|a\rangle\,\rho^{(\text{eq})}_{aa}\,\langle a|\,\hat{\mu}^{(I)}_{\alpha_1}(0)\,|b\rangle\langle b|\hat{\mu}^{(I)}_{\alpha_2}(\tau_1)\,|c\rangle\langle c| \\ & -|c\rangle\langle c|\,\hat{\mu}^{(I)}_{\alpha_2}(\tau_1)|b\rangle\langle b|\,\hat{\mu}^{(I)}_{\alpha_1}(0)\,|a\rangle\,\rho^{(\text{eq})}_{aa}\,\langle a|\,\hat{\mu}^{(I)}_{\alpha_3}(\tau_1+\tau_2)\,|d\rangle\langle d| \\ & +|c\rangle\langle c|\,\hat{\mu}^{(I)}_{\alpha_2}(\tau_1)\,|a\rangle\,\rho^{(\text{eq})}_{aa}\,\langle a|\,\hat{\mu}^{(I)}_{\alpha_1}(0)\,|b\rangle\langle b|\hat{\mu}^{(I)}_{\alpha_3}(\tau_1+\tau_2)\,|d\rangle\langle d| \\ & +|b\rangle\langle b|\,\hat{\mu}^{(I)}_{\alpha_1}(0)\,|a\rangle\,\rho^{(\text{eq})}_{aa}\,\langle a|\,\hat{\mu}^{(I)}_{\alpha_2}(\tau_1)\,|c\rangle\langle c|\hat{\mu}^{(I)}_{\alpha_3}(\tau_1+\tau_2)\,|d\rangle\langle d| \\ & -|a\rangle\,\rho^{(\text{eq})}_{aa}\,\langle a|\,\hat{\mu}^{(I)}_{\alpha_1}(0)\,|b\rangle\langle b|\hat{\mu}^{(I)}_{\alpha_2}(\tau_1)\,|c\rangle\langle c|\hat{\mu}^{(I)}_{\alpha_3}(\tau_1+\tau_2)\,|d\rangle\langle d| \Big\} \end{aligned}$$

Third Order: Eigenstate Expansion

$\hat{\mu}_{\alpha_2}^{(I)}$ induces a transition to state c at $t = \tau_1$

$$
\begin{aligned}
&\left[\hat{\mu}_{\alpha_3}^{(I)}(\tau_1+\tau_2), \left[\hat{\mu}_{\alpha_2}^{(I)}(\tau_1), \left[\hat{\mu}_{\alpha_1}^{(I)}(0), \hat{\rho}_{\text{eq}}\right]\right]\right] \\
&\quad = \sum_{abcd} \Big\{ |d\rangle\langle d|\,\hat{\mu}_{\alpha_3}^{(I)}(\tau_1+\tau_2)|c\rangle\langle c|\,\hat{\mu}_{\alpha_2}^{(I)}(\tau_1)|b\rangle\langle b|\,\hat{\mu}_{\alpha_1}^{(I)}(0)\,|a\rangle\,\rho_{aa}^{(\text{eq})}\,\langle a| \\
&\qquad - |d\rangle\langle d|\,\hat{\mu}_{\alpha_3}^{(I)}(\tau_1+\tau_2)|c\rangle\langle c|\,\hat{\mu}_{\alpha_2}^{(I)}(\tau_1)\,|a\rangle\,\rho_{aa}^{(\text{eq})}\,\langle a|\,\hat{\mu}_{\alpha_1}^{(I)}(0)\,|b\rangle\langle b| \\
&\qquad - |d\rangle\langle d|\,\hat{\mu}_{\alpha_3}^{(I)}(\tau_1+\tau_2)|b\rangle\langle b|\,\hat{\mu}_{\alpha_1}^{(I)}(0)\,|a\rangle\,\rho_{aa}^{(\text{eq})}\,\langle a|\,\hat{\mu}_{\alpha_2}^{(I)}(\tau_1)\,|c\rangle\langle c| \\
&\qquad + |d\rangle\langle d|\,\hat{\mu}_{\alpha_3}^{(I)}(\tau_1+\tau_2)\,|a\rangle\,\rho_{aa}^{(\text{eq})}\,\langle a|\,\hat{\mu}_{\alpha_1}^{(I)}(0)\,|b\rangle\langle b|\hat{\mu}_{\alpha_2}^{(I)}(\tau_1)\,|c\rangle\langle c| \\
&\qquad - |c\rangle\langle c|\,\hat{\mu}_{\alpha_2}^{(I)}(\tau_1)|b\rangle\langle b|\,\hat{\mu}_{\alpha_1}^{(I)}(0)\,|a\rangle\,\rho_{aa}^{(\text{eq})}\,\langle a|\,\hat{\mu}_{\alpha_3}^{(I)}(\tau_1+\tau_2)\,|d\rangle\langle d| \\
&\qquad + |c\rangle\langle c|\,\hat{\mu}_{\alpha_2}^{(I)}(\tau_1)\,|a\rangle\,\rho_{aa}^{(\text{eq})}\,\langle a|\,\hat{\mu}_{\alpha_1}^{(I)}(0)\,|b\rangle\langle b|\hat{\mu}_{\alpha_3}^{(I)}(\tau_1+\tau_2)\,|d\rangle\langle d| \\
&\qquad + |b\rangle\langle b|\,\hat{\mu}_{\alpha_1}^{(I)}(0)\,|a\rangle\,\rho_{aa}^{(\text{eq})}\,\langle a|\,\hat{\mu}_{\alpha_2}^{(I)}(\tau_1)\,|c\rangle\langle c|\hat{\mu}_{\alpha_3}^{(I)}(\tau_1+\tau_2)\,|d\rangle\langle d| \\
&\qquad - |a\rangle\,\rho_{aa}^{(\text{eq})}\,\langle a|\,\hat{\mu}_{\alpha_1}^{(I)}(0)\,|b\rangle\langle b|\hat{\mu}_{\alpha_2}^{(I)}(\tau_1)\,|c\rangle\langle c|\hat{\mu}_{\alpha_3}^{(I)}(\tau_1+\tau_2)\,|d\rangle\langle d| \Big\}
\end{aligned}
$$

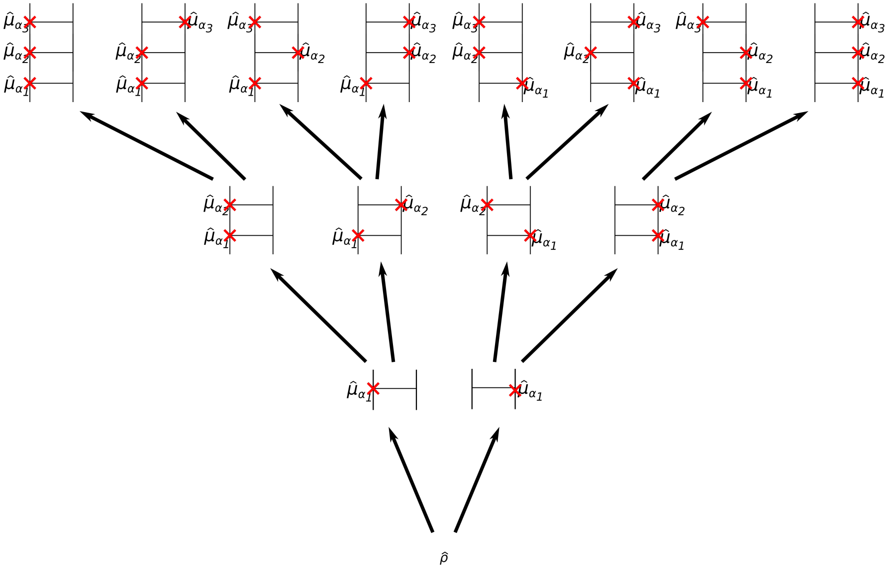
Third Order: Eigenstate Expansion

$\hat{\mu}_{\alpha_3}^{(I)}$ induces a transition to state d at $t = \tau_1 + \tau_2$

$$\left[\hat{\mu}_{\alpha_3}^{(I)}(\tau_1+\tau_2), \left[\hat{\mu}_{\alpha_2}^{(I)}(\tau_1), \left[\hat{\mu}_{\alpha_1}^{(I)}(0), \hat{\rho}_{\text{eq}}\right]\right]\right]$$

$$\begin{aligned}
= \sum_{abcd} \Big\{ & |d\rangle\langle d|\,\hat{\mu}_{\alpha_3}^{(I)}(\tau_1+\tau_2)|c\rangle\langle c|\,\hat{\mu}_{\alpha_2}^{(I)}(\tau_1)|b\rangle\langle b|\,\hat{\mu}_{\alpha_1}^{(I)}(0)\,|a\rangle\,\rho_{aa}^{(\text{eq})}\,\langle a| \\
& - |d\rangle\langle d|\,\hat{\mu}_{\alpha_3}^{(I)}(\tau_1+\tau_2)|c\rangle\langle c|\,\hat{\mu}_{\alpha_2}^{(I)}(\tau_1)\,|a\rangle\,\rho_{aa}^{(\text{eq})}\,\langle a|\,\hat{\mu}_{\alpha_1}^{(I)}(0)\,|b\rangle\langle b| \\
& - |d\rangle\langle d|\,\hat{\mu}_{\alpha_3}^{(I)}(\tau_1+\tau_2)|b\rangle\langle b|\,\hat{\mu}_{\alpha_1}^{(I)}(0)\,|a\rangle\,\rho_{aa}^{(\text{eq})}\,\langle a|\,\hat{\mu}_{\alpha_2}^{(I)}(\tau_1)\,|c\rangle\langle c| \\
& + |d\rangle\langle d|\,\hat{\mu}_{\alpha_3}^{(I)}(\tau_1+\tau_2)\,|a\rangle\,\rho_{aa}^{(\text{eq})}\,\langle a|\,\hat{\mu}_{\alpha_1}^{(I)}(0)\,|b\rangle\langle b|\hat{\mu}_{\alpha_2}^{(I)}(\tau_1)\,|c\rangle\langle c| \\
& - |c\rangle\langle c|\,\hat{\mu}_{\alpha_2}^{(I)}(\tau_1)|b\rangle\langle b|\,\hat{\mu}_{\alpha_1}^{(I)}(0)\,|a\rangle\,\rho_{aa}^{(\text{eq})}\,\langle a|\,\hat{\mu}_{\alpha_3}^{(I)}(\tau_1+\tau_2)\,|d\rangle\langle d| \\
& + |c\rangle\langle c|\,\hat{\mu}_{\alpha_2}^{(I)}(\tau_1)\,|a\rangle\,\rho_{aa}^{(\text{eq})}\,\langle a|\,\hat{\mu}_{\alpha_1}^{(I)}(0)\,|b\rangle\langle b|\hat{\mu}_{\alpha_3}^{(I)}(\tau_1+\tau_2)\,|d\rangle\langle d| \\
& + |b\rangle\langle b|\,\hat{\mu}_{\alpha_1}^{(I)}(0)\,|a\rangle\,\rho_{aa}^{(\text{eq})}\,\langle a|\,\hat{\mu}_{\alpha_2}^{(I)}(\tau_1)\,|c\rangle\langle c|\hat{\mu}_{\alpha_3}^{(I)}(\tau_1+\tau_2)\,|d\rangle\langle d| \\
& - |a\rangle\,\rho_{aa}^{(\text{eq})}\,\langle a|\,\hat{\mu}_{\alpha_1}^{(I)}(0)\,|b\rangle\langle b|\hat{\mu}_{\alpha_2}^{(I)}(\tau_1)\,|c\rangle\langle c|\hat{\mu}_{\alpha_3}^{(I)}(\tau_1+\tau_2)\,|d\rangle\langle d| \Big\}
\end{aligned}$$

Back to the Diagrams



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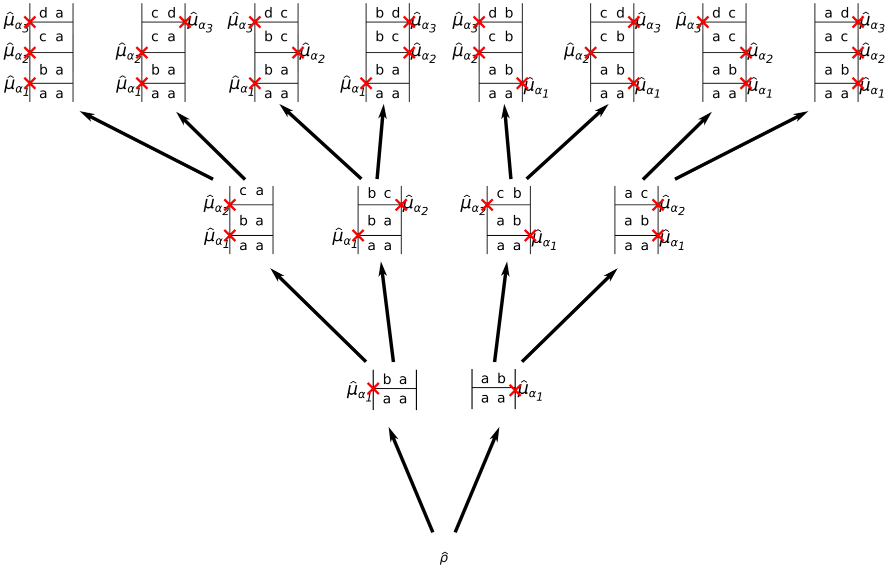

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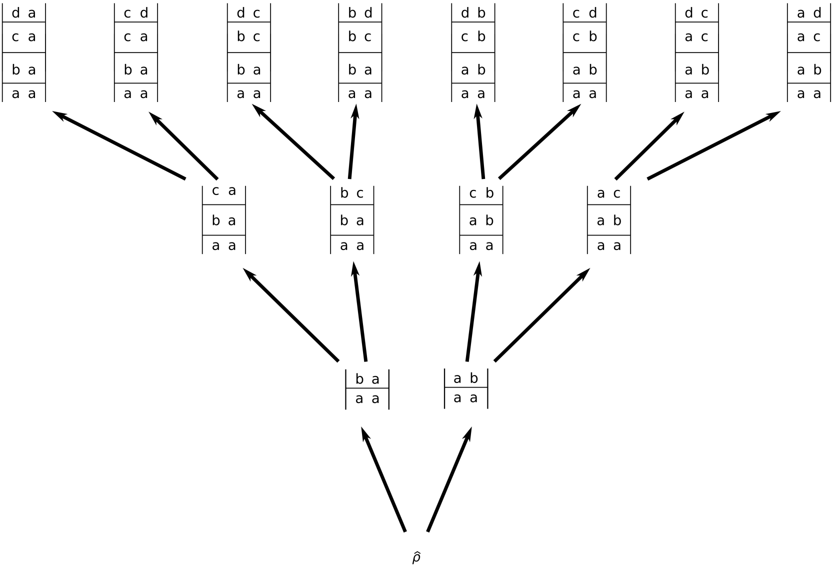

Transition Dipoles

Back to the Response Function

Our diagrams so far represent components

$$|x\rangle \langle y|$$

of the perturbed density matrix. E.g.,

$$|b\rangle \langle b| \hat{\mu}_{\alpha_1}^{(I)}(0) |a\rangle \rho_{aa}^{(\text{eq})} \langle a| \hat{\mu}_{\alpha_2}^{(I)}(\tau_1) |c\rangle \langle c| \hat{\mu}_{\alpha_3}^{(I)}(\tau_1 + \tau_2) |d\rangle \langle d|$$

Back to the Response Function

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Back to the Response Function

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In the response function, we have terms of the form

$$\begin{aligned} &\text{Tr}\left\{\hat{\mu}_{\alpha}^{(n)} |x\rangle \langle y|\right\} \\ &= \sum_n \langle n| \hat{\mu}_{\alpha} |x\rangle \langle y| n\rangle \\ &= \langle y| \hat{\mu}_{\alpha} |x\rangle \end{aligned}$$

In our response function expansion:

$$\mathrm{Tr}\Big\{\hat{\mu}_{\alpha}^{(I)}(\tau_1+\tau_2+\tau_3)\Big[\hat{\mu}_{\alpha_3}^{(I)}(\tau_1+\tau_2),\Big[\hat{\mu}_{\alpha_2}^{(I)}(\tau_1),\Big[\hat{\mu}_{\alpha_1}^{(I)}(0),\hat{\rho}_{\text{eq}}\Big]\Big]\Big]\Big\}$$

$$= \mathrm{Tr}\Big\{\sum_{abcd}\Big\{$$

$$+\hat{\mu}_{\alpha}^{(I)}(\tau_1+\tau_2+\tau_3)\,|d\rangle\langle d|\,\hat{\mu}_{\alpha_3}^{(I)}(\tau_1+\tau_2)\,|c\rangle\langle c|\,\hat{\mu}_{\alpha_2}^{(I)}(\tau_1)\,|b\rangle\langle b|\,\hat{\mu}_{\alpha_1}^{(I)}(0)\,|a\rangle\,\rho_{aa}^{(\text{eq})}\,\langle a|$$

$$-\hat{\mu}_{\alpha}^{(I)}(\tau_1+\tau_2+\tau_3)\,|d\rangle\langle d|\,\hat{\mu}_{\alpha_3}^{(I)}(\tau_1+\tau_2)\,|c\rangle\langle c|\,\hat{\mu}_{\alpha_2}^{(I)}(\tau_1)\,|a\rangle\,\rho_{aa}^{(\text{eq})}\,\langle a|\,\hat{\mu}_{\alpha_1}^{(I)}(0)\,|b\rangle\langle b|$$

$$-\hat{\mu}_{\alpha}^{(I)}(\tau_1+\tau_2+\tau_3)\,|d\rangle\langle d|\,\hat{\mu}_{\alpha_3}^{(I)}(\tau_1+\tau_2)\,|b\rangle\langle b|\,\hat{\mu}_{\alpha_1}^{(I)}(0)\,|a\rangle\,\rho_{aa}^{(\text{eq})}\,\langle a|\,\hat{\mu}_{\alpha_2}^{(I)}(\tau_1)\,|c\rangle\langle c|$$

$$+\hat{\mu}_{\alpha}^{(I)}(\tau_1+\tau_2+\tau_3)\,|d\rangle\langle d|\,\hat{\mu}_{\alpha_3}^{(I)}(\tau_1+\tau_2)\,|a\rangle\,\rho_{aa}^{(\text{eq})}\,\langle a|\,\hat{\mu}_{\alpha_1}^{(I)}(0)\,|b\rangle\langle b|\,\hat{\mu}_{\alpha_2}^{(I)}(\tau_1)\,|c\rangle\langle c|$$

$$-\hat{\mu}_{\alpha}^{(I)}(\tau_1+\tau_2+\tau_3)\,|c\rangle\langle c|\,\hat{\mu}_{\alpha_2}^{(I)}(\tau_1)\,|b\rangle\langle b|\,\hat{\mu}_{\alpha_1}^{(I)}(0)\,|a\rangle\,\rho_{aa}^{(\text{eq})}\,\langle a|\,\hat{\mu}_{\alpha_3}^{(I)}(\tau_1+\tau_2)\,|d\rangle\langle d|$$

$$+\hat{\mu}_{\alpha}^{(I)}(\tau_1+\tau_2+\tau_3)\,|c\rangle\langle c|\,\hat{\mu}_{\alpha_2}^{(I)}(\tau_1)\,|a\rangle\,\rho_{aa}^{(\text{eq})}\,\langle a|\,\hat{\mu}_{\alpha_1}^{(I)}(0)\,|b\rangle\langle b|\,\hat{\mu}_{\alpha_3}^{(I)}(\tau_1+\tau_2)\,|d\rangle\langle d|$$

$$+\hat{\mu}_{\alpha}^{(I)}(\tau_1+\tau_2+\tau_3)\,|b\rangle\langle b|\,\hat{\mu}_{\alpha_1}^{(I)}(0)\,|a\rangle\,\rho_{aa}^{(\text{eq})}\,\langle a|\,\hat{\mu}_{\alpha_2}^{(I)}(\tau_1)\,|c\rangle\langle c|\,\hat{\mu}_{\alpha_3}^{(I)}(\tau_1+\tau_2)\,|d\rangle\langle d|$$

$$-\hat{\mu}_{\alpha}^{(I)}(\tau_1+\tau_2+\tau_3)\,|a\rangle\,\rho_{aa}^{(\text{eq})}\,\langle a|\,\hat{\mu}_{\alpha_1}^{(I)}(0)\,|b\rangle\langle b|\,\hat{\mu}_{\alpha_2}^{(I)}(\tau_1)\,|c\rangle\langle c|\,\hat{\mu}_{\alpha_3}^{(I)}(\tau_1+\tau_2)\,|d\rangle\langle d|\;\Big\}$$

In our response function expansion:

$$\text{Tr}\Big\{\hat{\mu}_{\alpha}^{(I)}(\tau_1+\tau_2+\tau_3)\Big[\hat{\mu}_{\alpha_3}^{(I)}(\tau_1+\tau_2),\Big[\hat{\mu}_{\alpha_2}^{(I)}(\tau_1),\Big[\hat{\mu}_{\alpha_1}^{(I)}(0),\hat{\rho}_{\text{eq}}\Big]\Big]\Big]\Big\}$$

$$= \text{Tr}\Big\{\sum_{abcd}\Big\{$$

$$+\langle a|\,\hat{\mu}_{\alpha}^{(I)}(\tau_1+\tau_2+\tau_3)\,|d\rangle\,\langle d|\,\hat{\mu}_{\alpha_3}^{(I)}(\tau_1+\tau_2)\,|c\rangle\,\langle c|\,\hat{\mu}_{\alpha_2}^{(I)}(\tau_1)\,|b\rangle\,\langle b|\,\hat{\mu}_{\alpha_1}^{(I)}(0)\,|a\rangle\,\rho_{aa}^{(\text{eq})}$$

$$-\langle b|\,\hat{\mu}_{\alpha}^{(I)}(\tau_1+\tau_2+\tau_3)\,|d\rangle\,\langle d|\,\hat{\mu}_{\alpha_3}^{(I)}(\tau_1+\tau_2)\,|c\rangle\,\langle c|\,\hat{\mu}_{\alpha_2}^{(I)}(\tau_1)\,|a\rangle\,\rho_{aa}^{(\text{eq})}\,\langle a|\,\hat{\mu}_{\alpha_1}^{(I)}(0)\,|b\rangle$$

$$-\langle c|\,\hat{\mu}_{\alpha}^{(I)}(\tau_1+\tau_2+\tau_3)\,|d\rangle\,\langle d|\,\hat{\mu}_{\alpha_3}^{(I)}(\tau_1+\tau_2)\,|b\rangle\,\langle b|\,\hat{\mu}_{\alpha_1}^{(I)}(0)\,|a\rangle\,\rho_{aa}^{(\text{eq})}\,\langle a|\,\hat{\mu}_{\alpha_2}^{(I)}(\tau_1)\,|c\rangle$$

$$+\langle c|\,\hat{\mu}_{\alpha}^{(I)}(\tau_1+\tau_2+\tau_3)\,|d\rangle\,\langle d|\,\hat{\mu}_{\alpha_3}^{(I)}(\tau_1+\tau_2)\,|a\rangle\,\rho_{aa}^{(\text{eq})}\,\langle a|\,\hat{\mu}_{\alpha_1}^{(I)}(0)\,|b\rangle\,\langle b|\,\hat{\mu}_{\alpha_2}^{(I)}(\tau_1)\,|c\rangle$$

$$-\langle d|\,\hat{\mu}_{\alpha}^{(I)}(\tau_1+\tau_2+\tau_3)\,|c\rangle\,\langle c|\,\hat{\mu}_{\alpha_2}^{(I)}(\tau_1)\,|b\rangle\,\langle b|\,\hat{\mu}_{\alpha_1}^{(I)}(0)\,|a\rangle\,\rho_{aa}^{(\text{eq})}\,\langle a|\,\hat{\mu}_{\alpha_3}^{(I)}(\tau_1+\tau_2)\,|d\rangle$$

$$+\langle d|\,\hat{\mu}_{\alpha}^{(I)}(\tau_1+\tau_2+\tau_3)\,|c\rangle\,\langle c|\,\hat{\mu}_{\alpha_2}^{(I)}(\tau_1)\,|a\rangle\,\rho_{aa}^{(\text{eq})}\,\langle a|\,\hat{\mu}_{\alpha_1}^{(I)}(0)\,|b\rangle\,\langle b|\,\hat{\mu}_{\alpha_3}^{(I)}(\tau_1+\tau_2)\,|d\rangle$$

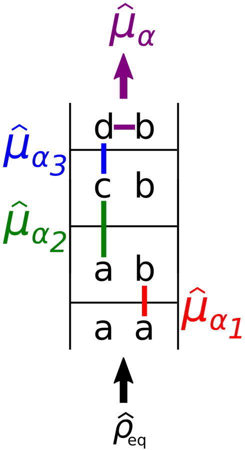
$$+\langle d|\,\hat{\mu}_{\alpha}^{(I)}(\tau_1+\tau_2+\tau_3)\,|b\rangle\,\langle b|\,\hat{\mu}_{\alpha_1}^{(I)}(0)\,|a\rangle\,\rho_{aa}^{(\text{eq})}\,\langle a|\,\hat{\mu}_{\alpha_2}^{(I)}(\tau_1)\,|c\rangle\,\langle c|\,\hat{\mu}_{\alpha_3}^{(I)}(\tau_1+\tau_2)\,|d\rangle$$

$$-\langle d|\,\hat{\mu}_{\alpha}^{(I)}(\tau_1+\tau_2+\tau_3)\,|a\rangle\,\rho_{aa}^{(\text{eq})}\,\langle a|\,\hat{\mu}_{\alpha_1}^{(I)}(0)\,|b\rangle\,\langle b|\,\hat{\mu}_{\alpha_2}^{(I)}(\tau_1)\,|c\rangle\,\langle c|\,\hat{\mu}_{\alpha_3}^{(I)}(\tau_1+\tau_2)\,|d\rangle\Big\}$$

Dipole Moment Matrix Elements

We can now generate simple rules for identifying dipole matrix elements from our diagrams:

- Matrix elements of the **interaction dipoles** $\hat{\mu}^{(I)}_{\alpha_1}, \ldots, \hat{\mu}^{(I)}_{\alpha_n}$ are taken **across consecutive rungs** of the ladder
- The matrix element of the **signal dipole** $\hat{\mu}_\alpha$ is taken **along the final rung** of the ladder



$$\langle b|\, \hat{\mu}^{(I)}_{\alpha}(\tau_1+\tau_2+\tau_3)|d\rangle\, \langle d|\, \hat{\mu}^{(I)}_{\alpha_3}(\tau_1+\tau_2)|c\rangle\, \langle c|\, \hat{\mu}^{(I)}_{\alpha_2}(\tau_1)\, |a\rangle\, \rho^{(\mathrm{eq})}_{aa}\, \langle a|\, \hat{\mu}^{(I)}_{\alpha_1}(0)\, |b\rangle$$

Frequency Components

Frequency Components

Recall that

$$\hat{\mu}_{\alpha}^{(I)}(t) \equiv e^{\frac{i}{\hbar}\hat{H}_o t}\hat{\mu}_{\alpha}e^{-\frac{i}{\hbar}\hat{H}_o t}.$$

Frequency Components

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$$\hat{\mu}_{\alpha}^{(I)}(t) \equiv e^{\frac{i}{\hbar}\hat{H}_o t}\hat{\mu}_{\alpha}e^{-\frac{i}{\hbar}\hat{H}_o t}.$$

Taking matrix elements:

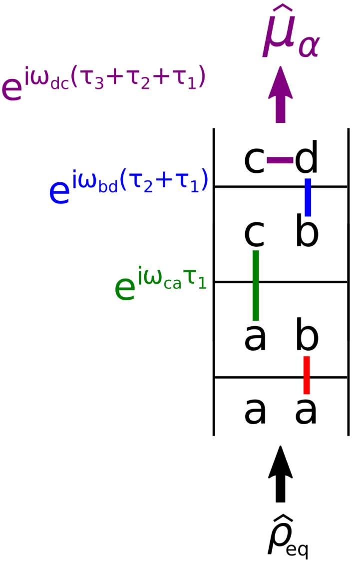
$$\begin{aligned}
\langle x|\,\hat{\mu}_{\alpha}^{(I)}(t)\,|y\rangle &= \langle x|\,e^{\frac{i}{\hbar}\hat{H}_o t}\hat{\mu}_{\alpha}e^{-\frac{i}{\hbar}\hat{H}_o t}\,|y\rangle \\
&= \langle x|\,e^{i\omega_x t}\hat{\mu}_{\alpha}e^{-i\omega_y t}\,|y\rangle \\
&= e^{i\omega_{xy} t}\,\langle x|\,\hat{\mu}_{\alpha}\,|y\rangle\,.
\end{aligned}$$

Each term in the response function oscillates as

$$e^{i(\Omega_1\tau_1+\ldots+\Omega_n\tau_n)}$$

where each transition *above* rung m contributes to Ω_m as follows:

- An $x \to y$ transition on the *left* contributes a frequency ω_{xy}



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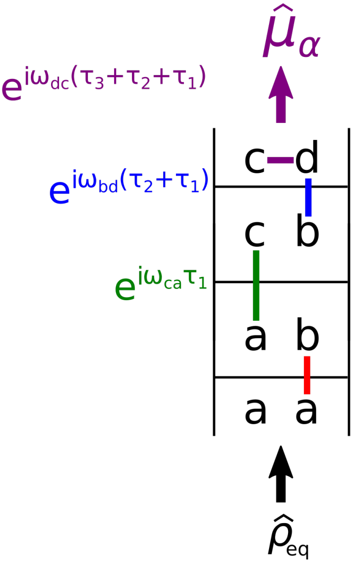
- An $x \to y$ transition on the *left* contributes a frequency ω_{xy}
- An $x \to y$ transition on the *right* contributes a frequency $-\omega_{xy}$



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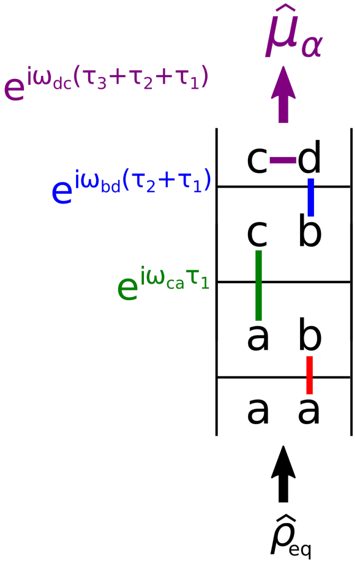
where each transition *above* rung m contributes to Ω_m as follows:

- An $x \to y$ transition on the *left* contributes a frequency ω_{xy}
- An $x \to y$ transition on the *right* contributes a frequency $-\omega_{xy}$
- Signal indices xy at the *top* of the ladder contribute a frequency $-\omega_{xy}$

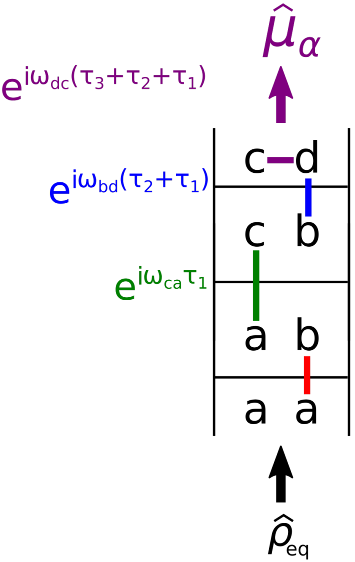


Each term in the response function oscillates as

$$e^{i(\Omega_1 \tau_1 + \ldots + \Omega_n \tau_n)}$$

where each transition *above* rung m contributes to Ω_m as follows:

- An $x \to y$ transition on the *left* contributes a frequency ω_{xy}
- An $x \to y$ transition on the *right* contributes a frequency $-\omega_{xy}$
- Signal indices xy at the *top* of the ladder contribute a frequency $-\omega_{xy}$



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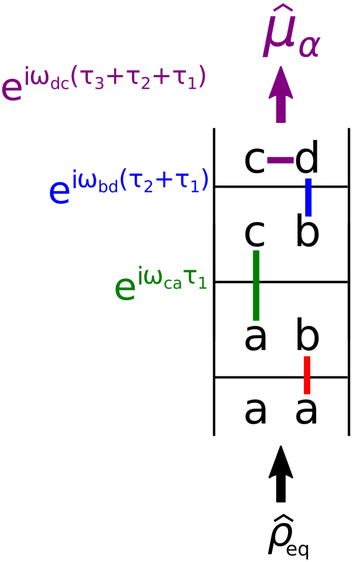


NB: τ_m appears in all exponentials **above** rung m.

Adding all contributions:

$$\begin{aligned}
\Omega_m &= (\text{left signal state frequency}) - (m^{\text{th}} \text{ left rung state frequency}) \\
&\quad - (\text{right signal state frequency}) + (m^{\text{th}} \text{ right rung state frequency}) \\
&\quad + (\text{left signal state frequency}) - (\text{right signal state frequency}) \\
&= (m^{\text{th}} \text{ right rung state frequency}) - (m^{\text{th}} \text{ left rung state frequency})
\end{aligned}$$

Key Point: For each τ_m, our expansion terms oscillate as $e^{-i\omega_{xy}\tau_m}$, where x and y are the *eigenstate indices between the* m *and* $m+1$ *rungs.*

Summary

Each n^{th}-order term is a product of of

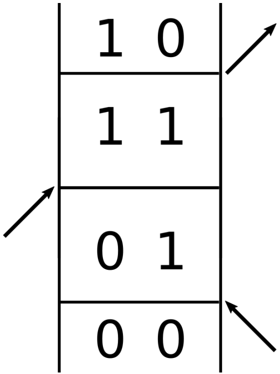
- Prefactors $\left(\frac{i}{\hbar}\right)^n \Theta(\tau_1)...\Theta(\tau_n)$
- One dipole $\mu_{\alpha_m}^{xy}$ for each transition $x \to y$ on the **right side** of the diagram
- One dipole $\mu_{\alpha_m}^{yx}$ for each transition $x \to y$ on the **left side** of the diagram
- An exponential $e^{-i\omega_{xy}\tau_m}$ for the pair of states x, y **above** each rung
- Add an overall minus sign if there are an odd number of arrows on the right

Arrow-Ladder Diagrams

Adding Arrows

To keep track of indices, it's useful to add arrows:

- Arrow pointing **in** means **absorption**: eigenstate index increases
- Arrow pointing **out** means **emission**: eigenstate index decreases



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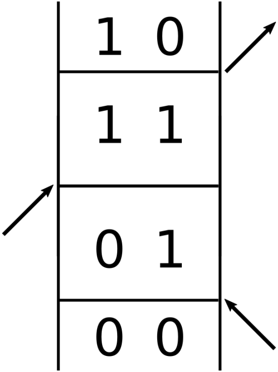

But wait! There's more!

Note that

- A **positive** transition **frequency** on the **left** corresponds to **absorption**
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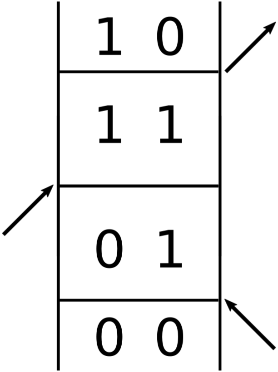


But wait! There's more!

Note that

- A **positive** transition **frequency** on the **left** corresponds to **absorption**
- A **positive** transition **frequency** on the **right** corresponds to **emission**

So what?

Adding Arrows

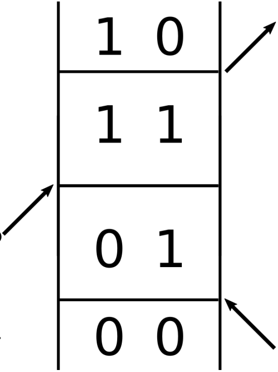
So:

- **Right-pointing** arrows correspond to **positive interaction frequencies** with the field
- **Left-pointing** arrows correspond to **negative interaction frequencies** with the field

And:

The sign of the n^{th} **interaction frequency** is tied to the sign of the n^{th} **interaction k-vector**

Key Point: Each wavevector sum condition corresponds to a particular sequence (e.g., "left-left-right" or "right-left-right") of arrows on ladder diagrams



Example: Third-Order Diagrams