Diagrammatic Expansions

Mike Reppert

October 28, 2019

Previously on CHM676...

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

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

and studied its properties in the $n = 1$ case.

Today: Diagrammatic expansions

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

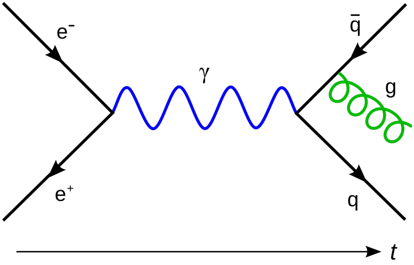
Diagrammatic Expansions

Q: What is a diagrammatic expansion?

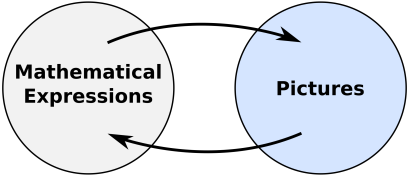
A: A one-to-one mapping between a particular set of mathematical expressions and symbolic diagrams

Q: Why do we use them?

A: *Because humans are better at reading pictures than mathematical expressions.*



https://en.wikipedia.org/wiki/Feynman_diagram



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:

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

Double Commutator:

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

Examples

Triple Commutator:

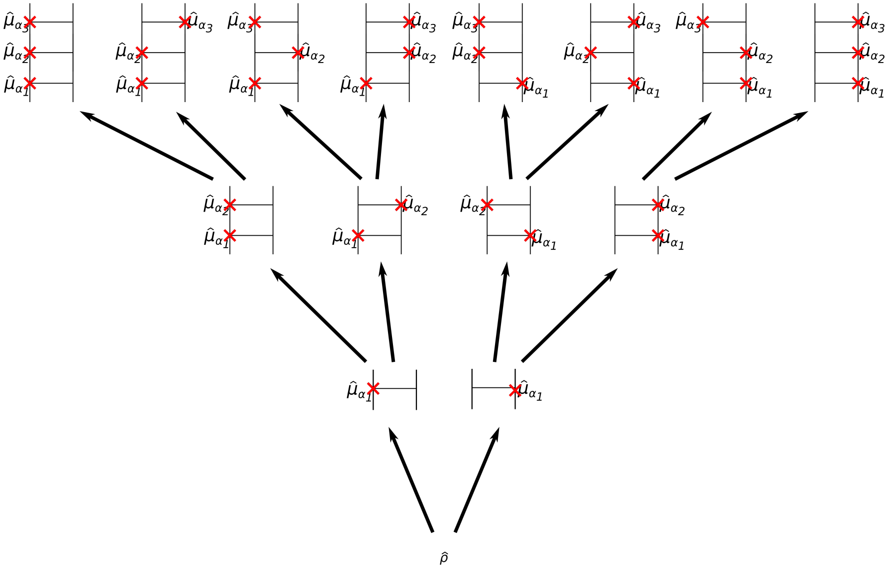
$$\left[\hat{\mu}^{(I)}_{\alpha_3}(\tau_1+\tau_2),\left[\hat{\mu}^{(I)}_{\alpha_2}(\tau_1),\left[\hat{\mu}^{(I)}_{\alpha_1}(0),\hat{\rho}_{\text{eq}}\right]\right]\right]$$

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

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



Commutator Diagram Rules

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

- Draw 2^n "ladders", with n rungs each.
- On each rung, mark an "interaction" on either right or left
  - Start with all interactions on left
  - On the n^{th} rung *from the top*, alternate left vs. right every 2^{n-1} diagrams
- Add the density matrix $\hat{\rho}$ to the bottom of the ladder
- Add interaction dipoles $\hat{\mu}^{(I)}_{\alpha_n}$ at the n^{th} rung from the bottom, on the side of the interaction.
- Write down the corresponding commutator term:
  - Start with $\hat{\rho}$ at the center
  - Add all left-side dipoles to the left of $\hat{\rho}$, ordered right-to-left according to ordering *up* the ladder
  - Add all right-side dipoles to the right of $\hat{\rho}$, ordered left-to-right according to ordering *up* the ladder
  - 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 $\hat{\rho}_{\text{eq}} = \sum_a |a\rangle\, \rho_{aa}^{(\text{eq})}\, \langle a|$
- Insert the identity $\hat{1} = \sum_b |b\rangle \langle b|$ on the side of $\hat{\mu}_{\alpha_1}^{(I)}$ *away* from $\hat{\rho}_{\text{eq}}$
- Insert the identity $\hat{1} = \sum_c |c\rangle \langle c|$ on the side of $\hat{\mu}_{\alpha_2}^{(I)}$ *away* from $\hat{\rho}_{\text{eq}}$
- 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 $\hat{\rho}_{\text{eq}}$

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

Third Order: Eigenstate Expansion

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

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

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

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 $\hat{\rho}_{\text{eq}}$.

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

Third Order: Eigenstate Expansion

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] \\
&\quad = \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| \\
&\qquad - |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| \\
&\qquad + |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| \\
&\qquad - |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| \\
&\qquad + |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| \\
&\qquad - |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| \\
&\qquad + |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| \\
&\qquad - |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 $|a\rangle\langle a|$

$$
\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] \\
&\quad=\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| \\
&\qquad-|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| \\
&\qquad+|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| \\
&\qquad-|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| \\
&\qquad+|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| \\
&\qquad-|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| \\
&\qquad+|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| \\
&\qquad-|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

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

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

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

Third Order: Eigenstate Expansion

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

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

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

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