Time-Dependent Perturbation Theory

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Previously on CHM676...

The **density matrix**

$$\hat{\rho} \equiv \frac{1}{N} \sum_{n=1}^{N} |\psi_n\rangle \langle\psi_n|$$

accounts for both *quantum* and *classical* uncertainty in experimental measurements. Its dynamics follow the **quantum Liouville equation**

$$i\hbar \frac{d\rho}{dt} = \left[\hat{H}, \rho\right],$$

the mixed state (ensemble) equivalent of the Schrödinger equation. In the eigenbasis of a **static Hamiltonian**, density matrix elements evolve as

$$\rho_{mn}(t) = e^{-i\omega_{mn} t} \rho_{mn}(0).$$

Today: Time-dependent Perturbation Theory

Two Approaches to Quantum Dynamics

Static Hamiltonian: Hilbert Space Dynamics

The time-dependent Schrödinger equation

$$\frac{d}{dt}|\psi\rangle = -\frac{i}{\hbar}\hat{H}|\psi\rangle$$

can be solved formally solved (check it!) as

$$|\psi(t)\rangle = e^{-\frac{i}{\hbar}\hat{H}t}|\psi(0)\rangle .$$

Here $e^{-\frac{i}{\hbar}\hat{H}t}$ is the *operator exponential*

$$e^{-\frac{i}{\hbar}\hat{H}t} = \sum_{n=0}^{\infty}\left(-\frac{i}{\hbar}\right)^n \frac{\hat{H}^n}{n!}.$$

NB: By extension, the *density matrix* must follow

$$\hat{\rho}(t) \equiv \sum_n |\psi_n(t)\rangle\langle\psi_n(t)| = \left(e^{-\frac{i}{\hbar}\hat{H}t}\right)\hat{\rho}(0)\left(e^{\frac{i}{\hbar}\hat{H}t}\right).$$

Static Hamiltonian: Liouville-Space Solution

In **exactly the same way**, the Liouville equation is formally solved (check it!) by the expansion

$$\begin{aligned}\hat{\rho}(t) &= \hat{\rho}(0) + \frac{t}{i\hbar}\left[\hat{H}, \hat{\rho}\right] + \frac{t^2}{2(i\hbar)^2}\left[\hat{H}, \left[\hat{H}, \hat{\rho}\right]\right] + \ldots \\ &= \sum_{n=0}^{\infty} \frac{(-it)^n}{n!}\frac{1}{\hbar^n}\left[\hat{H}, \ldots, \left[\hat{H}, \hat{\rho}\right]\ldots\right] \\ &\equiv e^{-i\hat{\mathcal{L}}t}\hat{\rho} = \left(e^{-\frac{i}{\hbar}\hat{H}t}\right)\hat{\rho}\left(e^{\frac{i}{\hbar}\hat{H}t}\right)\end{aligned}$$

where

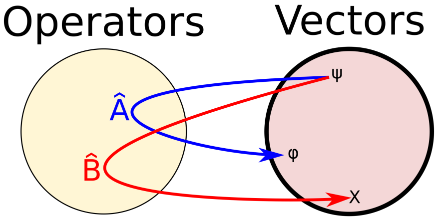
$$\hat{\mathcal{L}} \equiv \frac{1}{\hbar}\left[\hat{H}, \quad\right]$$

is the **Liouvillian** *super*operator.

Superoperators

So what the heck is a superoperator?

A **superoperator** maps operators to other operators – just like operators map vectors to other vectors.



Why superoperators?

Con: A new layer of abstraction

Pro: Drastically simplify many quantum dynamics calculations.

Key Point: Superoperators are "operator operators"! Anything (almost) you can do with operators (exponentiation, differentiation, integration, etc.), you can also do with superoperators.

The Interaction Picture

Time-dependent Perturbation Theory

In spectroscopy, we deal with a Hamiltonian of the form

$$\hat{H}(t) = \underset{\substack{\Uparrow \\ \text{Matter}}}{\hat{H}_o} - \underset{\substack{\Uparrow \qquad \Uparrow \\ \text{Field-Dipole}}}{\mathbf{E}(t) \cdot \hat{\boldsymbol{\mu}}}$$

The Liouville super-operator has the form

$$\hat{\mathcal{L}}(t) = \hat{\mathcal{L}}_o + \hat{\mathcal{L}}_E(t).$$

When $\mathbf{E}(t) = 0$, we know the dynamics. Can we build a perturbative expansion in $\mathbf{E}(t)$?

The Interaction Representation

Define an *interaction picture* density matrix:

$$\hat{\rho}_I(t) \equiv e^{i\hat{\mathcal{L}}_o t}\hat{\rho}(t),$$

where

$$\hat{\mathcal{L}}_o \equiv \frac{1}{\hbar}\left[\hat{H}_o, \quad\right].$$

Note that if $\boldsymbol{E}(t) = 0$, then $\hat{\rho}_I$ is constant in time since $e^{i\hat{\mathcal{L}}_o t}e^{-i\hat{\mathcal{L}}_o t} = \hat{1}$.

Big idea: $\hat{\rho}_I$ evolves **only** due to $\mathbf{E}(t)$ – so we can expand *perturbatively* in increasing powers of $\mathbf{E}$.

Interaction Picture Liouville Equation

How does $\hat{\rho}_I(t)$ evolve in time? Well...

$$\begin{aligned}\frac{d\hat{\rho}_I}{dt} &= \left(\frac{d}{dt}e^{i\hat{\mathcal{L}}_o t}\right)\hat{\rho}(t) + e^{i\hat{\mathcal{L}}_o t}\left(\frac{d}{dt}\hat{\rho}(t)\right) \\ &= i\hat{\mathcal{L}}_o e^{i\hat{\mathcal{L}}_o t}\hat{\rho}(t) + e^{i\hat{\mathcal{L}}_o t} - ie^{i\hat{\mathcal{L}}_o t}\left(\hat{\mathcal{L}}_o + \hat{\mathcal{L}}_E(t)\right)\hat{\rho}(t) \\ &= -ie^{i\hat{\mathcal{L}}_o t}\hat{\mathcal{L}}_E(t)\hat{\rho}(t) \\ &= -ie^{i\hat{\mathcal{L}}_o t}\hat{\mathcal{L}}_E(t)e^{-i\hat{\mathcal{L}}_o t}e^{i\hat{\mathcal{L}}_o t}\hat{\rho}(t) \\ &= -i\hat{\mathcal{L}}_E^{(I)}(t)\hat{\rho}_I(t),\end{aligned}$$

where

$$\hat{\mathcal{L}}_E^{(I)}(t) = e^{i\hat{\mathcal{L}}_o t}\hat{\mathcal{L}}_E(t)e^{-i\hat{\mathcal{L}}_o t}.$$

$\hat{\rho}_I(t)$ follows a Liouville equation determined by $\hat{\mathcal{L}}_E^{(I)}(t)$!

The Interaction-Picture Propagator

Let's look at $\hat{\mathcal{L}}_I^{(I)}(t)$ in a little more detail:

$$\begin{aligned}
\hat{\mathcal{L}}_E^{(I)}(t)\hat{\rho} &\equiv e^{i\hat{\mathcal{L}}_o t}\hat{\mathcal{L}}_E(t)e^{-i\hat{\mathcal{L}}_o t}\hat{\rho} \\
&= e^{i\hat{\mathcal{L}}_o t}\hat{\mathcal{L}}_E(t)\left(e^{-i\hat{H}_o t}\hat{\rho}e^{i\hat{H}_o t}\right) \\
&= e^{i\hat{\mathcal{L}}_o t}\left[(-\mathbf{E}(t)\cdot\hat{\boldsymbol{\mu}})\left(e^{-i\hat{H}_o t}\hat{\rho}e^{i\hat{H}_o t}\right) - \left(e^{-i\hat{H}_o t}\hat{\rho}e^{i\hat{H}_o t}\right)(-\mathbf{E}(t)\cdot\hat{\boldsymbol{\mu}})\right] \\
&= \left(-\mathbf{E}(t)\cdot e^{i\hat{H}_o t}\hat{\boldsymbol{\mu}}e^{-i\hat{H}_o t}\right)\hat{\rho} - \hat{\rho}\left(-\mathbf{E}(t)\cdot e^{i\hat{H}_o t}\hat{\boldsymbol{\mu}}e^{i\hat{H}_o t}\right) \\
&= -\mathbf{E}(t)\cdot\hat{\boldsymbol{\mu}}^{(I)}(t)\hat{\rho} - \hat{\rho}\left(-\mathbf{E}(t)\cdot\hat{\boldsymbol{\mu}}^{(I)}(t)\right).
\end{aligned}$$

$\hat{\mathcal{L}}_E^{(I)}(t)$ just represents *the commutator* with the *interaction picture* light-matter Hamiltonian

$$-\mathbf{E}(t)\cdot\hat{\boldsymbol{\mu}}^{(I)}(t) \equiv -\mathbf{E}(t)\cdot e^{i\hat{H}_o t}\hat{\boldsymbol{\mu}}e^{i\hat{H}_o t}.$$

Interaction Picture Observables

How do we calculate observables?
Trick: The trace is invariant under cyclic permutations

$$\begin{aligned}
\mathrm{Tr}\{\hat{A}\hat{B}\} &= \sum_n \left\langle n \left| \hat{A}\hat{B} \right| n \right\rangle \\
&= \sum_{n,m} \left\langle n \left| \hat{A} \right| m \right\rangle \left\langle m \left| \hat{B} \right| n \right\rangle \\
&= \sum_{n,m} \left\langle m \left| \hat{B} \right| n \right\rangle \left\langle n \left| \hat{A} \right| m \right\rangle = \mathrm{Tr}\{\hat{B}\hat{A}\}.
\end{aligned}$$

Thus

$$\begin{aligned}
\langle A \rangle &= \mathrm{Tr}\left\{ \hat{A} e^{-\frac{i}{\hbar}\hat{\mathcal{L}}_o t} \hat{\rho}_I(t) \right\} \\
&= \mathrm{Tr}\left\{ \hat{A} e^{-\frac{i}{\hbar}\hat{H}_o t} \rho_I(t) e^{\frac{i}{\hbar}\hat{H}_o t} \right\} = \mathrm{Tr}\left\{ e^{\frac{i}{\hbar}\hat{H}_o t} \hat{A} e^{-\frac{i}{\hbar}\hat{H}_o t} \rho_I(t) \right\} \\
&= \mathrm{Tr}\left\{ \hat{A}^{(I)}(t) \hat{\rho}_I(t) \right\}
\end{aligned}$$

A picture is worth a thousand expansion terms

What's happening in the "interaction picture"?

Suppose you want to calculate fuel requirements for a Chicago-Sau Paulo flight. Which representation do you use?

- Sun frame: Both targets move at $\sim$1000 MPH
- Earth frame: Earth's rotation is already incorporated – all motion due to engines

The **interaction picture** is like the Earth frame: Natural molecular motion is already included. All *dynamics* are induced by the field.

The Dyson Expansion

The Dyson Expansion

Formally, we can solve the dynamics exactly:

$$\frac{d}{dt}\hat{\rho}_I = -i\hat{\mathcal{L}}_E^{(I)}(t)$$

$$\Downarrow$$

$$\hat{\rho}_I(t) = \hat{\rho}_I(0) - i\int_0^t ds\hat{\mathcal{L}}_E^{(I)}(s)\hat{\rho}_I(s)$$

$$\Downarrow$$

$$\hat{\rho}_I(t) = \hat{\rho}_I(0) - i\int_0^t ds\hat{\mathcal{L}}_E^{(I)}(s)\left(\hat{\rho}_I(0) - i\int_0^t ds'\hat{\mathcal{L}}_E^{(I)}(s')\hat{\rho}_I(s')\right)$$

$$\Downarrow$$

$$\hat{\rho}_I(t) = \sum_{n=0}^{t}(-i)^n\int_0^\infty dt_n\int_0^{t_n} dt_{n-1}...\int_0^{t_2} dt_1 \\ \times \hat{\mathcal{L}}_E^{(I)}(t_n)\hat{\mathcal{L}}_E^{(I)}(t_{n-1})...\hat{\mathcal{L}}_E^{(I)}(t_1)\hat{\rho}(0).$$

Notation: Time-Ordered Exponentials

This solution is often termed a *time-ordered exponential*.

$$\begin{aligned}\hat{\rho}_I(t) &= \sum_{n=0}^{\infty}(-i)^n \int_0^t dt_n \int_0^{t_n} dt_{n-1}\ldots \int_0^{t_2} dt_1 \\ &\qquad \times \hat{\mathcal{L}}_E^{(I)}(t_n)\hat{\mathcal{L}}_E^{(I)}(t_{n-1})\ldots\hat{\mathcal{L}}_E^{(I)}(t_1)\hat{\rho}(0) \\ &\equiv \exp_{[+]}\left(-i\int_0^{\infty} ds\hat{\mathcal{L}}_E^{(I)}(s)\right)\hat{\rho}_I(0) \\ &\equiv \hat{\mathcal{T}}e^{-i\int_0^{\infty} ds\hat{\mathcal{L}}_E^{(I)}(s)}\rho_I(0)\end{aligned}$$

Why? Note that if $\hat{\mathcal{L}}_E^{(I)}(t)$ were static:

$$\hat{\rho}_I(t) = \sum_{n=0}^{\infty}\frac{(-it)^n}{n!}\hat{\mathcal{L}}_E^{(I)}\hat{\mathcal{L}}_E^{(I)}\ldots\hat{\mathcal{L}}_E^{(I)}\hat{\rho}(0) \qquad \equiv e^{-i\hat{\mathcal{L}}_E^{(I)}t}\hat{\rho}_I(0).$$

How do we calculate observables?

For observable averages:

$$\begin{aligned}\langle A\rangle &= \mathrm{Tr}\{\hat{A}^{(I)}(t)\hat{\rho}_I(t)\} \\ &= \sum_{n=0}^{\infty}(-i)^n \int_0^t dt_n \int_0^{t_n} dt_{n-1} \ldots \int_0^{t_2} dt_1 \\ &\qquad \times \mathrm{Tr}\left\{\hat{A}^{(I)}(t)\hat{\mathcal{L}}_E^{(I)}(t_n)\hat{\mathcal{L}}_E^{(I)}(t_{n-1})\ldots\hat{\mathcal{L}}_E^{(I)}(t_1)\hat{\rho}(0)\right\}\end{aligned}$$

This looks a lot – but not quite! – like response theory.

Response Theory

Response Theory

Four steps to response theory:

- Switch to time-intervals τ_n *between interactions* instead of absolute times t_n *of interactions*
- Assume the system starts at equilibrium
- Expand the propagators
- Shift the time axis using time-translation invariance

Step 1: Time intervals

To match response theory, we need to work in time intervals τ_n instead of absolute times t_n:

$$\begin{aligned}\tau_n &= t - t_n \\ \tau_{n-1} &= t_n - t_{n-1} \\ &\vdots \\ \tau_1 &= t_2 - t_1.\end{aligned}$$

Changing the integration variables:

$$\langle A \rangle = \sum_{n=0}^{\infty} \left(\frac{i}{\hbar}\right)^n \int_0^t d\tau_n \int_0^{t-\tau_n} d\tau_{n-1} \ldots \int_0^{t-\tau_n-\ldots-\tau_2} d\tau_1 \times \text{Tr}\left\{\hat{A}^{(I)}(t)\hat{\mathcal{L}}_E^{(I)}(t-\tau_n)\ldots\hat{\mathcal{L}}_E^{(I)}(t-\tau_n\ldots-\tau_1)\hat{\rho}(0)\right\}$$

Step 2: Initialize at Equilibrium

Next, assume that the system begins at equilibrium, i.e.

- $\hat{\mathcal{L}}_E^{(I)}(t) = 0$ for $t < 0$
- $\hat{\rho}(0) = \hat{\rho}_{\text{eq}}$

This lets us extend integration limits to ∞:

$$\langle A \rangle = \sum_{n=0}^{\infty} \left(\frac{i}{\hbar}\right)^n \int_0^{\infty} d\tau_n \int_0^{\infty} d\tau_{n-1} ... \int_0^{\infty} d\tau_1$$
$$\times \text{Tr} \left\{ \hat{A}^{(I)}(t) \hat{\mathcal{L}}_E^{(I)}(t - \tau_n) ... \hat{\mathcal{L}}_E^{(I)}(t - \tau_n - ... - \tau_1) \hat{\rho}_{\text{eq}} \right\}$$

Step 3: Expand the propagators

Now expand the propagators and factor out the field:

$$\langle A \rangle = \sum_{n=0}^{\infty} \left(\frac{i}{\hbar}\right)^n \sum_{\alpha_1,\ldots,\alpha_n} \int_0^{\infty} d\tau_n \ldots \int_0^{\infty} d\tau_1$$
$$\times E_{\alpha_n}(t-\tau_n)\ldots E_{\alpha_1}(t-\tau_n-\ldots-\tau_1)$$
$$\times \mathrm{Tr}\left\{\hat{A}^{(I)}(t)\left[\hat{\mu}^{(I)}_{\alpha_n}(t-\tau_n),\ldots\left[\hat{\mu}^{(I)}_{\alpha_1}(t-\tau_n-\ldots-\tau_1),\hat{\rho}_{\text{eq}}\right]\right]\right\}$$

Looks like response expansion **except** that "response function" depends on t!

Step 4: Shift the Time axis

Note that we can **shift the time axis** at will:

$$\begin{aligned}
&\text{Tr}\{\hat{X}_1^{(I)}(s_1)X_2^{(I)}(s_2)...X_n^{(I)}(t_n)\} \\
&= \text{Tr}\{e^{\frac{i}{\hbar}\hat{H}_o\tau}e^{-\frac{i}{\hbar}\hat{H}_o\tau}\hat{X}_1^{(I)}(s_1)...e^{\frac{i}{\hbar}\hat{H}_o\tau}e^{-\frac{i}{\hbar}\hat{H}_o\tau}\hat{X}_n^{(I)}(t_n)\} \\
&= \text{Tr}\{e^{-\frac{i}{\hbar}\hat{H}_o\tau}\hat{X}_1^{(I)}(s_1)e^{\frac{i}{\hbar}\hat{H}_o\tau}...e^{-\frac{i}{\hbar}\hat{H}_o\tau}\hat{X}_n^{(I)}(t_n)e^{\frac{i}{\hbar}\hat{H}_o\tau}\} \\
&= \text{Tr}\left\{\hat{X}_1^{(I)}(s_1-\tau)...\hat{X}_n^{(I)}(s_n-\tau)\right\}.
\end{aligned}$$

Shifting the time axis by $\tau_1 + ... + \tau_n - t$ gives:

$$\begin{aligned}
\langle A\rangle = &\sum_{n=0}^{\infty}\left(\frac{i}{\hbar}\right)^n \sum_{\alpha_1,...,\alpha_n}\int_0^{\infty} d\tau_n ... \int_0^{\infty} d\tau_1 \\
&\times E_{\alpha_n}(t-\tau_n)...E_{\alpha_1}(t-\tau_n-...-\tau_1) \\
&\times \text{Tr}\left\{\hat{A}^{(I)}(\tau_1+...+\tau_3)\left[\hat{\mu}_{\alpha_n}^{(I)}(\tau_1+...+\tau_{n-1}),...\left[\hat{\mu}_{\alpha_1}^{(I)}(0),\hat{\rho}_{\text{eq}}\right]\right]\right\}
\end{aligned}$$

Response Theory: A Microscopic Expression

Finally, since $\boldsymbol{P}(t) = \langle \boldsymbol{\mu}(t) \rangle$:

$$\boldsymbol{P}(t) = \sum_{n=0}^{\infty} \left(\frac{i}{\hbar}\right)^n \sum_{\alpha_1,\ldots,\alpha_n} \int_0^\infty d\tau_n \ldots \int_0^\infty d\tau_1$$
$$\times E_{\alpha_n}(t-\tau_n)\ldots E_{\alpha_1}(t-\tau_n-\ldots-\tau_1)$$
$$\times \operatorname{Tr}\left\{\hat{\boldsymbol{\mu}}^{(I)}(\tau_1+\ldots+\tau_3)\left[\hat{\mu}^{(I)}_{\alpha_n}(\tau_1+\ldots+\tau_{n-1}),\ldots\left[\hat{\mu}^{(I)}_{\alpha_1}(0),\hat{\rho}_{\mathsf{eq}}\right]\right]\right\}.$$

Comparing with our generic response-theory expansion:

$$R^{(n)}_{\alpha_1\ldots\alpha_n\alpha}(\tau_1,\ldots,\tau_n) = \Theta(\tau_1)\Theta(\tau_2)\ldots\Theta(\tau_n)\left(\frac{i}{\hbar}\right)^n$$
$$\times \operatorname{Tr}\left\{\hat{\mu}^{(I)}_{\alpha}(\tau_1+\ldots+\tau_3)\left[\hat{\mu}^{(I)}_{\alpha_n}(\tau_1+\ldots+\tau_{n-1}),\ldots\left[\hat{\mu}^{(I)}_{\alpha_1}(0),\hat{\rho}_{\mathsf{eq}}\right]\right]\right\}.$$