Brief summary and outlook

In previous lectures: 1) to calculate spectroscopic signals we need $\vec{P}(\vec{r},t)$

2) to calculate $\vec{P}(\vec{r},t) = \vec{P}(t)$ we need $\hat{\rho}(t)$

For perturbation theory we need only

$$\frac{\partial}{\partial t}\hat{\rho}(t) = ? \; \hat{\rho}(t)$$

independent of $\vec{E}$

How $\hat{\rho}(t)$ evolves when $\vec{E}(t) = 0$?

with different initial conditions

$\vec{E}$ causes sudden changes in $\hat{\rho}(t)$

Equations of motion for $\hat{\rho}(t)$ with $\vec{E} = 0$

$$\hat{W}(t) = |\Psi(t)\rangle\langle\Psi(t)|$$

Liouville-von Neumann eq.

$$\boxed{\frac{\partial}{\partial t}\hat{W}(t) = -\frac{i}{\hbar}\left[\hat{H}, \hat{W}(t)\right]}$$

useful tricks

we know
$$|\Psi(t)\rangle = \underbrace{\exp\left\{-\frac{i}{\hbar}\hat{H}(t-t_0)\right\}}_{\hat{U}(t-t_0)}|\Psi(t_0)\rangle$$

$$\Rightarrow \boxed{\hat{W}(t)} = \hat{U}(t-t_0)|\Psi(t)\rangle\langle\Psi(t)|\hat{U}^\dagger(t-t_0) = \boxed{\hat{U}(t-t_0)\hat{W}(t_0)\hat{U}^\dagger(t-t_0)}$$

evolution operators

Compare with Schrödinger eq.

- $|\Psi(t)\rangle = U(t-t_0)|\Psi(t)\rangle \rightarrow \hat{U}(t-t_0)\hat{W}(t_0)\hat{U}^\dagger(t-t_0)$

- $\frac{\partial}{\partial t}|\Psi(t)\rangle = -\frac{i}{\hbar}\hat{H}|\Psi(t)\rangle \rightarrow \boxed{\frac{\partial}{\partial t}\hat{W}(t) = -\frac{i}{\hbar}[\hat{H},\hat{W}(t)]}$

Super-operators ≡ „operators" on operators

$$\mathcal{L}\hat{A} = \frac{1}{\hbar}[\hat{H},\hat{A}] \quad \dots \quad \text{Liouvillian}$$

Liouville-von Neumann eq:
$$\frac{\partial}{\partial t}\hat{W}(t) = -i\mathcal{L}\hat{W}(t)$$

solution:
$$\hat{W}(t) = \underbrace{\exp\left\{-i\mathcal{L}(t-t_0)\right\}}_{\text{evolution super-operator}}\hat{W}(t_0)$$

$$\mathcal{U}(t-t_0) = \exp\{-i\mathcal{L}(t-t_0)\}$$

$$\frac{\partial}{\partial t}\mathcal{U}(t-t_0) = -i\mathcal{L}\,\mathcal{U}(t-t_0)$$

$$\mathcal{U}(0) = \mathbb{1}$$

$$\hat{W}(t) = \underline{\hat{U}(t-t_0)\,\hat{W}(t_0)\,\hat{U}^{\dagger}(t-t_0)} = \mathcal{U}(t-t_0)\,\hat{W}(t_0)$$

for closed system!

Open system: $\hat{\varrho}(t) = tr_B\{\hat{W}(t)\}$

$$\hat{\varrho}(t) = \bar{\mathcal{U}}(t-t_0)\,\hat{\varrho}(t_0)$$

Solution of the equation of motion for $\hat{\varrho}(t)$

Equation of motion for reduced density matrix

Hamiltonian

$$\hat{H} = \hat{H}_S + \hat{H}_B + \hat{H}_{S-B}$$

$$\frac{\partial}{\partial t}\hat{W}(t) = -\frac{i}{\hbar}[\hat{H}_S, \hat{W}(t)] - \frac{i}{\hbar}[\hat{H}_B, \hat{W}(t)] - \frac{i}{\hbar}[\hat{H}_{S-B}, \hat{W}(t)]$$

$$\Rightarrow \boxed{\frac{\partial}{\partial t}\hat{W}(t) = -i\mathcal{L}_S\hat{W}(t) - i\mathcal{L}_B\hat{W}(t) - i\mathcal{L}_{B-S}\hat{W}(t)}$$

note the notation

$$\mathcal{U}_S(t) = e^{-i\mathcal{L}_S t}$$

$$\mathcal{U}_B(t) = e^{-i\mathcal{L}_B t} \quad ; \quad \mathcal{U}_{S-B}(t) = e^{-i\mathcal{L}_{S-B} t}$$

Evolution back in time:

$$\text{operators} \Rightarrow \quad \hat{U}(t) \longrightarrow \hat{U}(-t) = \hat{U}^{+}(t)$$

$$\text{superoperators} \Rightarrow \quad \mathcal{U}(t) \rightarrow \mathcal{U}(-t)$$

Interaction picture

$$\boxed{\hat{W}^{(I)}(t)} = \underbrace{\hat{U}^{+}(t)\,\hat{W}(t)\,\hat{U}(t)}_{\text{closed systems}} = \boxed{\underbrace{\mathcal{U}(-t)\,\hat{W}(t)}_{\text{general}}}$$

with respect to $\hat{H}_B$, $\mathcal{L}_B$

$$\frac{\partial}{\partial t}\hat{W}^{(I)}(t) = \frac{\partial}{\partial t}\left(\mathcal{U}_B(-t)\,\hat{W}(t)\right)$$

$$= \left(\frac{\partial}{\partial t}\mathcal{U}_B(-t)\right)\hat{W}(t) + \mathcal{U}_B(-t)\frac{\partial}{\partial t}\hat{W}(t)$$

$$\frac{\partial}{\partial t}\mathcal{U}_B(-t) = i\mathcal{L}_B\,\mathcal{U}_B(-t)$$

$$\frac{\partial}{\partial t}\hat{W}^{(I)}(t) = i\mathcal{L}_B\underbrace{\mathcal{U}_B(-t)\hat{W}(t)}_{\hat{W}^{(I)}(t)} - \mathcal{U}_B(-t)\,i\mathcal{L}_S\,\hat{W}(t)$$

$$-i\,\mathcal{U}_B(-t)\,\mathcal{L}_B\,\hat{W}(t) - i\,\mathcal{U}_B(-t)\,\mathcal{L}_{S-B}\,\hat{W}(t)$$

$$\mathcal{U}_B(-t)\,\mathcal{L}_B = \mathcal{L}_B\,\mathcal{U}_B(-t) \quad \leftarrow \quad \mathcal{U}_B(-t) \text{ is an exponential of } \mathcal{L}_B$$

$$\mathcal{U}_B(-t)\,\mathcal{L}_S = \mathcal{L}_S\,\mathcal{U}_B(-t) \quad \leftarrow \quad \text{different Hilbert spaces}$$

Liouville space

$$\mathcal{U}_B(-t)\,\mathcal{L}_{S-B} \neq \mathcal{L}_{S-B}\,\mathcal{U}_B(-t)$$

$$\| \quad \mathcal{U}_B(-t)\,\mathcal{L}_{S-B}\,\underbrace{\mathcal{U}_B(t)\,\mathcal{U}_B(-t)}_{\mathbb{1}_B}$$

$$\frac{\partial}{\partial t}\hat{W}^{(I)}(t) = \cancel{i\,\mathcal{L}_B\,\mathcal{U}_B(-t)\,\hat{W}(t)} - i\,\mathcal{L}_S\,\hat{W}^{(I)}(t) \cancel{- i\,\mathcal{L}_B\,\hat{W}^{(I)}(t)}$$

$$- i\,\underbrace{\mathcal{U}_B(-t)\,\mathcal{L}_{S-B}\,\mathcal{U}_B(t)}_{\mathcal{L}_{S-B}^{(I)}(t)}\,\hat{W}^{(I)}(t)$$

$$\mathcal{L}_{S-B}^{(I)}(t) \quad \leftarrow \quad \text{interaction picture of interaction Liouvillian}$$

$$\boxed{\frac{\partial}{\partial t}\hat{W}^{(I)}(t) = -i\,\mathcal{L}_S\,\hat{W}^{(I)}(t) - i\,\mathcal{L}_{S-B}^{(I)}(t)\,\hat{W}^{(I)}(t)}$$

Very important observation

$$tr_B\left\{\hat{W}^{(I)}(t)\right\} = tr_B\left\{\hat{U}_B^{+}(t)\,\hat{W}(t)\,\hat{U}_B(t)\right\}$$

$$= tr_B \left\{ \sum_{nm} \hat{U}_B^\dagger(t)\, |n\rangle\langle n|\, \hat{W}(t)\, |m\rangle\langle m|\, \hat{U}_B(t) \right\}$$

$$= \sum_{nm} tr_B \left\{ \hat{U}_B^\dagger(t)\, \langle n| \hat{W}(t) |m\rangle\, \hat{U}_B(t) \right\} |n\rangle\langle m|$$

↑ bath operator

$$tr_B\{\hat{A}\hat{B}\hat{C}\} = tr_B\{\hat{C}\hat{A}\hat{B}\} = \dots$$

$$= \sum_{nm} \underbrace{tr_B \left\{ \langle n| \hat{W}(t) |m\rangle \right\}}_{\rho_{nm}(t)} |n\rangle\langle m| = \underline{\underline{\hat{\rho}(t)}}$$

trace tr_B eq. for $\hat{W}^{(I)}(t)$

$\Rightarrow$

$$\underbrace{\frac{\partial}{\partial t}\hat{\rho}(t) = -i\mathcal{L}_S\hat{\rho}(t)}_{\text{Liouville-von Neumann}} - i\underbrace{tr_B\left\{\mathcal{L}_{S-B}^{(I)}(t)\, \hat{W}^{(I)}(t)\right\}}_{= \mathcal{D}(t)\hat{\rho}(t)}$$

$$\boxed{\frac{\partial}{\partial t}\hat{\rho}(t) = -\frac{i}{\hbar}\left[\hat{H}_S, \hat{\rho}(t)\right] - \mathcal{D}(t)\hat{\rho}(t)}$$

relaxation super-operator

processes:
energy dissipation
decoherence

We will postulate a usefull, practical form of $\mathcal{D}(t)$

Phenomenological form of relaxation super-operator

Working in eigenstate basis of $\hat{H}_S$

→ these states are „visible" in spectroscopy
~ absorption

→ stable states – can be populated

Process of population transfer

$$\rho_{nn}(t) = P_n(t) \quad \leftarrow \text{population of state } |n\rangle$$

$$\hat{H}_S |n\rangle = E_n |n\rangle$$

Kinetic equations

$$\frac{\partial}{\partial t}\rho_{nn}(t) = \sum_{m\neq n} K_{nm}\,\rho_{mm}(t) - \left(\sum_{m\neq n} K_{mn}\right)\rho_{nn}(t)$$

conservation of population $\sum_n P_n = 1$

Process decoherence and dephasing

$n \neq m$

$$\frac{\partial}{\partial t}\rho_{nm}(t) = -\Gamma_{nm}\,\rho_{nm}(t)$$

$$\Gamma_{nm} = \underbrace{\frac{1}{2}\left(\sum_{k\neq n} K_{kn} + \sum_{k\neq m} K_{km}\right)}_{\text{dephasing due to population transfer}} + \gamma_{nm}$$

Pure dephasing

How does the equation of motion looks like?

$$\mathcal{D}(t)\hat{\rho}(t) = ?$$

$$\rightarrow \langle n|\mathcal{D}(t)\hat{\rho}(t)|m\rangle = \sum_{kl} \mathcal{D}_{nmkl}^{(t)}\,\rho_{kl}(t)$$

Coherences $n\neq m$

$$\hat{H}_S|n\rangle = E_n|n\rangle$$

$$\frac{\partial}{\partial t}\rho_{nm}(t) = -\frac{i}{\hbar}\langle n|\hat{H}_S\hat{\rho}(t)-\hat{\rho}(t)\hat{H}_S|m\rangle - \mathcal{D}_{nmnm}^{(t)}\,\rho_{nm}(t)$$

$$= -i\,\omega_{nm}\,\rho_{nm}(t) - \mathcal{D}_{nmnm}^{(t)}\,\rho_{nm}(t)$$

$$\boxed{\mathcal{D}_{nmnm}^{(t)} = \Gamma_{nm}}$$

Populations

$$\frac{\partial}{\partial t} \rho_{nn}(t) = - \sum_{\substack{kl \\ k \neq l}} \mathcal{D}_{nnkl}(t)\, \rho_{kl}(t)$$

$$= - \sum_{k} \mathcal{D}_{nnkk}(t)\, \rho_{kk}(t)$$

$$\boxed{\mathcal{D}^{(t)}_{nnkk} = - K_{nk} \quad k \neq n}$$

$$\boxed{\mathcal{D}^{(t)}_{nnnn} = \sum_{k \neq n} K_{kn}}$$

All other elements of $\mathcal{D}$ are equal to zero!

$\boxed{\text{Secular approximation}}$ ~ non-secular terms

! $\mathcal{D}(t)$; $\hat{\rho}(t_0)$

depends on initial conditions

$$\hat{W}(t_0) = \hat{\rho}(t_0)\, \hat{w}(t_0)$$

$$\mathcal{D}(t, \hat{w}(t_0))$$

Summary

$$\boxed{\frac{\partial}{\partial t}\hat{\rho}(t) = -\frac{i}{\hbar}[\hat{H}_S, \hat{\rho}(t)] - \mathcal{R}\hat{\rho}(t)}$$

Master equation

$$\hat{\rho}(t) = \bar{\mathcal{U}}(t-t_0)\hat{\rho}(t_0)$$

for now it depends only on $t-t_0$

reduced evolution superoperator

Elements of evolution super-operator in secular approximation

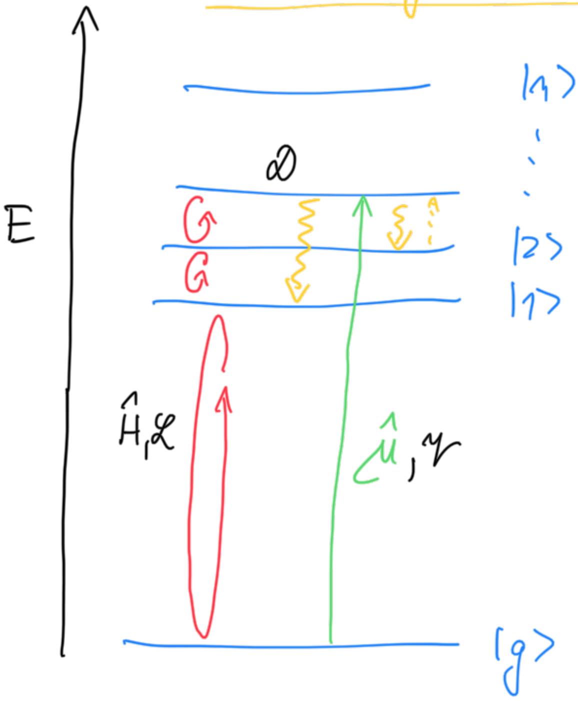
Populations

$$\frac{\partial}{\partial t}\rho_{nn}(t) = \sum_m K_{nm}\rho_{mm}(t) \Rightarrow \boxed{\bar{\mathcal{U}}_{nnmm}(t)} = \Omega_{nm}(t) = \boxed{\exp(Kt)\big|_{nm}}$$

Coherences

$$\boxed{\bar{\mathcal{U}}_{nmnm}(t) = e^{-\Gamma_{nm}t}}$$

Summary before perturbation theory



general eq. of motion

$$\boxed{\frac{\partial}{\partial t}\hat{\rho}(t) = -i\mathcal{L}_S\hat{\rho}(t) - \mathcal{D}(t)\hat{\rho}(t) + i\mathcal{V}\hat{\rho}(t)E(t)}$$

$$\mathcal{V}\hat{A} = \frac{1}{\hbar}[\hat{\mu}, \hat{A}]$$

In eigenstates of $\hat{H}_S$

$$\frac{\partial}{\partial t}\rho_{nm}(t) = -i\omega_{nm}\rho_{nm}(t) - \sum_{kl}\mathcal{D}_{nmkl}(t)\rho_{kl}(t)$$

$$+ i\sum_{kl}\mathcal{V}_{nmkl}\rho_{kl}(t)E(t)$$

details of $\mathcal{V}$ and μ will be crucial