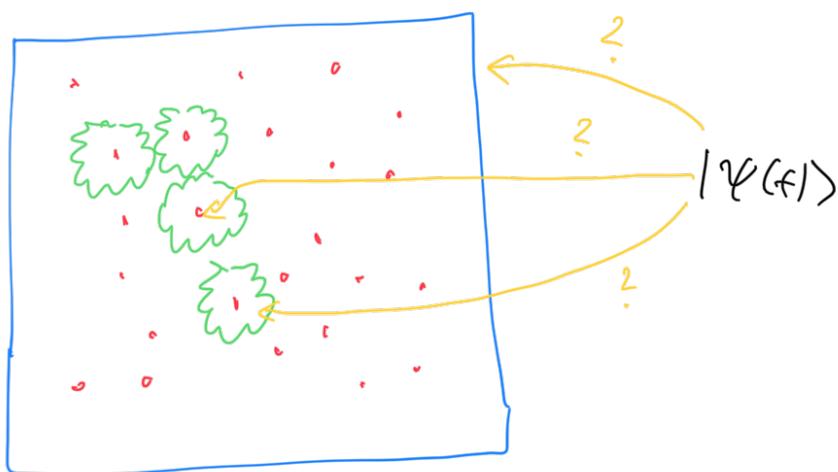


Minimal approach to open quantum systems

Quantum mechanics

$$\boxed{\frac{\partial}{\partial t} |\psi(t)\rangle = -\frac{i}{\hbar} \hat{H} |\psi(t)\rangle}$$



$|\psi(t)\rangle \rightarrow$ relevant degrees of freedom of the molecular system + its environment

Polarization

$$\vec{P}(\vec{r}, t) \sim \left\langle \langle \psi(t) | \vec{\mu} | \psi(t) \rangle \right\rangle_{\Delta V, \vec{r}}$$

average in ΔV
around \vec{r}

$\vec{\mu}$
transition dipole
operator of a
molecule

$$\langle \psi(t) | \hat{\mu} | \psi(t) \rangle = \langle \psi(t) | \sum_{\alpha} \langle \alpha | \hat{\mu} | \alpha \rangle \alpha | \psi(t) \rangle$$

↑
 independent
 of environment
 DOF

T
 \prod_S
 B

$$= \sum_{\alpha} \sum_m \langle \alpha | \langle m | \hat{\mu} | \psi(t) \rangle \langle \psi(t) | m \rangle | \alpha \rangle$$

$$= \text{Tr}_B \left\{ \text{Tr}_S \left\{ \langle \hat{\mu} | \psi(t) \rangle \langle \psi(t) | \right\} \right\}$$

$$= \text{Tr}_S \left\{ \hat{\mu} \text{Tr}_B \left\{ \langle \psi(t) \rangle \langle \psi(t) | \right\} \right\}$$

↓
 $\hat{W}(t)$... total statistical operator
 ↑ S + B

$\hat{\rho}(t)$
 Reduced statistical
 operator

$$= \text{Tr}_S \left\{ \hat{\mu} \hat{\rho}(t) \right\}$$

(density matrix)

$$\hat{\rho}(t) = \text{Tr}_B \left\{ \langle \psi(t) \rangle \langle \psi(t) | \right\} = \text{Tr}_B \left\{ \hat{W}(t) \right\}$$

Equation of motion for RDM

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

$$\text{Schrödinger eq.} \Rightarrow \frac{\partial}{\partial t} |\psi(t)\rangle = -\frac{i}{\hbar} \hat{H} |\psi(t)\rangle$$

\Rightarrow Liouville-von Neumann eq.

$$\boxed{\frac{\partial}{\partial t} \hat{W}(t) = \frac{\partial}{\partial t} (\langle \psi(t) | \psi(t) \rangle) = \left(\frac{\partial}{\partial t} |\psi(t)\rangle \right) \langle \psi(t) | + |\psi(t)\rangle \frac{\partial}{\partial t} \langle \psi(t) |}$$

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

$$\boxed{\frac{\partial}{\partial t} \hat{W}(t) = -i \mathcal{L} \hat{W}(t)}$$

$$\partial \hat{A} = \frac{1}{i} [\hat{H}, \hat{A}]$$

• does not depend on time

• does not depend on initial condition

This does not apply to eq. of motion for $\hat{\rho}(t)$

Hamiltonian of the problem

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

bath/environment
molecule(s)
of interest
- just its relevant DOF
 $\vec{\mu} \cdot \vec{E}(t)$
classical
electric
field
semiclassical
Hamiltonian
operator: transition
dipole
moment

--- --- --- --- --- ---
(--- --- ---)
Quantum evolution
(--- --- ---)
in full
perturbation theory

approximations
related to the "reduction"

$$\hat{W}(t) \rightarrow \hat{S}(t)$$

$$\hat{P}(t) = \text{tr} \left\{ \hat{U} \hat{S}(t) \right\}$$