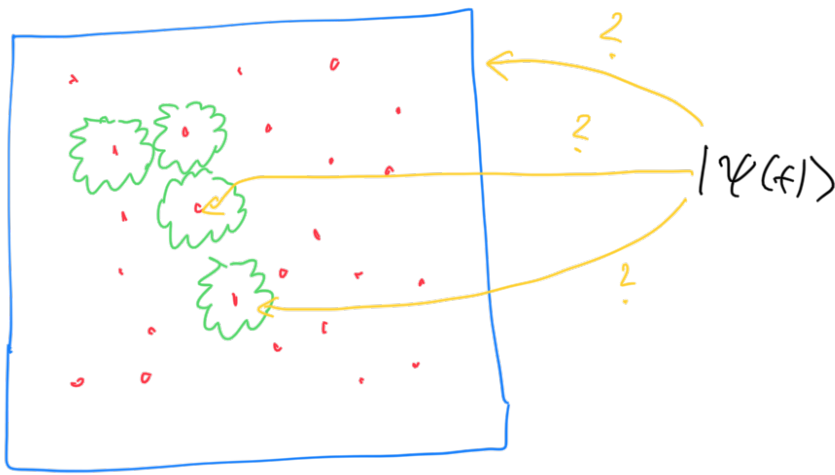


# Minimal approach to open quantum systems

Quantum mechanics

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



$|\psi(t)\rangle \rightarrow$  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  $\Delta V$  around  $\vec{r}$

↑  
transition dipole operator of a molecule

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

↑
↑
↑

independent
 $\mathbb{I}_S$ 
 $\mathbb{I}_B$

of environmental

DOF

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

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

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

↑
total statistical operator

$\hat{W}(t)$ 
 $S+B$

↑
 $\hat{\rho}(t)$

Reduced statistical operator

(density matrix)

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

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

Equation of motion for RDM

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

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

$\Rightarrow$  Liouville-von Neumann eq.

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

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

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

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

- does not depend on time
- does not depend on initial condition

$\rightarrow$  This does not apply to eq. of motion for  $\vec{S}(t)$

## Hamiltonian of the problem

$$\hat{H} = \hat{H}_S + \hat{H}_B + \hat{H}_{S-B} - \vec{\mu} \cdot \vec{E}(t)$$

$\hat{H}_S$ : molecule(s) of interest - just its relevant DOF  
 $\hat{H}_B$ : bath/environment  
 $\hat{H}_{S-B}$ : interaction between S and B  
 $-\vec{\mu} \cdot \vec{E}(t)$ : classical electric field  
 semiclassical Hamiltonian  
 operator: transition dipole moment

Quantum evolution in full  
 approximations related to the "reduction"  
 perturbation theory

$$\hat{\rho}(t) \longrightarrow \hat{\rho}(t)$$

$$\vec{P}(t) = \text{tr} \{ \vec{\mu} \hat{\rho}(t) \}$$