

# Simulations

Design Overview and Introduction to WrightSim Project

# Liouville Equation

- For this talk, we focus our attention to the equation we use most frequently in the group, the Liouville equation with phenomenological dephasing:

$$\frac{d\rho}{dt} = [H, \rho] - \Gamma\rho,$$
$$H = H_0 + \mu \cdot E(t)$$

$$\text{or } \frac{d\rho_{ij}}{dt} = -(i\omega_{ij} + \Gamma_{ij})\rho_{ij} - \frac{i}{\hbar} \sum_k (\mu_{ik} E(t) \rho_{kj} - \mu_{jk} E(t) \rho_{ki})$$

- This equation is very general—we often make simplifications from this point.
- These oscillating polarizations create observable e-fields:

$$E_{\text{out}}(t) \approx i\mu_{ij}\rho_{ij}(t)$$

# Liouville Equation – Parameterization

$$\frac{d\rho_{ij}}{dt} = -(i\omega_{ij} + \Gamma_{ij})\rho_{ij} - \frac{i}{\hbar}(\mu_{ik}E(t)\rho_{kj} - \mu_{jk}E(t)\rho_{ki})$$

Both the coherence and the optical fields have a characteristic parameters, so bake those into this equation:

$$\rho_{ij} = \tilde{\rho}_{ij} e^{i\omega_{ij}t}$$
$$E(t) = c(t - \tau)(e^{i(kz - \omega(t - \tau))} + c.c.)$$

# Liouville Equation – Parameterization

For each coherence, four terms to think about:

$$\begin{aligned}
 \frac{d\tilde{\rho}_{ij}}{dt} = & \quad -\Gamma_{ij}\tilde{\rho}_{ij} \\
 & \quad \quad \quad \overbrace{k \leftrightarrow i} \\
 & + \frac{i}{2\hbar} \mu_{ik} \tilde{E}_l(t - \tau_l) \left[ \overbrace{e^{-ik_l z} e^{+i\omega_l(t-\tau_l)} e^{-i\omega_{ki}t}}^{\omega_k > \omega_i} + \overbrace{e^{ik_l z} e^{-i\omega_l(t-\tau_l)} e^{-i\omega_{ki}t}}^{\omega_k < \omega_i} \right] \tilde{\rho}_{kj} \\
 & - \frac{i}{2\hbar} \mu_{kj}^* \tilde{E}_l(t - \tau_l) \left[ \overbrace{e^{-ik_l z} e^{+i\omega_l(t-\tau_l)} e^{-i\omega_{jk}t}}^{\omega_k < \omega_j} + \overbrace{e^{ik_l z} e^{-i\omega_l(t-\tau_l)} e^{-i\omega_{jk}t}}^{\omega_k > \omega_j} \right] \tilde{\rho}_{ik} \\
 & \quad \quad \quad \underbrace{\hspace{10em}}_{k \leftrightarrow j}
 \end{aligned}$$

# Liouville Equation

Alternative notation:

$$\frac{d\tilde{\rho}_{ij}}{dt} = -\Gamma_{ij}\tilde{\rho}_{ij} + \frac{i\lambda\mu}{2\hbar} c(t - \tau) \underbrace{e^{i\kappa(kz + \omega_{\text{laser}}\tau)}}_{\text{phase factor}} e^{+i\kappa\Omega t} \tilde{\rho}_i(t)$$

$\lambda \in \{1, -1\}$ ; ket side (+1) vs. bra-side (-1) transition

$\kappa \in \{-1, 1\}$ ; wavevector sign (also,  $\kappa = \lambda$  for absorption and  $\kappa = -\lambda$  for emission)

$\Omega = |\omega_{\text{FID}}| - \omega_{\text{laser}}$ ; detuning

Neglect phase factor here (for simplicity)

# Liouville Equation: Driven Limit

This limit assumes slow electric field fluctuations compared to system dynamics. System evolution mimics the behavior of the pulse. Appropriate when dephasing is much faster than the pulses used, or when lasers are far detuned.

$$\tilde{\rho}_f(t) = \frac{\lambda \mu}{2\hbar} \frac{c(t - \tau) e^{i\Omega t}}{\kappa\Omega - i\Gamma} \tilde{\rho}_i(t)$$

These are the most common equations for resonance used in the group. When resonances are spectrally narrower than pulses, convolve resulting spectrum by pulse envelopes.

# Liouville Equation: Impulsive Limit

This limit assumes system dynamics are much slower than the fluctuations of the electric fields. System evolves freely. Appropriate when lasers are much faster than the dephasing rates and near resonance.

$$\tilde{\rho}_f(t) = \frac{i}{2} \lambda \mu \tilde{\rho}_i(\tau_x) \int c(u) du \times \Omega(t - \tau_x) e^{-\Gamma_f(t - \tau_x)}$$

Note that this equation approximates with delta function excitation—though system dynamics may be much slower, your experiment might resolve the rise time stuff, which makes this equation inadequate.

# Strategies for Simulation: Numerical Integrate WMEL pathways

- Appropriate to call non-perturbative wrt pulse behavior, but perturbative with fluence (higher-order effects neglected)
- Typically requires integration (e.g. improved Euler, RK4).



# Strategies for Simulation: Compute Entire Polarization

- When you don't isolate the phase-matched components beforehand
- Non-linear signals need to be isolated in similar ways to experiments

$$P_{lmn}(t) = \int_0^{2\pi} \int_0^{2\pi} \int_0^{2\pi} e^{i(l\phi_1 + m\phi_2 + n\phi_3)} P(t; \phi_1, \phi_2, \phi_3) d\phi_1 d\phi_2 d\phi_3$$

# Simulations Abstracted

Evaluate  $f(\{\vec{\omega}, \vec{\tau}, |E|, \dots\}; \{\Gamma, \omega_{vg}, \dots\})$

Experimental parameters are scanned; system parameters are fixed

How to organize the workflow in a way that:

- is robust to many different forms of  $f$ ?
- allows easy, readable access to system and experimental parameters?
- gives organized solutions that can easily be viewed and manipulated (i.e. measured)?

**Usability** is crucial!

# WrightSim: Design

$$f(\{\vec{\omega}, \vec{\tau}, |E|, \dots\}; \{\Gamma, \omega_{vg}, \dots\}) \rightarrow f\left(g(\vec{\omega}, \vec{\tau}, |E|, \dots); h(\Gamma, \omega_{vg}, \dots)\right)$$

$g$  and  $h$  are translator “functions”. They take the easy assortment of parameters and convert them into the framework that is suitable for use in a more general calculation,  $f$

# WrightSim: Design

$$f(\{\vec{\omega}, \vec{\tau}, |E|, \dots\}; \{\Gamma, \omega_{vg}, \dots\}) \rightarrow f\left(g(\vec{\omega}, \vec{\tau}, |E|, \dots); h(\Gamma, \omega_{vg}, \dots)\right)$$

```
# experiment
trive = ws.experiments.builtin('TRIVE')
trive.d2.points = np.linspace(0, 1, 100)
trive.d2.active = True
```

g works through an “experiment” module that defines the experimental space, and how to convert those variables to meaningful inputs in the simulation

# WrightSim: Design

$$f(\{\vec{\omega}, \vec{\tau}, |E|, \dots\}; \{\Gamma, \omega_{vg}, \dots\}) \rightarrow f\left(g(\vec{\omega}, \vec{\tau}, |E|, \dots); h(\Gamma, \omega_{vg}, \dots)\right)$$

```
# system
system_py_path = ws.mixed.builtin_systems('a') # this is essentially h
system_params = wt.kit.INI('PbSe.ini').dictionary

# run the simulation
response = ws.mixed.scan(system_py_path, system_params)
```

# Application: library of functions useful for computing mixed domain signals

Which Liouville pathways are equivalent? Note that if

$$\frac{d\tilde{\rho}_f}{dt} = -\Gamma_f \tilde{\rho}_f + \frac{i}{2} \lambda_f \mu_f c_x(t - \tau_x) e^{i\kappa_f(\bar{k}_x z + \omega_x \tau_x)} e^{+i\kappa_f \Omega_{fx} t} \tilde{\rho}_i(t)$$

then

$$\begin{aligned} \tilde{\rho}_f(t) &= \frac{i}{2} \lambda_f \mu_f e^{i\kappa_f \omega_x \tau_x} e^{+i\kappa_f \Omega_{fx} t} \\ &\times \int_{-\infty}^{\infty} c_x(t - u - \tau_x) \tilde{\rho}_i(t - u) \Theta(u) e^{-(\Gamma_f + i\kappa_f \Omega_{fx})u} du, \end{aligned}$$

# For a string of interactions

- $E_L(t) =$   
 $\pm \frac{i}{8} \lambda_1 \lambda_2 \lambda_3 \mu_1 \mu_2 \mu_3 \mu_4 e^{i(\kappa_1 \omega_x \tau_x + \kappa_2 \omega_y \tau_y + \kappa_3 \omega_z \tau_z)} e^{-i(\kappa_3 \omega_z + \kappa_2 \omega_y + \kappa_1 \omega_x)t} \times$   
 $\iiint_{-\infty}^{\infty} c_z(t - u - \tau_z) c_y(t - u - v - \tau_y) c_x(t - u - v - w - \tau_x) \times R_L(u, v, w) dw dv du,$
- $R_L(u, v, w) = \Theta(w) e^{-(\Gamma_1 + i\kappa_1 \Omega_{1x})w}$   
 $\times \Theta(v) e^{-(\Gamma_2 + i[\kappa_1 \Omega_{1x} + \kappa_2 \Omega_{2y}])v}$   
 $\times \Theta(u) e^{-(\Gamma_3 + i[\kappa_1 \Omega_{1x} + \kappa_2 \Omega_{2y} + \kappa_3 \Omega_{3z}])u}$

# Constructing a library

- Resonances with different states are accommodated by translation (same principle behind convolution technique)
- Different Liouville pathways within the same time ordering have different signs (lambda product)
- ONLY unique strings of kappa need to be computed to get the end result (for trive, we need  $\{1,-1,1\}$ ,  $\{-1,1,1\}$ , and  $\{1,1,-1\}$ )
- A generalized library would store pathways as a function of system space  $\vec{\Gamma}$  (relative to pulse duration) and experimental space  $\vec{\Omega}, \vec{\tau}, \vec{\kappa}$ --  
~nine dimensions!



# Liouville Equation

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

where

$$H(t) = H_0 - \vec{\mu} \cdot \vec{E}(t)$$

For a complete basis,  $\{\phi_i(r)\}$ , the time-dependence,  $c_i(t)$ , is given by

$$\frac{dc_m(t)}{dt} = -\frac{i}{\hbar} \sum_n H_{mn} c_n(t)$$

There is no way to write a wavefunction of a statistical average:

$$\begin{aligned}\langle A \rangle &= \langle \psi(t) | A | \psi(t) \rangle \\ &= \sum_{m,n} c_m^* c_n A_{mn} = \sum_{m,n} \rho_{nm} A_{mn} \\ &= \text{Tr}(\rho A)\end{aligned}$$

We typically want to evaluate oscillating polarization,  $\langle \mu \rangle$ , since this creates the electric field.

So we really want the time dependence of the density matrix

$$\frac{d\rho_{nm}}{dt} = \left( \frac{dc_n}{dt} \right) c_m^* + c_n \left( \frac{dc_m^*}{dt} \right)$$

# Liouville Equation

$$\frac{d\rho_{nm}}{dt} = \left(\frac{dc_n}{dt}\right)c_m^* + c_n\left(\frac{dc_m^*}{dt}\right)$$

Substitute in evolution of coefficients:

$$\frac{dc_m(t)}{dt} = -\frac{i}{\hbar} \sum_n H_{mn} c_n(t)$$

$$\begin{aligned}\frac{d\rho_{nm}}{dt} &= -\frac{i}{\hbar} \sum_i H_{ni} \rho_{im} + \frac{i}{\hbar} \sum_j H_{jm} \rho_{mj} \\ &= -\frac{i}{\hbar} [H, \rho]_{nm}\end{aligned}$$

Also add in dephasing/relaxation:

$$\frac{d\rho_{nm}}{dt} = \Gamma_{nm} \rho_{nm} - \frac{i}{\hbar} [H, \rho]_{nm}$$

For a two-state system (and using the basis of eigenstates):

$$\frac{d\rho_{ij}}{dt} = -(i\omega_{ij} + \Gamma_{ij})\rho_{ij} - \frac{i}{\hbar} \sum_k (\mu_{ik} E(t) \rho_{kj} - \mu_{jk} E(t) \rho_{ki})$$