QuTiP:

Applications from quantum technology and quantum biology

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Resources: https://arxiv.org/abs/2412.04705, Lambert at al., v5 review.
www.qutip.org
https://qutip2024.wordpress.com/ v5 release developer's conference
https://github.com/nwlambert/AutumnSchool/ Python code and more details adapted from here

QuTiP development recently supported by:

Here begins our new MIRAI
MOONSHOT
RESEARCH & DEVELOPMENT PROGRAM

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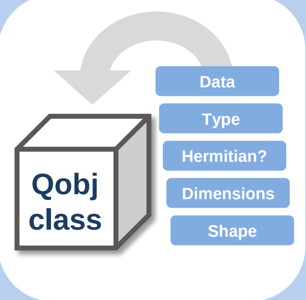
UNIVERSITÉ DE SHERBROOKE

Google Summer of Code

Overview of QuTiP Functionality

1. QuTiP-Core

Qobj



Data Layer

Dense, CSR and DIA

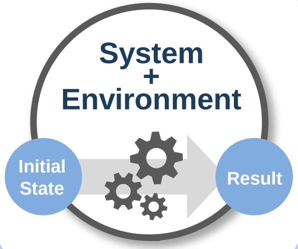
Functions

Eigenstates, Matrix elements, Norms, etc.

Utility Functions

Entanglement measures, Distances, Superoperator representations (Choi, Kraus, etc.), Channels, ENR states, Two-time correlation functions and spectra, MPI support, etc.

Solvers



mesolve
Lindblad master equation

mcsolve + nm_mcsolve
Monte-Carlo master equation

brmesolve
Bloch-Redfield master equation

fmmesolve
Floquet master equation

krylovsolve
Krylov subspace solver

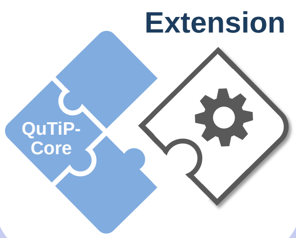
smesolve
Stochastic master equation

HEOMsolver
Hierarchical equations of motion

PIQS
Permutational invariant systems

2. QuTiP-Packages

Packages



QIP: Pulse-based Quantum Circuit Simulator

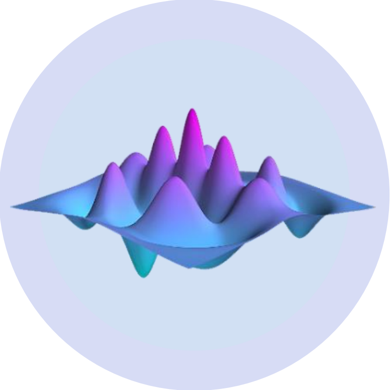
allows circuits to be run on different hardware backend simulations at the level of time-dependent pulses and noise.

QOC: Quantum Optimal Control Package

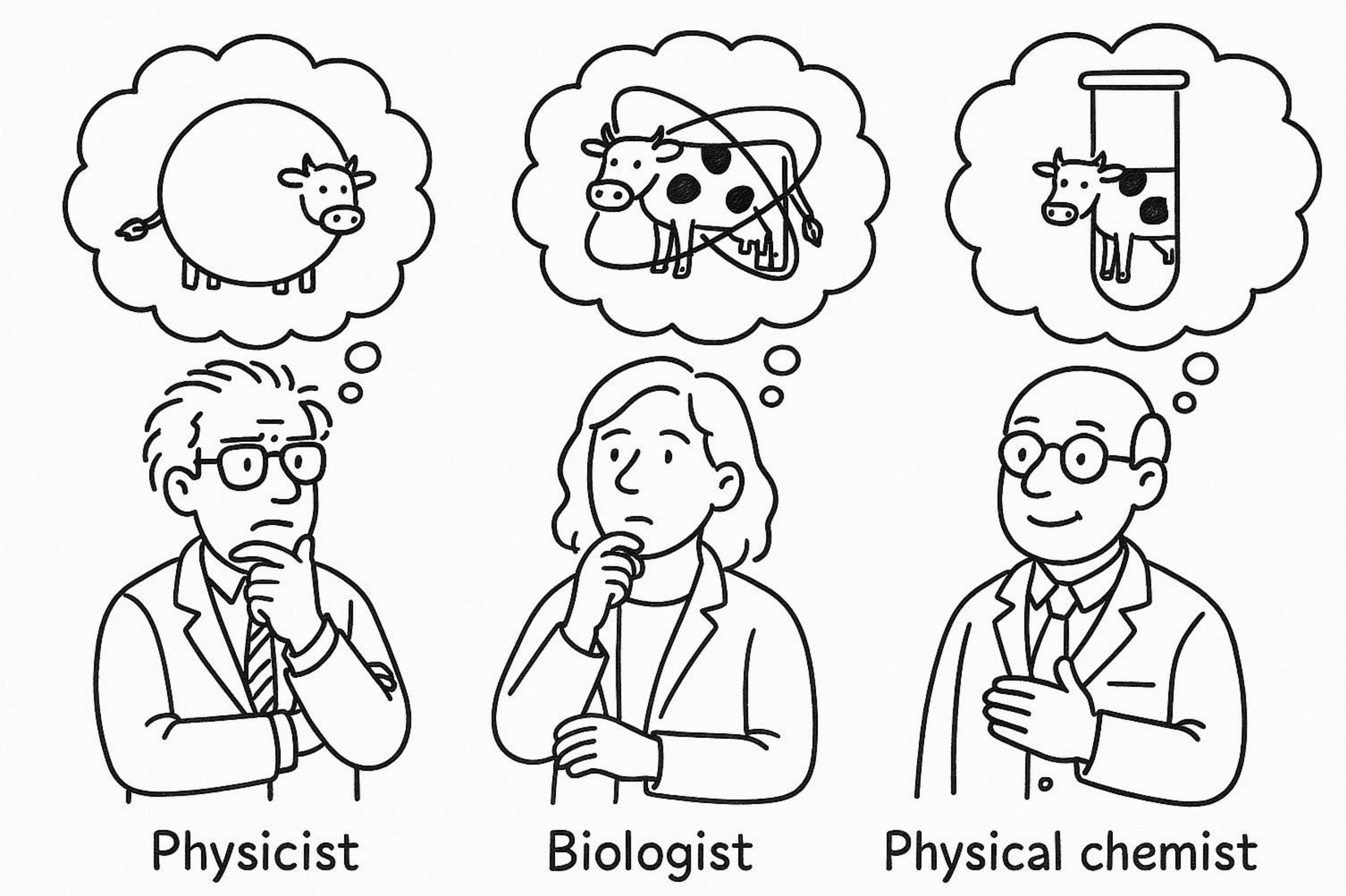
supports for CRAB, GRAPE and GOAT algorithms.

JAX: JAX Data Layer

supports the popular JAX package, allowing for GPU and autograd.



Part 2: An example from quantum biology: photosynthesis, and a more nuanced explanation of noise with non-Markovian methods (HEOM)



Overview:

- **Very short background summary**
- Photosynthesis: a physicist's picture
- Photosynthesis: the role of noise, master equation derivation
- Photosynthesis: non-Markovian noise, HEOM
- Does coherence really survive the noise? Recent contradictory results
- What is the right question?
- Conclusions

Part 2: pre-amble, when should we expect something to be quantum (or non-classical)?

- Low temperature (relative to relevant energy scale $\hbar\omega_i \ll k_{\mathrm{B}}T$. $\rho(t \to \infty) = \sum_i \frac{e^{-\hbar\omega_i/k_{\mathrm{B}}T}}{Z} |\psi_i\rangle\langle\psi_i|$

- This is kind of an equilibrium argument, but many processes in biology and chemistry are transient or non-equilibrium
    - “Living matter evades the decay to equilibrium”, Schrodinger

- If coupling to environment is weak enough, and system starts in a non-equilibrium state, we may expect coherence and entanglement to survive

Timeline of quantum effects in biology (focus on photosynthesis and magnetoreception)

2007-??: Large range of explanations for the role of coherence and noise in optimal efficiency (Plenio, Aspuru-Guzik, Manczel, etc)

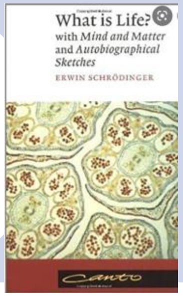
1944 Schrodinger:

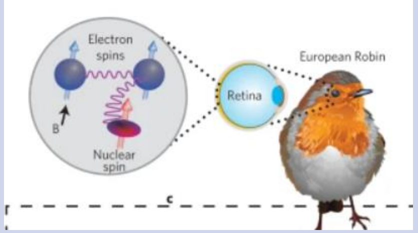
Quantum effects important in some biological processes?

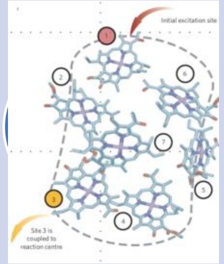
2007: Engel et al. demonstrate beating in FMO complex @ 77K

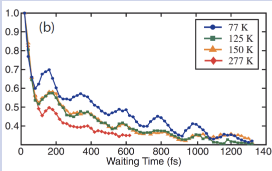
2017/2021: Repeated FMO experiments show limited coherence (Thorwart, Miller). Focus on the influence of noise?

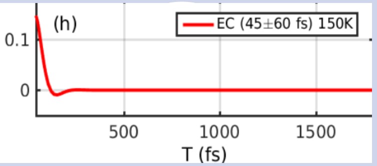
2021: Demonstration of magnetic sensitivity in cryptochrome from migratory songbird (Xu, Hore, Nature)

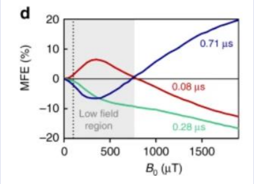


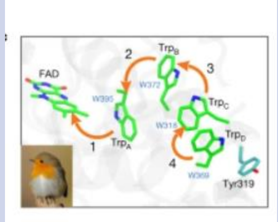












1978:

Radical-pair magneto-reception proposal (Schulten et al.)

2010: FMO complex experiment repeated at room temperature (PNAS)

2019: Kerpal et al, Nat. Comms, Demonstration of sensitivity of radical pair to 50 micro-tesla

1972: Wiltschko: Bird's have an inclination compass:

2006/2010: Wiltschko: Bird's ability to navigate dependent on ambient light, affected by external oscillating Magnetic fields.
Hore/Schulten: Cryptochromes.
Maeda: Demonstration in solution

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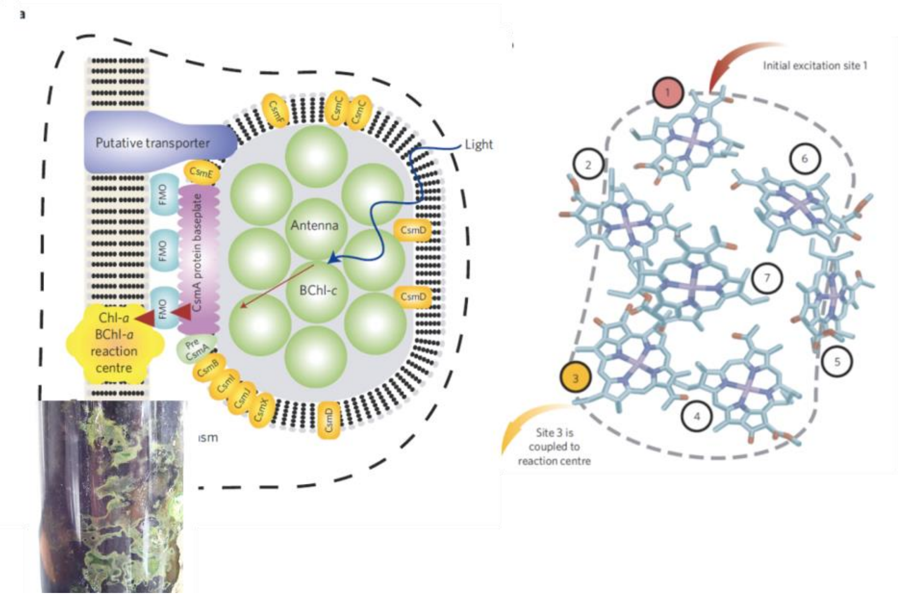
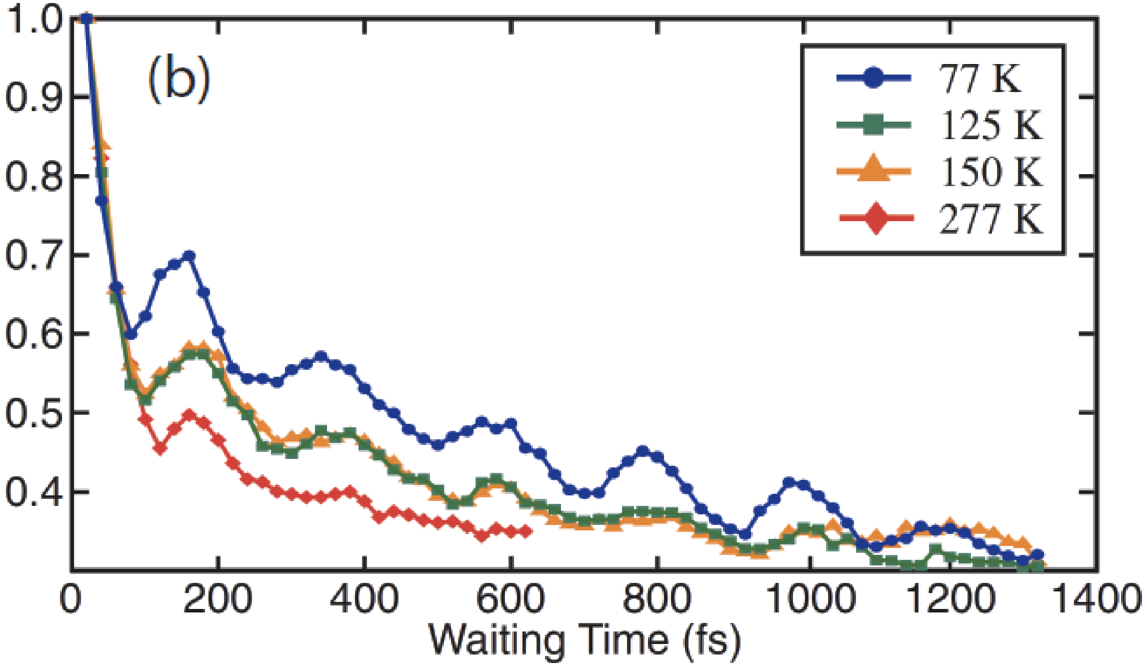
Photosynthesis: A simple physics picture

Light-harvesting in the Fenna-Matthews-Olsen complex: does quantum coherence persist on time scales relevant for energy transfer?





Panitchayangkoon G, et al. (2010) Long-lived quantum coherence in photosynthetic complexes at physiological temperature. Proc Natl Acad Sci USA 107:12766–12770.

Modelling the energy transfer might be tricky:

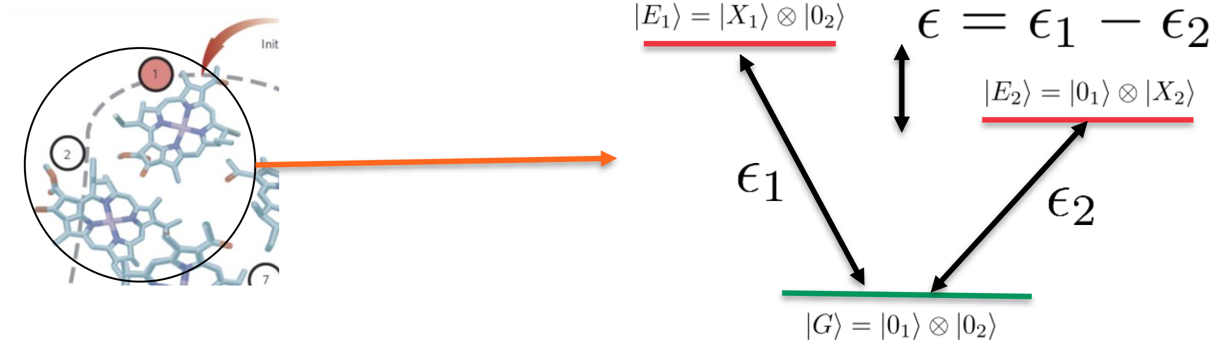
- Electrical excitations strongly couple to nuclear motion
- Thermal energy is on the same order as reorganization energy, electronic coupling, etc

If there is quantum coherence on >100 fs time scale, does it mean anything?

Here we will show how to accurately model noise effects.

Photosynthesis: A simple physics picture

- A minimal model of a single excitation being transported through the complex: lets focus on just two sites



$$|E_1\rangle = |X_1\rangle \otimes |0_2\rangle$$

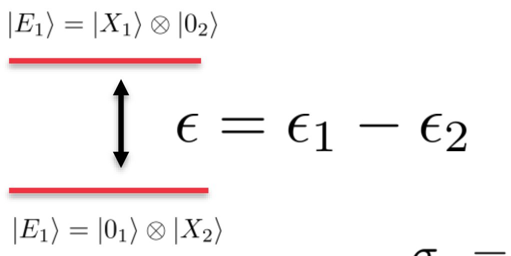
$$\epsilon = \epsilon_1 - \epsilon_2$$

$$|E_2\rangle = |0_1\rangle \otimes |X_2\rangle$$

ϵ_1 ϵ_2

$$|G\rangle = |0_1\rangle \otimes |0_2\rangle$$

- If we focus on a single excitation subspace, we can just describe the two molecules as an effective spin:



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$$\epsilon = \epsilon_1 - \epsilon_2$$

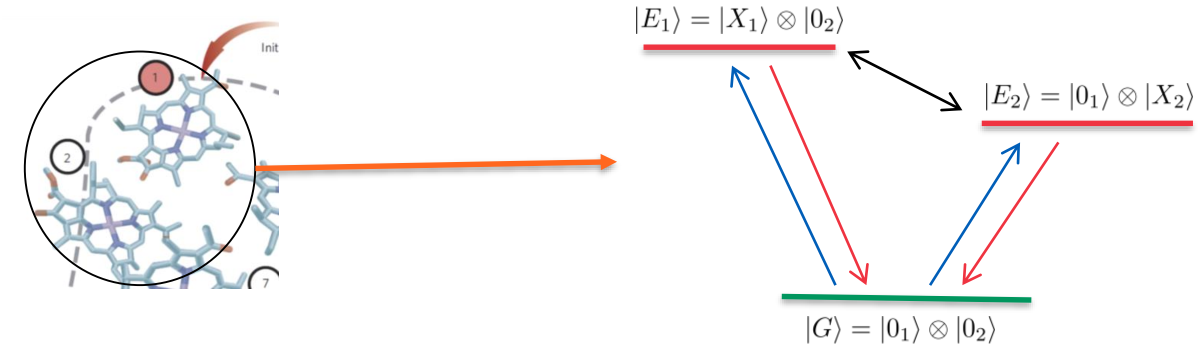
$$|E_1\rangle = |0_1\rangle \otimes |X_2\rangle$$

$$H_E = \frac{\epsilon}{2}\sigma_z$$

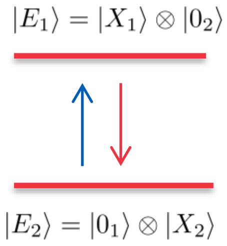
$$\sigma_z = |X_1, 0_2\rangle\langle X_1, 0_2| - |0_1, X_2\rangle\langle 0_1, X_2|$$

Photosynthesis: A simple physics picture

- Energy transfer between sites is given by dipole coupling:



- Energy transfer between sites does not involve an actual movement of charge. We can also capture the contribution to the total energy (Hamiltonian) with two-site model

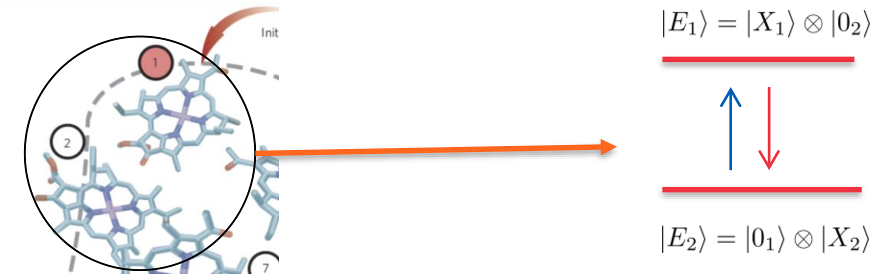


$$H_D = \frac{\Delta}{2}\sigma_x$$

$$\sigma_x = |X_1, 0_2\rangle\langle 0_1, X_2| + |0_1, X_2\rangle\langle X_1, 0_2|$$

Photosynthesis: A simple physics picture

- Given we have this simple model of two coupled chromophores:



$$H = H_S + H_D = \frac{\epsilon}{2}\sigma_z + \frac{\Delta}{2}\sigma_x$$

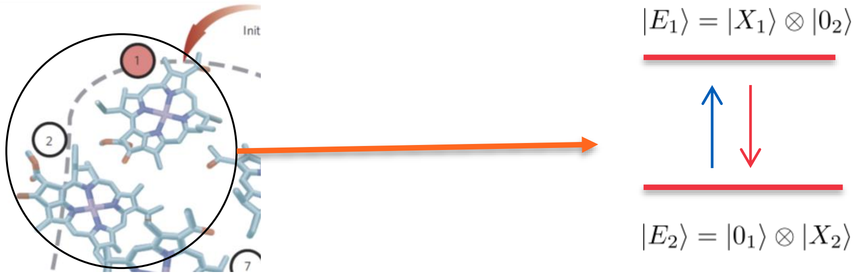
Maybe a photon arrives at one chromophore. If we allow it to evolve under this simple Hamiltonian, what happens?

The initial condition is $$|\psi(t=0)\rangle = |X_1, 0_2\rangle$$

And the dynamics are given by the time-independent Schrodinger equation, as we saw yesterday

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

Photosynthesis: A simple physics picture



$|E_1\rangle = |X_1\rangle \otimes |0_2\rangle$

$|E_2\rangle = |0_1\rangle \otimes |X_2\rangle$

$$H = H_S + H_D = \frac{\epsilon}{2}\sigma_z + \frac{\Delta}{2}\sigma_x$$

We need some parameters. The literature tells us some reasonable choices are

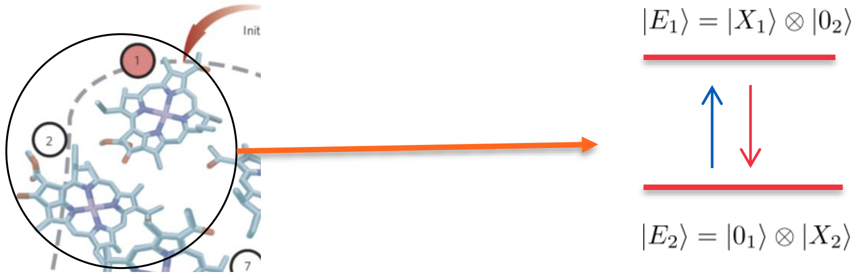
$\epsilon = -120$ cm^{-1}, and $\Delta = 87$ cm^{-1}.

Inverse centimeters??? Why?? Let's convert to something useful

1 cm^{-1} = $100 \times h \times c$ Joules, c = speed of light, h = Planck's constant.

In units of s^{-1}, 100 cm^{-1} corresponds to $10^4 \times h \times c/2\pi\hbar = 3 \times 10^{12} s^{-1} = 3THz$, i.e., a frequency with a time-scale of ~333 femto-seconds.

Photosynthesis: A simple physics picture



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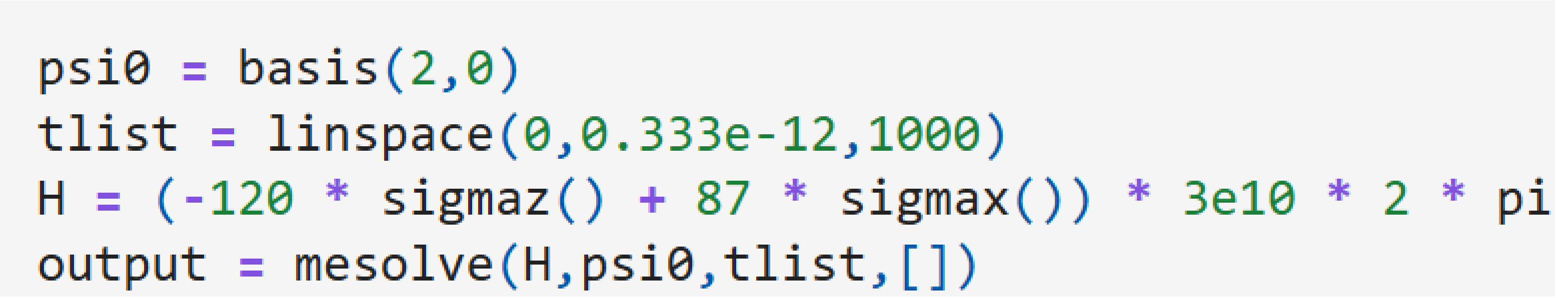
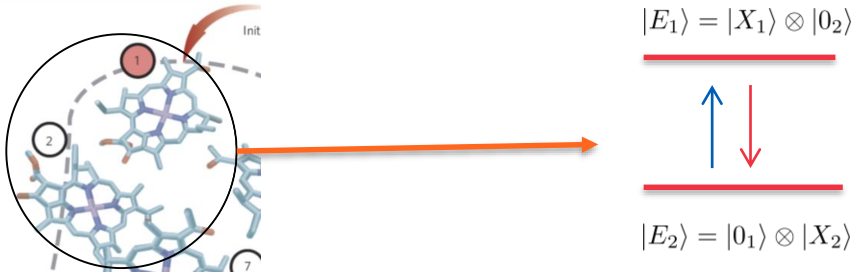


```
psi0 = basis(2,0)
tlist = linspace(0,0.333e-12,1000)
H = (-120 * sigmaz() + 87 * sigmax()) * 3e10 * 2 * pi
output = mesolve(H,psi0,tlist,[])
```

Photosynthesis: A simple physics picture

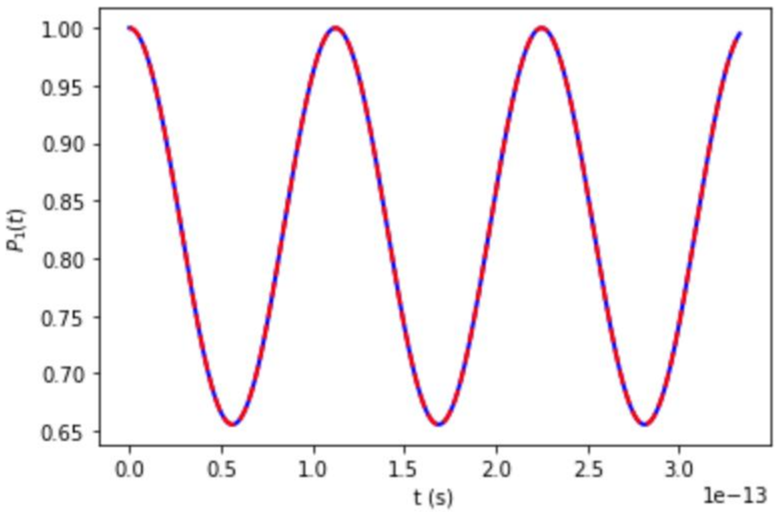


$$H = H_S + H_D = \frac{\epsilon}{2}\sigma_z + \frac{\Delta}{2}\sigma_x$$

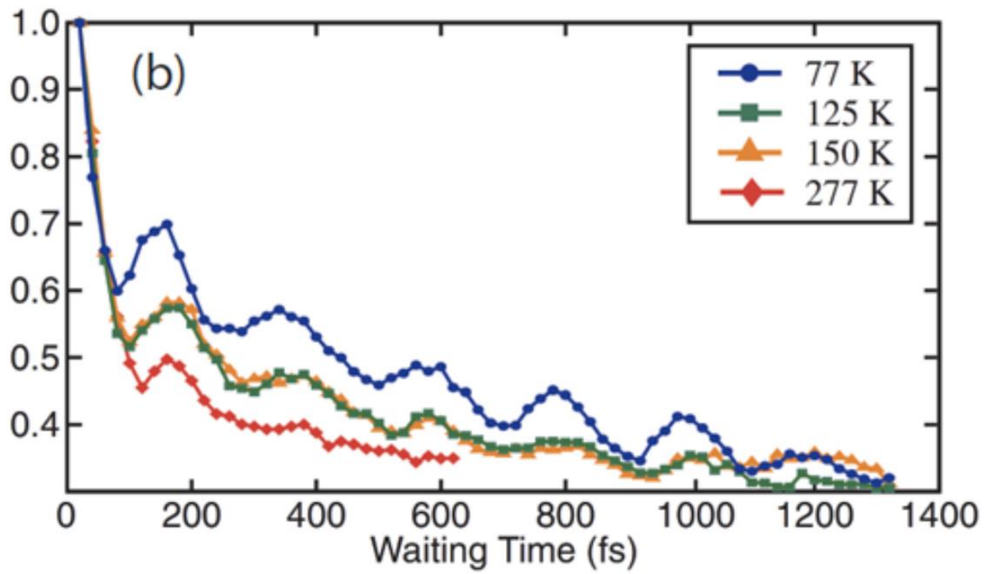
Plot the probability of the excitation being in the first chromophore as a function of time

```
fig, ax = plt.subplots(1, 1)
ax.plot(tlist,expect(psi0*psi0.dag(),output.states), 'b', lw=2)
ax.plot(tlist,Pana, 'r--', lw=2)
ax.set_xlabel('t (s)')
ax.set_ylabel('$P_1(t)$')

plt.show()
```



Frequencies are sort of similar to those plots we saw before!



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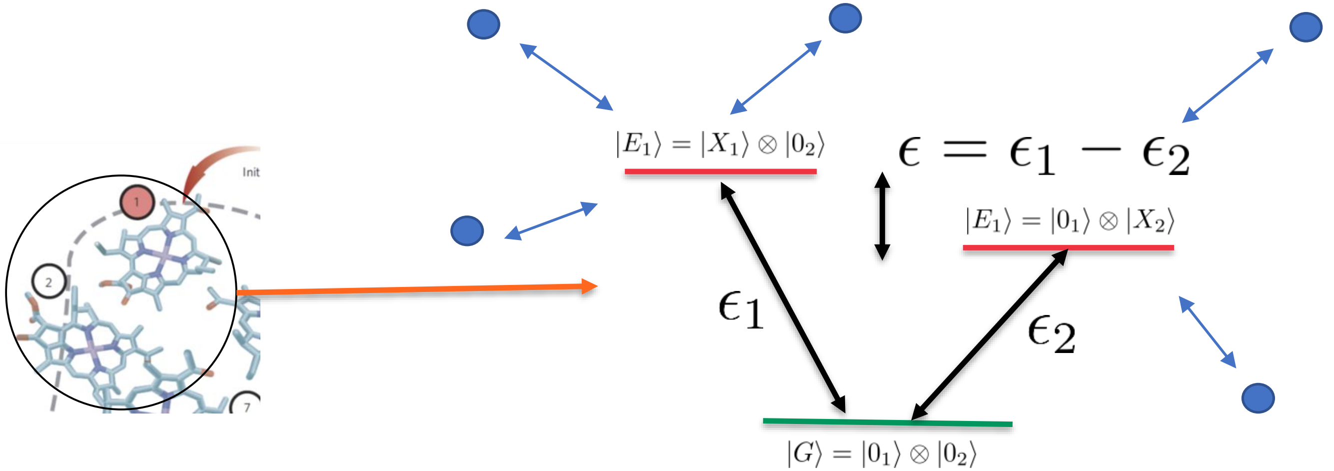
Introducing noise: spin-boson model

- The nuclear motion+molecular vibrations and protein scaffold, modulate the eletronic excitation energy. We describe these with a bath of harmonic oscillators (Ishizaki and Fleming, PNAS)



a_k Is the annihilation operator for mode k
In the environment (destroys a vibrotational
Excitation at frequency ω_k)

$[a_k, a_k^\dagger] = 1$

$$H_{\mathrm{SB}} = \frac{\epsilon}{2}\sigma_z + \frac{\Delta}{2}\sigma_x + \sum_k \omega_k a_k^\dagger a_k + \sigma_z \sum_k \frac{g_k}{\sqrt{2\omega_k}}(a_k + a_k^\dagger)$$

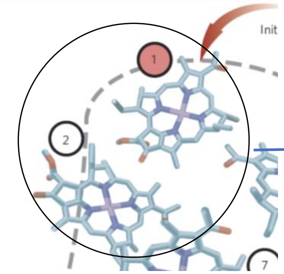
$$\sigma_x = |X_1, 0_2\rangle\langle 0_1, X_2| + |0_1, X_2\rangle\langle X_1, 0_2| \qquad \sigma_z = |X_1, 0_2\rangle\langle X_1, 0_2| - |0_1, X_2\rangle\langle 0_1, X_2|$$

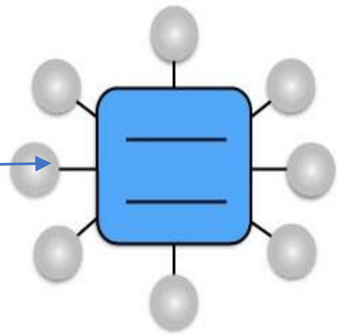
- Note that in general, each chromophore couples to an independent bath (though correlated baths have been studied).

Spin-boson model

- The nuclear motion+molecular vibrations and protein scaffold, modulate the eletronic excitation energy. We can describe these at the Hamiltonian level with a bath of harmonic oscillators

$$H_{\mathrm{SB}} = \tfrac{\epsilon}{2}\sigma_z + \tfrac{\Delta}{2}\sigma_x + \textstyle\sum_k \omega_k a_k^\dagger a_k + \sigma_z \sum_k g_k (a_k + a_k^\dagger)$$





Environment characterized by spectral density and correlation functions

$$J(\omega) = \pi \sum_k |g_k|^2 \, \delta(\omega - \omega_k).$$

$$X = \sum_k g_k (a_k + a_k^\dagger).$$

$$C(\tau) = \langle \bar{X}(t+\tau)\bar{X}(t)\rangle = \int_0^\infty d\omega \frac{J(\omega)}{\pi}[\coth(\beta\omega/2)\cos(\omega\tau) - i\sin(\omega\tau)]$$

$$S(\omega) = \int_{-\infty}^{\infty} \mathrm{d}t \, C(t) \, \mathrm{e}^{\mathrm{i}\omega t},$$

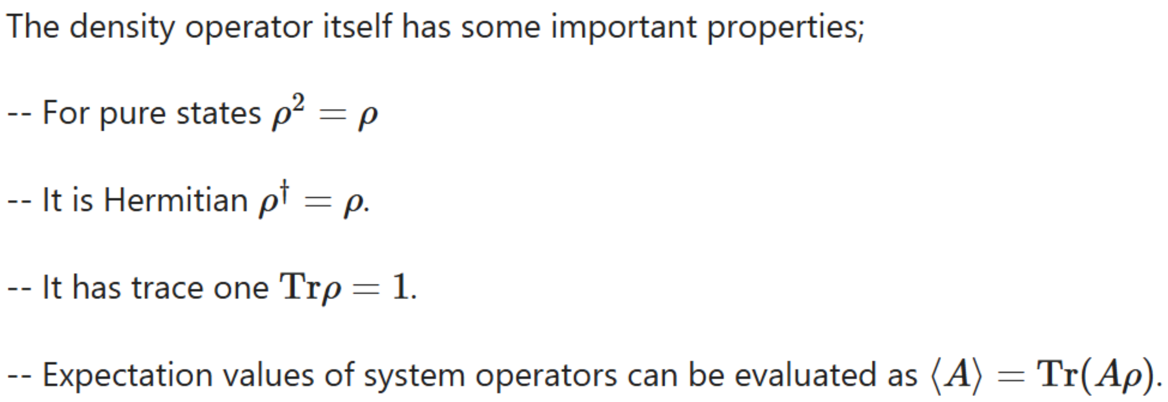
$$S(\omega) = \mathrm{sign}(\omega)\, J(|\omega|) \left[\coth\left(\frac{\beta\omega}{2}\right) + 1\right].$$

Spin-boson model

$$H_{\mathrm{SB}} = \frac{\epsilon}{2}\sigma_z + \frac{\Delta}{2}\sigma_x + \sum_k \omega_k a_k^\dagger a_k + \sigma_z \sum_k \frac{g_k}{\sqrt{2\omega_k}}(a_k + a_k^\dagger)$$

- Recall in Part 1 we introduced the concept of a density operator and a Lindblad master equation, derived from this microscopic model (not the only way to get it!)

$$\rho = \sum_k p_k |\psi_k\rangle\langle\psi_k|$$



The density operator itself has some important properties;

-- For pure states $\rho^2 = \rho$

-- It is Hermitian $\rho^\dagger = \rho$.

-- It has trace one $\mathrm{Tr}\rho = 1$.

-- Expectation values of system operators can be evaluated as $\langle A \rangle = \mathrm{Tr}(A\rho)$.

$$\dot{\rho}(t) = -\frac{i}{\hbar}[H(t), \rho(t)] + \sum_n \frac{1}{2}\left[2C_n\rho(t)C_n^\dagger - \rho(t)C_n^\dagger C_n - C_n^\dagger C_n \rho(t)\right]$$

How is this justified and derived? Under what approximation?

Spin-boson model

The derivation is very long.

I want to highlight a few steps though.

Normally we start with:

$$H_{\mathrm{SB}} = \underbrace{\tfrac{\epsilon}{2}\sigma_z + \tfrac{\Delta}{2}\sigma_x}_{} + \underbrace{\textstyle\sum_k \omega_k a_k^\dagger a_k}_{} + \underbrace{\sigma_z \textstyle\sum_k \frac{g_k}{\sqrt{2\omega_k}}(a_k + a_k^\dagger)}_{}$$

$$H = H_S + H_E + H_I$$

$$\tilde{H}_I(t) = e^{i(H_S+H_E)t} H_I e^{-i(H_S+H_E)t}$$

$$\frac{d}{dt}|\psi(t)\rangle = \frac{-i}{\hbar} H|\psi(t)\rangle \quad \Longrightarrow \quad \frac{\partial}{\partial t}\tilde{\rho}(t) = -i[\tilde{H}_I(t), \tilde{\rho}(t)]$$

Spin-boson model

Formally, this equation can be integrated,

$$\tilde{\rho}(t) = \rho(0) - i\int_0^t ds[\tilde{H}_I(s), \tilde{\rho}(s)]$$

Lets plug this back into what we had before

$$\frac{\partial}{\partial t}\tilde{\rho}(t) = -i[\tilde{H}_I(t), \tilde{\rho}(t)]$$

And trace out the environment degrees of freedom

$$\rho_S(t) = \mathrm{Tr}_E[\rho(t)]$$

$$\frac{\partial}{\partial t}\tilde{\rho}_S(t) = -i\mathrm{Tr}_E[\tilde{H}_I(t), \tilde{\rho}(0)] - \int_0^t ds\mathrm{Tr}_E[\tilde{H}_I(t), [\tilde{H}_I(s), \tilde{\rho}(s)]$$

Spin-boson model

This is still exact! No approximation! To make it solvable, people normally take the following approximations:

- **Born approximation:** $\rho(t) = \rho_S(t)\rho_E(0)$

Basically means the environment is large and never changes (always factorizes, no dynamics and no entanglement)

- **Markov:** Means in the integral, the system state only depends on its current time, not the past (no memory, local in time equation)

$$\tilde{\rho}_S(s) \to \tilde{\rho}_S(t)$$

- This gives us this formula, which is basically most of the way there!

$$\frac{\partial}{\partial t}\tilde{\rho}_S(t) = -\int_0^\infty d\tau \mathrm{Tr}_E[\tilde{H}_I(t), [\tilde{H}_I(t-\tau), \tilde{\rho}_S(t)\rho_E]$$

Spin-boson model

$$\frac{\partial}{\partial t}\tilde{\rho}_S(t) = -\int_0^\infty d\tau \mathrm{Tr}_E[\underbrace{\tilde{H}_I(t)}_{\sigma_z \sum_k g_k(a_k + a_k^\dagger)}, [\tilde{H}_I(t-\tau), \tilde{\rho}_S(t)\rho_E]$$

$$X = \sum_k g_k(a_k + a_k^\dagger).$$

$$\begin{aligned} C(\tau) &= \langle \bar{X}(t+\tau)\bar{X}(t)\rangle \\ &= \mathrm{Tr}\left[\sum_k g_k(a_k e^{-i\omega_k\tau} + a_k^\dagger e^{i\omega_k\tau}) \sum_{k'} g_{k'}(a_{k'} + a_{k'}^\dagger)\rho_B\right] \\ &= \sum_k g_k^2[n(\omega_k,\beta)e^{i\omega_k\tau} + \{1 + n(\omega_k,\beta)\}e^{-i\omega_k\tau}] \\ &= \int_0^\infty d\omega \frac{J(\omega)}{\pi}[n(\omega,\beta)e^{i\omega\tau} + \{1 + n(\omega,\beta)\}e^{-i\omega\tau}] \\ &= \int_0^\infty d\omega \frac{J(\omega)}{\pi}[\coth(\beta\omega/2)\cos(\omega\tau) - i\sin(\omega\tau)] \end{aligned}$$

$$J(\omega) = \pi \sum_k |g_k|^2 \, \delta(\omega - \omega_k).$$

$$n(\omega) = (e^{\omega/k_B T} - 1)^{-1}$$

Spin-boson model

With a bit more work (!) one can arrive at something like

For eigenstates $|\psi_j\rangle$ of H_S, and $c_{j,l} = \langle\psi_j|\sigma_z|\psi_l\rangle$ $\Delta_{j,l} = E_j - E_l$ is the difference in eigenenergies.

$$\frac{\partial}{\partial t}\rho_S(t) = -i[H_S, \rho(t)]$$

$$+\sum_{j>l,l} J(\Delta_{j,l})|c_{j,l}|^2 \left(n(\Delta_{j,l}) + 1\right) \left[2|\psi_l\rangle\langle\psi_j|\rho_S(t)|\psi_j\rangle\langle\psi_l| - \{|\psi_j\rangle\langle\psi_j|, \rho_S\}\right]$$

$$+\sum_{j>l,l} J(\Delta_{j,l})|c_{j,l}|^2 n(\Delta_{j,l}) \left[2|\psi_j\rangle\langle\psi_l|\rho_S(t)|\psi_l\rangle\langle\psi_j| - \{|\psi_l\rangle\langle\psi_l|, \rho_S\}\right]$$

The first part is the coherent system evolution, the second part describes spontaneous and stimulated emission, and the third part describes absorption. $n(\omega) = (e^{\omega/T} - 1)^{-1}$

To recap, it is valid when:

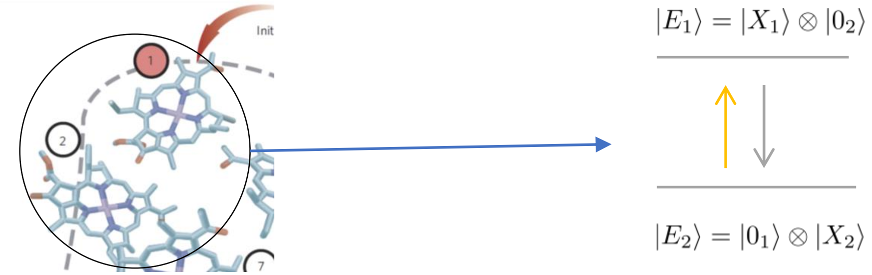
- The **Born approximation** applies: the coupling is weak such that we can assume $\rho(t) = \rho_S(t) \otimes \rho_E$
- The **Markov approximation** applies: the bath returns to equilibrium on a time scale τ_E which is faster than the relaxation of the system induced by that bath τ_R.
- The **secular approximation** applies: the system time scales are small (i.e., higher frequency) than the relaxation time scales. In other words, $\epsilon > \quad J(\epsilon)(n(\epsilon)+1)$.

$$\tau_E \ll \tau_S \ll \tau_R$$

** Two questions **:

- Can we use this model to describe the environment affecting energy transport in FMO?
- Does noise slow down transport, or speed it up?

Photosynthesis: A simple physics picture



$|E_1\rangle = |X_1\rangle \otimes |0_2\rangle$

$|E_2\rangle = |0_1\rangle \otimes |X_2\rangle$

$$H = H_S + H_D = \frac{\epsilon}{2}\sigma_z + \frac{\Delta}{2}\sigma_x$$

To add noise to our old example, Lets assume the **spectral density** is flat

$$J(\Delta_{j,l})|c_{j,l}|^2 = \gamma.$$

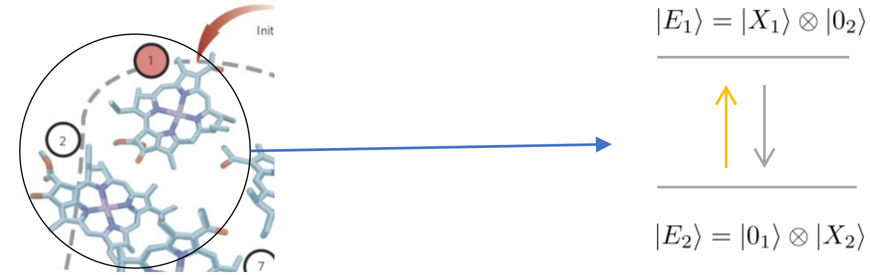
Here we have two operators; one which causes emission,

$$\sum_{j>l,l} \gamma\,(n+1)\left[2|\psi_l\rangle\langle\psi_j|\rho_S(t)|\psi_j\rangle\langle\psi_l| - \{|\psi_j\rangle\langle\psi_j|, \rho_S\}\right]$$

the other absorption

$$\sum_{j>l,l} \gamma n\left[2|\psi_j\rangle\langle\psi_l|\rho_S(t)|\psi_l\rangle\langle\psi_j| - \{|\psi_l\rangle\langle\psi_l|, \rho_S\}\right]$$

Photosynthesis: A simple physics picture

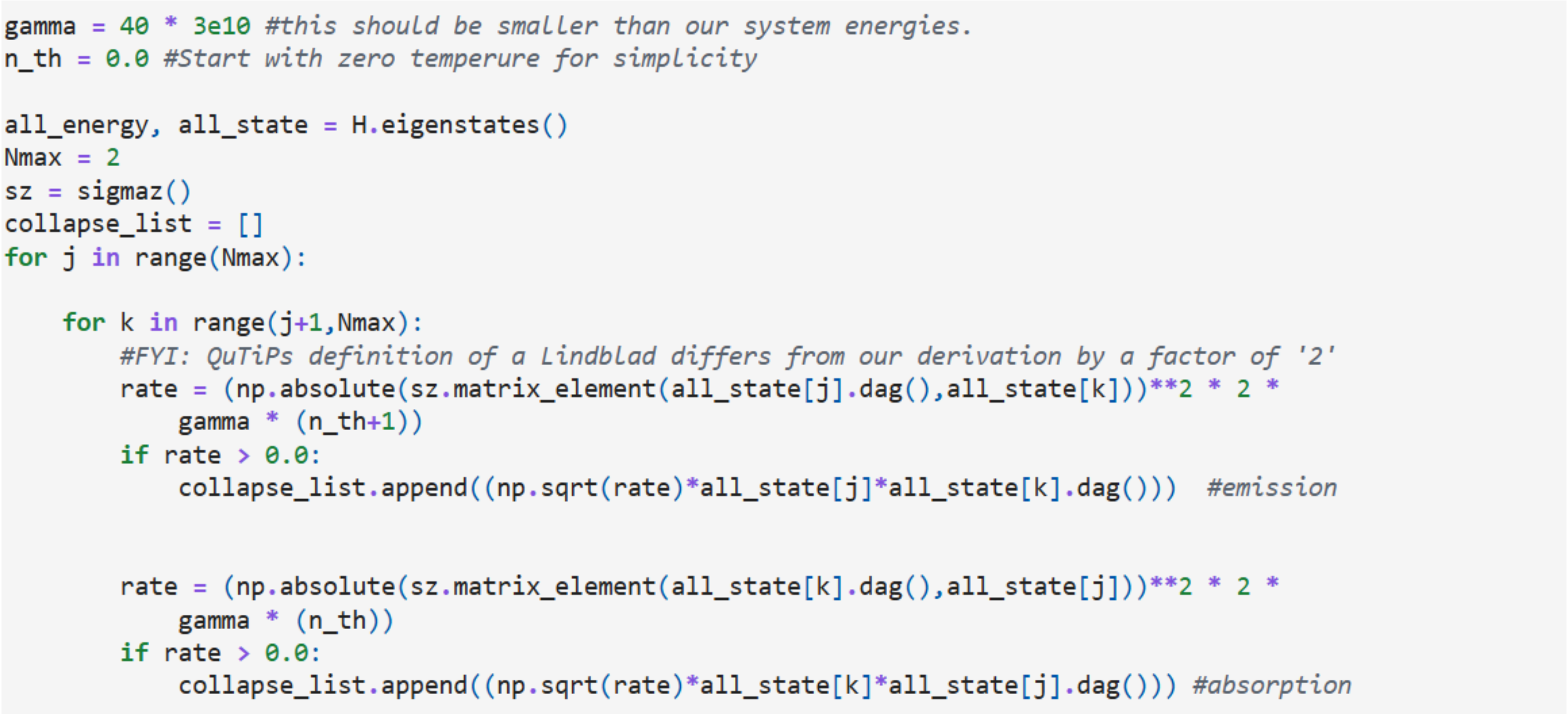


$|E_1\rangle = |X_1\rangle \otimes |0_2\rangle$

$|E_2\rangle = |0_1\rangle \otimes |X_2\rangle$

$$H = H_S + H_D = \frac{\epsilon}{2}\sigma_z + \frac{\Delta}{2}\sigma_x$$

To implement this in QuTiP, we can use the **Bloch-Redfield solver (brmesolve()),** which will diagonalize and construct this equation for us. But lets show how we might do it manually:

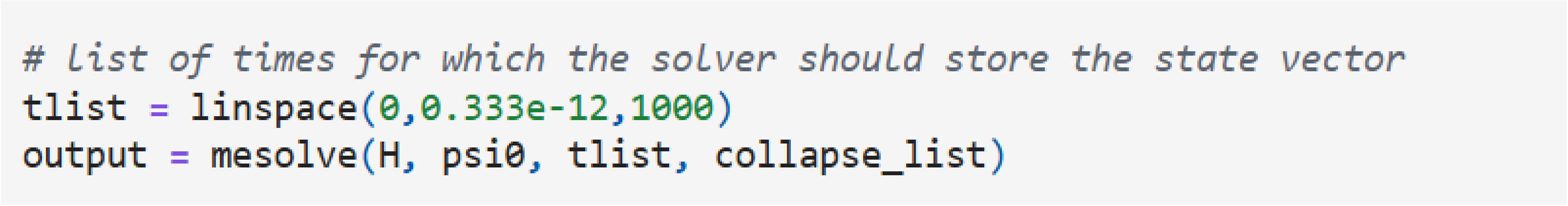


```
gamma = 40 * 3e10 #this should be smaller than our system energies.
n_th = 0.0 #Start with zero temperure for simplicity

all_energy, all_state = H.eigenstates()
Nmax = 2
sz = sigmaz()
collapse_list = []
for j in range(Nmax):

    for k in range(j+1,Nmax):
        #FYI: QuTiPs definition of a Lindblad differs from our derivation by a factor of '2'
        rate = (np.absolute(sz.matrix_element(all_state[j].dag(),all_state[k]))**2 * 2 *
            gamma * (n_th+1))
        if rate > 0.0:
            collapse_list.append((np.sqrt(rate)*all_state[j]*all_state[k].dag()))  #emission


        rate = (np.absolute(sz.matrix_element(all_state[k].dag(),all_state[j]))**2 * 2 *
            gamma * (n_th))
        if rate > 0.0:
            collapse_list.append((np.sqrt(rate)*all_state[k]*all_state[j].dag())) #absorption
```

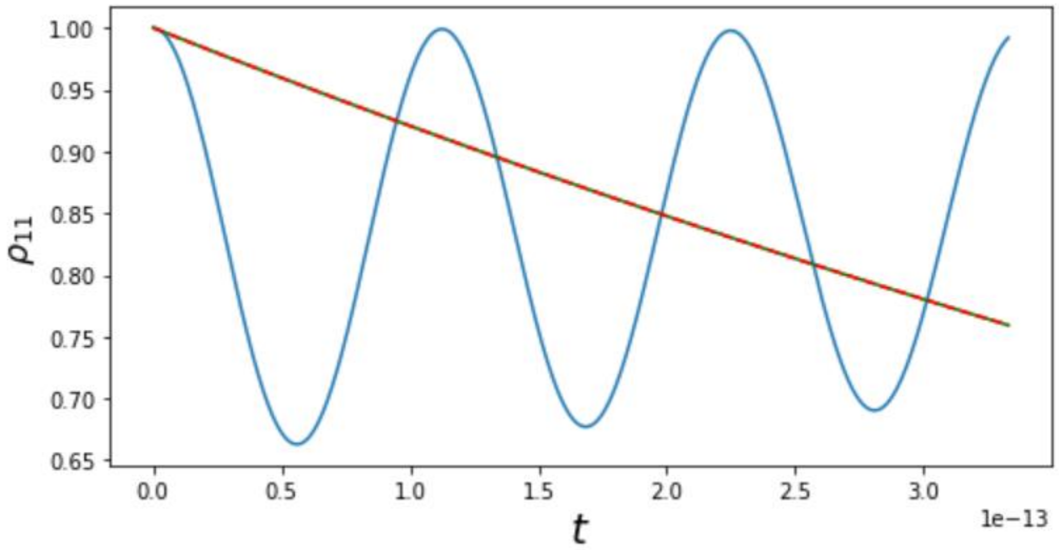
Photosynthesis: A simple physics picture

$$H = H_S + H_D = \frac{\epsilon}{2}\sigma_z + \frac{\Delta}{2}\sigma_x$$

With this list of ‘collapse operators’ between eigenstates, we can use mesolve() as usual:



```
# list of times for which the solver should store the state vector
tlist = linspace(0,0.333e-12,1000)
output = mesolve(H, psi0, tlist, collapse_list)
```

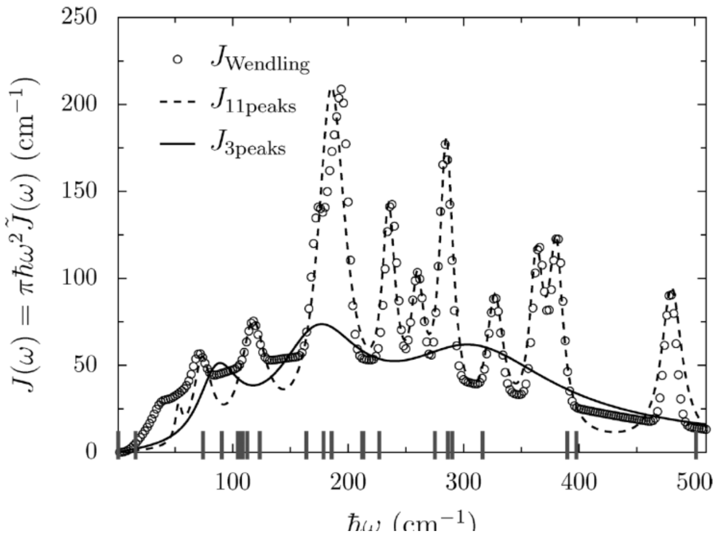


Zero temperature, small decay (40 cm^{-1}) gives
Very slow decay!

Note: Starting in an eigenstate, we see no coherent oscillations, just slow decay

Is this an accurate description of noise in FMO?

- Modelling of the dynamics of a real photosynthetic complex is hard because of the complex environment. Are these simple perturbative methods sufficient?



Kreisbeck and Kramer,
J. Phys. Chem. Lett. 2012

What does the spectral density tell us about validity of master equations?

- Both the magnitude and the structure are important:
  - Large magnitude = strong coupling = Born approximation may break
  - What about Markov approximation?
    - Implies bath correlation time is short.
    - **Extreme limit:** delta-function correlated = white noise at all frequencies **(positive and negative)**

$$C(t) = \int_0^\infty \frac{d\omega}{\pi} J(\omega)\left[\coth\left(\frac{\beta\omega}{2}\right)\cos(\omega t) - i\sin(\omega t)\right],$$

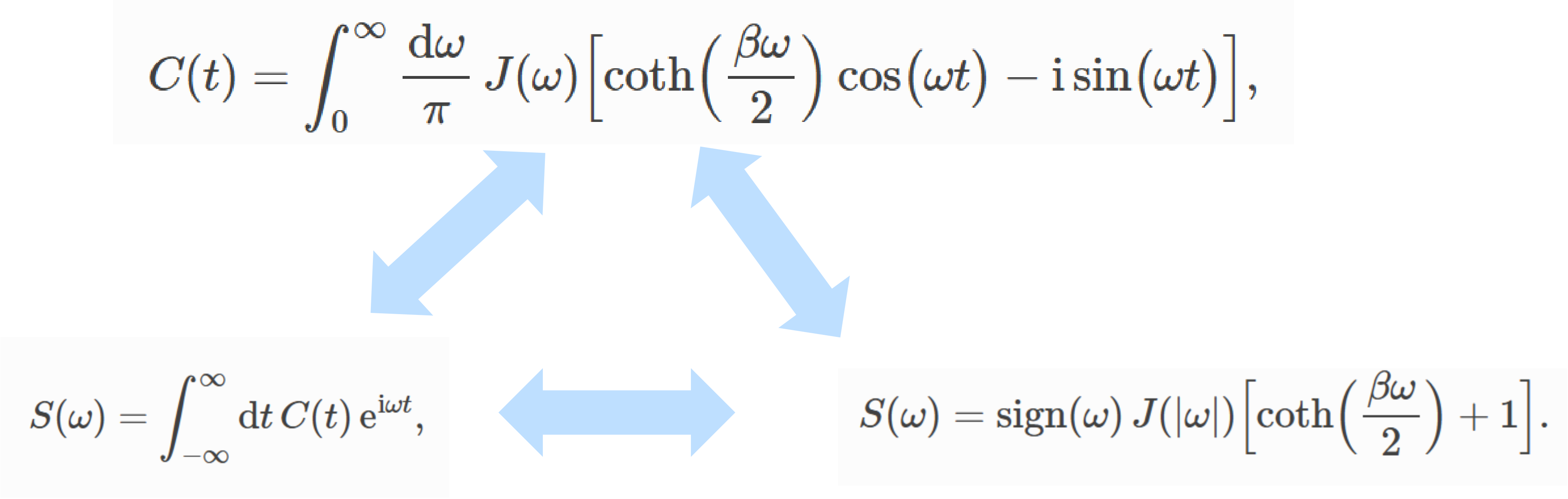
$$S(\omega) = \int_{-\infty}^{\infty} dt\, C(t)\, e^{i\omega t},$$

$$S(\omega) = \mathrm{sign}(\omega)\, J(|\omega|)\left[\coth\left(\frac{\beta\omega}{2}\right) + 1\right].$$

QuTiP Environment class

In QuTiP v5 we provide a handy **environment class** to deal with this description, and provides an easy consistent interface! https://qutip.readthedocs.io/en/qutip-5.1.x/guide/guide-environments.html

Contains **pre-defined and user-defined** options (via input of J(w)+T, S(w), or C(t)).
When one of the three provided, the others can be reconstructed with different means



$$C(t) = \int_0^\infty \frac{\mathrm{d}\omega}{\pi} J(\omega) \left[\coth\left(\frac{\beta\omega}{2}\right) \cos(\omega t) - \mathrm{i} \sin(\omega t)\right],$$

$$S(\omega) = \int_{-\infty}^{\infty} \mathrm{d}t \, C(t) \, \mathrm{e}^{\mathrm{i}\omega t},$$

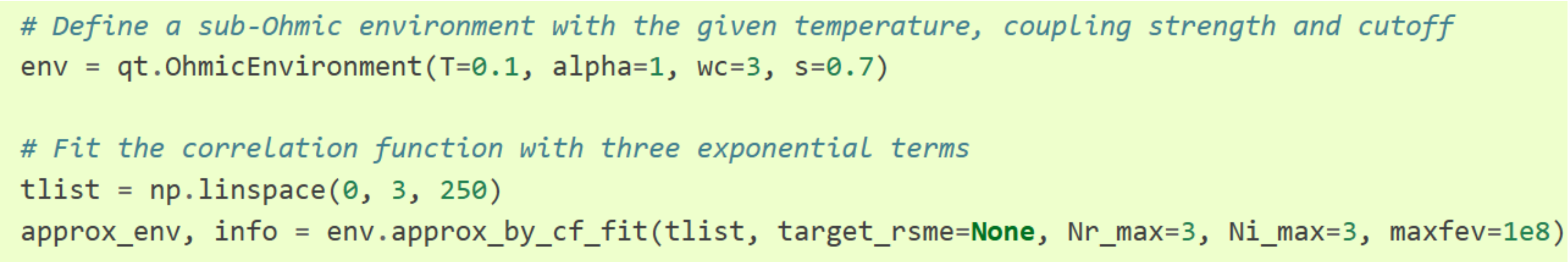
$$S(\omega) = \mathrm{sign}(\omega) \, J(|\omega|) \left[\coth\left(\frac{\beta\omega}{2}\right) + 1\right].$$

QuTiP Environment class

Predefined spectral densities:

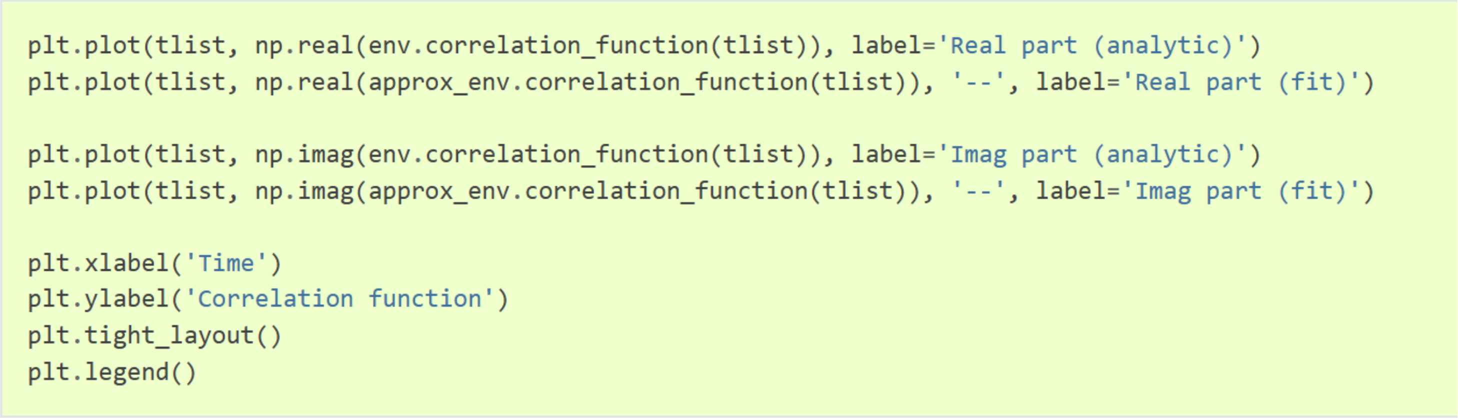
- ‘Ohmic’ class with exponential cut-off

$$J(\omega) = \alpha \frac{\omega^s}{\omega_c^{s-1}} e^{-\omega/\omega_c},$$

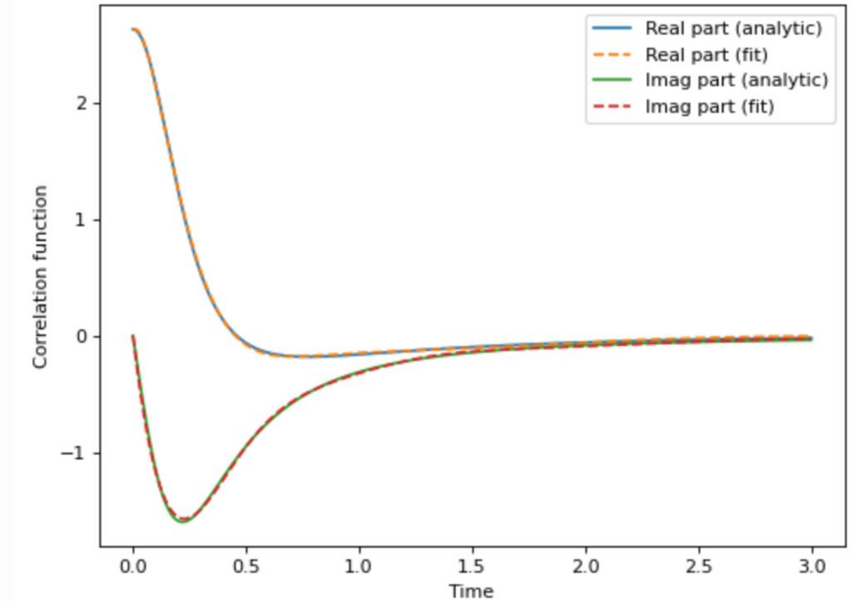


```
# Define a sub-Ohmic environment with the given temperature, coupling strength and cutoff
env = qt.OhmicEnvironment(T=0.1, alpha=1, wc=3, s=0.7)

# Fit the correlation function with three exponential terms
tlist = np.linspace(0, 3, 250)
approx_env, info = env.approx_by_cf_fit(tlist, target_rsme=None, Nr_max=3, Ni_max=3, maxfev=1e8)
```

- Get exact or approximate fit of correlation functions:



```
plt.plot(tlist, np.real(env.correlation_function(tlist)), label='Real part (analytic)')
plt.plot(tlist, np.real(approx_env.correlation_function(tlist)), '--', label='Real part (fit)')

plt.plot(tlist, np.imag(env.correlation_function(tlist)), label='Imag part (analytic)')
plt.plot(tlist, np.imag(approx_env.correlation_function(tlist)), '--', label='Imag part (fit)')

plt.xlabel('Time')
plt.ylabel('Correlation function')
plt.tight_layout()
plt.legend()
```

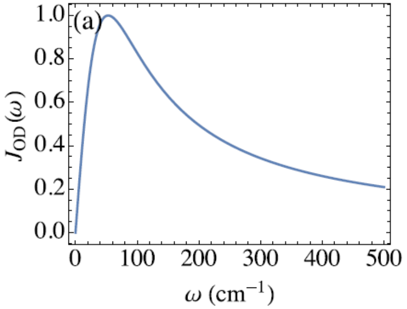


QuTiP Environment class

Predefined spectral densities:

- **‘Drude-Lorentz’**

$$J(\omega) = \frac{2\lambda\gamma\omega}{\gamma^2+\omega^2},$$



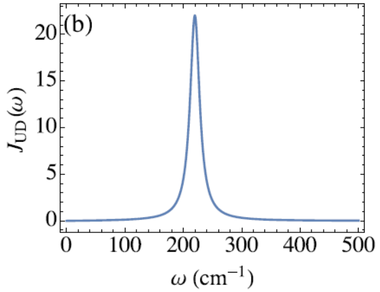
Correlation functions can be decomposed as Matsubara, Pade, or fit with least squares, AAA, etc

$$C(t) = \sum_{k=0}^{\infty} c_k e^{-\nu_k t}$$

$$\nu_k = \begin{cases} \gamma & k=0 \\ 2\pi k/\beta & k\geq 1 \end{cases}, \qquad c_k = \begin{cases} \lambda\gamma[\cot(\beta\gamma/2)-i] & k=0 \\ \frac{4\lambda\gamma\nu_k}{(\nu_k^2-\gamma^2)\beta} & k\geq 1 \end{cases}.$$

- **‘Underdamped ‘Brownian Motion**’

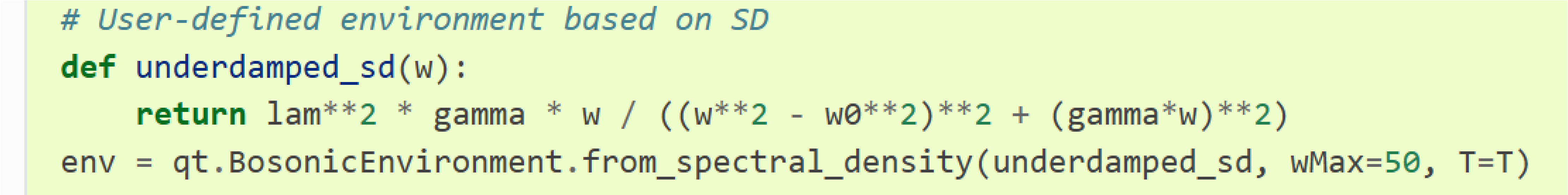
$$J(\omega) = \frac{\lambda^2\Gamma\omega}{(\omega_0^2-\omega^2)^2+\Gamma^2\omega^2},$$



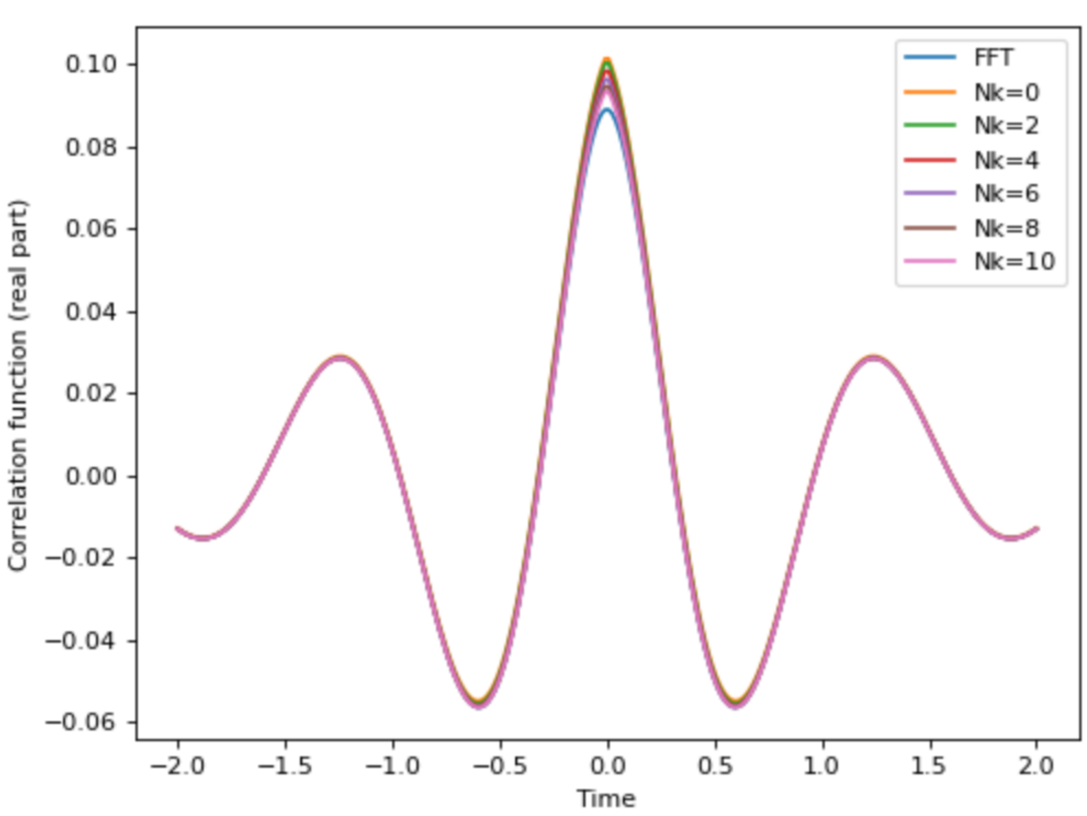
Correlation functions can be decomposed as Matsubara, or fit with least squares, AAA, etc

QuTiP Environment class

User-defined bath example: from spectral density:



```python
# User-defined environment based on SD
def underdamped_sd(w):
    return lam**2 * gamma * w / ((w**2 - w0**2)**2 + (gamma*w)**2)
env = qt.BosonicEnvironment.from_spectral_density(underdamped_sd, wMax=50, T=T)
```



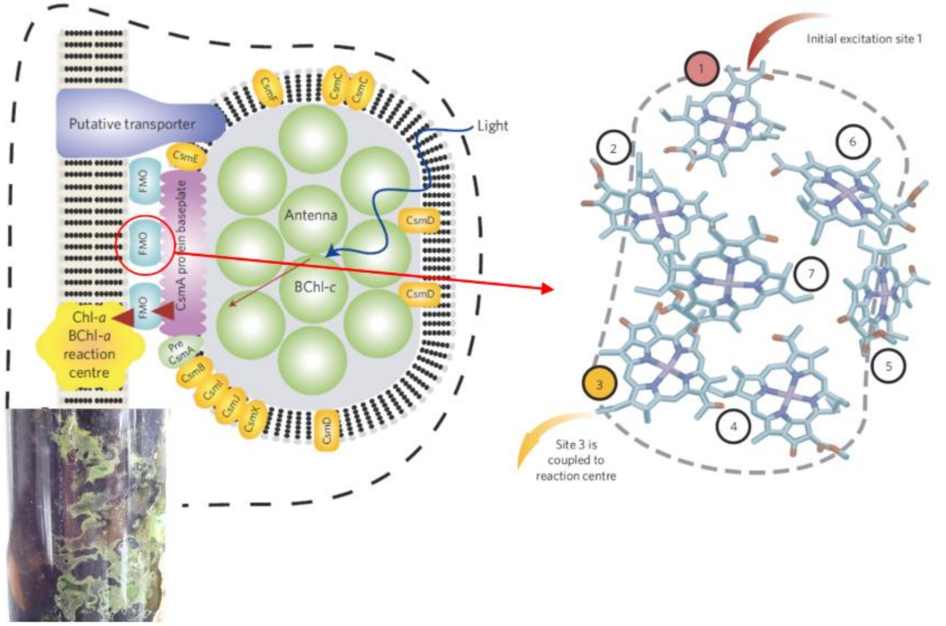
Photosynthesis: A simple physics picture

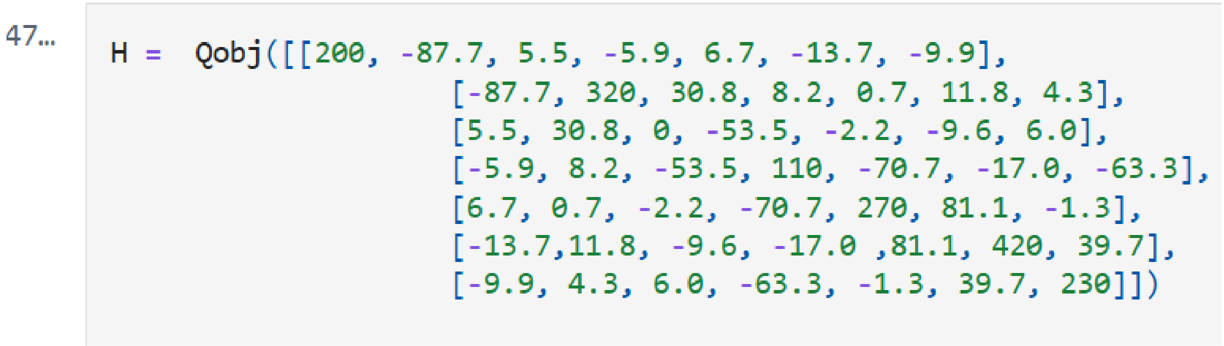
Lets do two things at once: move from the two-site picture to **the full 7-site picture,** and then lets Introduce frequency-dependent **spectral density**

In the single-excitation limit, we wrote 2-sites as a 2-level system.

For 7-sites we can write a 7-level system with Hamiltonian

$$H = \sum_{j=1}^{7} \epsilon_j |j\rangle\langle j| + \sum_{j,j'} J_{j,j'} \left(|j\rangle\langle j'| + c.c\right)$$




47…

```
H =  Qobj([[200, -87.7, 5.5, -5.9, 6.7, -13.7, -9.9],
                   [-87.7, 320, 30.8, 8.2, 0.7, 11.8, 4.3],
                   [5.5, 30.8, 0, -53.5, -2.2, -9.6, 6.0],
                   [-5.9, 8.2, -53.5, 110, -70.7, -17.0, -63.3],
                   [6.7, 0.7, -2.2, -70.7, 270, 81.1, -1.3],
                   [-13.7,11.8, -9.6, -17.0 ,81.1, 420, 39.7],
                   [-9.9, 4.3, 6.0, -63.3, -1.3, 39.7, 230]])
```

This type of data is found via ab-initio modeling and spectroscopy

Photosynthesis: A simple physics picture

The interaction with the bath becomes a little more complicated. Now each chromophore is assumed to interact with an independent bath. Each bath modules the energy of that chromophore via coupling to the operator:

$$H_I = \sum_{m=1}^{7} |m\rangle\langle m| \sum_k g_{k,m}(b_{k,m} + b_{k,m}^\dagger)$$

The full spectrum we showed earlier is a bit complicated: in Ishizaki and Fleming PNAS 2012 they argue that the environment has a decay time of between 50 fs and 200 fs. We can capture this with a Drude-Lorentz spectral density:

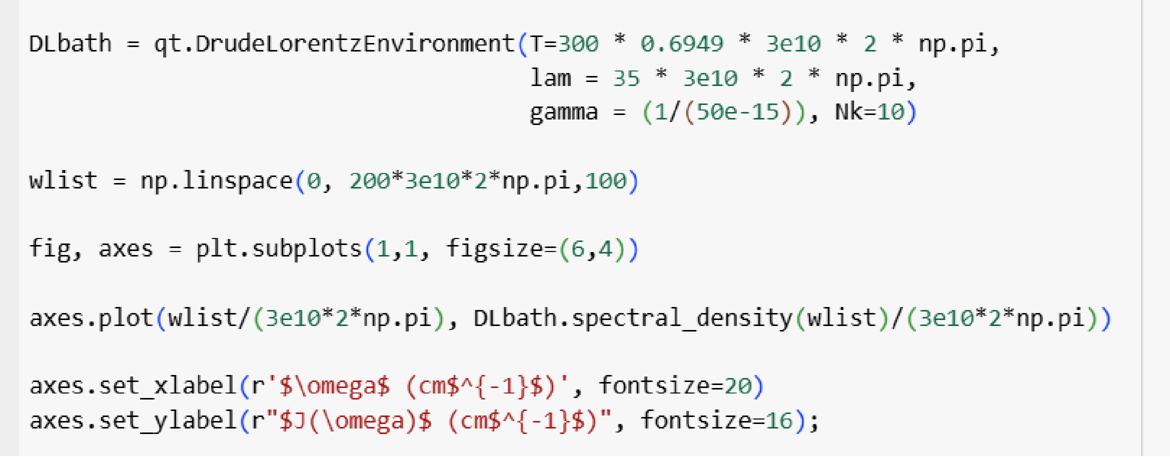
$$J(\omega) = \frac{2\lambda\gamma\omega}{\pi(\omega^2 + \gamma^2)}$$

λ tells us how strong the overall interaction with the environment is

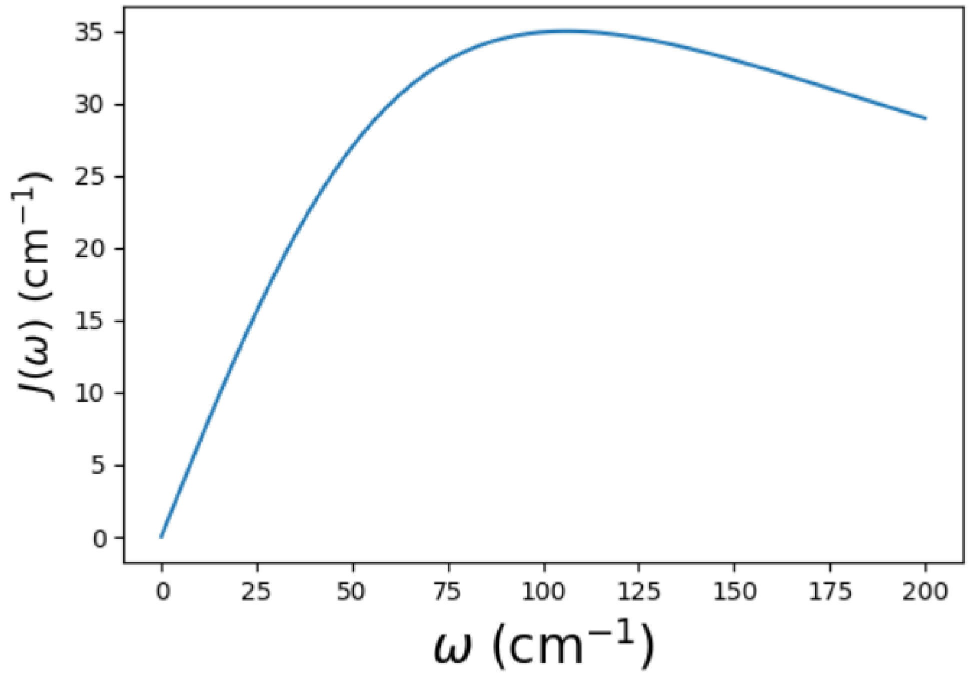
γ tell us the bath cut-off, or decay rate, so is inverse of the bath memory time.

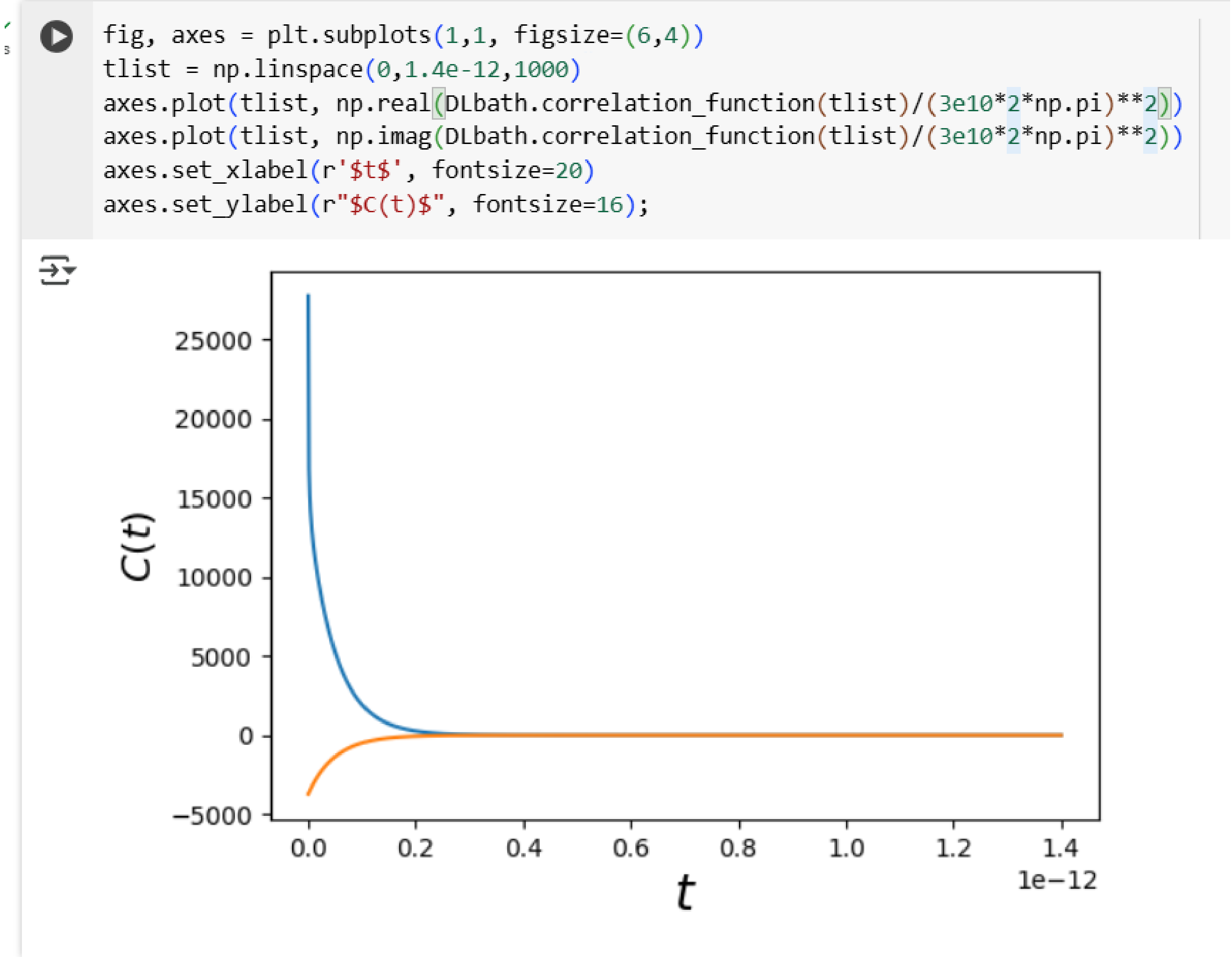
Photosynthesis: A simple physics picture

Use predefined bath-class:



```
DLbath = qt.DrudeLorentzEnvironment(T=300 * 0.6949 * 3e10 * 2 * np.pi,
                                    lam = 35 * 3e10 * 2 * np.pi,
                                    gamma = (1/(50e-15)), Nk=10)

wlist = np.linspace(0, 200*3e10*2*np.pi,100)

fig, axes = plt.subplots(1,1, figsize=(6,4))

axes.plot(wlist/(3e10*2*np.pi), DLbath.spectral_density(wlist)/(3e10*2*np.pi))

axes.set_xlabel(r'$\omega$ (cm$^{-1}$)', fontsize=20)
axes.set_ylabel(r"$J(\omega)$ (cm$^{-1}$)", fontsize=16);
```

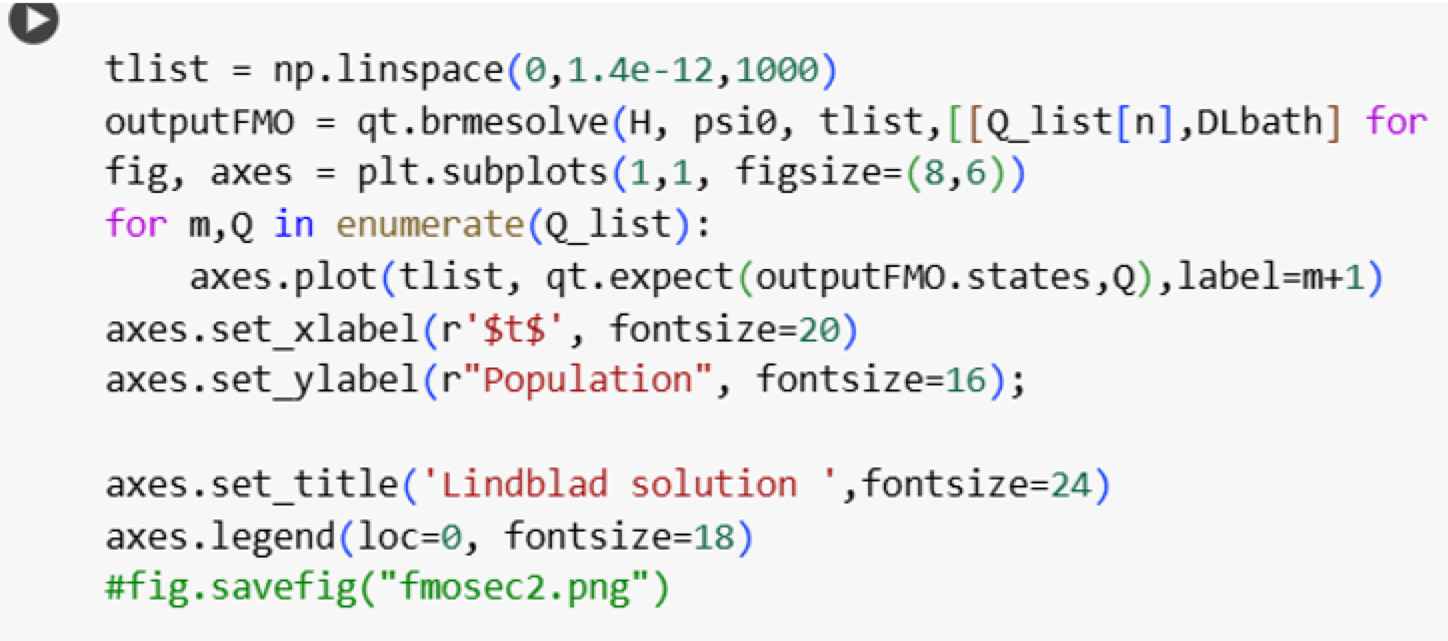




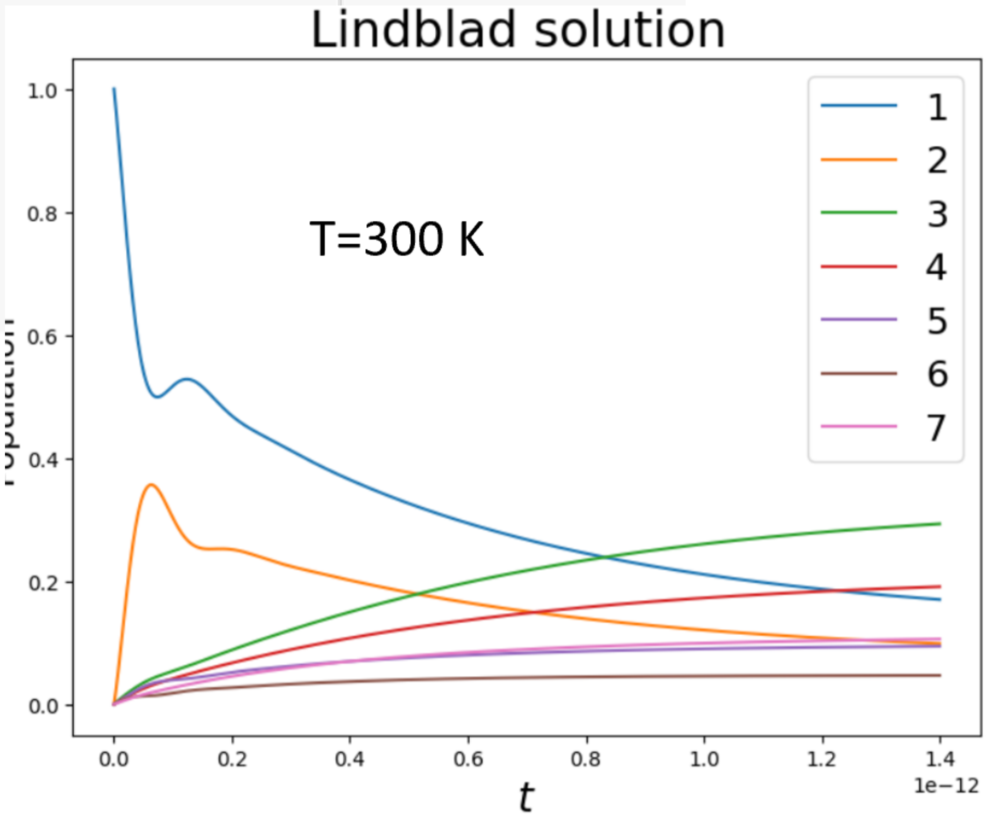
```
fig, axes = plt.subplots(1,1, figsize=(6,4))
tlist = np.linspace(0,1.4e-12,1000)
axes.plot(tlist, np.real(DLbath.correlation_function(tlist)/(3e10*2*np.pi)**2))
axes.plot(tlist, np.imag(DLbath.correlation_function(tlist)/(3e10*2*np.pi)**2))
axes.set_xlabel(r'$t$', fontsize=20)
axes.set_ylabel(r"$C(t)$", fontsize=16);
```

Photosynthesis: A simple physics picture

Lets combine 7-site model with spectral density Bloch-Redfield solver with a bath on each site!a

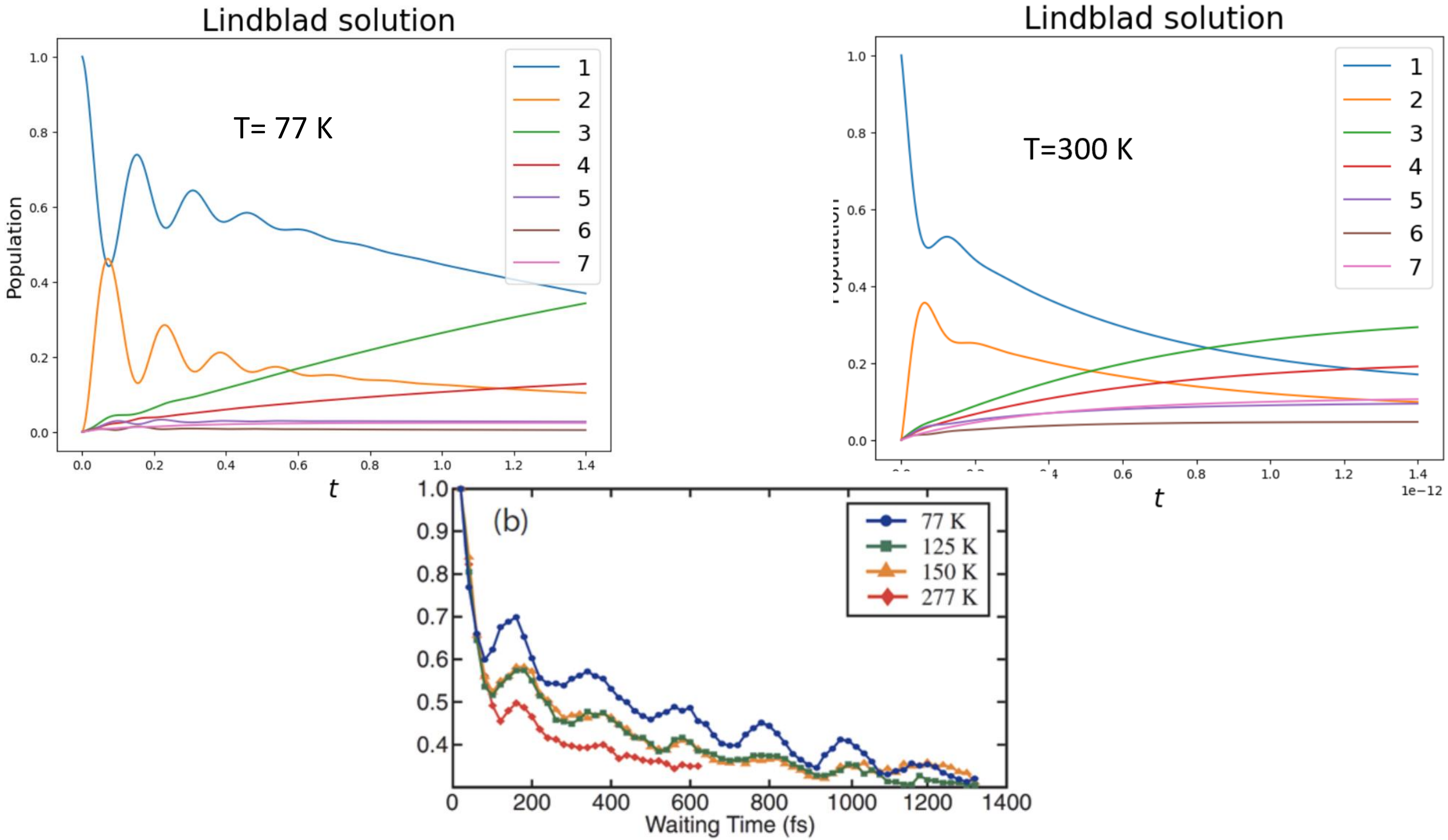


```
tlist = np.linspace(0,1.4e-12,1000)
outputFMO = qt.brmesolve(H, psi0, tlist,[[Q_list[n],DLbath] for n in range(Nmax)])
fig, axes = plt.subplots(1,1, figsize=(8,6))
for m,Q in enumerate(Q_list):
    axes.plot(tlist, qt.expect(outputFMO.states,Q),label=m+1)
axes.set_xlabel(r'$t$', fontsize=20)
axes.set_ylabel(r"Population", fontsize=16);

axes.set_title('Lindblad solution ',fontsize=24)
axes.legend(loc=0, fontsize=18)
#fig.savefig("fmosec2.png")
```



Photosynthesis: A simple physics picture

Compare back to experimental result



Overview:

- Very short background summary
- Photosynthesis: a physicist's picture
- Photosynthesis: the role of noise, master equation derivation
- **Photosynthesis: non-Markovian noise, HEOM**
- Does coherence really survive the noise? Recent contradictory results
- What is the right question?
- Conclusions

Non-Markovian noise models

- Temperature, bath coupling, bath decay time, and system frequencies are all **‘of the same order’.**
- Maybe we need a more accurate way to treat open quantum systems?
- In QuTiP we provide the HEOM solver method:

HEOM= Hierarchical-equations-of-motion (Tanimura and Kubo).

Applied to model FMO experimental data by Ishizaki and Fleming PNAS 2009, and many more improvements/variations by others.

-Our open-source implementation in QuTiP, Lambert et al, PRR 2023.

Advantages: More efficient that some other methods, allows arbitrary system model, time-dependence, etc.

Disadvantages: Scales exponentially for low temps/many baths, somewhat difficult to implement, use and **interpret.**

Other options:

Quasi-adiabatic path integral: (A. Strathearn, Nat. Comms. 2018)

Discrete models + tensor networks: (e.g., Chin et al. Nat. Phys. 2013)

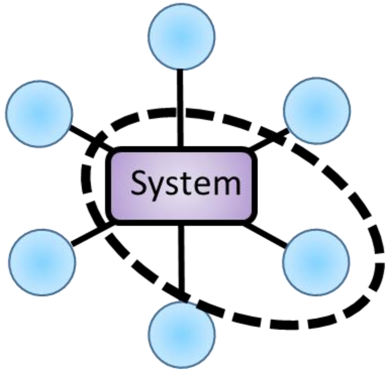
Collective reaction-coordinate: (Iles-smith, Lambert, Nazir, Phys. Rev. A. 2014)

Pseudomodes: B. Garraway 1997, Imamoglu 1994, M. Plenio 2018, Pleasance (2021), Lambert (2021),

Different Strategies to model non-Markovian effects

Physical Approach

Model the most relevant **physical** environmental degrees of freedom

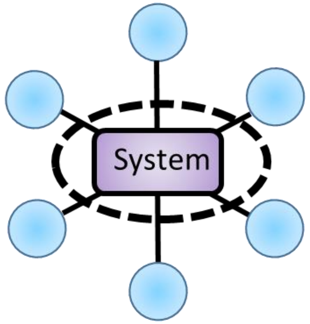


✓ Compute both system and bath dynamics

Ex. Polaron transformation, Bath discretizations, Reaction Coordinate...

Effective Approach

Reproduce **the effects** of the environment on the system



✓ Minimal knowledge
✓ More efficient
X Only system dynamics

Ex. **HEOM,** Dissipatons, **Pseudomodes**.

Hierarchical equations of motion

- Lets start with a quick sketch of how this is derived…. Our starting point is as with the master equation, we assume the system is coupled to a big bath of bosons!

- Under the assumption this bath is Gaussian, instead of following the recipe for the master equation, there is a known formal solution, the **Feynman-Vernon influence functional**

$$\bar{\rho}_S(t) = \mathcal{T}\exp\left\{-\int_0^t dt_2 \int_0^{t_2} dt_1 Q^\times(t_2)\left[C_R(t_2-t_1)Q(t_1)^\times + iC_I(t_2-t_1)Q^o(t_1)\right]\right\}\bar{\rho}_S(0)$$

$A^\times B \equiv [A, B]$ and $A^\circ B = \{A, B\}$.

Note in this complicated formula, Q(t) are the system operators which couple to the bath, and the bath has been traced out…. The system only depends on the two-time correlation functions, like in the master equation!

$$C(t) = \int_0^\infty d\omega J(\omega)\left[\coth\left(\frac{\beta\omega}{2}\right)\cos(\omega t) - i\sin(\omega t))\}\right]$$

This is a consequence of the Gaussianity + Wick's theorem (we contract higher-order correlations into two-time ones)

Directly solving or using this equation is intractable because of the time-ordering at the front.

The HEOM!

$$\bar{\rho}_S(t) = \mathcal{T} \exp\left\{ -\int_0^t dt_2 \int_0^{t_2} dt_1 Q^\times(t_2) \left[C_R(t_2 - t_1) Q(t_1)^\times + i C_I(t_2 - t_1) Q^o(t_1) \right] \right\} \bar{\rho}_S(0)$$

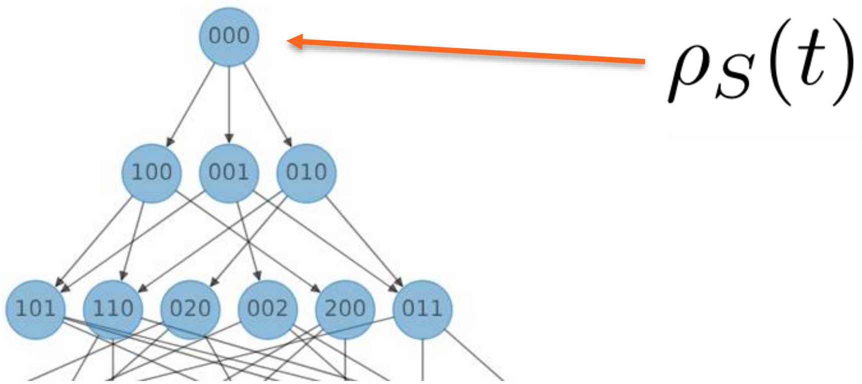
The HEOM assumes that the **correlation functions can be expressed as a sum of exponentials** (with complex parameters):

$$C(t) = C_R(t) + \mathrm{i} C_I(t), \qquad C_{R,I}(t) = \sum_{k=1}^{N_{R,I}} c_k^{R,I} \exp[-\nu_k^{R,I} t]$$

$$\dot{\rho}^{n}(t) = \left(\mathcal{L} - \sum_{j=\mathrm{R,I}} \sum_{k=1}^{N_j} n_{jk} \gamma_k^j \right) \rho^{n}(t) - \mathrm{i} \sum_{k=1}^{N_\mathrm{R}} c_k^\mathrm{R} n_{\mathrm{R}k} Q^\times \rho^{n^-_{\mathrm{R}k}}(t) + \sum_{k=1}^{N_\mathrm{I}} c_k^\mathrm{I} n_{\mathrm{I}k} Q^\circ \rho^{n^-_{\mathrm{I}k}}(t) - \mathrm{i} \sum_{j=\mathrm{R,I}} \sum_{k=1}^{N_j} Q^\times \rho^{n^+_{jk}}(t)$$

$n = \{n_1, n_2, ..n_m, \ldots, n_M\}$: it contains M indices, 0 to M, a cut-off in the number of exponentials.

$n_{jk} \in \{0..N_c\}$, and N_c is a cut-off parameter



The HEOM applied to FMO

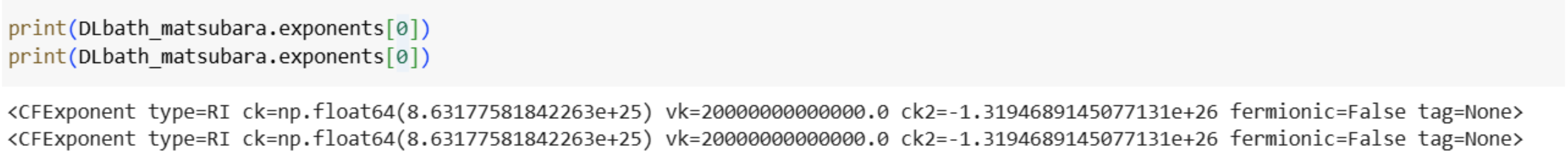
It is exact, up to:

- convergence in **Nk** number of exponentials (and how accurately they capture the true bath functions),
- the convergence parameter **Nc,** which truncates the set of equations in much the same way as truncating a Fock space

$$J(\omega) = \frac{2\lambda\gamma\omega}{\gamma^2 + \omega^2},$$

$$C(t) = \sum_{k=0}^{\infty} c_k e^{-\nu_k t}$$

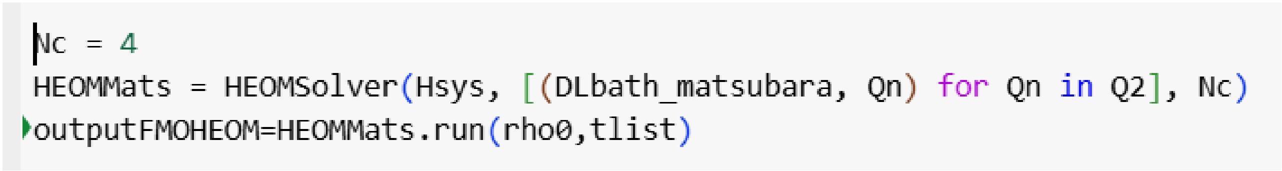
$$\nu_k = \begin{cases} \gamma & k = 0 \\ 2\pi k/\beta & k \geq 1 \end{cases}, \qquad c_k = \begin{cases} \lambda\gamma[\cot(\beta\gamma/2) - i] & k = 0 \\ \frac{4\lambda\gamma\nu_k}{(\nu_k^2 - \gamma^2)\beta} & k \geq 1 \end{cases}.$$



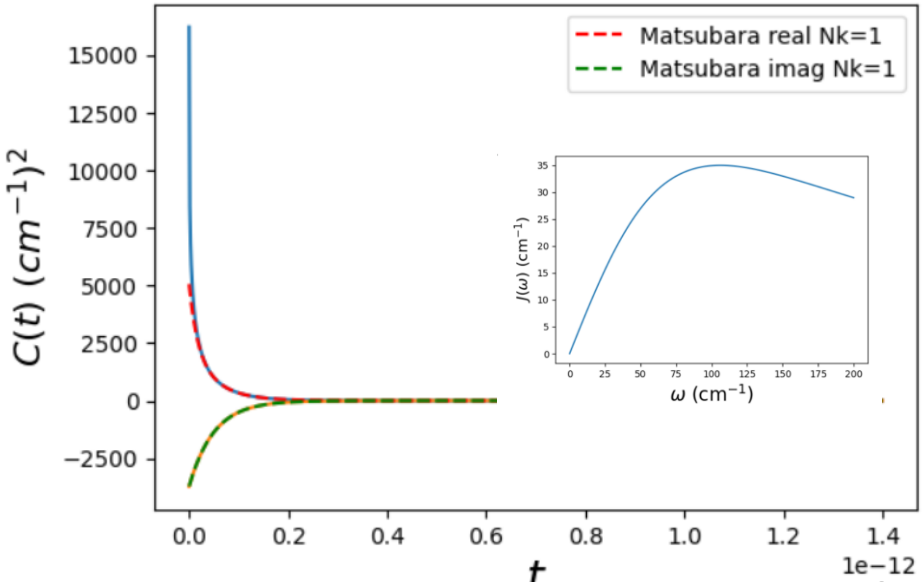
```
print(DLbath_matsubara.exponents[0])
print(DLbath_matsubara.exponents[0])
```

```
<CFExponent type=RI ck=np.float64(8.63177581842263e+25) vk=20000000000000.0 ck2=-1.3194689145077131e+26 fermionic=False tag=None>
<CFExponent type=RI ck=np.float64(8.63177581842263e+25) vk=20000000000000.0 ck2=-1.3194689145077131e+26 fermionic=False tag=None>
```

- To use the HEOM implementation in QuTiP, the interface is similar to what we did in brmesolve()



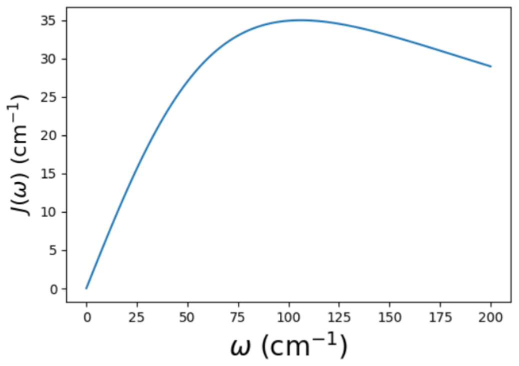
```
Nc = 4
HEOMMats = HEOMSolver(Hsys, [(DLbath_matsubara, Qn) for Qn in Q2], Nc)
outputFMOHEOM=HEOMMats.run(rho0,tlist)
```

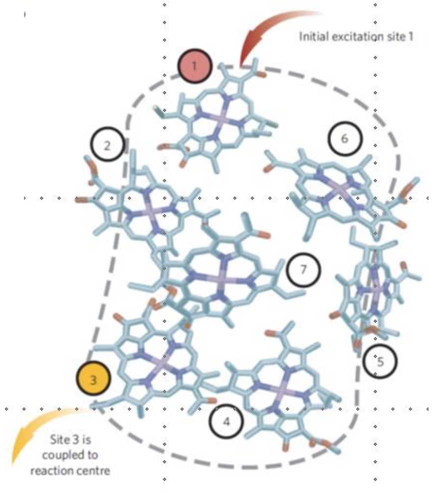


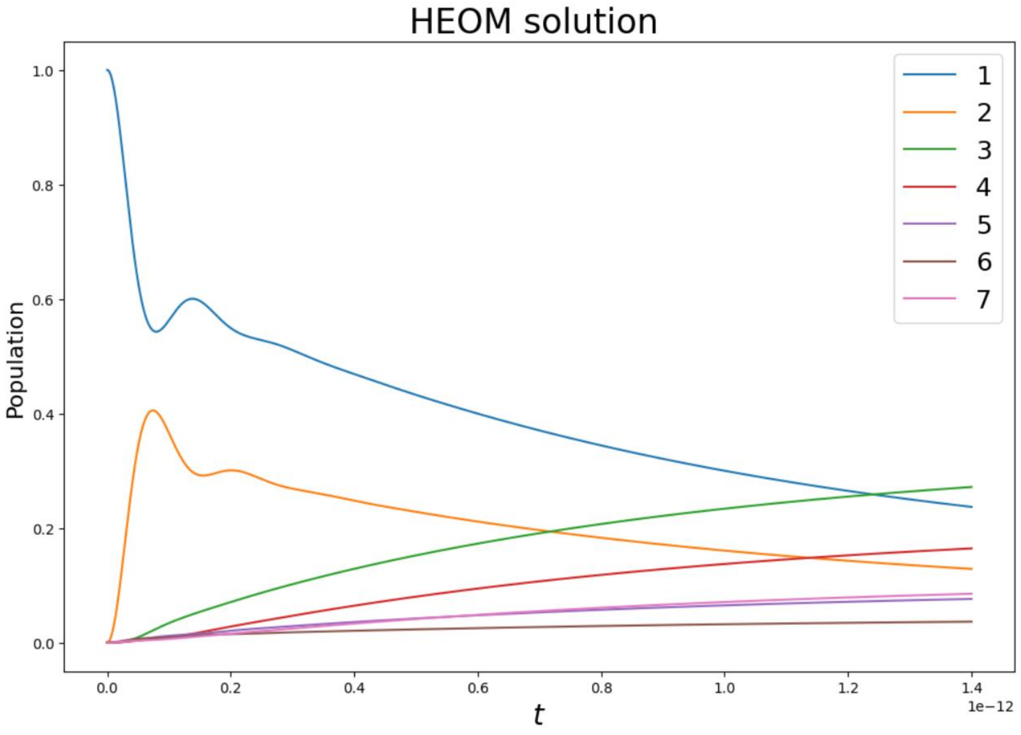
The HEOM applied to FMO

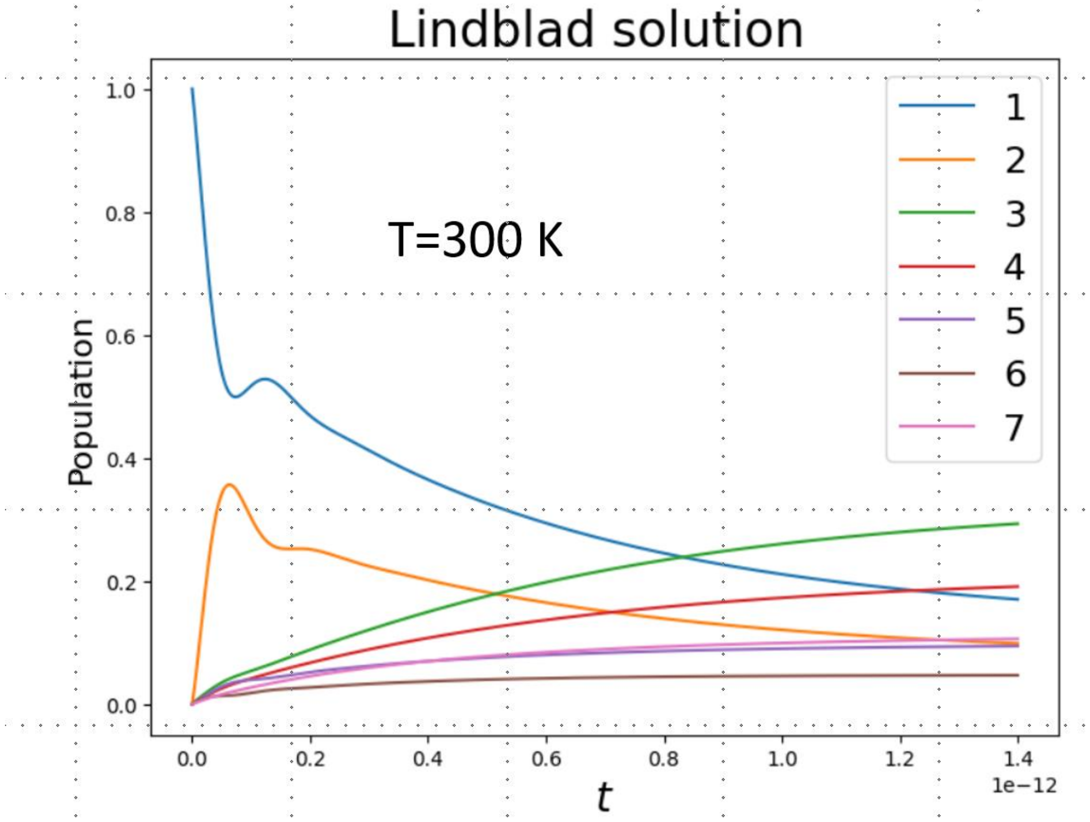
Lets compare HEOM and BRmesolve

$$\lambda = 35\ \mathrm{cm}^{-1},\ 1/\gamma = 50\ \mathrm{fs},\ T = 300\mathrm{K},$$





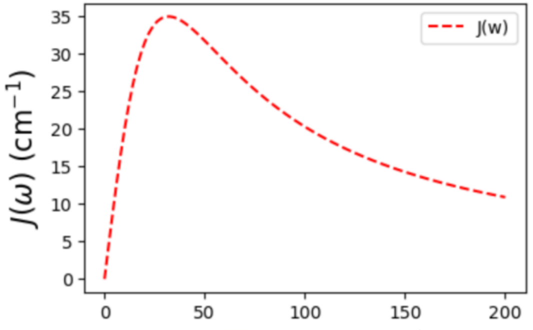


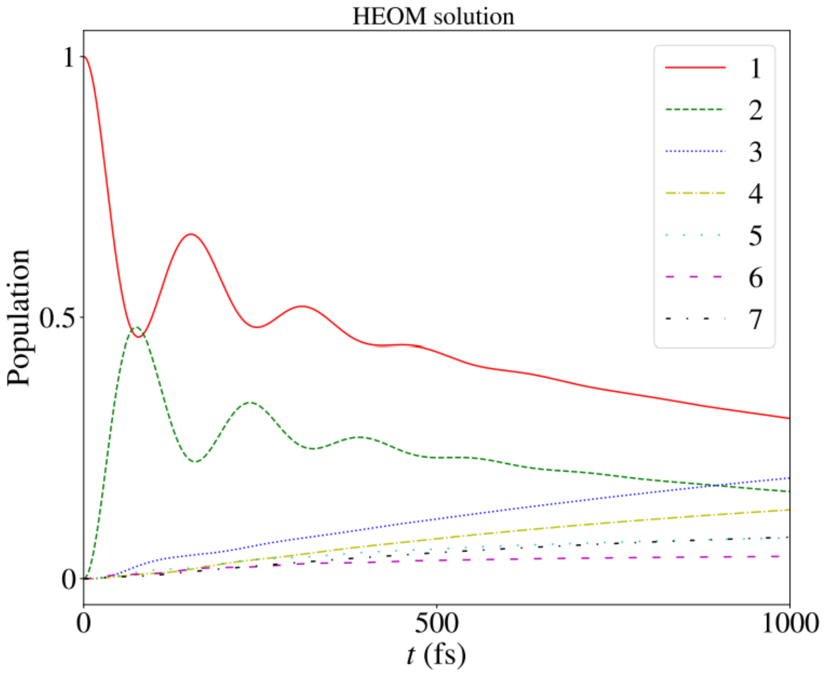


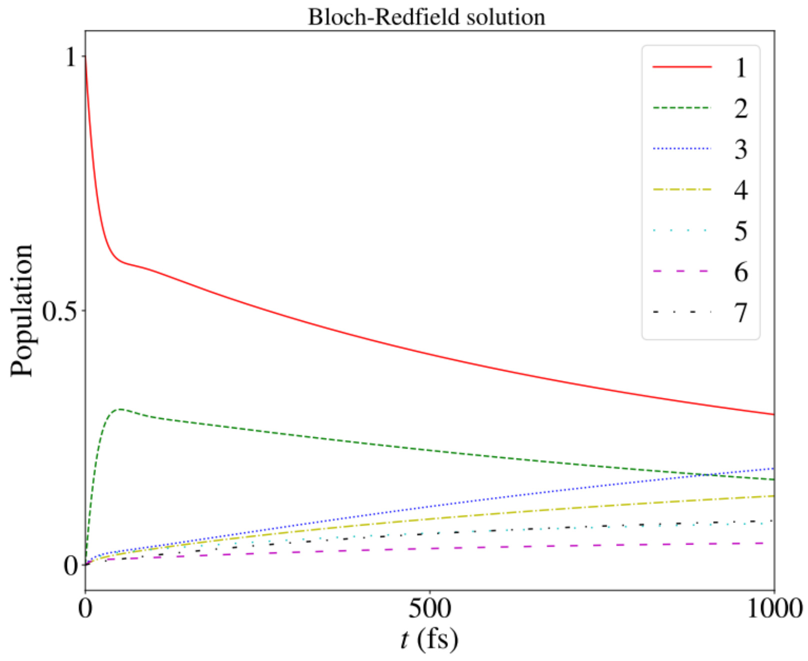
The HEOM applied to FMO

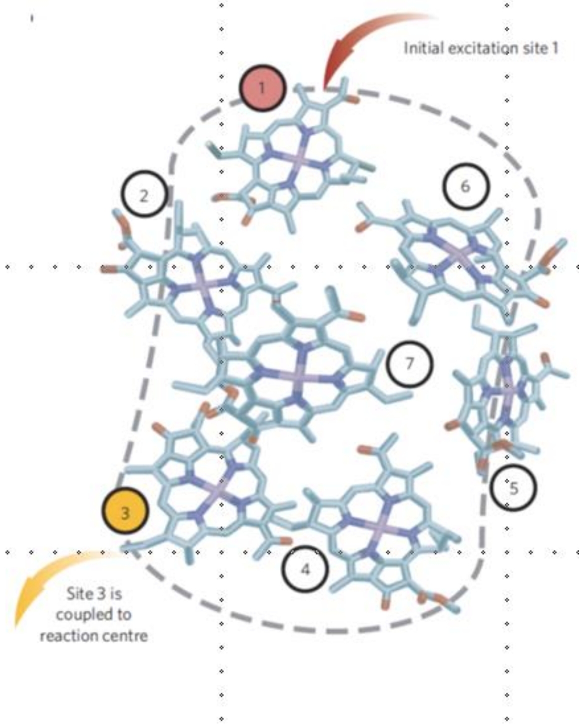
Ishizaki and Fleming pointed out that if the bath is much more ‘non-Markovian’ (i.e., narrower, and hence has longer lived Correlation functions), the difference is more pronounced:

$$\lambda = 35\ \mathrm{cm}^{-1},\ \gamma^{-1} = 166\,\mathrm{fs}\quad T = 300\ \mathrm{K}.$$









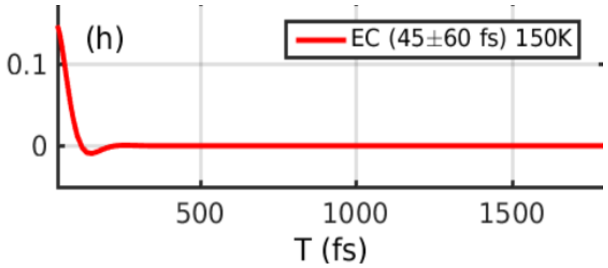
Coherence survives more than expected. But still does not explain all experimental data.

Overview:

- Very short background summary
- Photosynthesis: a physicist's picture
- Photosynthesis: the role of noise, master equation derivation
- Photosynthesis: non-Markovian noise, HEOM
- **Does coherence really survive the noise? Recent contradictory results**
- What is the right question?
- Conclusions

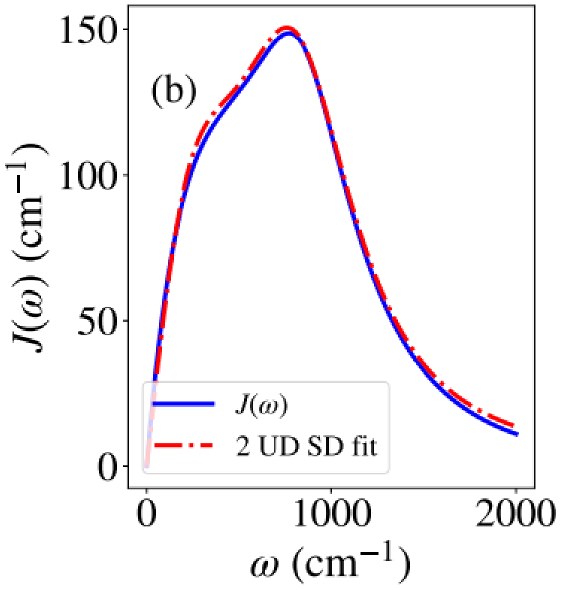
The HEOM applied to FMO

More recent (Duan,Thorwart, Miller, et al., PNAS) work attempted to improve earlier experiments, and compensating for ‘ground-state vibrational coherence’ they observe almost no ‘electronic’ coherence at all

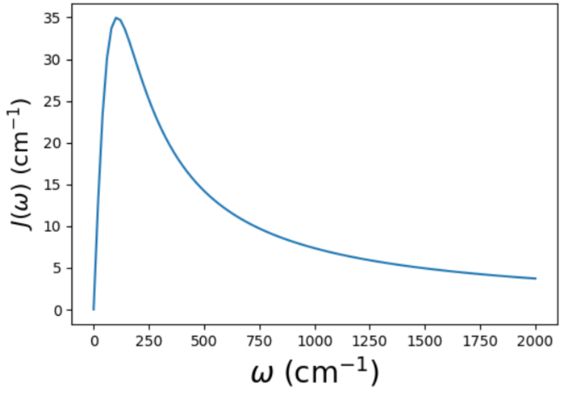


Interestingly they posited a theoretical model where the spectral density was extremely large, to justify this overdamped behaviour…

$$J(\omega) = \gamma_{\mathrm{Ohm}}\,\omega e^{-\omega/\omega_c^{\mathrm{Ohm}}} + \frac{2}{\pi}\frac{S\Omega_{\mathrm{r}}^3\omega\Gamma_{\mathrm{r}}}{(\Omega_{\mathrm{r}}^2-\omega^2)^2+\omega^2\Gamma_{\mathrm{r}}^2}$$



Very different from our previous choice:

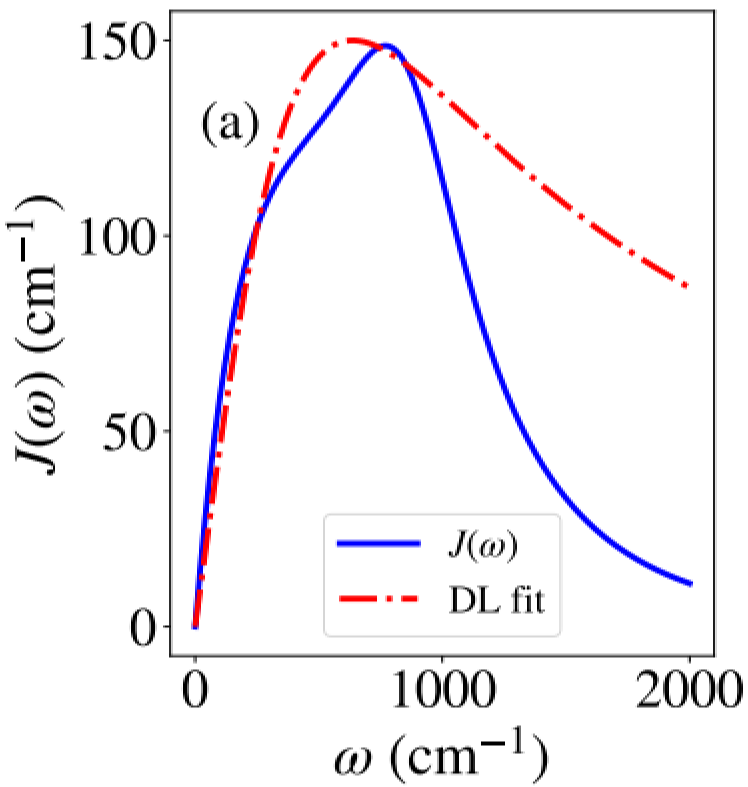


The HEOM applied to FMO

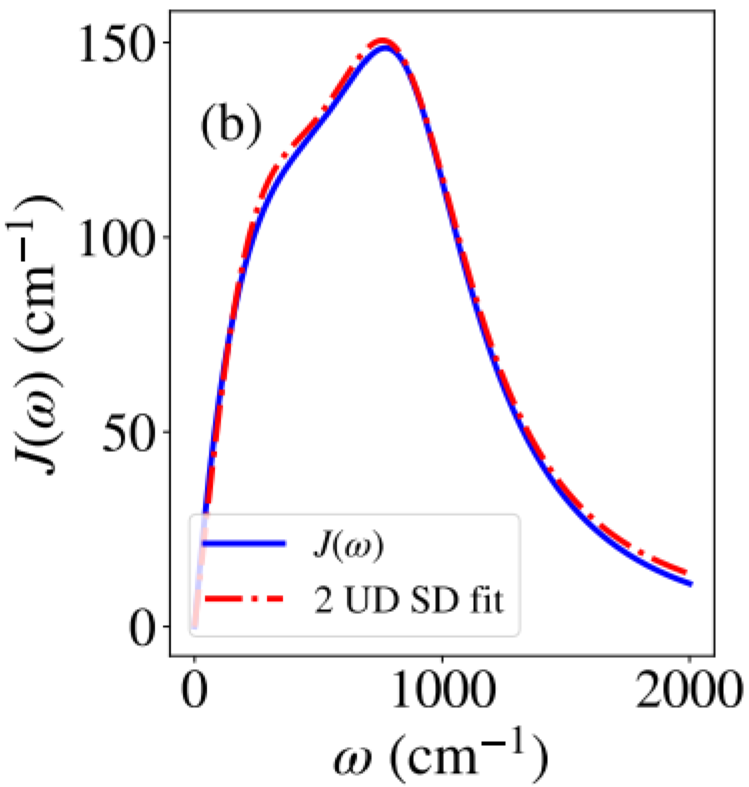
We can treat this in HEOM with fitting. We can either:

- Fit the correlation functions
- Fit the power spectrum
- **Fit the spectral density and decompose fitting functions with Matsubara/Pade**

Left: Fit with one Drude-Lorentz function

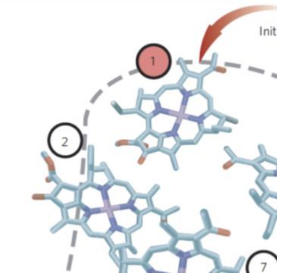


Left: Fit with two underdamped functions

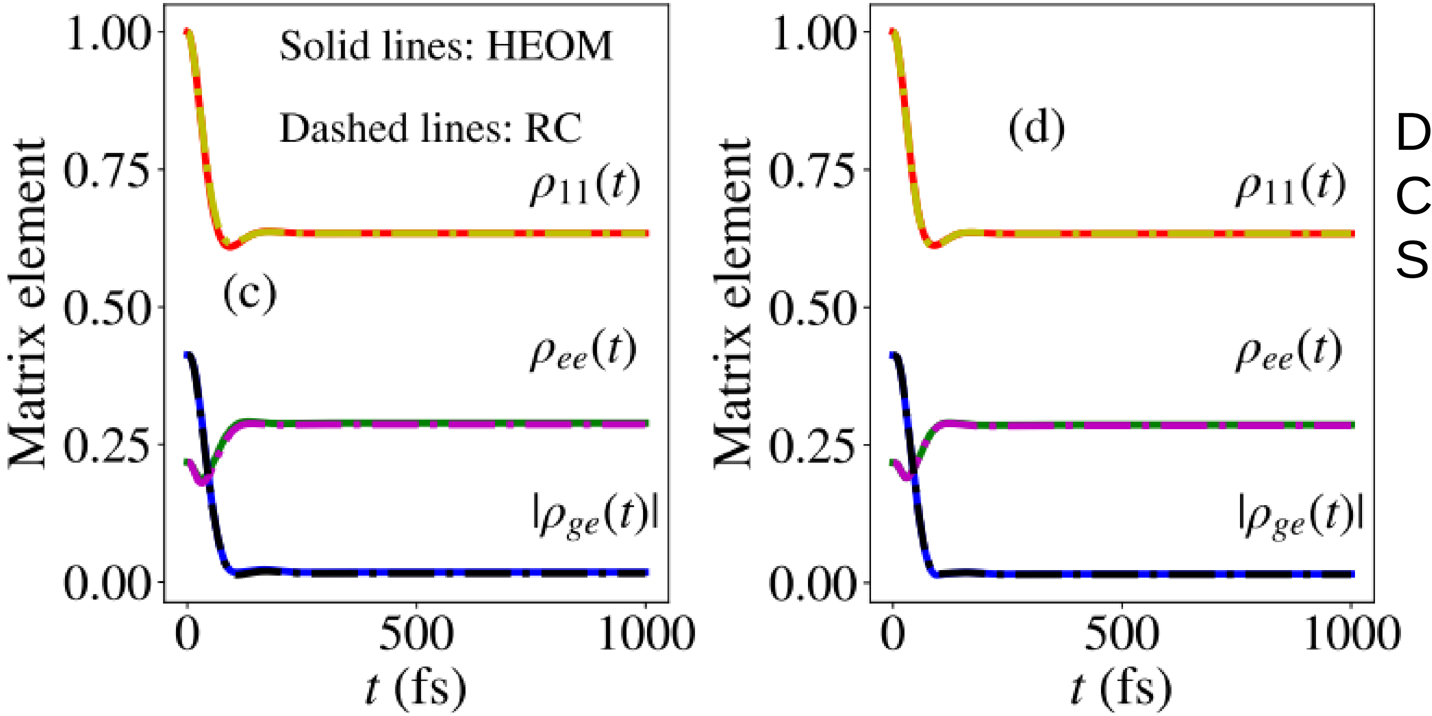


The HEOM applied to FMO

This gets a bit numerically challenging, so we **go back to two-site model**



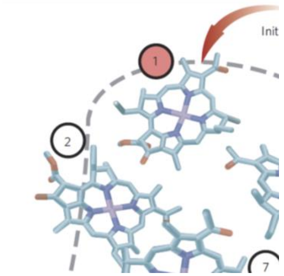
$$H = H_S + H_D = \frac{\epsilon}{2}\sigma_z + \frac{\Delta}{2}\sigma_x$$



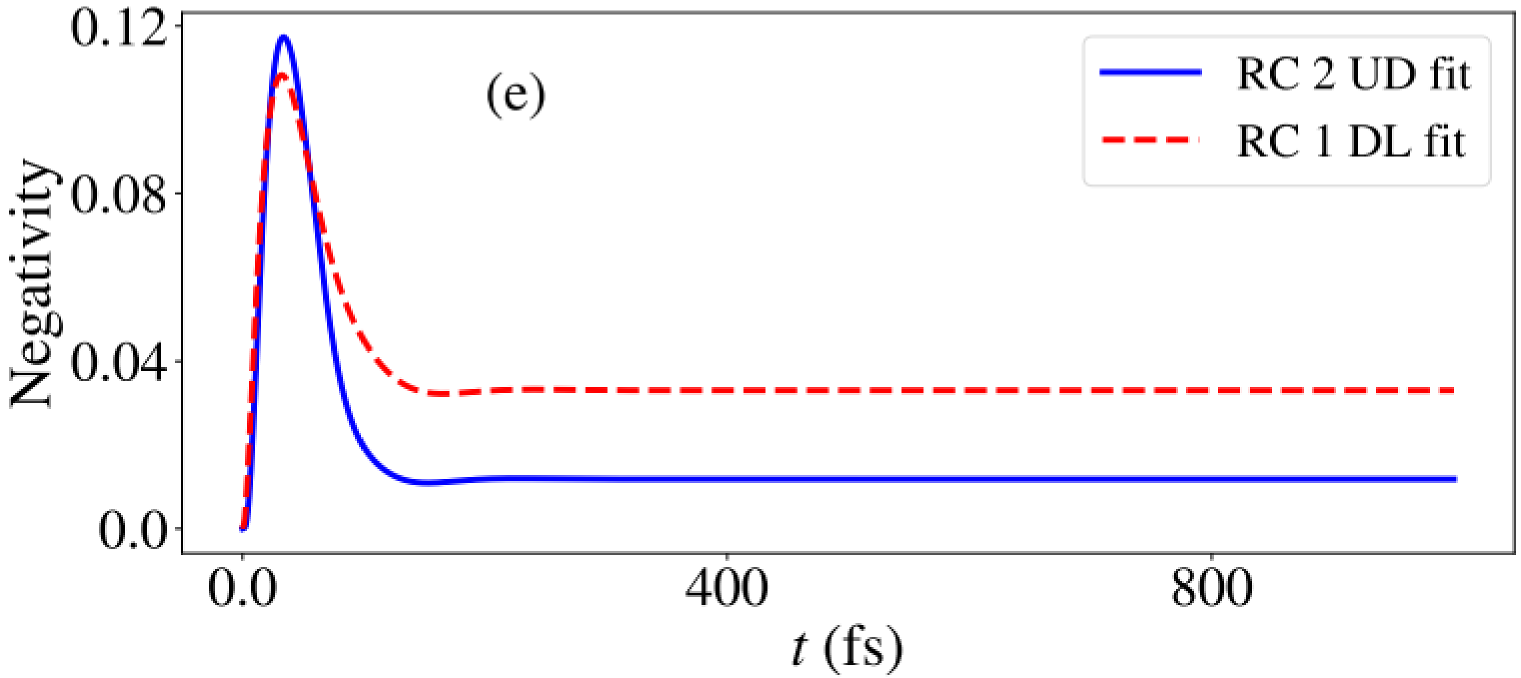
Does having such strong
Coupling to the environment mean
Something non-classical still survives?

The HEOM applied to FMO

This gets a bit numerically challenging, so we **go back to two-site model**



$$H = H_S + H_D = \frac{\epsilon}{2}\sigma_z + \frac{\Delta}{2}\sigma_x$$



Is it meaningful to think about system-environment entanglement?

Is this system-environment entanglement?

Overview:

- Very short background summary
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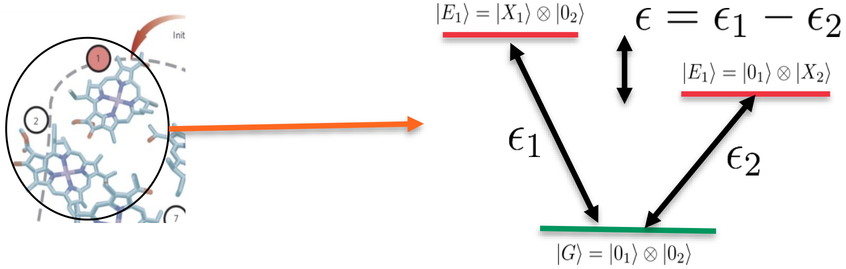
- Conclusions

Alternative perspective: optimize bath properties for faster transport

Illes-Smith, Lambert, Nazir, Phys. Rev. A (2014), and J. Chem. Phys. (2016) , Ishizaki and Fleming, J. Chem. Phys. (2009)

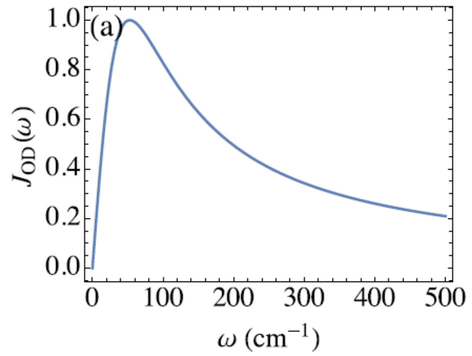
Parameterize the speed of energy transfer by fitting an effective ‘rate’ to the movement of an excitation from one site to another:



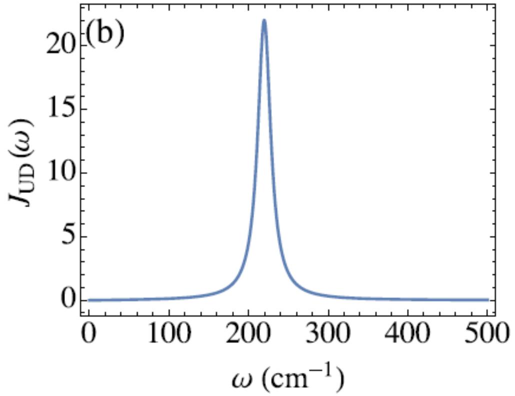
$$\frac{dP_1(t)}{dt} = -k_{1\to 2}P_1 + k_{2\to 1}P_2,$$
$$\frac{dP_2(t)}{dt} = k_{1\to 2}P_1 - k_{2\to 1}P_2.$$

Using non-perturbative method, we can study resonant vs. broad environments:

$$J_{\rm SB}^{\rm OD}(\omega) = \alpha_{\rm OD}\omega_c \frac{\omega}{\omega^2 + \omega_c^2}.$$

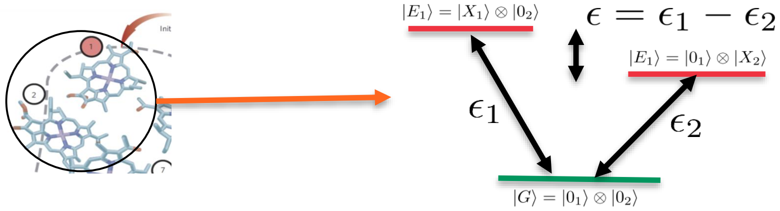


$$J_{\rm SB}^{\rm UD}(\omega) = \frac{\alpha_{\rm UD}\Gamma\omega_0^2\omega}{(\omega_0^2 - \omega^2)^2 + \Gamma^2\omega^2}$$

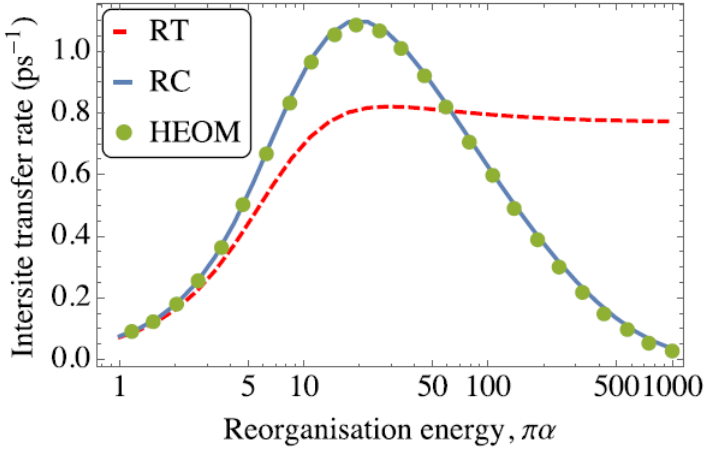


$\epsilon = 100$ cm^{-1}, $\Delta = 40$ cm^{-1}, $\omega_c = 53$ cm^{-1}, and $T = 300$ K.

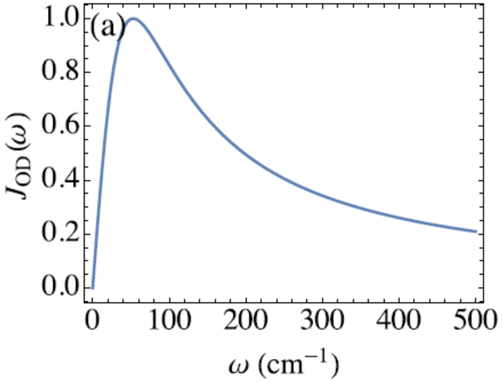
Which is better for faster transport?

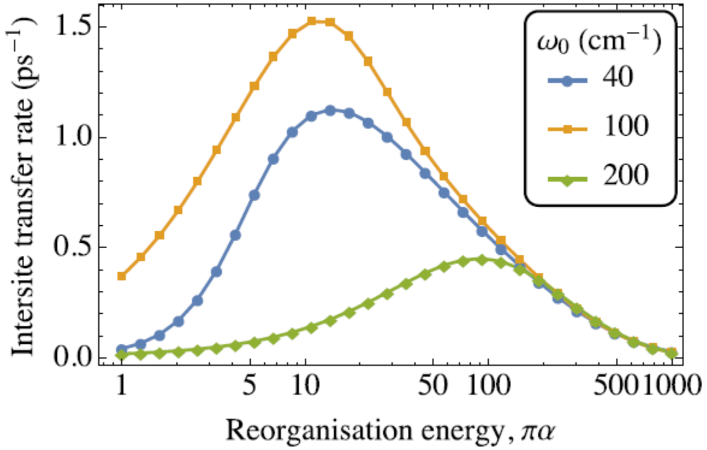


$$\frac{dP_1(t)}{dt} = -k_{1\to 2}P_1 + k_{2\to 1}P_2,$$
$$\frac{dP_2(t)}{dt} = k_{1\to 2}P_1 - k_{2\to 1}P_2.$$

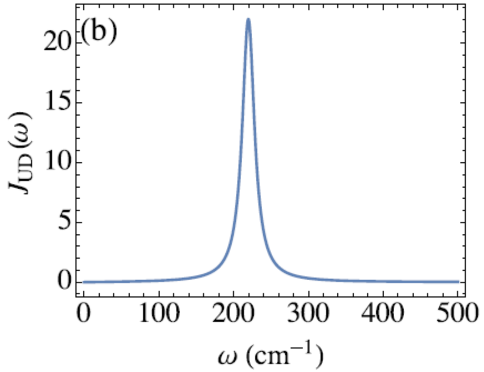


$$J_{\rm SB}^{\rm OD}(\omega) = \alpha_{\rm OD}\omega_c \frac{\omega}{\omega^2 + \omega_c^2}.$$



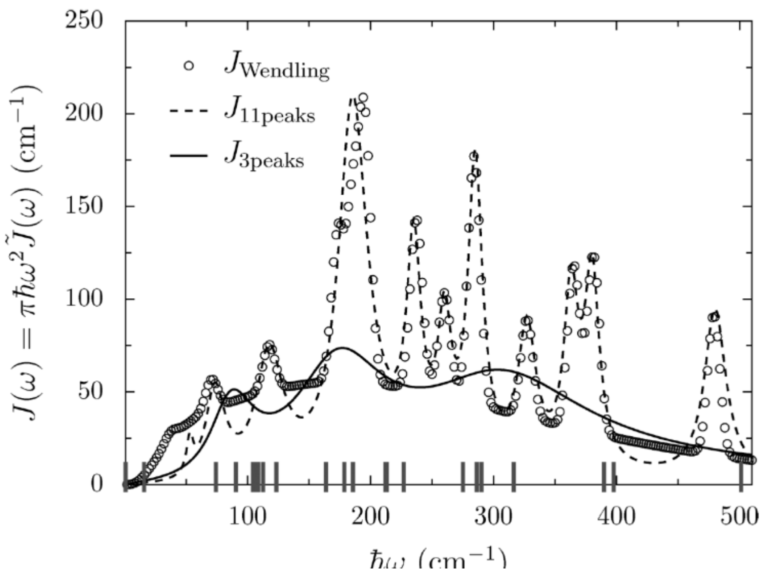


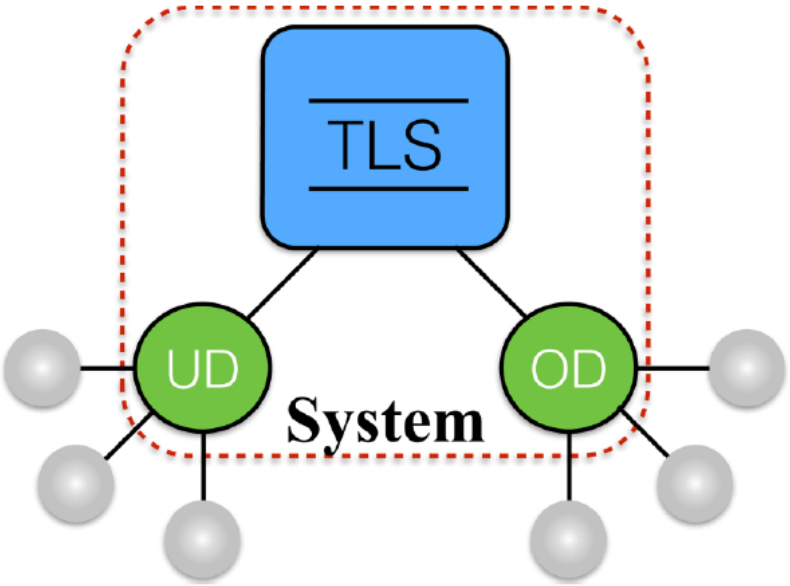
$$J_{\rm SB}^{\rm UD}(\omega) = \frac{\alpha_{\rm UD}\Gamma\omega_0^2\omega}{(\omega_0^2 - \omega^2)^2 + \Gamma^2\omega^2}$$

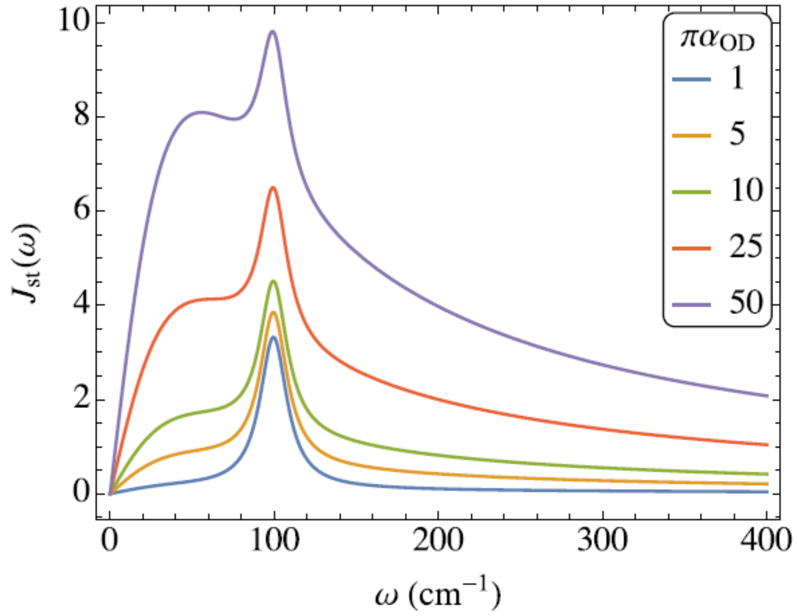


$\epsilon = 100$ cm^{-1}, $\Delta = 40$ cm^{-1}, $\omega_c = 53$ cm^{-1}, and $T = 300$ K.

What about when both broad and resonant baths co-exist?

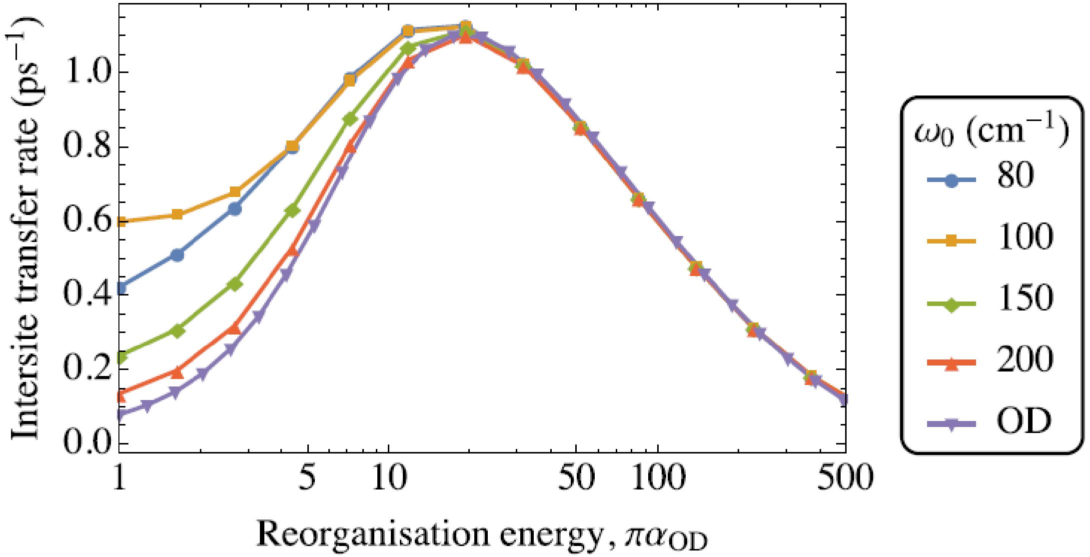




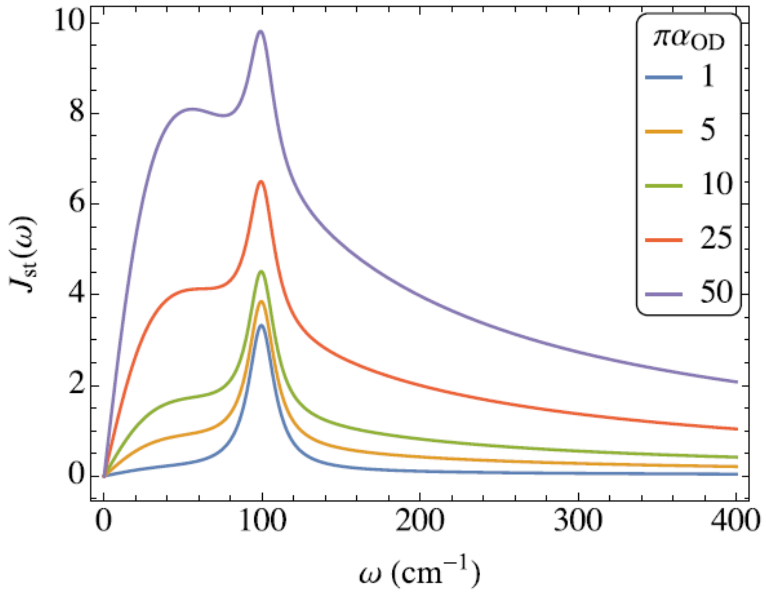


$\omega_0 = 100\ \mathrm{cm}^{-1}$, with $\Gamma = 20\ \mathrm{cm}^{-1}$ and $\pi\alpha_{\mathrm{UD}} = 2\ \mathrm{cm}^{-1}$.

What about when both broad and resonant baths co-exist?



$\epsilon = 100\ cm^{-1}$, $\Delta = 40\ cm^{-1}$, $\omega_c = 53\ cm^{-1}$, and $T = 300$ K.



$\omega_0 = 100\ cm^{-1}$, with $\Gamma = 20\ cm^{-1}$ and $\pi\alpha_{UD} = 2\ cm^{-1}$.

Resonant structured baths enhance energy transfer, but their influence is diminished if the broad background is sufficiently strong

Conclusions

The study of open quantum systems lets us model how a system interacts with it environment in various limits:

- Weak coupling, no bath memory (Markov), and weak damping gives us the Lindblad Born-Markov-Secular master equation

$$\tau_E \ll \tau_S \ll \tau_R$$

- Exact methods (HEOM, reaction coordinate, pseudo-modes (Lambert et al, Nat. Comm. 2019) give insight into strongly correlated system-bath problems when this approximation no longer holds, and everything occurs on comparable time-scales

$$\tau_E \approx \tau_S \approx \tau_R$$

How does this help us study light-harvesting?

- Comparing exact models, approximate models, and experimental data gives us insight more than each one alone.
- E.g., in this example we saw that while the noise suppresses coherent oscillations, non-Markovian (resonant) environments can speed-up the transfer time of electronic energy across the whole complex, which may be important for improving efficency.

All of these tools are useful for studying in noise in any type of quantum system:

1- quantum computers, understanding and mitigating noise

2- quantum optics, measurement and control

3- condensed matter systems, electron transport, Fermionic environments ....