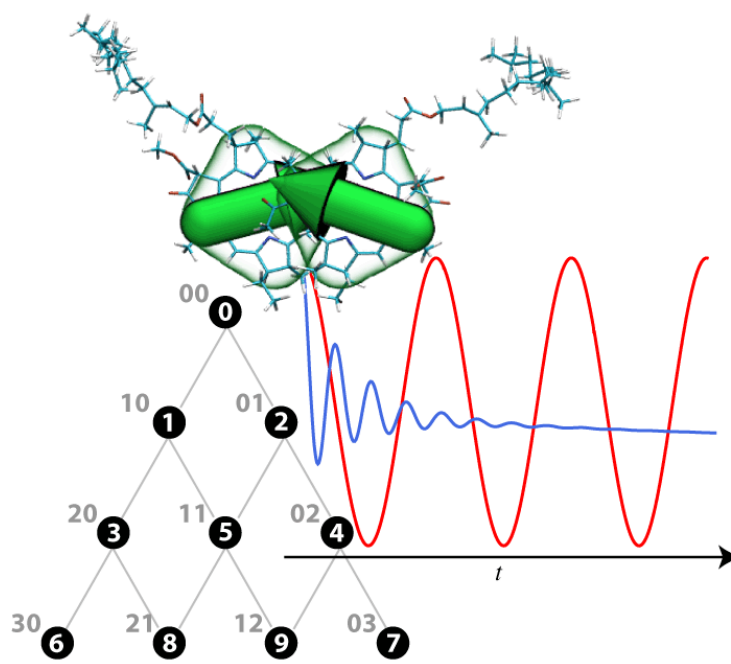


PHI: Open quantum dynamics of multi-molecule systems



Johan Strümpfer
July 13, 2012

Please visit www.ks.uiuc.edu/Research/phi/ to get the latest version of this tutorial, to obtain more tutorials like this one, or to join the tutorial-1@ks.uiuc.edu mailing list for additional help.

Abstract

This tutorial provides some basic examples to explain how to calculate the dynamics of a quantum system in contact with a thermal environment using the hierarchy equations of motion integration software PHI.

Contents

1. Introduction	4
2. Theory of open quantum systems	5
3. Hierarchy structure	8
4. Dynamics	10
5. Matsubara Terms, Hierarchy Integration & Hierarchy Truncation	14

1. Introduction

The goal of this tutorial is to:

- Introduce the hierarchy equations of motion as implemented in PHI
- Show how to use PHI to determine hierarchy structure
- Provide guidance for performing density dynamics calculations using PHI.

Completion of this tutorial requires:

- Files contained in the archive `phi_tutorial_files.zip`
- PHI 1.0 or later (<http://ks.uiuc.edu/Research/phi>)

Some basic understanding of Linux/Unix shell interaction, particularly text editing and file parsing, is also assumed. This tutorial should be used in conjunction with the PHI 1.0 User's Guide (see <http://ks.uiuc.edu/Research/phi>). The reader would benefit also from reading the PHI paper: Strümpfer & Schulten, "Open Quantum Dynamics Calculations with the Hierarchy Equations of Motion on Parallel Computers" *J. Chem. Theor. Comp.*, (2012).

2. Theory of open quantum systems

Open quantum systems refers to quantum systems that are embedded in some environment. An example is a molecule in water, where the “system” of interest is the excited states of the molecule. In general, the system consists of many coupled quantum states that are coupled to a thermal bath. This tutorial focuses on systems found in photosynthesis, i.e. excited pigments embedded in a biological environment. There are many resources for more information on the theory of open quantum systems such as:

- H.P Breuer and F. Petruccione. “The theory of open quantum systems.”
Oxford University Press. 2002
- U. Weiss. “Dissipative quantum systems.”
World Scientific. 2008

The reader is also strongly encouraged to read the PHI manual as it includes some more theoretical details beyond the need for the tutorial.

In general, the system is modeled by an effective Hamiltonian that includes only a subset of the quantum states $|n\rangle$, $n = 1, \dots, N$. The system Hamiltonian is

$$H_S = \sum_{n=1}^N E_n |n\rangle \langle n| + \sum_{n=1}^N \sum_{m=1}^n V_{nm} (|n\rangle \langle m| + |m\rangle \langle n|) = \begin{pmatrix} E_1 & V_{12} & \cdots & V_{1N} \\ V_{12} & E_2 & \cdots & V_{2N} \\ \vdots & \vdots & \ddots & \vdots \\ V_{1N} & V_{2N} & \cdots & E_N \end{pmatrix}, \quad (1)$$

where E_n is the energy level of state n (also called the site energy), and V_{nm} is the interaction energy between states n and m . In this tutorial $|n\rangle$ refers to the first excited state of the n 'th molecule. Although the general framework of open quantum systems includes multiple excited states of a molecule, PHI 1.0 is currently only capable of calculating dynamics in the single-excitation manifold.

The environment in which the system is embedded is described by an infinite series of harmonic oscillators q_ξ with vibration frequencies ω_ξ . The coupling of the quantum states in the system to each environment oscillator is assumed to be linear and is described by the interaction Hamiltonian:

$$H_I = \sum_{a=1}^M \hat{F}_a \sum_{\xi} c_{a\xi} q_\xi. \quad (2)$$

The coupling operators

$$\hat{F}_a = \sum_m \sum_n f_{a,mn} |m\rangle \langle n|, \quad (3)$$

can in principle take any form. The computational expense associated with arbitrary operators is significant, and thus PHI 1.0 is restricted to only diagonal forms $\hat{F}_a = \sum_m f_{a,m} |m\rangle \langle m|$.

The coupling strengths, $c_{a\xi}$ in Eq. 2 is defined through the spectral density $J_a(\omega)$. There are many types of spectral densities that are often employed. Spectral densities are a kind of power spectrum, in that they describe the “importance” of each frequency in a given biological system (e.g, the C=O bond vibration). The primary difference is that spectral densities define how strongly the normal mode vibrations of a system couple to a given quantum state. The spectral densities is thus often referred to as the weighted density of vibrational states.

The hierarchy equations of motion implemented in PHI are restricted to Drude spectral densities of the form

$$J_a(\omega) = \frac{\lambda_a}{2} \frac{\gamma_a \omega}{\gamma_a^2 + \omega^2}. \quad (4)$$

The important parameters here are the reorganization energy λ_a and bath response frequency γ_a of each coupling.

The Hamiltonian parameters needed to perform a calculation of excited state dynamics using PHI are summarized as:

1. N – the number of excited pigments in the system
2. E_n – the site energy of each excited pigment
3. V_{nm} – the coupling between the excited pigments
4. M – the number of system-environment coupling terms
5. λ_a – the reorganization energy for each coupling term
6. γ_a – the response frequency for each coupling term

The hierarchy equations of motion (HEOM) are a set of equations that furnishes the noise-averaged time evolution of the system density matrix

$$\hat{\rho}(t) = \sum_{n=1}^N \sum_{m=1}^N \rho_{nm}(t) |n\rangle \langle m|. \quad (5)$$

The density matrix is Hermitian, positive definite and has trace 1: i.e.,

$$\begin{aligned} \rho(t)^\dagger &= \rho(t) \\ \mathbf{z}^\dagger \rho(t) \mathbf{z} &> 0 \quad \forall \mathbf{z} \neq \mathbf{0} \\ \text{tr} \{ \rho(t) \} &= 1 \end{aligned}$$

The system density matrix describes in full the current state of the quantum system at time t . In the HEOM formalism, additional density matrices are introduced to account for the non-Markovian dynamics arising from the system-environment interaction. To account for all the matrices an index vector $\mathbf{n} = (n_1, n_2, \dots)$ is used. The density matrix with index vector containing all zeros, $\mathbf{n} = (0, \dots, 0)$, is exactly the system density matrix. All other density matrices have positive integer entries in the index vector. The set of density matrices and the coupling arising from the HEOM is referred to as the ‘‘hierarchy’’.

The matrices in the hierarchy need to be truncated at some level greater than or equal to $L = \sum n_i$, which depends on how non-Markovian the system is, i.e. how much ‘‘memory’’ the bath has. There are two types of truncation: (1) Time-Nonlocal truncation that simply sets the matrices at level L to zero; and (2) Time-Local truncation that employs the Markovian approximation for the matrices at level L . Typically it is best to use Time-Local truncation. There is an additional set of matrices that account for low temperature effects. The term ‘‘low’’ is somewhat misleading as in this case it means anything less than very high temperature. The number of ‘‘low temperature’’ terms, more correctly called Matsubara terms, K to include is in fact system dependent. The total number of matrices \mathcal{N} in the hierarchy depends on M , K and L through

$$\mathcal{N} = \frac{(M(K+1) + L - 1)!}{(M(K+1))! (L - 1)!}. \quad (6)$$

In summary, the additional parameters needed to calculate $\rho(t)$ using the HEOM in PHI are:

1. L – the hierarchy truncation

2. K – the number of Matsubara terms
3. Truncation method: TimeLocal or Time-Nonlocal
4. dt – the integration timestep

As such there are TWO distinct parameters sets: (1) Model parameters (that determine the Hamiltonian); (2) Integration parameters (that specify the HEOM). The following example calculations highlight some of the features of PHI and show how to specify the different parameters and obtain converged results.

The simplest example that could be described using the HEOM is that of a single excited state. While this is indeed very simple, it is a little too simple for this tutorial. The next simplest case is the pigment dimer where $N = 2$. In the rest of the tutorial the two level system (TLS) representing the pigment dimer is investigated to highlight some of the features of PHI and to illustrate the effects of different HEOM parameters.

3. Hierarchy structure

Although an equation has been given that provides the number of matrices in the hierarchy for a given truncation scheme and number of interacting states, this can also be calculated using PHI, and for a two level system. The hierarchy of a TLS with $K = 0$ (zero Matsubara terms) is shown in Figure 1. It can be

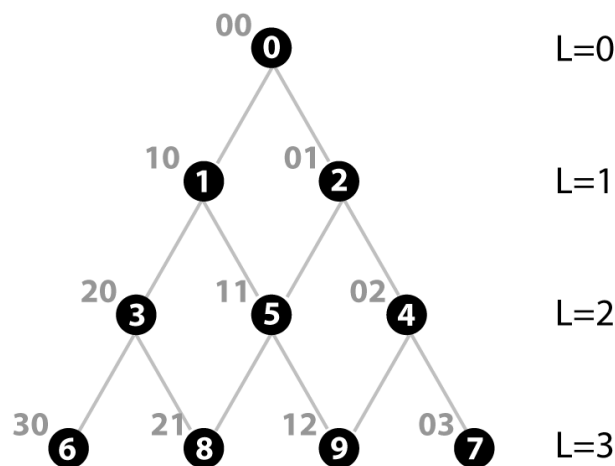


Figure 1: Hierarchy of a two level system with $K = 0$ showing the matrices in each level L . Each filled circle is a matrix. The lines connecting the matrices indicate their coupling through the HEOM.

seen from Figure 1 that the number of matrices grow rapidly with truncation. The hierarchy for a TLS

can be viewed as a form of Pascal's triangle. Indeed, in higher dimensions (with higher M or K), the hierarchy can be viewed as a $d = M(K + 1)$ dimensional Pascal's simplex.

PHI can be used to print out the indices for the matrices in the hierarchy of any system. For this functionality, the input file needs to only specify N and L . The assumption in this case is that $M = N$ and $K = 0$.

Step 1: Create a new plaintext file called `TLS-NumMatrices.prm` and enter in the following:

```
NumStates=2
HierarchyTruncation=5
```

Step 2: In a command line run the following command:

```
$ phi TLS-NumMatrices.prm print
```

Part of the screen output from this command will be:

```
Heirarchy Level: 0
0: 0,0

Heirarchy Level: 1
1: 1,0
2: 0,1
      2 Matrices.

Heirarchy Level: 2
3: 2,0
4: 0,2
5: 1,1
      3 Matrices.

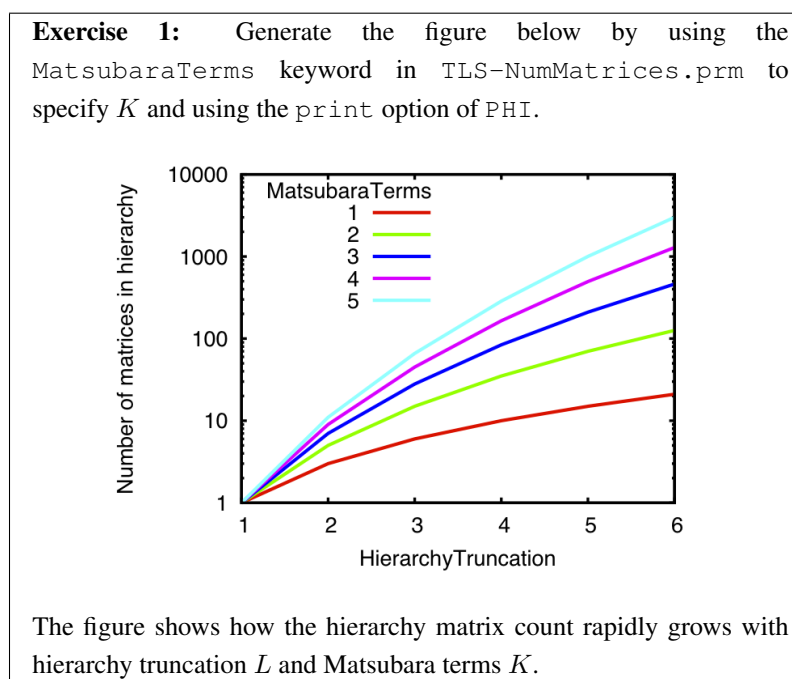
Heirarchy Level: 3
6: 3,0
7: 0,3
8: 2,1
9: 1,2
      4 Matrices.

Heirarchy Level: 4
10: 4,0
11: 0,4
12: 3,1
13: 1,3
14: 2,2
```

5 Matrices.

Total: 15 matrices

The output lists the matrices in each level and gives each associated index vector. E.g., it can be seen that: hierarchy level 3 contains four matrices, matrix 9 is associated with the index vector (1, 2) and for a pigment dimer with $K = 0$ and a truncation of 5 there are 15 matrices in the hierarchy.



4. Dynamics

The first system we consider is a pair of bacteriochlorophyll pigments found in the photosynthetic reaction center as is known as the “special pair” due to their close proximity and resulting strong interaction. The RC special pair is shown in Fig. 2 along their associated transition dipole moments.

To calculate the dynamics of the system we first need to specify the effective Hamiltonian. The site energy of each pigment is approximately $12,100 \text{ cm}^{-1}$ ($\sim 826 \text{ nm}$, $\sim 1.5 \text{ eV}$). In fact, a slight asymmetry results in one of the special pair pigments being lower in energy by about 100 cm^{-1} . Their close proximity results in an extremely large coupling of their excited states with an interaction energy of about 500 cm^{-1} . The special pair pigments can thus be modeled with the effective Hamiltonian:

$$H_S = 12\,100 |1\rangle \langle 1| + 12\,000 |2\rangle \langle 2| + 500(|1\rangle \langle 2| + |2\rangle \langle 1|) = \begin{pmatrix} 12\,100 & 500 \\ 500 & 12\,000 \end{pmatrix}. \quad (7)$$

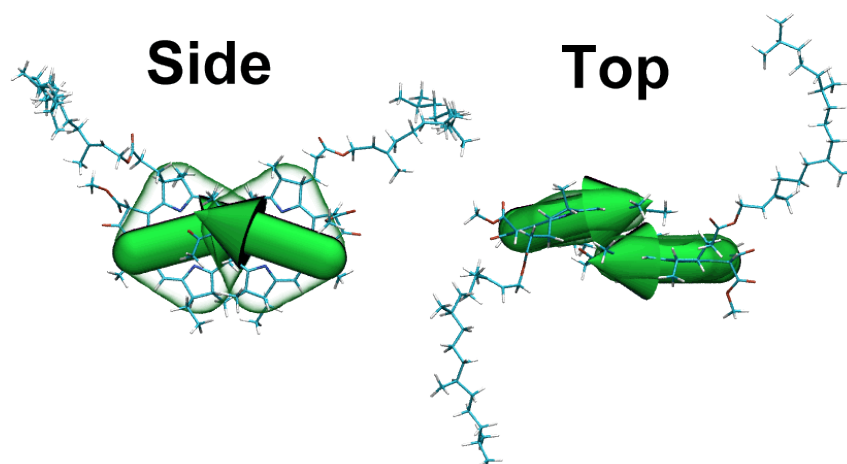


Figure 2: Side and top view of the special pair pigments in the photosynthetic reaction center. Arrows indicate the orientation of the transition dipole moments.

In the absence of any environment (in vacuum) excitation of one pigment results in so-called Rabi oscillations. A system in vacuum can be simulated by setting the hierarchy truncation to 1, and reorganization energies λ and response frequencies γ to 0.

Step 1: Input parameters. Create a file called `TLS-Dynamics_vacuum.prm` containing the following text

```
OutputFile=TLS-Dynamics_vacuum.out
NumStates=2
HierarchyTruncation=1
Temperature=0
Hamiltonian:
12100,500
500,12000
InitialDensityMatrix:
1.0,0.0
0.0,0.0
gamma:
0,0
lambda:
0,0
Timestep=0.0001
Time=0.1
```

Here the timestep is set to $dt = 0.1$ fs and the total simulation time is set to $t = 100$ fs. The Hamiltonian is specified exactly as in Eq. 7. Additionally, the initial density matrix has been specified such that the

higher energy pigment is initially excited, i.e., that

$$\rho(0) = |1\rangle\langle 1| = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix}. \quad (8)$$

Step 2: Run simulation. In a command line run the following command:

```
$ phi TLS-DynamicsVacuum.prm rk4
```

This command specifies that PHI reads the simulation parameters from the file `TLS-DynamicsVacuum.prm` and perform Runge-Kutta 4 (`rk4`) integration.

Step 3: Examine screen output. PHI will output some basic status information to the screen (`STDOUT`).

The verbosity of the screen output can be altered with the `verbose` keyword (accepting values of `-1`, `0`, `1`, `2`, `3`. The default is `1`). Of interest here is that for the current set of parameters, PHI requires only about 0.95 kB of RAM for `rk4` integration (more memory is used to store the program in memory, but this is negligible, particularly for larger calculations).

Step 4: Examine file output. The body of the output is written to the file specified by the `OutputFile` keyword. Open `TLS-DynamicsVacuum.out` in a text editor. All lines beginning with `#` are comments that either specify what input parameters were used to generate the output in the current file, or give information about the calculation time, integration method and memory used. The first few non-comment lines are

```
0 (1,0) (0,0) (0,0) (0,0)
0.0001 (0.999645,-2.50483e-18) (3.54772e-05,-0.018832) (3.54772e-05,0.018832) (0.000354772,1.09161e-20)
0.0002 (0.999645,-2.50483e-18) (3.54772e-05,-0.018832) (3.54772e-05,0.018832) (0.000798118,2.9362e-20)
0.0003 (0.999202,7.74338e-18) (7.98118e-05,-0.0282396) (0.000141858,0.0376371) (0.00141858,6.42733e-20)
```

In each non-commented output line the first number is the timestep followed by the density matrix, in this case $\rho_{00}(t)$ $\rho_{01}(t)$ $\rho_{10}(t)$ $\rho_{11}(t)$. PHI outputs the density matrix for each timestep on one line in row-major order. Plotting $\rho_{00}(t)$ shows the expected Rabi oscillations as seen in Fig. 3

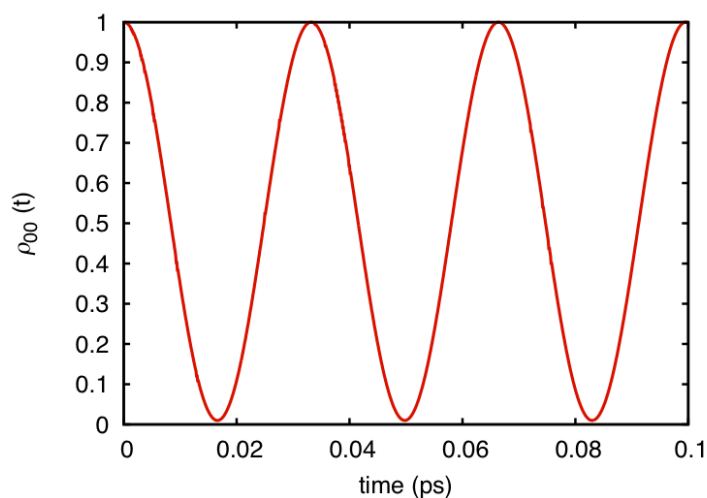
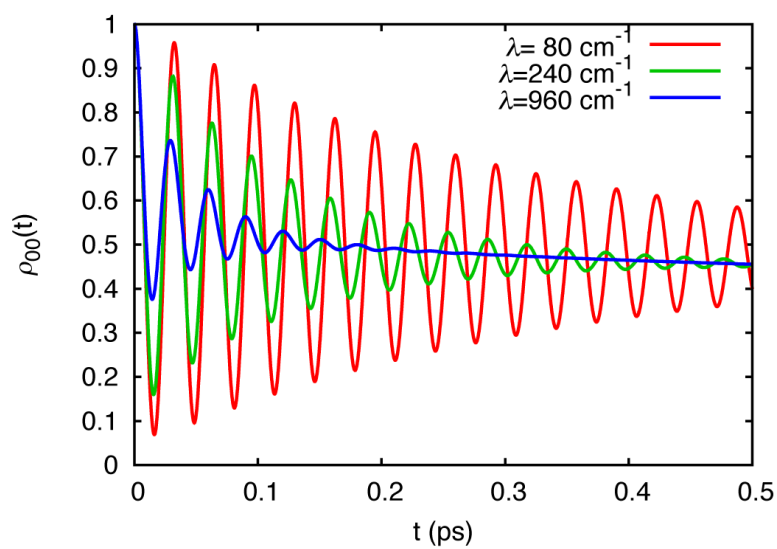


Figure 3: Rabi oscillations arising in the coherently coupled pigment dimer in the absence of a thermal environment.

Exercise 2: Damped oscillations Determine the effect of increased environmental coupling. Modify the input script `TLS-Dynamics.Vacuum.prm` to increase the hierarchy truncation to 10, set the response frequencies to $\gamma = 10 \text{ ps}^{-1}$ and set the temperature to 300 K. Plot the dynamics of the initially excited pigment in the special pair for reorganization energies of $\lambda = 80, 240$ and 960 . (N.B.: remember to change the `OutputFile` keyword for each calculation!)



5. Matsubara Terms, Hierarchy Integration & Hierarchy Truncation

Up to now the examples provided use HEOM integration parameters to obtain the results without knowing how “good” they are or whether the result were converged for different values of K and L . Although converged results can be obtained with sufficiently large values of K and L , such calculations are often prohibitively expensive. It is thus vital for larger calculations to use optimal parameters that yield converged results in a reasonable time. We again examine a pigment dimer, however at a much lower temperature of $T = 77$ K, and investigate the effect of different K and L values.

Step 1: Input parameters. Create a file called `TLS-Dynamics_77K.prm` containing the following text (note the different model parameters to those in the prior examples).

```
OutputFile=TLS-Dynamics_77K_L5K0.out
NumStates=2
HierarchyTruncation=5
Temperature=77
MatsubaraTerms=0
Hamiltonian:
100,200
200,0
InitialDensityMatrix:
1.0,0.0
0.0,0.0
gamma:
10,10
lambda:
300,300
Timestep=0.0001
Time=1.0
```

Step 2: Integrate the HEOM using PHI. Run the following command

```
$ phi TLS-Dynamics_77K.prm rk4
```

to calculate the dynamics of the TLS at 77 K with zero Matsubara terms.

Step 3: Modify Matsubara terms. Modify the `OutputFile` and `MatsubaraTerms` parameters in the input file and repeat step 2 in order to obtain the density matrix dynamics for $K = 1, 2, 3$. The dynamics of the initially excited pigment is shown in Fig. 4. It can be seen that the difference between $K = 2$ and $K = 3$ is quite small but still non-zero.

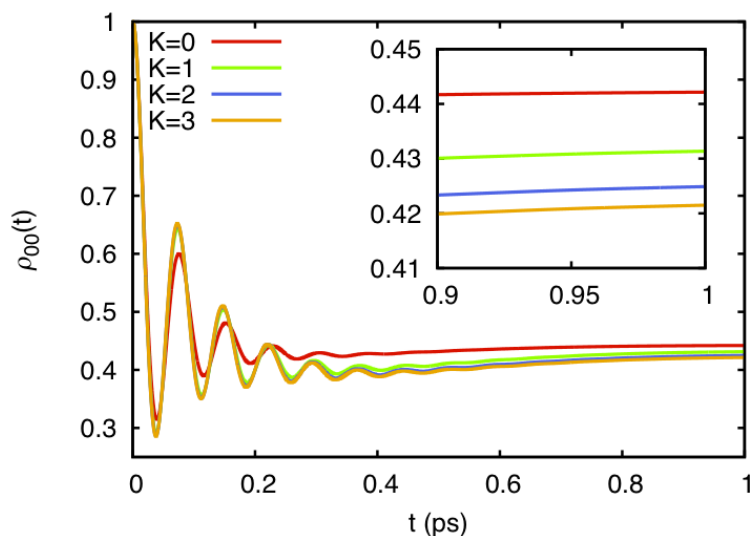


Figure 4: Dynamics of initially excited pigment with different number of Matsubara terms.

Step 4: Reduce the calculation time. Notice that the calculation with $K = 3$ took a little while longer than the others. This is due to the larger number of equations (495 compared to 70 for $K = 2$) that have to be integrated. To improve the calculation time use the adaptive Runge-Kutta-Fehlberg 4/5 integrator instead by running PHI with the following command:

```
$ phi TLS-Dynamics_77K.prm rkf45
```

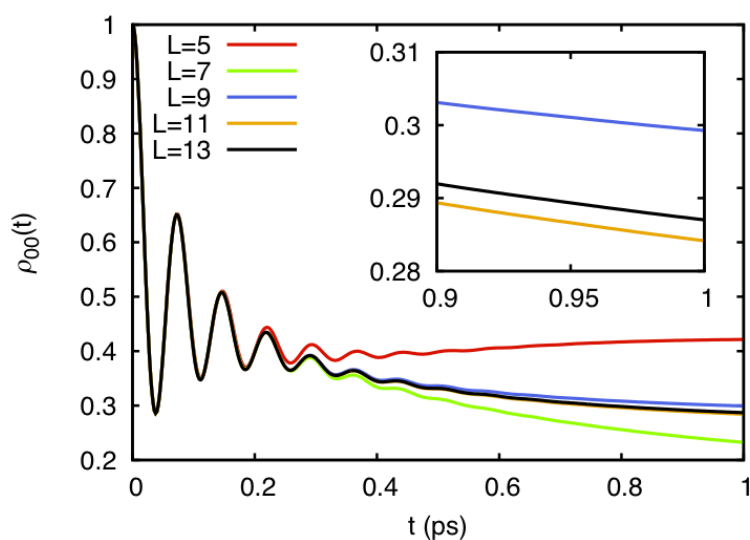
Notice that the calculation was much faster! It took only 297 integration steps (compared to 10 000 with `rk4`), 5 of which it had to discard due to integration errors. Although better performance for the `rk4` integrator could also be obtained with a larger step size, it is tedious to find the optimal step size for each system. Take note also from the PHI screen output that the `rkf45` integrator uses more memory than the `rk4` integrator.

Even faster calculation can be obtained by using multiple threads if you have a multi-core CPU. To use N integration threads, add N to the end of the PHI run command. E.g., to use 2 integration threads (for a dual-core CPU) use the following command:

```
$ phi TLS-Dynamics_77K.prm rkf45 2
```

Benchmarking should be done to utilize the most efficient number of cores for a calculation, and never specify more integration threads than number of physical cores.

Exercise 3: Optimal hierarchy truncation. Determine the minimum hierarchy truncation L to obtain converged results. Modify the input file `TLS-Dynamics_77K.prm` (see Step 1 of the current section) to set `MatsubaraTerms=3`. Calculate the density matrix dynamics from 0 to 1 ps, employing the `rkf45` integrator, for hierarchy truncations of $L = 5, 7, 9, 11, 13$. Be aware, the calculation for $L = 13$ will take some time (>30 mins on a single processor). Plot $\rho_{00}(t)$ for each value of L as shown below.



The error with using a too low truncation is readily apparent showing reasonable convergence with $L = 13$. Care must be used when determining the appropriate truncation level for a given set of model parameters.

Although the steps taken above will indicate the optimal K and L values to employ, only the initially excited pigment population has been considered. In practice the whole density matrix ought to be checked for convergence: all the population and coherence terms.

Acknowledgements

Development of this tutorial was supported by the National Institutes of Health (P41-RR005969 - Resource for Macromolecular Modeling and Bioinformatics).