

# Technical note: GPU-HEOM on nanohub.org

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February 28, 2013, release 1.0

## Abstract

Technical note describing the implementation and algorithms used in GPU-HEOM on nanohub.org. Further details are given in the cited literature. Some examples and use cases for running the tool are given at [quantumdynamics.wordpress.com](http://quantumdynamics.wordpress.com).

## 1 Setting up the model Hamiltonian

The total Hamiltonian which includes the exciton system and the environment is given by [1]

$$\mathcal{H} = \mathcal{H}_{\text{ex}} + \mathcal{H}_{\text{phon}} + \mathcal{H}_{\text{ex-phon}} + \mathcal{H}_{\text{reorg}}. \quad (1)$$

The exciton system is denoted by  $\mathcal{H}_{\text{ex}}$  and the harmonic vibrations of the bath by  $\mathcal{H}_{\text{phon}} = \sum_{m,\xi} \hbar\omega_{\xi,m} b_{\xi,m}^\dagger b_{\xi,m}$ . The coupling terms between the exciton and vibrational degrees of freedom are expressed by the last two parts. For a system with  $N$  sites, the exciton Hamiltonian reads

$$\mathcal{H}_{\text{ex}} = \sum_{m=1}^N \varepsilon_m^0 a_m^\dagger a_m + \sum_{m>n} J_{mn} (a_m^\dagger a_n + a_n^\dagger a_m), \quad (2)$$

where  $a_m^\dagger$  ( $a_m$ ) is defined as the creation (annihilation) operator of electronic excitations at site  $m$ . The state  $|m\rangle = a_m^\dagger|0\rangle$  corresponds to an electronic excitation at site  $m$  while the electronic configuration of all other sites remains in the ground

state. The state  $|0\rangle$  is defined as the ground state without any electronic excitations (all sites in the electronic ground state). The reorganization energy is given by

$$\mathcal{H}_{\text{reorg}} = \sum_{m=1}^N \lambda_m a_m^\dagger a_m. \quad (3)$$

The provided user input of the Hamiltonian must include the reorganisation energy  $\varepsilon_m = \varepsilon_m^0 + \lambda_m$  in the specified Hamiltonian. For numerical convenience we suggest to shift the diagonal elements of the Hamiltonian to center its eigenvalues around zero.

The model assumes a linear coupling of the exciton system to the vibrational environment

$$\mathcal{H}_{\text{ex-phon}} = \sum_{m=1}^N V_m B_m, \quad (4)$$

with

$$V_m = a_m^\dagger a_m \quad \text{and} \quad B_m = \sum_{\xi} \hbar \omega_{\xi,m} d_{\xi,m} (b_{\xi,m}^\dagger + b_{\xi,m}). \quad (5)$$

The coupling strength of the vibronic modes to the exciton system is given by the spectral density

$$J_m(\omega) = \pi \sum_{\xi} \hbar^2 \omega_{\xi,m}^2 d_{\xi,m}^2 \delta(\omega - \omega_{\xi,m}). \quad (6)$$

The spectral density is related to the reorganization energy by

$$\int_0^\infty d\omega \frac{J_m(\omega)}{\pi \hbar \omega} = \lambda_m. \quad (7)$$

The nanohub.org implementation assumes that all independent baths have the same form of spectral density. The spectral density itself is specified by a superposition of shifted Lorentzian peaks [2]

$$J(\omega) = \sum_{k=1}^M \left[ \frac{\nu_k \lambda_k \omega}{\nu_k^2 + (\omega + \Omega_k)^2} + \frac{\nu_k \lambda_k \omega}{\nu_k^2 + (\omega - \Omega_k)^2} \right]. \quad (8)$$

## 2 Reduced hierarchy equations of motions on the GPU

The tool calculates the time-evolution of the reduced density matrix, where the bath degrees of freedom are traced out. The calculation is performed on massively

parallel Graphics Processing Units (GPU) [3]. For faster computation speed, a high-temperature approximation (HTA) is employed [4], which requires that

$$\hbar\nu_k\beta < 1. \quad (9)$$

The transfer dynamics of the exciton system is described by the reduced density operator  $\rho(t) = \text{Tr}\{R(t)\}$ , which is obtained after tracing out the vibrational degrees of freedom of the total density operator  $R(t)$ . At  $t_0$  we assume that system and bath degrees of freedom factorize  $R(t_0) = \rho(t_0) \otimes \rho_{\text{phon}}$ , where  $\rho_{\text{phon}}$  describes the bath density operator. The Gaussian nature of the phonon bath reduces bath correlations to two-time correlation functions expressed by the symmetrized correlation  $S_m(t) = 1/2 \text{Tr}_{\text{phon}}\{[\tilde{B}_m(t), \tilde{B}_m(0)]_+\}$  and response function  $\chi_m(t) = 1/2 \text{Tr}_{\text{phon}}\{[\tilde{B}_m(t), \tilde{B}_m(0)]\}$  with  $\tilde{B}_m(t) = \sum_{\xi} \hbar\omega_{\xi,m} d_{\xi,m} (\tilde{b}_{\xi,m}^{\dagger}(t) + \tilde{b}_{\xi,m}(t))$ . Operators with tilde are defined as interaction picture operators with respect to  $\mathcal{H}_0 = \mathcal{H}_{\text{ex}} + \mathcal{H}_{\text{phon}}$ . The derivation of HEOM relies on an exponential form of  $S_m(t)$  and  $\chi_m(t)$ . Such a form is guaranteed for a spectral density that is constructed by a super-position of shifted Drude-Lorentz peaks (8). Within a high temperature approximation the bath correlation functions are expressed as follows

$$S_m^{HTA}(t) = \sum_k^M \sum_{s=\pm 1} \left[ \frac{\lambda_k}{\beta\hbar} \left( 1 - \frac{2(\nu_k + is\Omega_k)^2}{\gamma_1^2 - (\nu_k + is\Omega_k)^2} \right) e^{-(\nu_k + is\Omega_k)t} + \frac{\lambda_k}{\beta\hbar} \frac{2\nu_k}{(\gamma_1 + is\Omega_k)^2 - \nu_k^2} \delta(t) \right], \quad (10)$$

and

$$\chi(t) = \sum_{k=1}^M \sum_{s=\pm 1} \lambda_k / \hbar (\nu_k + is\Omega_k) e^{-(\nu_k + is\Omega_k)t}. \quad (11)$$

The first Matsubara frequency is denoted by  $\gamma_1 = 2\pi/\beta$ . The shifts  $\Omega_k$  induce oscillatory components in the correlation functions.

The time evolution of the reduced density operator is then given in terms of a system of hierarchically coupled equations of motion [5, 4]

$$\frac{d}{dt}\rho(t) = -\frac{i}{\hbar}\mathcal{L}_{\text{ex}}\rho(t) + \sum_{m,k=1,s=\pm 1}^{N,M} \frac{i}{\hbar}V_m^{\times}\sigma_{\vec{n}_0}^{\dagger}(t) \quad (12)$$

with

$$\begin{aligned}
\frac{d}{dt}\sigma^{\vec{n}}(t) &= -\frac{i}{\hbar}\mathcal{L}_{\text{ex}}\sigma^{\vec{n}}(t) \\
&\quad - \sum_{m,k=1,s=\pm 1}^{N,M} n_{m,k,s}(\nu_k + s i\Omega_k)\sigma^{\vec{n}}(t) \\
&\quad + \sum_{m,k=1,s=\pm 1}^{N,M} \left(\frac{i}{\hbar}V_m^\times\sigma^{\vec{n}_{m,k,s}^+}(t) + \theta_{m,k,s}\sigma^{\vec{n}_{m,k,s}^-}(t)\right). \quad (13)
\end{aligned}$$

Here we define operators

$$\mathcal{L}_{\text{ex}}\rho = -i\hbar[\mathcal{H}_{\text{ex}},\rho] - \sum_{m=1}^N \sum_{k=1}^M \sum_{s=\pm 1} \frac{2}{\beta\hbar^2} \frac{\lambda_k\nu_k}{(\gamma_1 + is\Omega_k)^2 - \nu_k^2} V_m^\times V_m^\times \rho \quad (14)$$

and

$$\theta_{m,k,s} = \frac{i}{2} \left( \frac{2\lambda_k\beta}{\hbar} V_m^\times - i\lambda_k(\nu_k + s i\Omega_k) V_m^\circ - \frac{2\lambda_k}{\beta\hbar^2} \frac{(\nu_k + is\Omega_k)^2}{\gamma_1^2 - (\nu_k + is\Omega_k)^2} V_m^\times \right) \quad (15)$$

with  $V_m^\times\sigma = [a_m^\dagger a_m, \sigma]$  and  $V_m^\circ\sigma = [a_m^\dagger a_m, \sigma]_+$ . The index  $\vec{n}$  of the auxiliary matrix  $\sigma^{\vec{n}}$  is defined as tuple  $\vec{n} = (n_{1,1,s}, \dots, n_{1,M,s}, \dots, n_{N,1,s}, \dots, n_{N,M,s})$  where  $n_{m,k,s} \in \mathbb{N}$ . The label  $m = 1, \dots, N$  covers the number of sites, the label  $k = 1, \dots, M$  covers the number of shifted Drude-Lorentz peaks and the label  $s = \pm 1$  takes into account the sign of the frequency shift  $\pm\Omega_k$ . We further define  $\vec{n}_{m,k,s}^\pm = (n_{1,k,s}, \dots, n_{m,k,s} \pm 1, \dots, n_{N,M,s})$ . The hierarchy converges for a sufficiently large truncation level  $N_{\text{max}} = \sum_{m,k,s} n_{m,k,s}$ . Convergence of the hierarchy must be verified by comparison with higher truncation levels.

### 3 Supported calculation modes

#### 3.1 Population dynamics

The tool calculates the time evolution of the site population. The initial site  $i$  is specified by the user and sets

$$\rho(t=0) = |i\rangle\langle i| \quad (16)$$

### 3.2 Exciton coherences

The tool calculates the time-evolution of the coherence between two exciton eigenstates. The eigenstates  $|E_i\rangle$  are sorted by increasing eigenvalue. The initial reduced density matrix is given by

$$\rho(t=0) = |E_i\rangle\langle E_j| \quad (17)$$

where  $|E_i\rangle$  is given by the user as  $|ket\rangle$  and  $\langle E_j|$  as  $\langle bra|$ .

### 3.3 Absorption spectra

To calculate absorption-spectra we have to expand the system and add the ground state  $|0\rangle$  to the basis. The dipole matrix is constructed as

$$\mu = \begin{pmatrix} 0 & \mu_{1\text{ex}}^- \\ \mu_{1\text{ex}}^+ & 0 \end{pmatrix}, \quad (18)$$

where  $\mu_{1\text{ex}}^+ = \mu_{1\text{ex}}^-^\top$ . The zero to single excitation dipole block reads

$$\mu_{1\text{ex}}^+ = \sum_{k=1}^{N_{\text{sites}}} \mu_k |k\rangle \langle 0| \quad (19)$$

with the dipole moments  $\mu_k$  given for every site  $k$ .

The absorption spectrum is calculated as

$$I_{1\text{d}}(\omega) = \left\langle \int_0^\infty dt e^{i\omega t} \text{tr} (\mu(t) \mu(0) \rho_0) \right\rangle_{\text{rot}}, \quad (20)$$

where  $\rho_0 = |0\rangle \langle 0|$  is the density operator for no excitation. Rotational averaging is automatically performed by the program and consists of summing up the results for three orthogonal polarisation vectors of the laser beam (“xyz”-averaging) [6].

### 3.4 Two-dimensional echo spectra

The 2d echo-spectra are calculated in two configurations which correspond to the rephasing (RP) and non-rephasing (NR) contributions of the third order response function [7, 8]

$$S^{(3)}(t_3, t_2, t_1) = \left(\frac{i}{\hbar}\right)^3 \Theta(t_3)\Theta(t_2)\Theta(t_1) \text{tr} (\mu(t_3 + t_2 + t_1) [\mu(t_2 + t_1), [\mu(t_1), [\mu(0), \rho_0]]]) \quad (21)$$

Using the impulsive approximation which assumes  $\delta$ -functions for the temporal envelopes of the pulses, the two components of the spectrum corresponding to  $S^{(3)}(t_3, t_2, t_1) = S_{\text{RP}}^{(3)}(t_3, t_2, t_1) + S_{\text{NR}}^{(3)}(t_3, t_2, t_1)$  read

$$I_{\text{RP}}(\omega_3, t_2, \omega_1) = \int_{-\infty}^{\infty} dt_1 \int_{-\infty}^{\infty} dt_3 e^{i\omega_3 t_3 - i\omega_1 t_1} S_{\text{RP}}^{(3)}(t_3, t_2, t_1), \quad (22)$$

$$I_{\text{NR}}(\omega_3, t_2, \omega_1) = \int_{-\infty}^{\infty} dt_1 \int_{-\infty}^{\infty} dt_3 e^{i\omega_3 t_3 + i\omega_1 t_1} S_{\text{NR}}^{(3)}(t_3, t_2, t_1). \quad (23)$$

Sorting this expression for the rephasing and the non-rephasing parts yields six different pathways, which represent the stimulated emission, the ground-state bleach and the excited state absorption. By taking the time between second and third pulse as a control parameter as done in (22) and (23) one can study the exciton dynamics which is probed by recording the emitted signal pulse. Due to the excited state absorption the dynamics is more involved compared to the one dimensional case. Including a double excited manifold, we construct an enlarged exciton Hamiltonian  $H_e^{2d}$  which is block diagonal and of the form

$$H_e^{2d} = \begin{pmatrix} H_e^{\text{gs}} & 0 & 0 \\ 0 & H_e^{1\text{ex}} & 0 \\ 0 & 0 & H_e^{2\text{ex}} \end{pmatrix}, \quad (24)$$

where  $H_e^{\text{gs}} = 0$  represents the ground state,  $H_e^{1\text{ex}}$  is the single-exciton Hamiltonian with  $N_{\text{sites}}^2$  elements, and the energy levels of the two excitons are described by  $H_e^{2\text{ex}}$ . The two-exciton Hamiltonian  $H_e^{2d}$  has  $[N_{\text{sites}}(N_{\text{sites}} - 1)/2]^2$  entries which are constructed from the matrix elements of  $H_e^{1\text{ex}}$  following [8]. In site basis, we denote the two exciton states by  $|ij\rangle$ , where  $0 < i < j \leq N_{\text{sites}}$ , and the diagonal entries of  $H_e^{2\text{ex}}$  are given by

$$\langle ij | H_e^{2\text{ex}} | ij \rangle = \langle i | H_e^{1\text{ex}} | i \rangle + \langle j | H_e^{1\text{ex}} | j \rangle. \quad (25)$$

The off-diagonal elements are given by

$$\begin{aligned} \langle ij | H_e^{2\text{ex}} | kl \rangle = & \delta_{ik} (1 - \delta_{jl}) \langle j | H_e^{1\text{ex}} | l \rangle + \delta_{il} (1 - \delta_{jk}) \langle j | H_e^{1\text{ex}} | k \rangle \\ & + \delta_{jk} (1 - \delta_{il}) \langle i | H_e^{1\text{ex}} | l \rangle + \delta_{jl} (1 - \delta_{ik}) \langle i | H_e^{1\text{ex}} | k \rangle \end{aligned} \quad (26)$$

Following [8], we construct the dipole operator associated with the extended Hamiltonian

$$\mu = \begin{pmatrix} 0 & \mu_{1\text{ex}}^- & 0 \\ \mu_{1\text{ex}}^+ & 0 & \mu_{2\text{ex}}^- \\ 0 & \mu_{2\text{ex}}^+ & 0 \end{pmatrix}. \quad (27)$$

The zero to single excitation operators  $\mu_{1\text{ex}}^{\pm}$  are defined as before. The single to double excitation operators are defined according to

$$\langle ij | \mu_{2\text{ex}}^+ | k \rangle = \delta_{ik} \langle j | \mu_{1\text{ex}}^+ | 0 \rangle + \delta_{jk} \langle i | \mu_{1\text{ex}}^+ | 0 \rangle \quad (28)$$

and  $\mu_{2ex}^- = (\mu_{2ex}^+)^T$ .

An approximation to full rotational averaging is available by selecting one of four polarisation directions of the laser beam and adding up all the resulting spectra (this corresponds to an octahedral approximation of the sphere). Due to runtime limitations the icosahedral averaging mode is not available at this time.

## 4 Acknowledgements

This program was developed by Christoph Kreisbeck in collaboration with Tobias Kramer, Birgit Hein, and Mirta Rodríguez. We acknowledge funding by the Emmy-Noether program of the DFG, grant KR 2889/2 and by the German Academic Exchange Service (DAAD) within the Acciones Integradas Hispano-Alemanas. Further we thank Gerhard Klimeck and Steven Clark at nanohub.org for their support and providing the resources for making GPU computing possible at nanohub.org.

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