

Constructing more realistic molecular bath models

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Introduction

Charge and energy transport between the excited states of small molecules is important to the design of photosynthetic materials. The rates of relaxation and energy transfer are controlled by coupling the system of interest to its environmental degrees of freedom, or a "bath", held at thermal equilibrium. Constructing realistic bath models is crucial in modeling of these quantum phenomena. However, it remains a challenge because the number of degrees of freedom in the dynamics of a many-body system grows exponentially with the number of physical particles. The continuous coupling to the bath is represented by a function called Spectral Density (SD). High computation cost currently limits the construction of SDs to a few parameters.

In this work, we introduce a new method to construct thermal bath models cheaply and more physically, which is demonstrated with a butadiynyl fluorophore (Dimer 1cd) recently synthesized by Pati *et al.*^[1]

Procedure

1. Perform a Quantum Mechanics/ Molecular Mechanics (QM/MM) simulation of the system of interest and its environment. The atomic energy fluctuation is computed by TDDFT calculations in intervals. (Most expensive step)
2. Construct a classical correlation function of the energy fluctuation obtained from the dynamics.
3. Obtain atomic orbital SDs $J(\omega)$ in Drude-Lorentz form, utilizing a sparse L1 signal-processing technique called Super Resolution developed by Markovich *et al.*^[2]
4. Compute atom-specific reorganization energies.
5. Compute the rates of bath-induced relaxation and dephasing by the second-order time-convolutionless perturbation theory (TCL-2):

$$i \frac{P_{\mu\nu}}{dt} = [\hat{F}, P] + \kappa_{\mu\nu, \lambda\sigma} P_{\lambda\sigma}$$

$\kappa \propto J(\omega)$

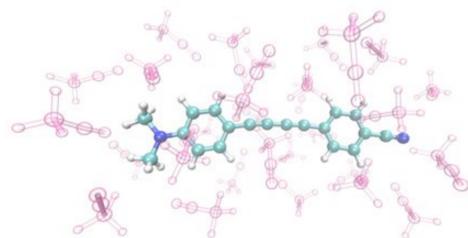
Advantages

1. Atomistic bath models are more realistic: (1) include molecular vibrations and other physical effects, (2) depend on the system of interest, temperature, and environment.
2. Super Resolution technique reduces the MD wall-time required to capture SDs accurately by a factor of 8, compared to the standard Fast Fourier Transform (FFT) of the correlation function, therefore enabling construction of bath models for larger systems.
3. The SDs obtained by Super Resolution can be directly used to obtain relaxation and dephasing rates induced by the bath.

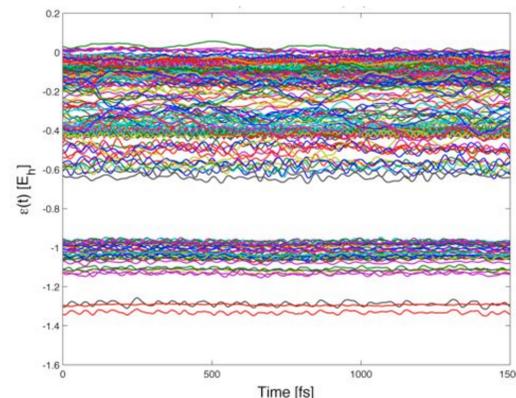
Dynamics Simulation

10-ps QM/MM simulation of dimer 1cd (a butadiynyl derivative) solvated in acetonitrile at 300 (K) is performed using the Q-Chem 4.0 package.^[3]

The QM region with the dimer is described using standard B3LYP/6-31G. The MM region of solvent molecules is treated by the CHARMM27 force field.

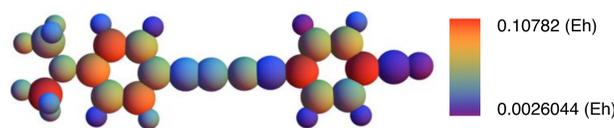


Dimer 1cd - Atomic Orbital Fock energies



Atomic orbital energies of the dimer are collected at each 0.5-fs timestep using TDDFT calculations. The last 5-ps dynamics shows energy of each atomic orbital fluctuates within 40 (mEh) (25 kcal/mol).

Reorganization Energy



Atom-specific reorganization energy is calculated as:

$$\int_0^\infty \frac{J(\omega)}{\omega} d\omega = \lambda$$

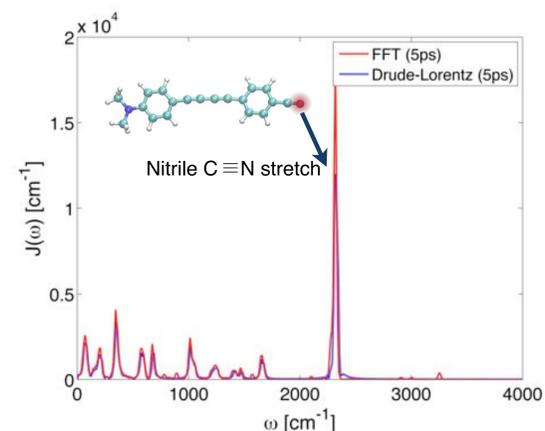
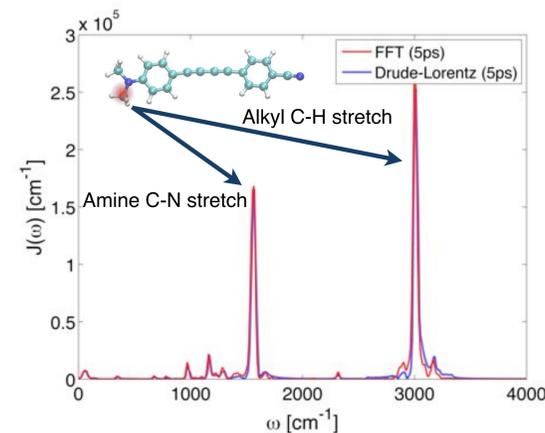
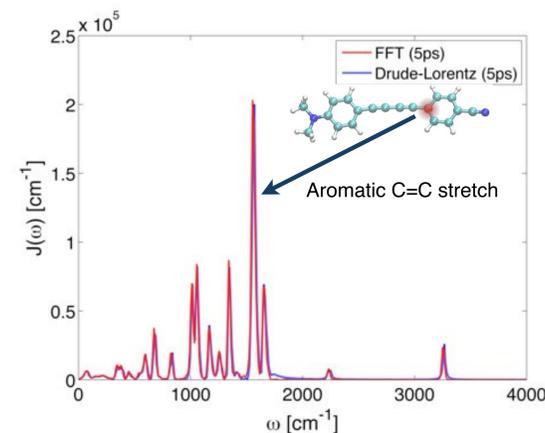
Vibronic structure dominates the reorganization.

Atomic Spectral Density

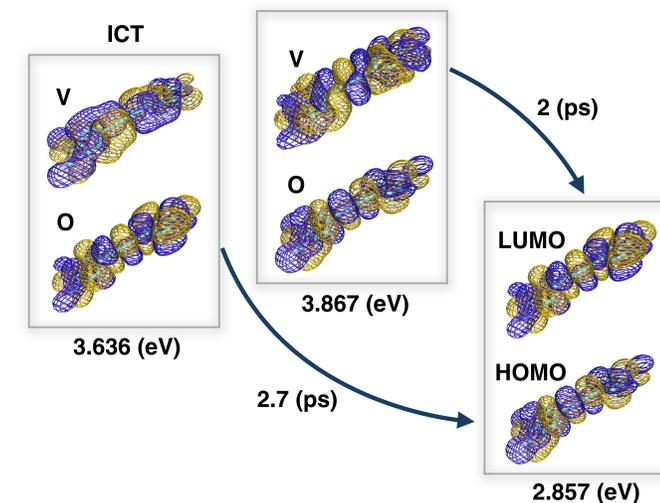
Super Resolution yields atomic orbital SDs in Drude-Lorentz form (frequency-dependent strength of system-bath coupling):

$$J(\omega) = \frac{\lambda_{ij}}{\sqrt{\pi}} \left(\frac{\beta \hbar \omega \gamma_i}{\gamma_i^2 + (\omega - \Omega_j)^2} + \frac{\beta \hbar \omega \gamma_i}{\gamma_i^2 + (\omega + \Omega_j)^2} \right)$$

Compared with SDs from FFT technique, these SDs faithfully capture fine vibration details.



Excited State Decay Rates



Delayed fluorescence of the butadiynyl derivative is a mixture of the bright absorption state, an intramolecular charge transfer (ICT) state and localized states.

The Markov rates computed by TCL-2 reproduce the decay of these states.^[1]

Conclusion

More realistic bath models can be constructed cheaper using the Super Resolution technique to generate accurate SDs in Drude-Lorentz form.

We demonstrate that our bath model of a butadiynyl fluorophore reproduces the experimental relaxation and dephasing rates.

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References:

1. Pati, A. *et al.* Deciphering the photophysical role of conjugated diyne in butadiynyl fluorophores: Synthesis, photophysical and theoretical study. *J. Phys. Chem. A.* 117 (30), 6548-6560 (2013)
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3. Shao, Y. *et al.* Advances in methods and algorithms in a modern quantum chemistry program package. *Phys. Chem. Chem. Phys.* 8, 3172 (2006)