VISTA

Benchmarking surface hopping method to include nuclear quantum effects

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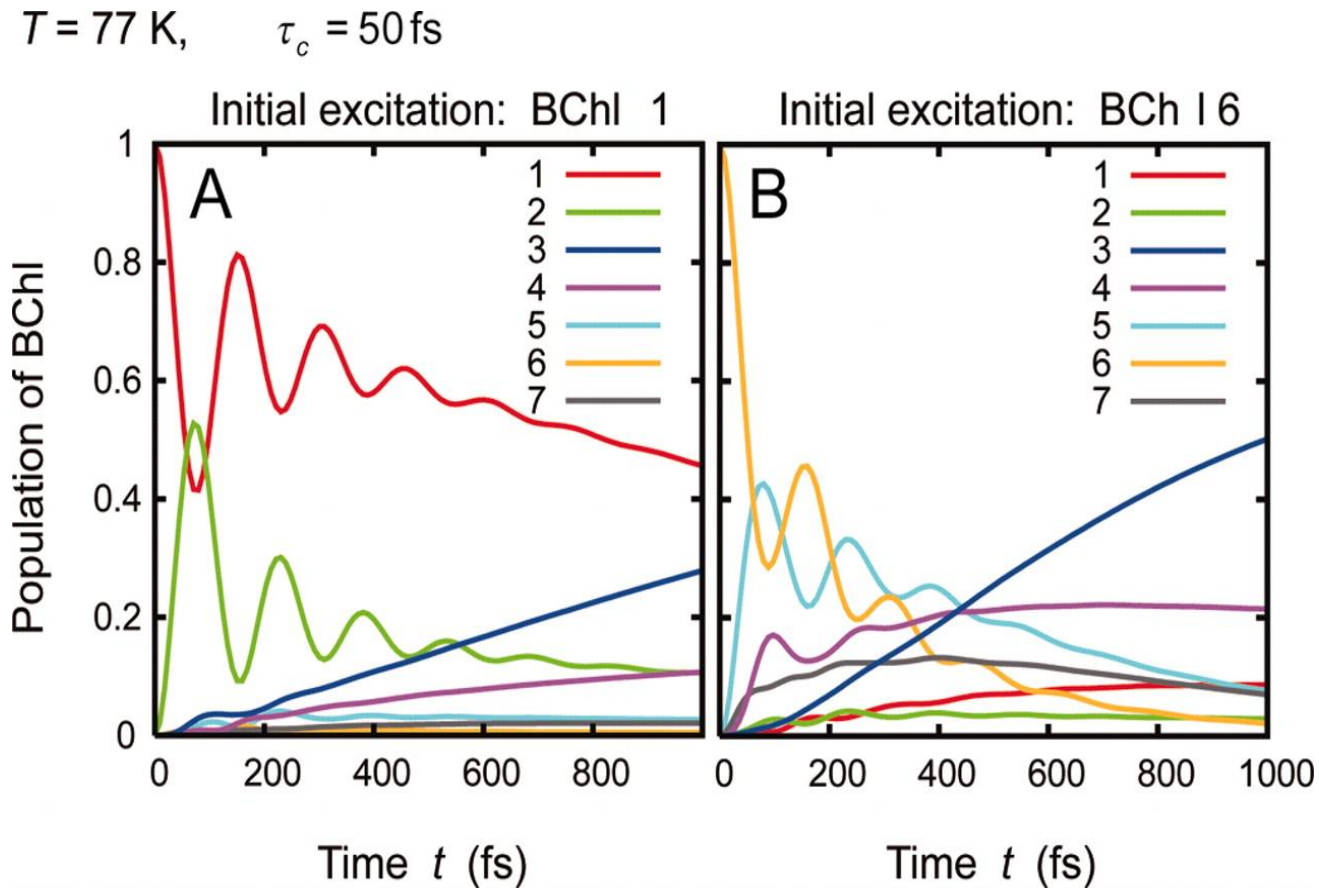
(Group of Prof. Amber Jain)

From where we started ...

Fenna-Matthews Olson complex (FMO)

- **A protein-pigment complex found in green Sulphur bacteria**
- **Plays a crucial role in photosynthesis process by efficiently transfer electronic energy from absorption to reaction center**
- **Widely used to study the EET dynamics because of its well defined structure**



Engel GS, et al. Nature 446:782–786 (2007)
Ishizaki A. and Fleming G.R., PNAS, 106 : 17255-17260 (2009).

Fewest Switches Surface Hopping (FSSH)

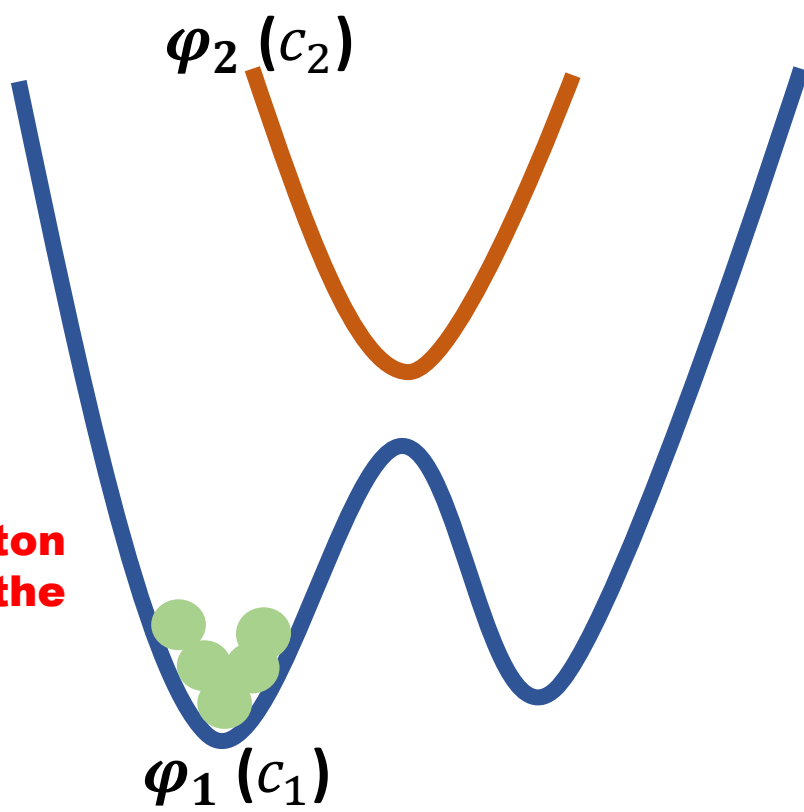
A molecular dynamics method which includes non-adiabatic effects (when more two or more PES becomes significant for a particular reaction).

For a n level system, choose adiabatic basis $\phi_i s$ (electronic or vibrational or vibronic) such that :

$$\psi(r, R, t) = \sum_i c_j(t)\varphi_j(r, R)$$

$\psi(r, R, t)$ can be put in Schrodinger Equation to get

$$i\hbar\dot{c}_j = \sum_k c_k(V_{jk} - i\hbar\dot{R}d_{jk})$$



At each classical set of coordinate R (that is evolved using Newton equation of motion), $c_j s$ can be found out by numerical integration of the above equation

Tully J.C., J. Chem. Phys., 93 : 1061-1071 (1990).

Events in FSSH to be taken care of :

- **Accurate treatment of Frustrated Hops**
- **Treatment of over-coherence in FSSH**

Treatment of Frustrated hops and Over-coherence

- The original FSSH algorithm do nothing for the events
- **For frustrated hops**, we are following the scheme given by Jasper and Truhlar [1] which is velocity is reversed when :

$$(\vec{F}_j \vec{d}_{\lambda j})(\vec{v} \vec{d}_{\lambda j}) < 0$$

where is the $\vec{F}_j$ force on jth adiabatic surface and λ is the active surface

- Algorithms for including **decoherence :**
  1. **Augmented FSSH (A-FSSH)[2]**
  2. **A-FSSH (2016)[3]**

1. Ahren W Jasper and Donald G Truhlar, Chem. Phys. Lett., 369(1-2):60–67, 2003
2. Joseph E Subotnik and Neil Shenvi, J. Chem. Phys., 134(2):024105, 2011
3. Amber Jain, Ethan Alguire, and Joseph E Subotnik., J. Chem. Theory Comput., 12(11):5256–5268, 2016

Model System for benchmarking FSSH

$$\hat{H}_{tot} = \hat{H}_e + \hat{H}_{n1} + \hat{H}_{en} + \hat{H}_{n2} + \hat{H}_b$$

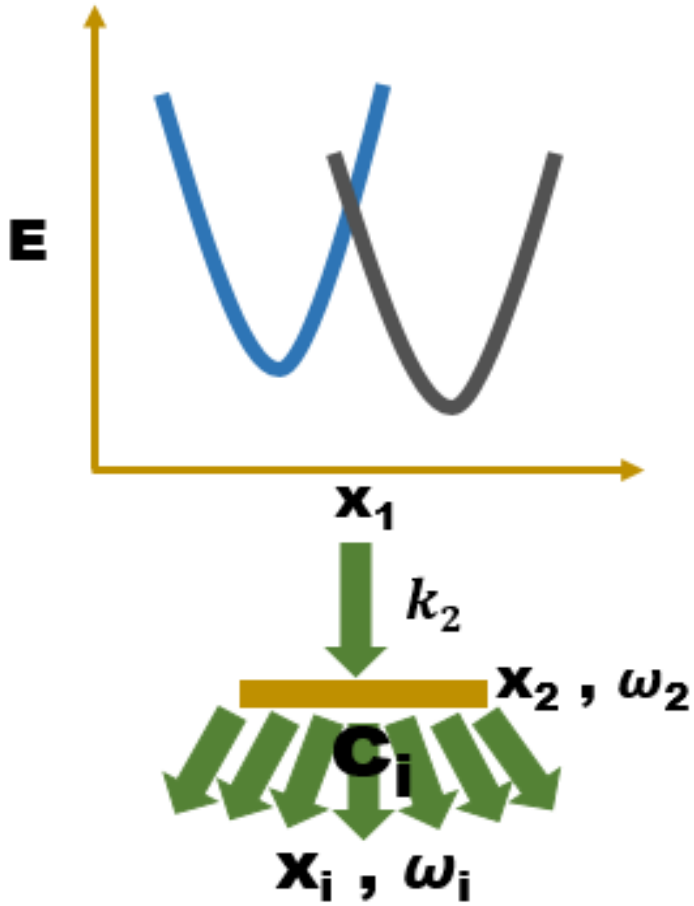
$$\hat{H}_e = \frac{\epsilon}{2}\left(|1\rangle\langle 1| - |2\rangle\langle 2|\right) + V_{12}\left(|1\rangle\langle 2| + |2\rangle\langle 1|\right)$$

$$\hat{H}_{n1} = \frac{P_1^2}{2m} + \frac{1}{2} m\omega_1^2 x_1^2$$

$$\hat{H}_{en} = k_1 x_1 \left(|1\rangle\langle 1| - |2\rangle\langle 2|\right)$$

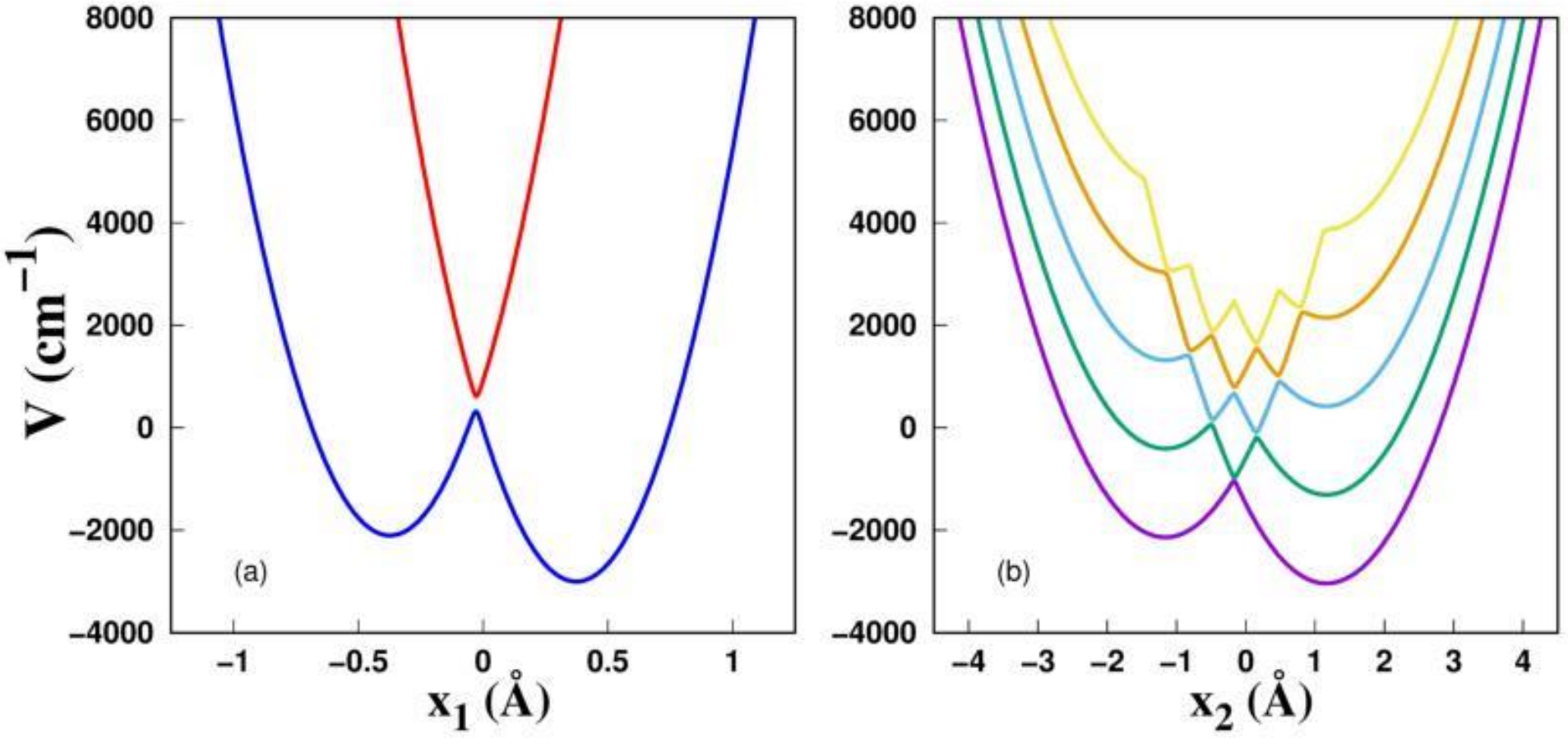
$$\hat{H}_{n2} = \frac{P_2^2}{2m} + \frac{1}{2} m\omega_2^2 \left(x_2 - \frac{k_2 x_1}{m\omega_2^2}\right)^2$$

$$\hat{H}_b = \sum_{i=3} \frac{P_i^2}{2m} + \sum_{i=3} \frac{1}{2} m\omega_i^2 \left(x_i - \frac{c_i x_2}{m\omega_i^2}\right)^2$$



Abraham Nitzan. Chemical dynamics in condensed phases: relaxation, transfer and reactions in condensed molecular systems. Oxford university press, 2006

Potential Energy Surfaces



(a) without including NQE **(b) including NQE**

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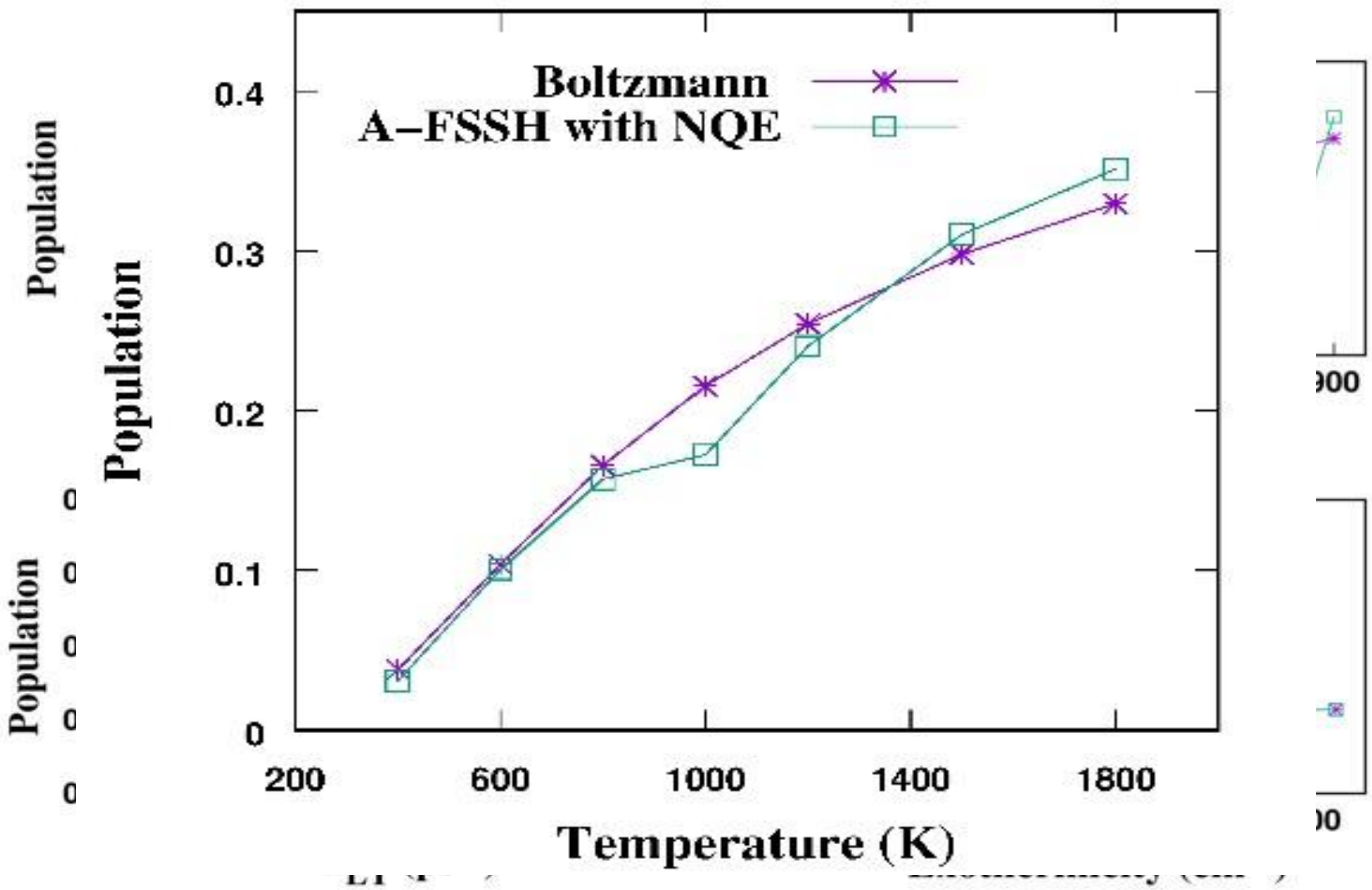
What are we comparing……??

- **The thermal population with that obtained from Boltzmann answer**

- **The rates obtained with that of Marcus rate (without quantization) and FGR (with quantization)**

RESULTS

Thermal Population



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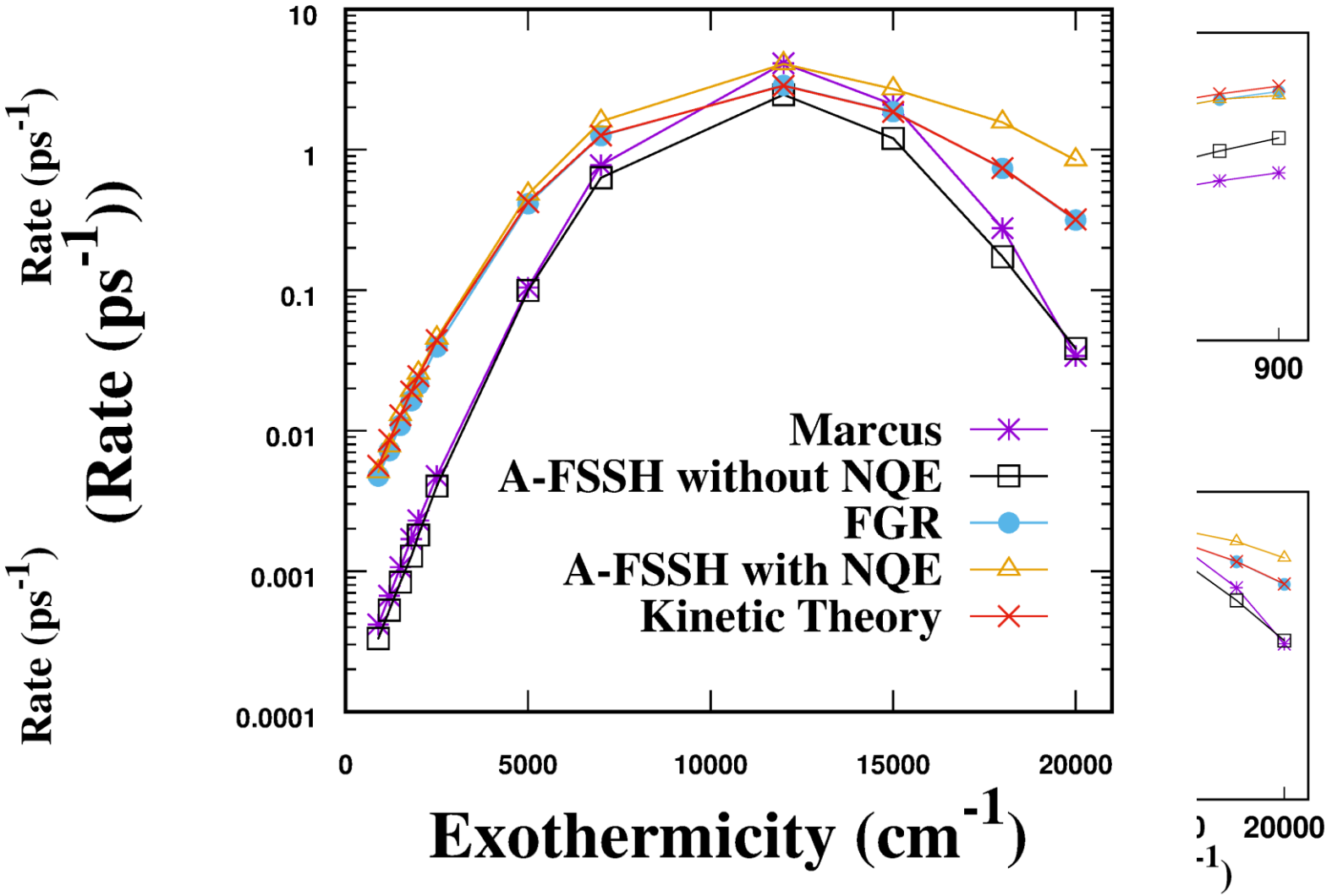
Rates



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JCTC Journal of Chemical Theory and Computation

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Benchmarking the Surface Hopping Method to Include Nuclear Quantum Effects

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Cite This: J. Chem. Theory Comput. 2021, 17, 655−665

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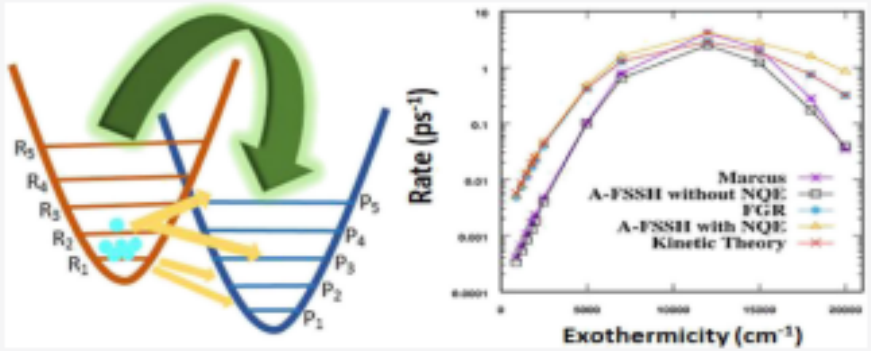
ABSTRACT: We have benchmarked the surface hopping method to capture nuclear quantum effects in the spin-Boson model in the deep tunneling regime. The thermal populations and the rate constants calculated using the surface hopping method are compared with those calculated using Boltzmann theory and Fermi's golden rule, respectively. Additionally, we have proposed a simple kinetic model that partially includes nuclear quantum effects within Marcus theory, and the results of the surface hopping method are analyzed under the framework of this simple kinetic model. A broad range of parameters are investigated to identify the regimes for the successes and failures of the surface hopping method. This work shows that with the accurate treatment of decoherence and velocity reversal, surface hopping can generally capture the nuclear quantum effects in the deep tunneling and weak diabatic coupling regime.

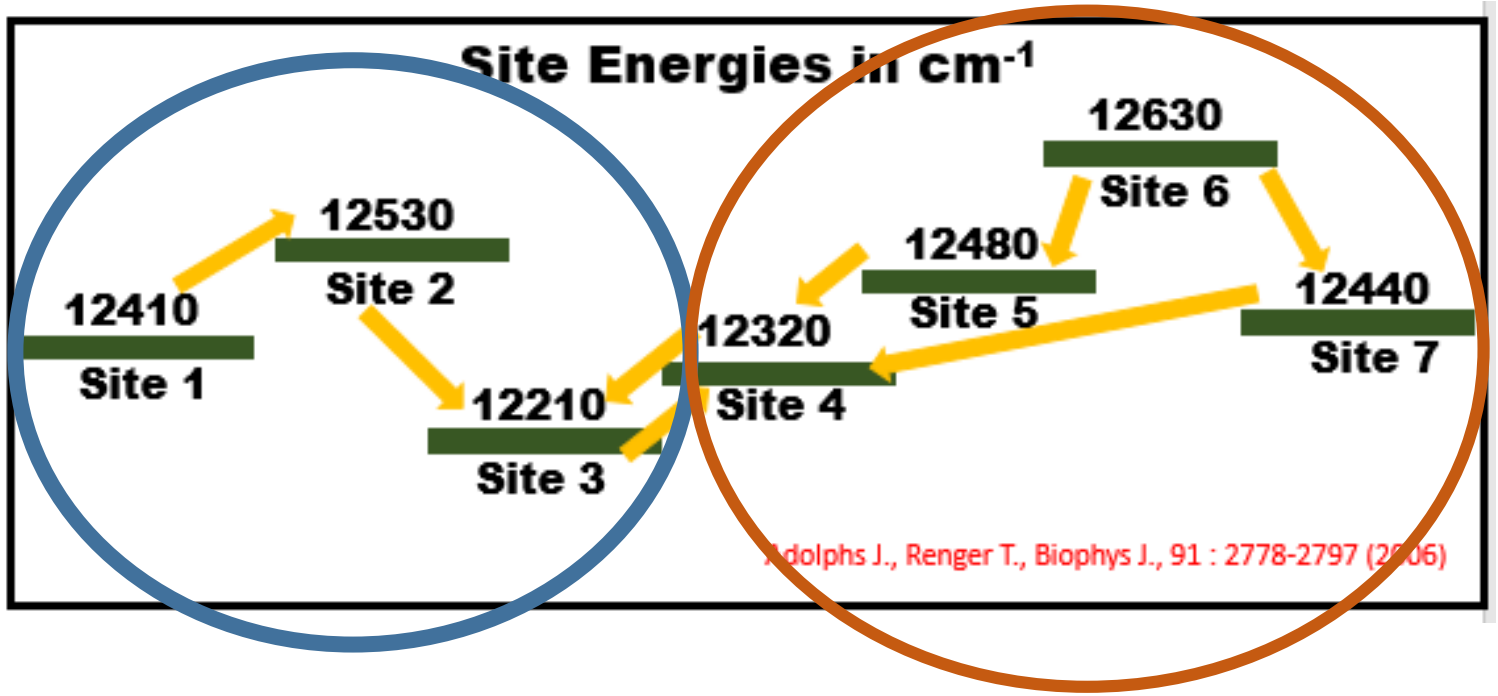


The FMO Model

Reorganization Energy , $\lambda = 35\ cm^{-1}$

Phonon Relaxation time, $1/\eta = 50$ fs

Temperature , $T = 77K$



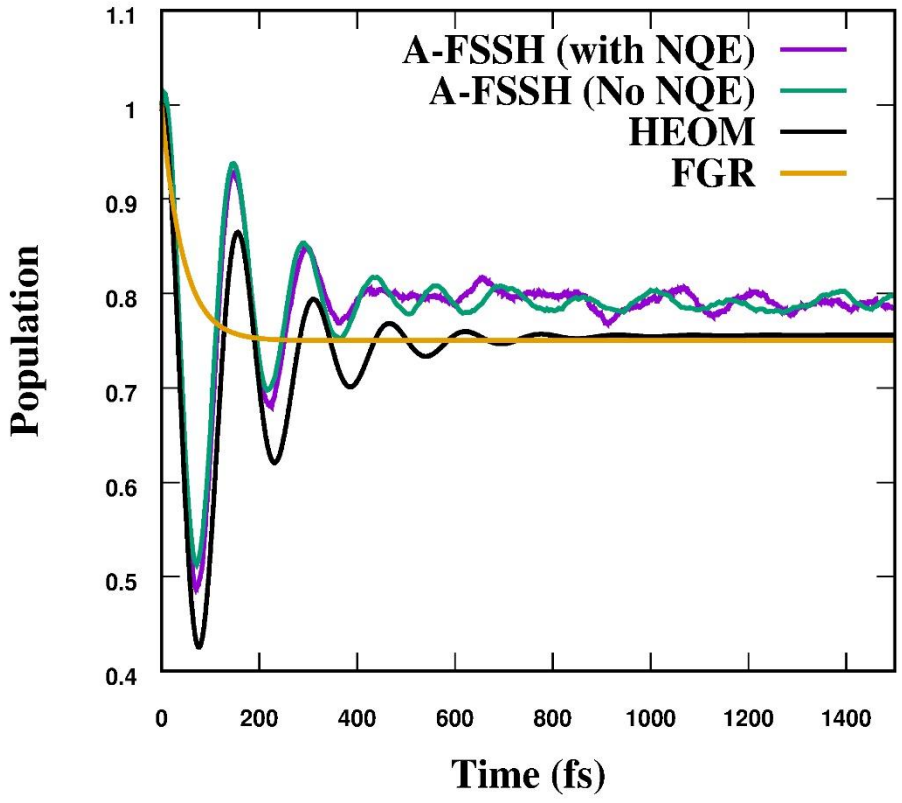
$V_{12} = -87.7$ $V_{23} = 30.8$ $V_{34} = -53.5$ $V_{47} = -63.3$

$V_{45} = -70.7$ $V_{56} = 81.8$ $V_{67} = 39.7$

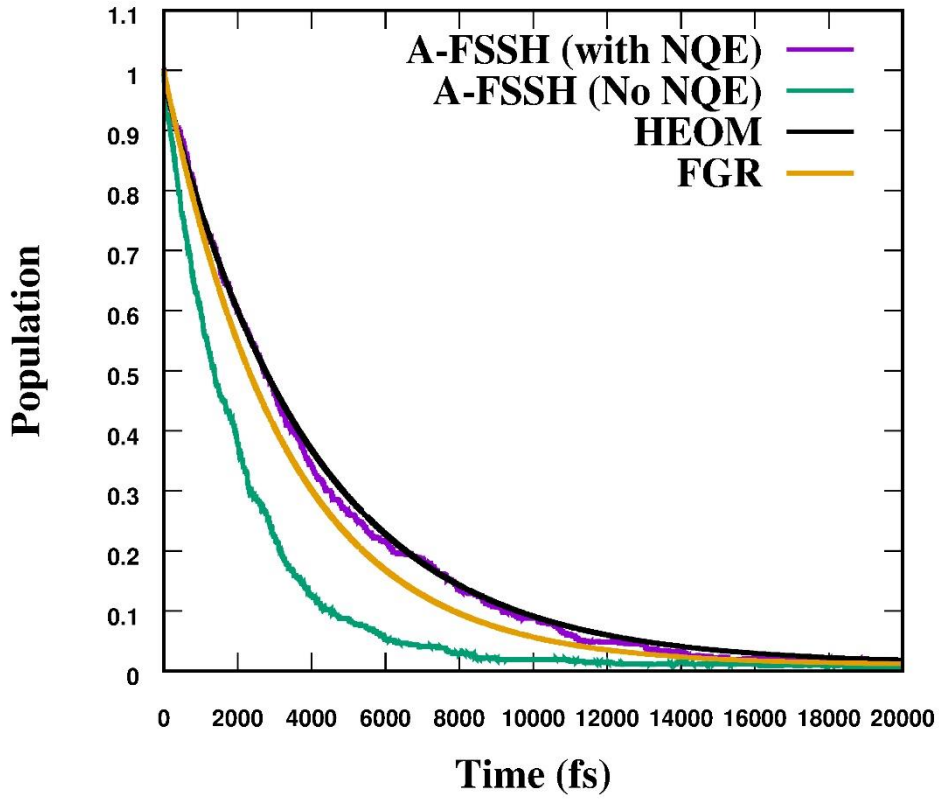
Adolphs J., Renger T., Biophys J., 91 : 2778-2797 (2006).
Ishizaki A. and Fleming G.R., PNAS, 106 : 17255-17260 (2009).

2-site models (1-2) and (2-3)

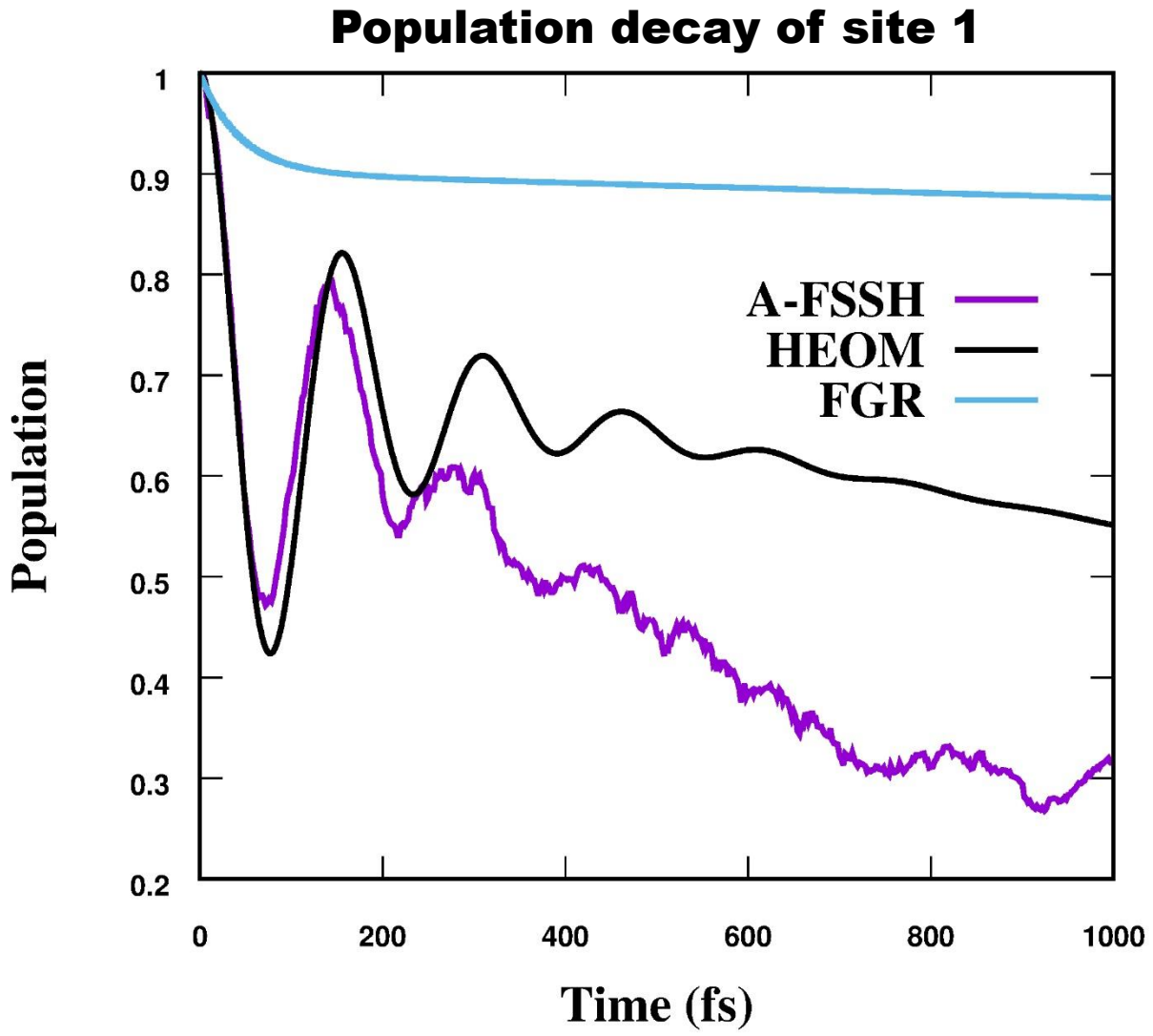
Site 1-2 (population decay of site 1)



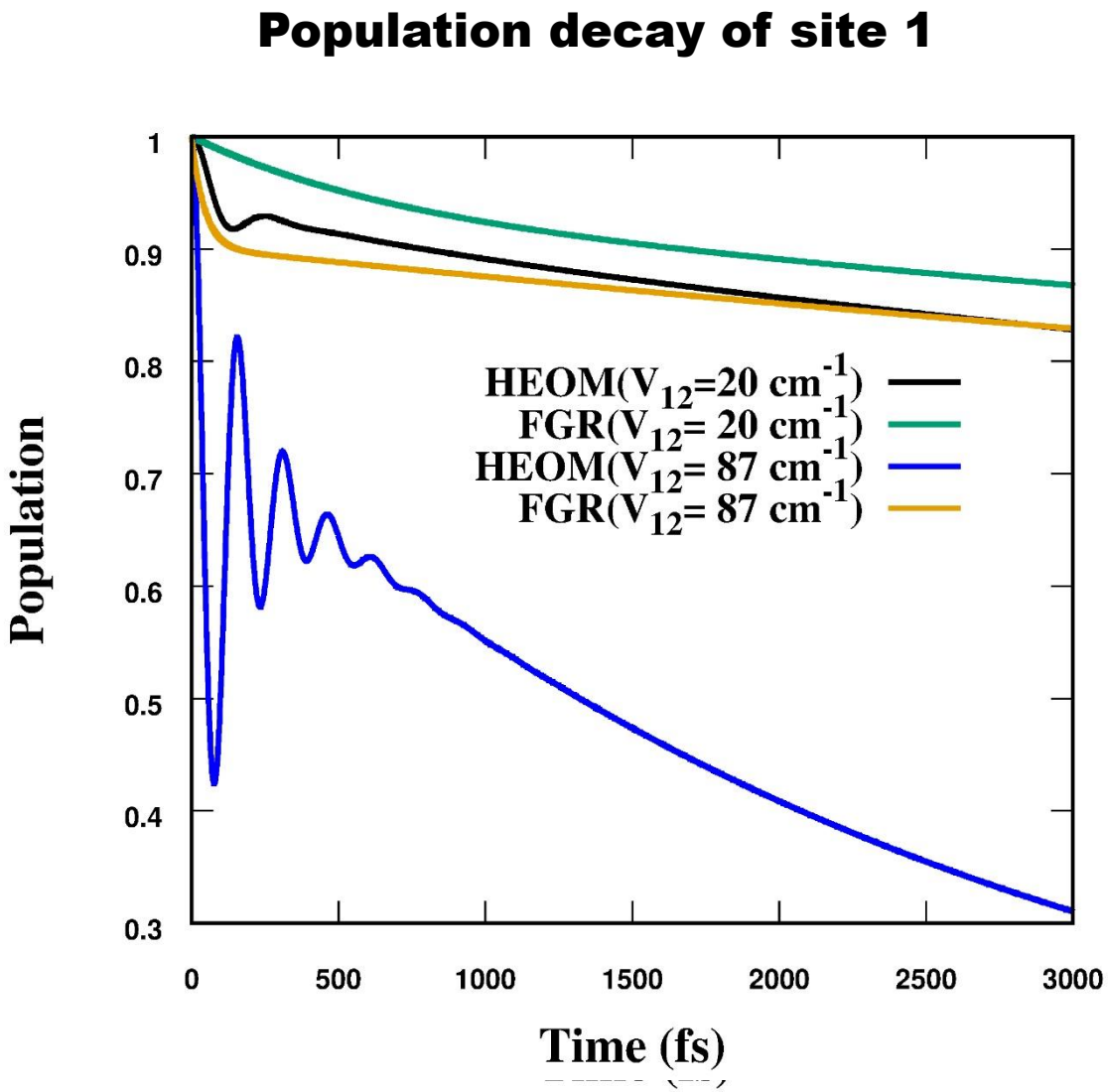
Site 2-3 (Population decay of site 2)



3-Site Model (1-2-3)



3-site Model (When the diabatic coupling (V_{12}) is changed to 20 cm^{-1})



Preliminary Conclusions

- **For the 2 site model, FSSH is in good agreement wit FGR as well as HEOM**
- **The 3 site model, FSSH population decays way faster than HEOM and FGR**
- **Coherences are clearly playing an important role in the dynamics.**

Future Plans

- **Quantifying the efficiency from simulations**
- **Checking of FSSH results (if it is actually the failure of the method or a bug)**
- **Once the 3 site dynamics is correctly set, extending the system to seven sites**

Acknowledgements

High Performance computational facility, Department of Chemistry, IIT Bombay

Questions and suggestions are welcome !!

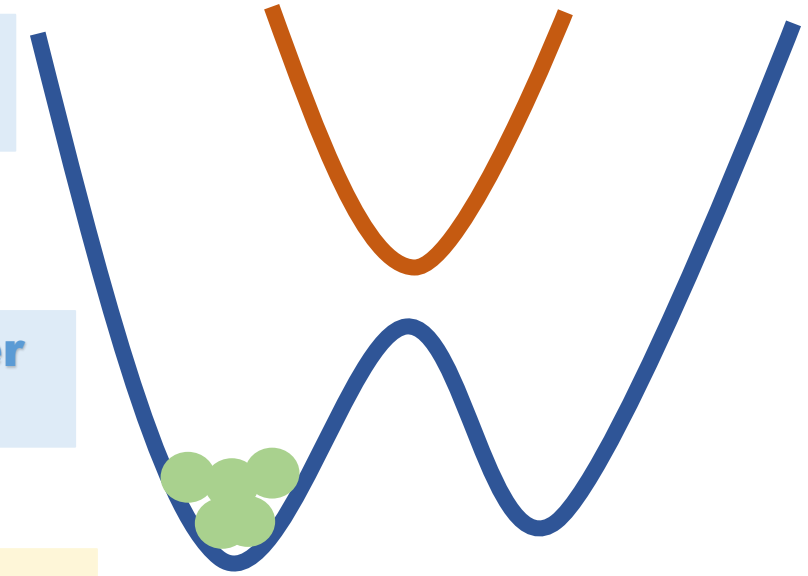
Additional Slides

Frustrated Hops

Check the probability of hopping

Hopping probability is greater than the random number

Let me hop

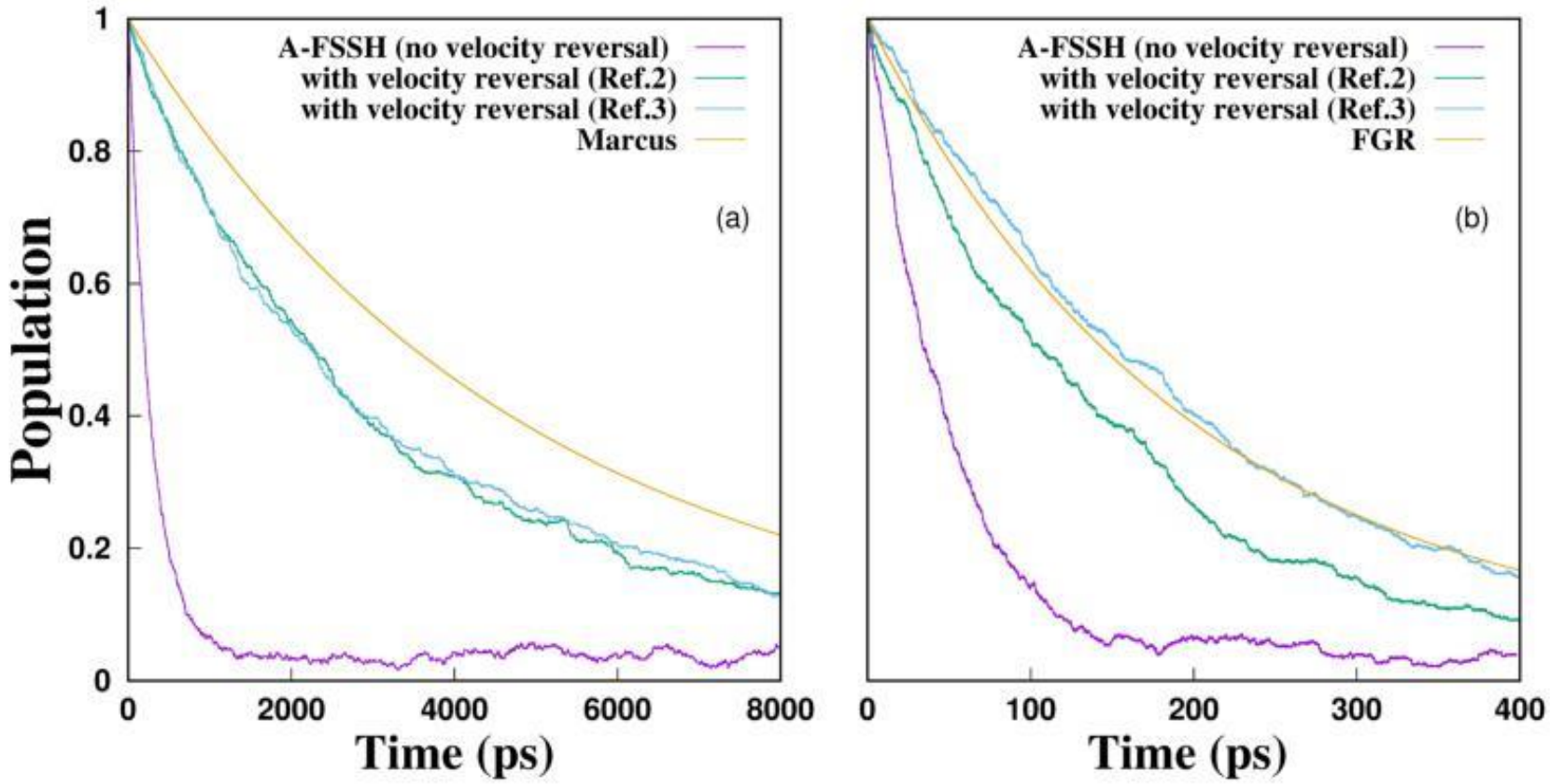


But, Do I have enough energy ?

No

I am Frustrated now

Treatment of Frustrated Hops



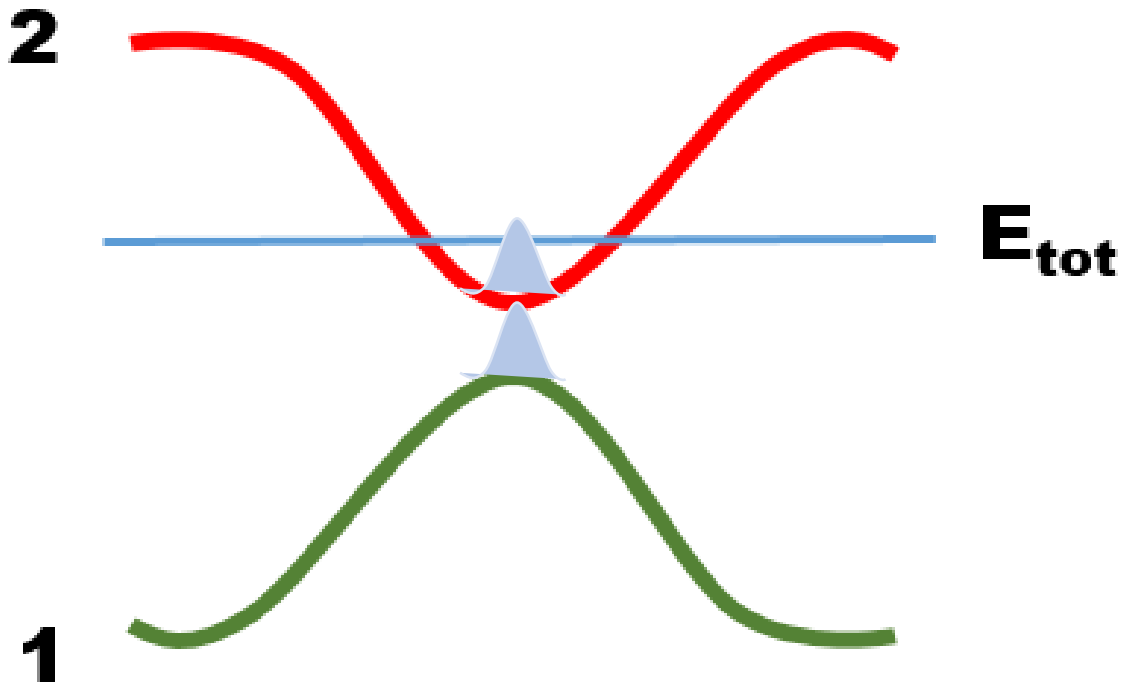
Population decay (a) without including NQE (b) including NQE

Decoherence

$\rho_{\text{final}} = |\phi_R\ 1><\phi_R\ 1| + |\phi_L\ 1><\phi_L\ 1|$

But from surface hopping,

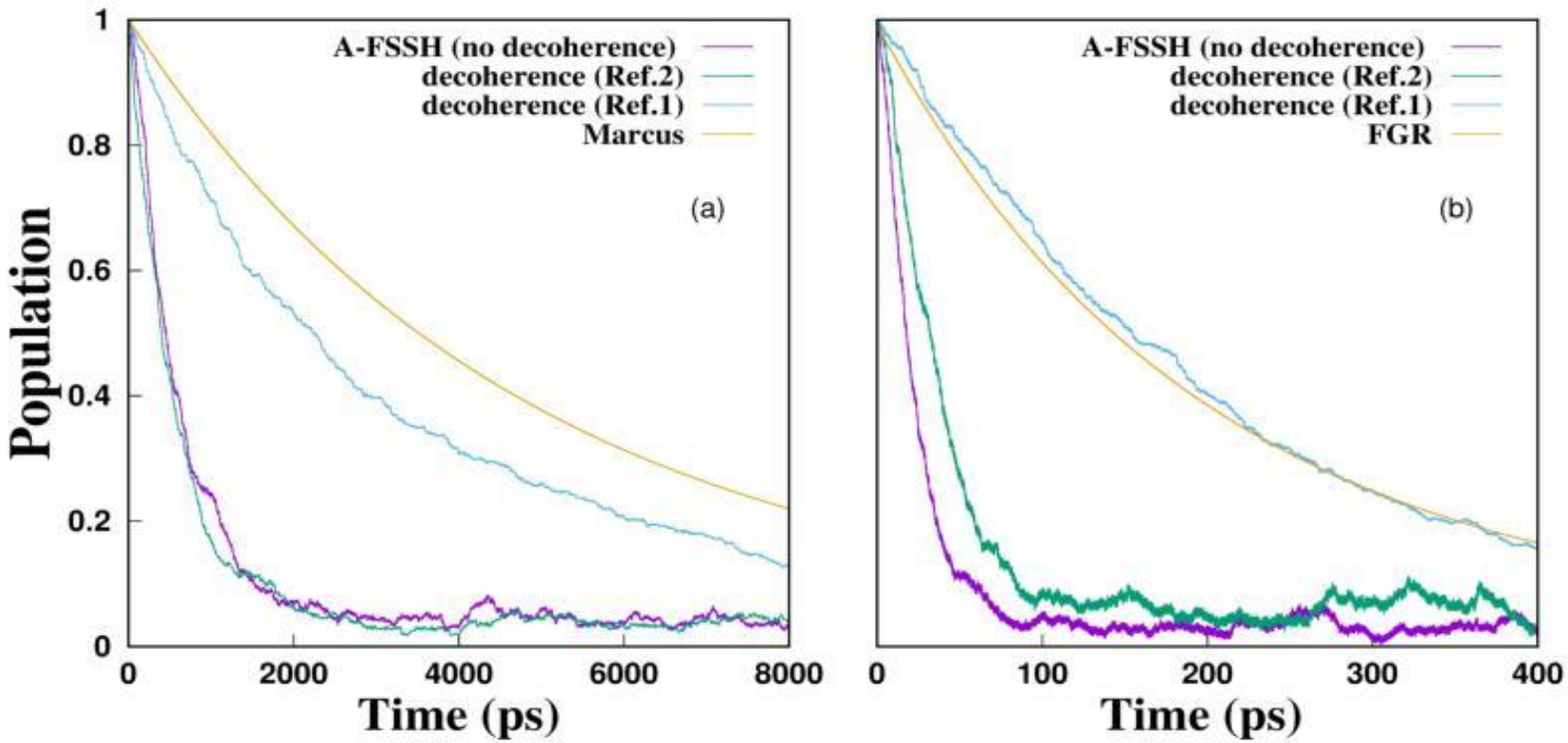
$\rho_{\text{FSSH}} = |\phi_R\ (c_1^R 1 + c_2^R 2)><\phi_R(c_1^R 1 + c_2^R 2)| + |\phi_L\ (c_1^L 1 + c_2^L 2)><\phi_L\ (c_1^L 1 + c_2^L 2)|$



Algorithms for including decoherence

1. **Augmented FSSH (A-FSSH)**
2. **A-FSSH (2016)**

Which version of decoherence is accurate...??



Population decay (a) without including NQE (b) including NQE

Where, $k_1 = \sqrt{0.5 m \omega_1^2 \lambda_1}$ (λ_1 is the reorganization energy for mode x_1)

And $k_2 = \sqrt{0.5 m \omega_2^2 \lambda_2}$

where λ_2 can be estimated by considering mode x_1 coupled to n harmonic oscillators by Brownian spectral density given by :

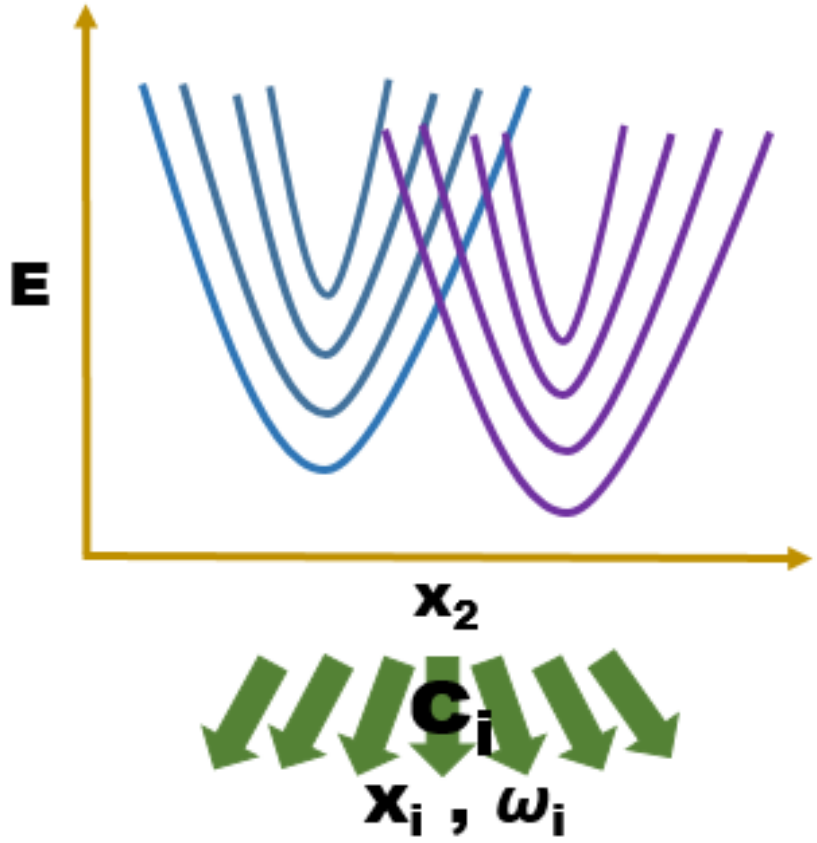
$$J_{brown}(\omega) = \frac{\lambda_2}{2} \frac{\omega_2 \eta \omega}{(\omega^2 - \omega_2^2) + \eta^2 \omega^2}$$

k_2 affects the vibrational energy relaxation rate within the vibrational state of mode x_1 which can be estimated by Landau-Teller Rate :

$$k_{LT} = \frac{\lambda_2}{2} \frac{1}{\beta \hbar \omega_1} \frac{J(\omega_1)}{\omega_1} \frac{\beta \hbar \omega_1}{1 - e^{-\beta \hbar \omega_1}}$$

Quantizing Vibrations

- Mode x_1 is treated quantum mechanically
- We used DVR basis for the purpose
- Eigen functions and Eigen energies are obtained
- Surface hopping dynamics is run on the surfaces in the same way as without quantization



Sharon Hammes-Schiffer and John C Tully, J. Chem. Phys., 101(6):4657–4667, 1994

Parameters

Parameter	Value
Mass (m)	1836 a.u.
Exothermicity (ϵ)	900 cm^{-1} (900 – 20000 cm^{-1})
Diabatic Coupling (V_{12})	150 cm^{-1} (150 – 900 cm^{-1})
Vibrational Energy relaxation rate (k_{LT})	10 ps^{-1} (2 - 25 ps^{-1})
Temperature (T)	400 K (400 - 1800 K)
Reorganization energy of mode x1 (λ_1)	12000 cm^{-1}
Frequency of mode x1 (ω_1)	1200 cm^{-1}
Frequency of mode x2 (ω_2)	400 cm^{-1}
Friction constant (η)	400 cm^{-1}

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Rate Theories

The expression for the Fermi's Golden Rule[1] rate is given by :

$$k_{FGR} = 2V_c^2 \ \mathrm{Re} \int_0^\infty dt e^{-i\epsilon t} \exp\{-\int_0^\infty d\omega \frac{4J(\omega)}{\pi\omega^2} [\coth(\beta\omega/2)(1-\cos\omega t)-i\sin\omega t]\}$$

And the Marcus rate[2] is as follows :

$$k_{Marcus} = \frac{2\pi V_c^2}{\sqrt{4\pi\lambda K_B T}} exp\left(-\frac{(\epsilon-\lambda)^2}{4\lambda K_B T}\right)$$

1. Weiwei Xie, Shuming Bai, Lili Zhu, and Qiang Shi, J. Phys. Chem. A, 117(29):6196–6204, 2013
2. Rudolph A Marcus., Annu. Rev. Phys. Chem., 15(1):155–196, 1964

The Simple kinetic theory assumes the following :

- The model is non-coherent
- Vibrational energy relaxation rate is much faster within in the reactant levels than the population transfer rate
- There is no back reaction i.e., the transmission coefficient is 1
- Works in weak diabatic limit

Discussion

- For the variation of k_{LT}, the rates obtained from FSSH with quantization shows deviation with that of FGR answer in the $k_{LT} < 5\ ps^{-1}$ regime

- To analyze this, we have looked a few pairs of reactant surface (n) and product surface (m), the table shows the FSSH, FGR and Marcus rate for a given pair :

n	m	Regime	P_n^R	K_{nm} (FSSH)	K_{nm} (Marcus)	K_{nm} (FGR)
1	1	**Barrier-less**	0.99	0.012	0.0024	0.0024
1	2	**Normal**	0.99	0.004	0.0035	0.0037
2	1	**Inverted**	0.01	0.027	0.0099	0.0092
2	2	**Barrier-less**	0.01	0.36	0.13	0.14

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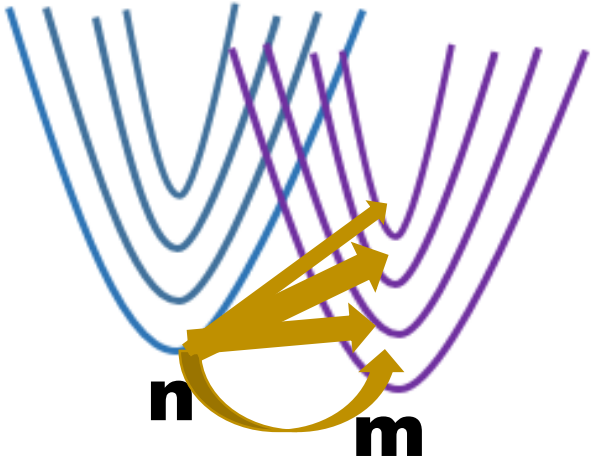
Simple Kinetic Theory

- The model is built to better understand the results obtained from Surface Hopping method
- It partially includes NQE in Marcus theory

The master equation for the rate :

$$k = \sum_n P_n^R \sum_m k_{nm}$$



where P_n^R is the probability of being on the nth reactant energy state and k_{nm} is the Marcus rate from nth reactant state to the mth product state

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