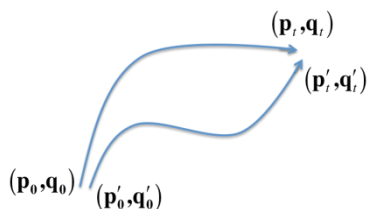


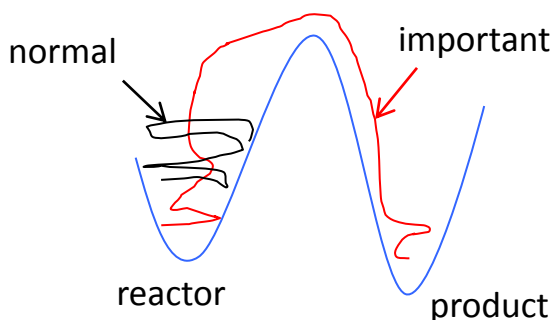
Quantum theory

The development of quantum molecular dynamics (QMD) will start from semiclassical (SC) initial value representation (IVR), incorporating the idea of transition path sampling (TPM) in statistical mechanics and the analysis of topology of phase space structure to improve the efficiency of QMD calculations.

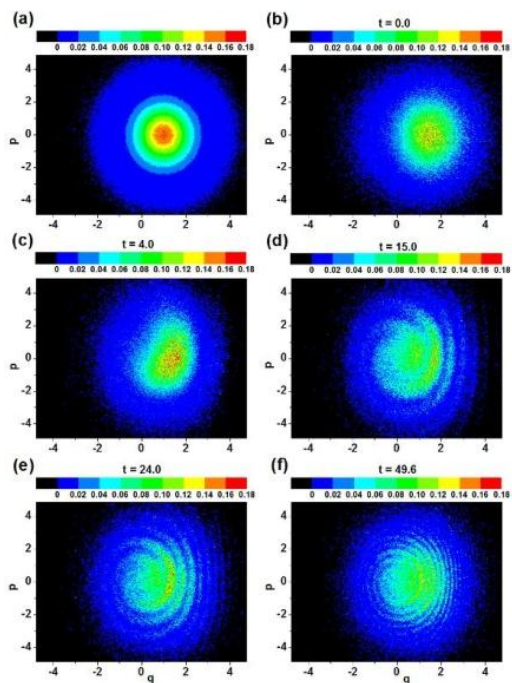
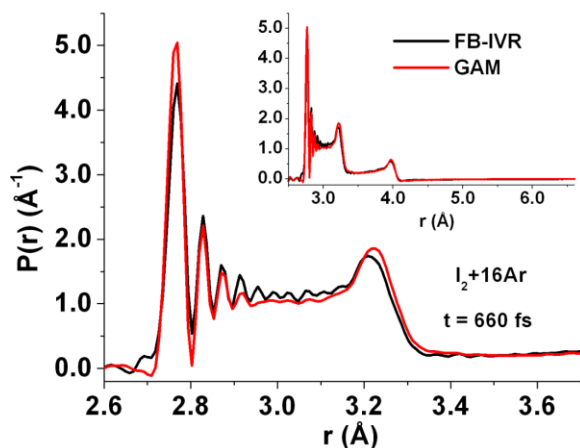
SC-IVR introduces quantum effects through the interferences of trajectories in the phase space average.



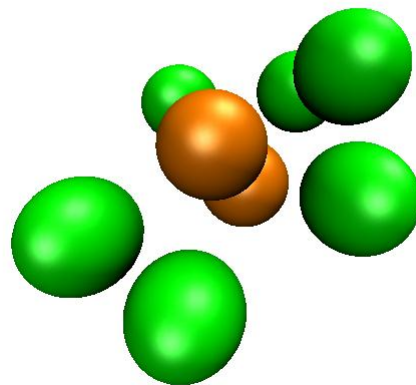
TPM enhance the statistical efficiency by sampling those rare but important trajectories.



Quantum effects in complex molecular systems can be well described by the importance sampling in Gaussian Approximation Method (GAM). The first demonstration of vibrational quantum coherence seen in the nonequilibrium relaxation of a 3D I₂-Ar cluster.



The time-dependent (TD) probability distribution of initial configurations in phase space in the TD-SC-IVR method.

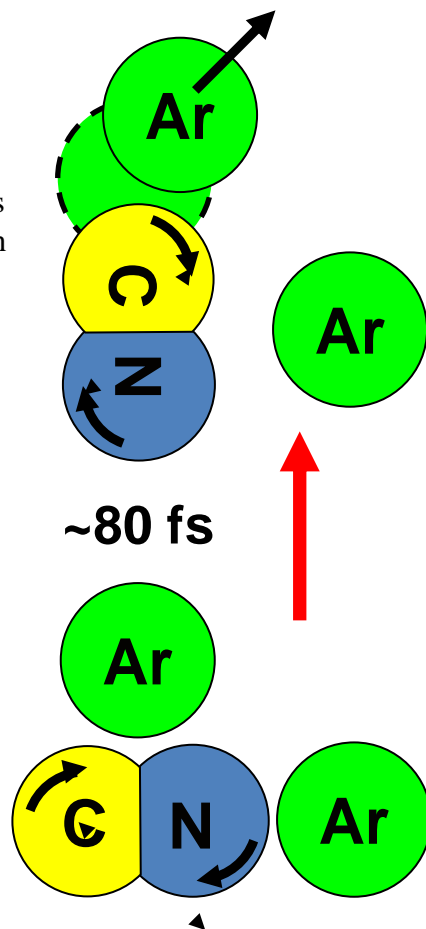
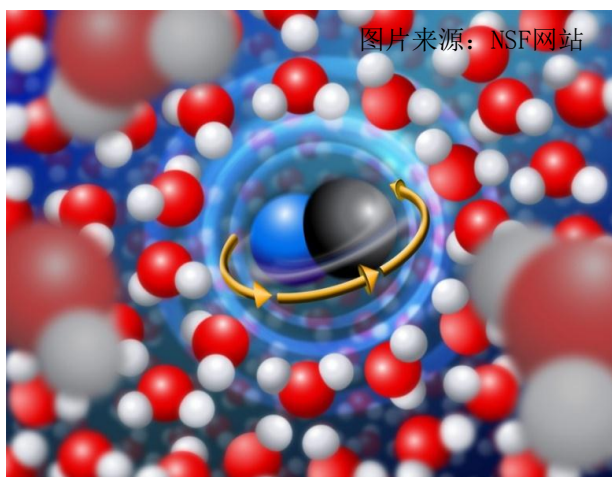


References:

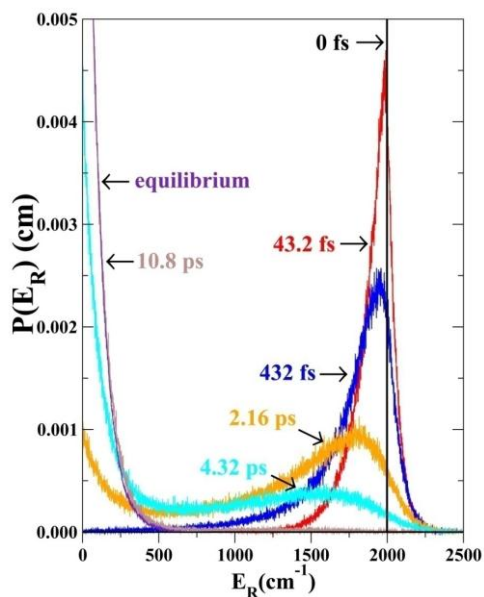
- Tao and Miller, J. Chem. Phys. **130**, 184108 (2009).
- Tao and Miller, J. Chem. Phys. **131**, 224107 (2009).
- Tao and Miller, J. Chem. Phys. **135**, 024104 (2011).
- Tao and Miller, J. Chem. Phys. Submitted.

Nonequilibrium dynamics

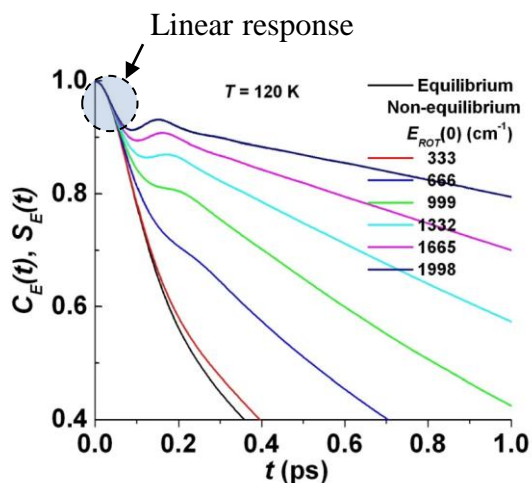
Traditional linear response theory (LRT) states that the nonequilibrium relaxation in the system may be approximated by the equilibrium dynamics. However, it is difficult to describe the far-from equilibrium dynamics in statistical mechanics. Our research found that in the high-energy rotational relaxation process in condensed phase, LRT still works at short time, but breaks down as the solute pushes away the surrounding solvents which slows down the relaxation.



Nonequilibrium rotational relaxation
CN Rotational Energy Distribution



Breakdown of linear response



References:

- A. C. Moskun, A. E. Jailaubekov and S. E. Bradforth
- G. Tao and R. M. Stratt, *Science*, 311, 1907 (2006).
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Nuclear-electronic coupling

Electronically nonadiabatic dynamics

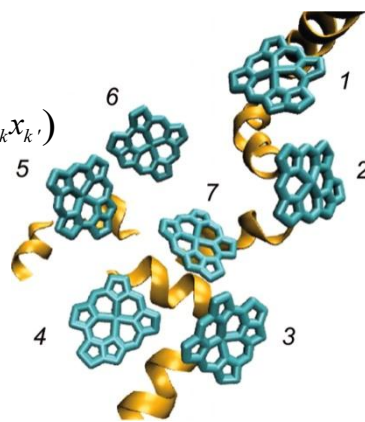
In many photochemical processes, such as photodissociation, valence electron transfer, pericyclic reactions, electron solvation/transfer in interfacial photovoltaic systems and photocatalytic water splitting, Born-Oppenheimer (BO) approximation breaks down while nonadiabatic transitions take place between different BO potential energy surfaces. The origin of electronically nonadiabatic dynamics (ND) is the nuclear-electronic coupling which is indispensable in characterizing important features in chemical reactions, such as reaction rate, branching ratio and catalytic (if any) mechanisms etc. ND is on the frontier of theoretical chemistry. We will develop the efficient nonadiabatic dynamics methodology starting from Meyer-Miller-Stock-Thoss (MMST) theory and SC-IVR. The applications include solar cell, lithium ion battery and 2D atomic crystal.

Nuclear-electronic couplings described by MMST

$$H(\mathbf{P}, \mathbf{R}, \mathbf{p}, \mathbf{x}) = \sum_{k=1}^N H_{kk}(R) \frac{1}{2} (p_k^2 + x_k^2 - 1) + \sum_{k < k'=1}^N H_{kk'}(R) (p_k p_{k'} + x_k x_{k'})$$

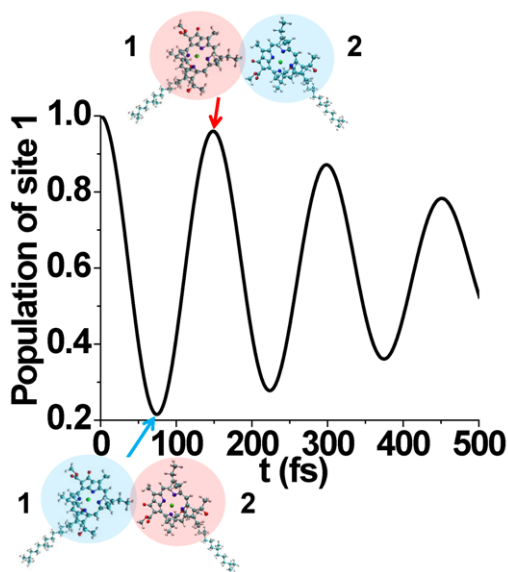
$$H = H^{el} + H^{ph}$$

$$= \begin{pmatrix} \varepsilon_1^0 & J_{12} \\ J_{21} & \varepsilon_2^0 \end{pmatrix} + \begin{pmatrix} H_1^{ph} & 0 \\ 0 & H_2^{ph} \end{pmatrix}$$

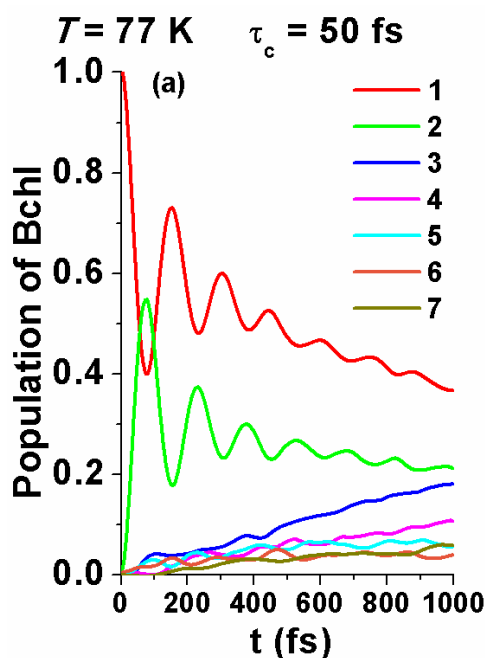


Quantum coherence transfer in excitation energy transfer of BChl molecules in photosynthesis.

Two-states model



7-states model for the FMO pigment-protein complex



References:

Isizaki and Fleming, PNAS, 106, 17255 (2009).

Tao and Miller, J. Phys. Chem. Lett. **1**, 891 (2010).