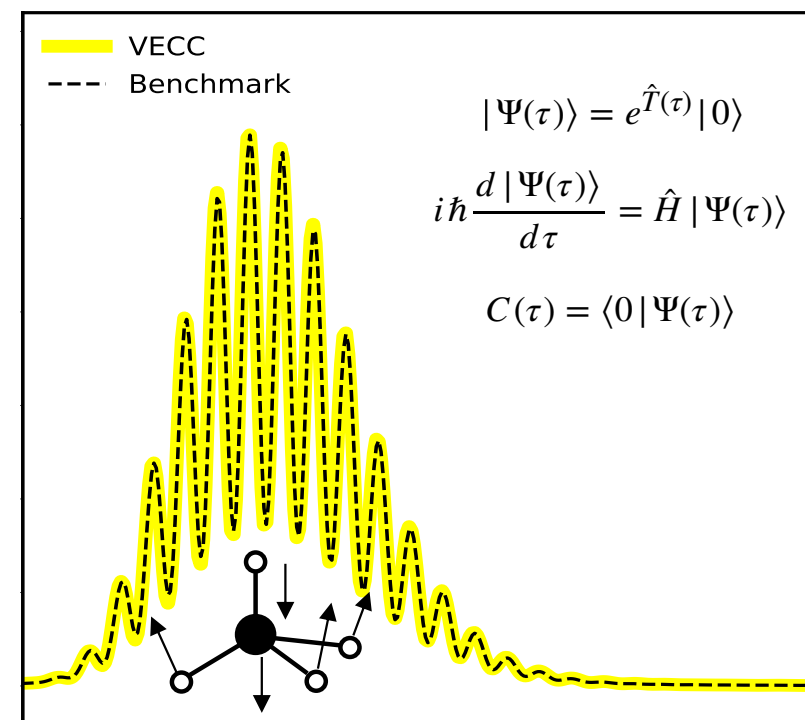
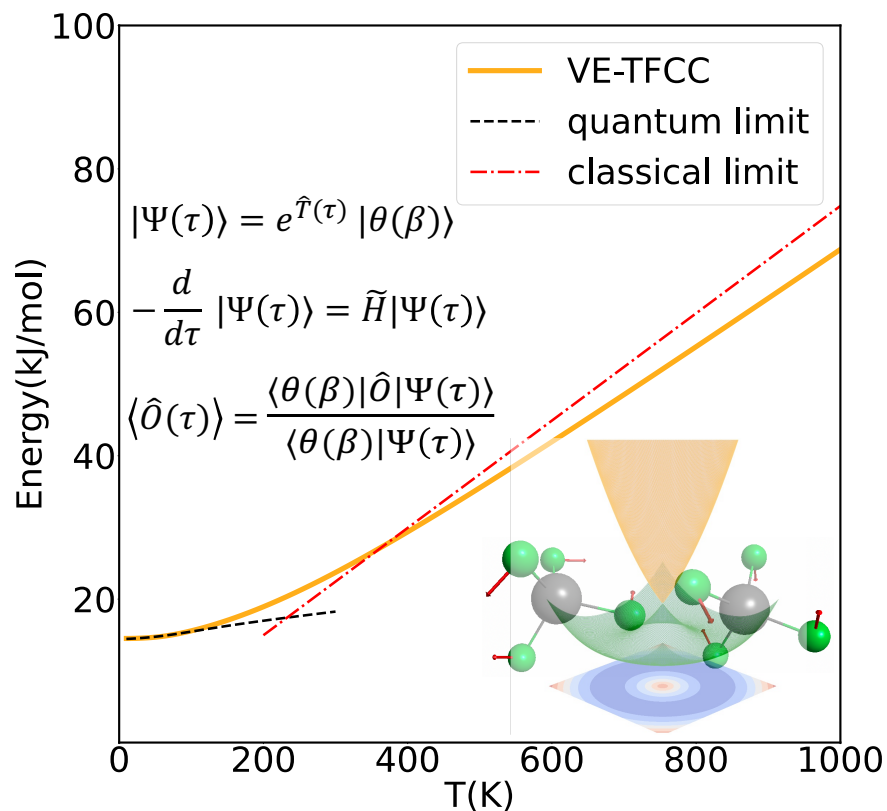


# VISTA talk: Simulating quantum dynamics and thermal equilibrium properties of vibronic coupling system using vibrational electronic coupled cluster (VECC) method

11/1/24

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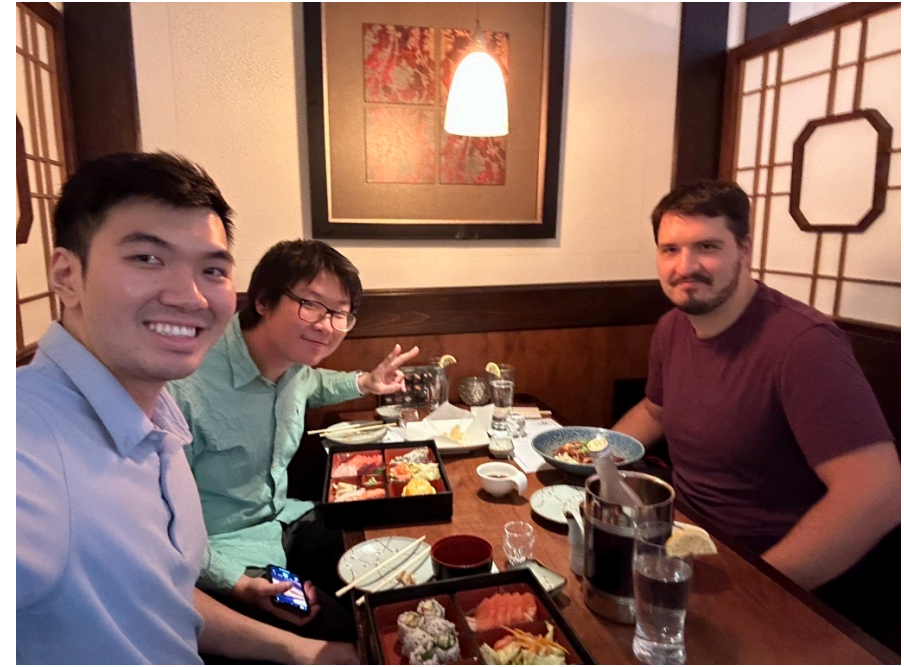
# My collaborator



Prof Marcel Nooijen,  
University of Waterloo



Prof Tao Zeng,  
York University



Dr Neil Raymond and Mr Benny Chen,  
University of Waterloo



# Motivation

- Simulating quantum dynamics of vibronic coupling systems helps understand photo-electron chemical process
- Simulating statistical mechanics of vibronic coupling systems helps understand mechanism of chemical reactions

1. Yaghoubi Jouybari, Martha, et al. *Journal of Chemical Theory and Computation* 16.9 (2020): 5792-5808.
2. Retrieved from: [https://en.wikipedia.org/wiki/Transition\\_state\\_theory](https://en.wikipedia.org/wiki/Transition_state_theory)

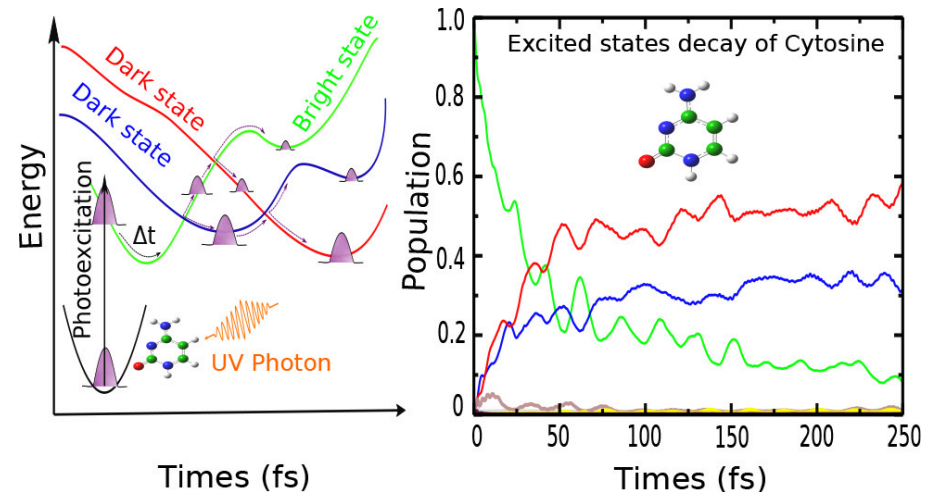


Illustration of the non-adiabatic dynamics process [1]

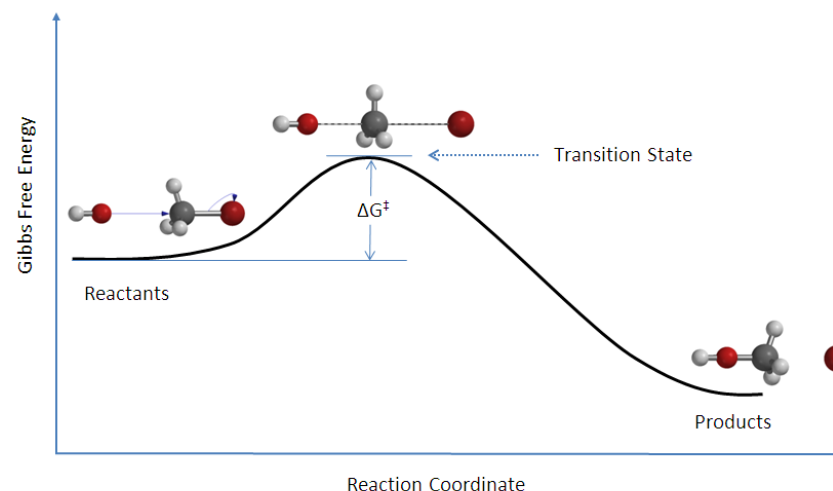


Illustration of the chemical reaction pathway [2]

# Table of content

- General theory: TNOE and TFCC
- Application: electronic structure problem
- Application: vibronic coupling problem

# TNOE and TFCC theory

PHYSICAL REVIEW E

VOLUME 48, NUMBER 5

NOVEMBER 1993

## Thermal averaging in quantum many-body systems: a non-perturbative thermal cluster cumulant approach

Goutam Sanyal, Seikh Hannan Mandal and Debashis Mukherjee<sup>1</sup>

*Theory Group, Department of Physical Chemistry, Indian Association for the Cultivation of Science*

Received 31 January 1992

We present here a non-perturbative cluster cumulant approach for effecting thermal averaging in quantum many-body systems. We introduce a new representation of thermo field dynamics (TFD), with the associated cluster cumulant expansion, and replace the thermal averaging by a quantum mechanical one involving a thermal field theory. In the traditional TFD, only the physical variables appear in our formulation. The imaginary time evolution is treated by our recently developed time-dependent coupled cluster theory. The partition function is expressed as a contracted quantity involving  $|0_\beta\rangle$ . We have computed  $Z$  for an anharmonic oscillator with quartic perturbation. We also demonstrate numerically the validity of the Kohn-Luttinger theorem.

## Systematic nonperturbative approach for thermal averages in quantum many-body systems: The thermal-cluster-cumulant method

G. Sanyal, S. H. Mandal, S. Guha, and D. Mukherjee\*

*Theory Group, Department of Physical Chemistry, Indian Association for the Cultivation of Science, Calcutta 700 032, India*

(Received 5 January 1993)

We present in this paper a systematic nonperturbative cluster-cumulant method for deriving thermal averages of operators in quantum many-body systems. The method combines the advantages of the cumulant expansion scheme of thermodynamic perturbation theory, the approach of thermofield dynamics as a finite-temperature field theory, and the time-dependent coupled-cluster theory extended to “imaginary time.” We have generalized the concepts of cumulants in a nonperturbative manner and have positioned on the statistical operator an exponential-like ansatz containing connected, size-extensive operators in the exponent. These latter cumulantlike operators have been termed “cluster cumulants” by us. For a compact treatment, we have derived an alternative thermal field theory in which a time-ordered product is expanded in terms of “thermal normal products” of operators and thermal contractions—leading to a “thermal Wick’s theorem.” The thermal normal products are the finite-temperature analogs of the ordinary normal products and have zero thermal averages. Operators in these products commute (anticommute) under permutations for bosons (fermions). This thermal representation is shown to be unitarily related to the traditional thermofield dynamics formulation, but has the advantage of using only the physical variables. The imaginary-time evolution of the statistical operator is treated by our recently formulated time-dependent cluster-cumulant theory. The partition function is evaluated as an exponential of a connected quantity. As an illustrative example, we have computed the partition function of an anharmonic oscillator with equally weighted cubic and quartic perturbation for a wide range of coupling, extending to the strongly nonperturbative regime. We study the behavior of free energy in the low-temperature limit and verify numerically the validity of the Kohn-Luttinger theorem [Phys. Rev. **118**, 41 (1960)] for this system. We also show that our formalism is a natural nonperturbative analog of the thermodynamic perturbative theory by showing that a perturbative solution of the thermal-cluster-cumulant equations generates a variation of the Bloch-Balian-de Dominicis theory.

PACS number(s): 05.30.-d, 03.65.Ge

# TNOE and TFCC theory

- Calculate thermal properties:  $\hat{D} \equiv e^{-\beta \hat{H}}$        $\langle \hat{O} \rangle \equiv \frac{\text{Tr}(\hat{O}\hat{D})}{\text{Tr}(\hat{D})}$

$$\overline{\hat{p}^\dagger \hat{q}} \equiv \text{Tr}(\hat{p}^\dagger \hat{q} \hat{D}_0) \equiv f_p \delta_{pq},$$

- TNOE

$$\overline{\hat{p} \hat{q}^\dagger} \equiv \text{Tr}(\hat{p} \hat{q}^\dagger \hat{D}_0) \equiv \bar{f}_q \delta_{pq} \equiv (1 - f_q) \delta_{pq},$$

- TFCC

$$\{\hat{A}\}\{\hat{B}\} = \{\hat{A}\hat{B}\} + \sum \{\overline{\hat{A}\hat{B}}\} + \sum \{\overline{\overline{\hat{A}\hat{B}}}\} + \dots$$

$$|\theta\rangle = e^{-\frac{\beta \hat{h}_0}{2}} e^{\hat{u}} |0, \tilde{0}\rangle$$

$$\hat{H} \xrightarrow{\text{BV trans}} \tilde{H}$$

$$\hat{D} \rightarrow \{e^{\hat{s}}\} \hat{D}_0$$

$$\hat{D} \rightarrow e^{\hat{T}} |\theta\rangle$$

$$\langle \hat{O} \rangle \rightarrow o_0 + \left\langle \left( \{\hat{O}\} \{e^{\hat{s}}\} \right)_{f.c.} \right\rangle$$

$$\langle \hat{O} \rangle \rightarrow \langle \theta | \left( \hat{O} e^{\hat{T}} \right)_{f.c.} | \theta \rangle$$

- The two approaches are equivalent

## Thermofield Theory for Finite-Temperature Electronic Structure

Published as part of *The Journal of Physical Chemistry virtual special issue "MQM 2022: The 10th Triennial Conference on Molecular Quantum Mechanics"*.

Gaurav Harsha,\* Thomas M. Henderson, and Gustavo E. Scuseria

Cite This: *J. Phys. Chem. A* 2023, 127, 3063–3071

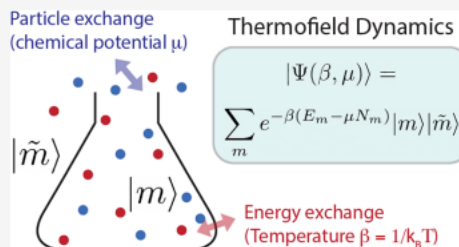
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**ABSTRACT:** Wave function methods have offered a robust, systematically improvable means to study ground-state properties in quantum many-body systems. Theories like coupled cluster and their derivatives provide highly accurate approximations to the energy landscape at a reasonable computational cost. Analogues of such methods to study thermal properties, though highly desirable, have been lacking because evaluating thermal properties involve a trace over the entire Hilbert space, which is a formidable task. Besides, excited-state theories are generally not as well studied as ground-state ones. In this mini-review, we present an overview of a finite-temperature wave function formalism based on thermofield dynamics to overcome these difficulties. Thermofield dynamics allows us to map the equilibrium thermal density matrix to a pure state, i.e., a single wave function, albeit in an expanded Hilbert space. Ensemble averages become expectation values over this so-called thermal state. Around this thermal state, we have developed a procedure to generalize ground-state wave function theories to finite temperatures. As explicit examples, we highlight formulations of mean-field, configuration interaction, and coupled cluster theories for thermal properties of Fermions in the grand-canonical ensemble. To assess the quality of these approximations, we also show benchmark studies for the one-dimensional Hubbard model, while comparing against exact results. We will see that the thermal methods perform similarly to their ground-state counterparts, while merely adding a prefactor to the asymptotic computational cost. They also inherit all the properties, good or bad, from the ground-state methods, signifying the robustness of our formalism and the scope for future development.



efficiently computed using a variational Lagrangian. We discuss the implementation for realistic systems and showcase the potential utility of the method with calculations of the exchange correlation energy of the uniform electron gas under warm dense matter conditions.

# heory body perturbation ical ensemble

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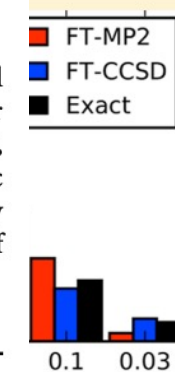
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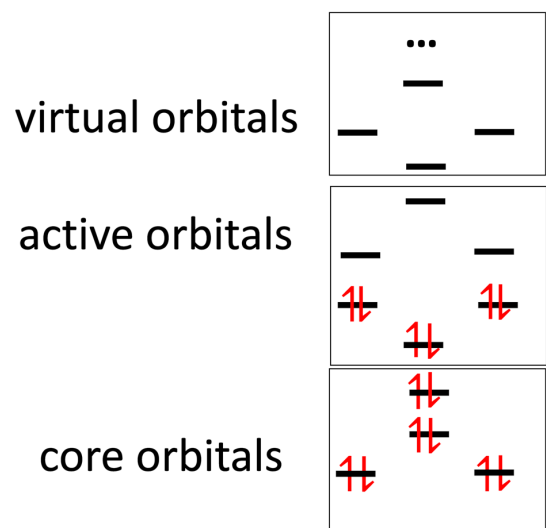
expands in power series the electronic grand potential, chemical potentials and sum-over-orbitals analytical formulas for the second-order correlation energies in a degenerate subspace as well as nine algebraic quantities and products thereof. They reproduce numerically thermal-full-configuration-interaction results for a wide range of



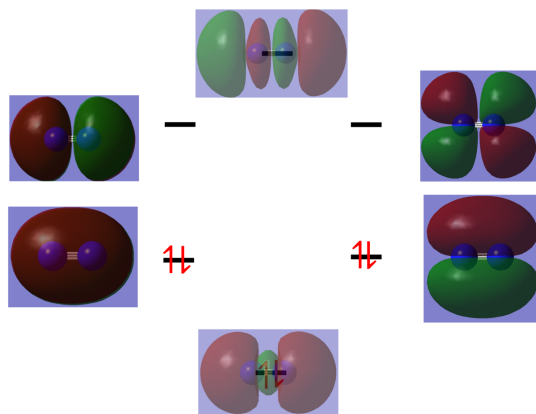
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$k_B T$  (Hartree)

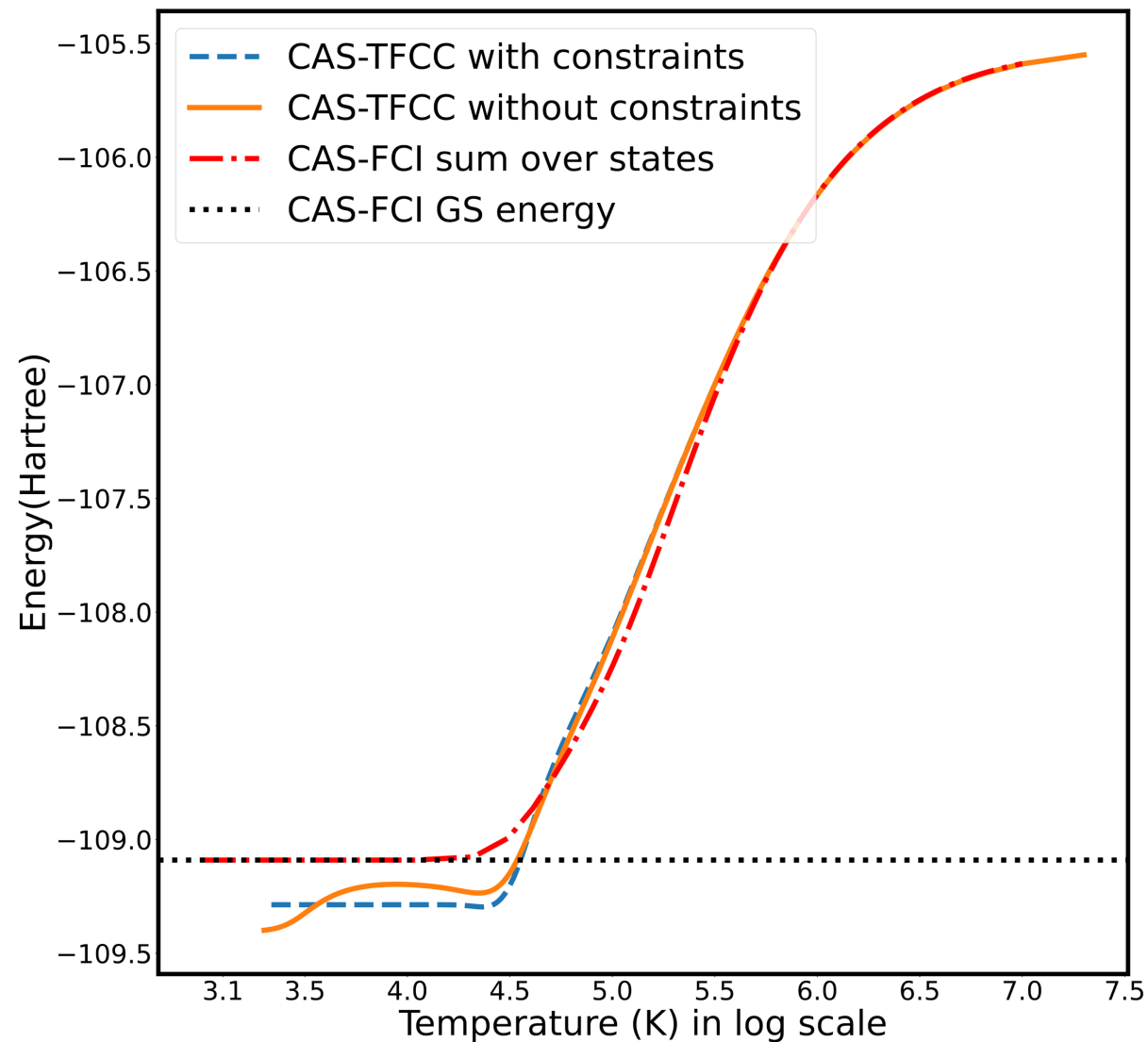
# Application: thermal electronic structure problem



(a) N<sub>2</sub> Occupation scheme



(b) N<sub>2</sub> active orbital





# Application: thermal electronic structure problem

- N-representability problem

$${}^N\hat{D} \equiv \sum_{\lambda} w_{\lambda} |\Psi_{\lambda}\rangle \langle \Psi_{\lambda}| \quad \forall \lambda, w_{\lambda} \geq 0 \text{ and } \sum_{\lambda} w_{\lambda} = 1$$

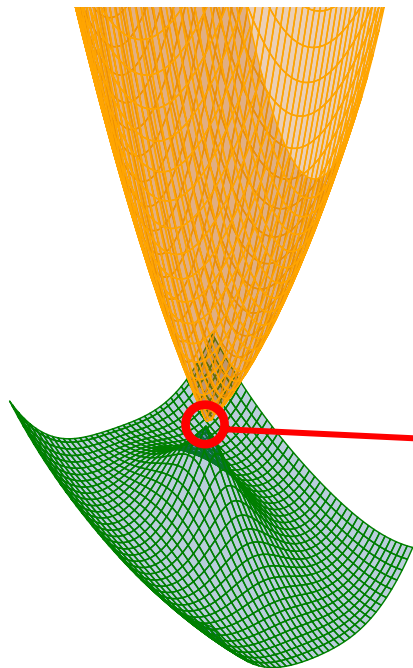
- Positivity constraints

$$\text{Tr}\left(\hat{o}_1^{\dagger}\hat{o}_1^N\hat{D}\right) = \sum_{\lambda} w_{\lambda} \langle \Psi_{\lambda} | \hat{o}_1^{\dagger}\hat{o}_1 | \Psi_{\lambda} \rangle = \sum_{\lambda} w_{\lambda} \langle \Phi_{\lambda} | \Phi_{\lambda} \rangle \geq 0$$

# Application: vibronic coupling problem

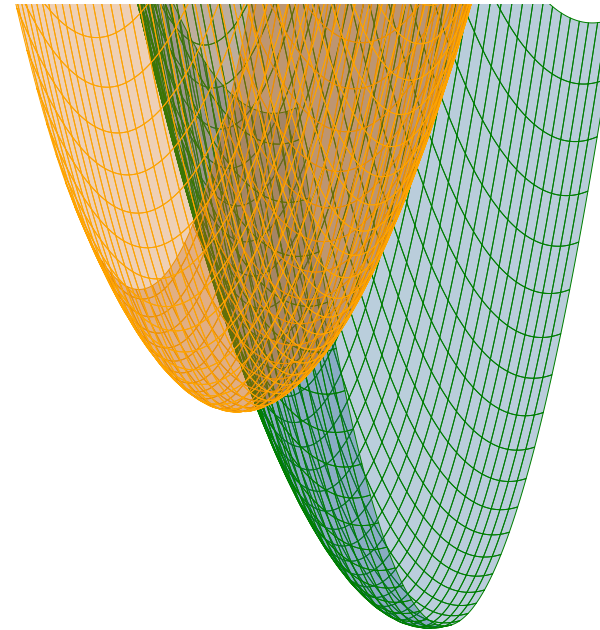
$$\begin{bmatrix} \hat{T}_1 & N.A.C. \\ N.A.C. & \hat{T}_2 \end{bmatrix} + \begin{bmatrix} E_1(\vec{R}) & 0 \\ 0 & E_2(\vec{R}) \end{bmatrix} \xrightarrow{\text{diabatization}} \begin{bmatrix} \hat{T}_1 & 0 \\ 0 & \hat{T}_2 \end{bmatrix} + \begin{bmatrix} \hat{V}_{11}(\vec{R}) & \hat{V}_{12}(\vec{R}) \\ \hat{V}_{21}(\vec{R}) & \hat{V}_{22}(\vec{R}) \end{bmatrix}$$

*Adiabatic PES*



Conical  
intersection

*Diabatic PES*



# Application: vibronic coupling problem

- Vibronic model Hamiltonian in second quantized representation:

$$\hat{H}_{vibr} = \sum_{ab} |a\rangle \langle b| (h_b^a + \sum_i h_b^{ai} \hat{i}^\dagger + \sum_i h_{bi}^a \hat{i} + \sum_{ij} h_{bj}^{ai} \{\hat{i}^\dagger \hat{j}\} + \frac{1}{2} \sum_{ij} h_b^{aij} \{\hat{i}^\dagger \hat{j}^\dagger\} + \frac{1}{2} \sum_{ij} h_{bij}^a \{\hat{i} \hat{j}\})$$

- Time dependent Schrödinger equation (TDSE):

$$i\hbar \frac{d}{dt} |\Psi(t)\rangle = \hat{H}_{vibr} |\Psi(t)\rangle$$

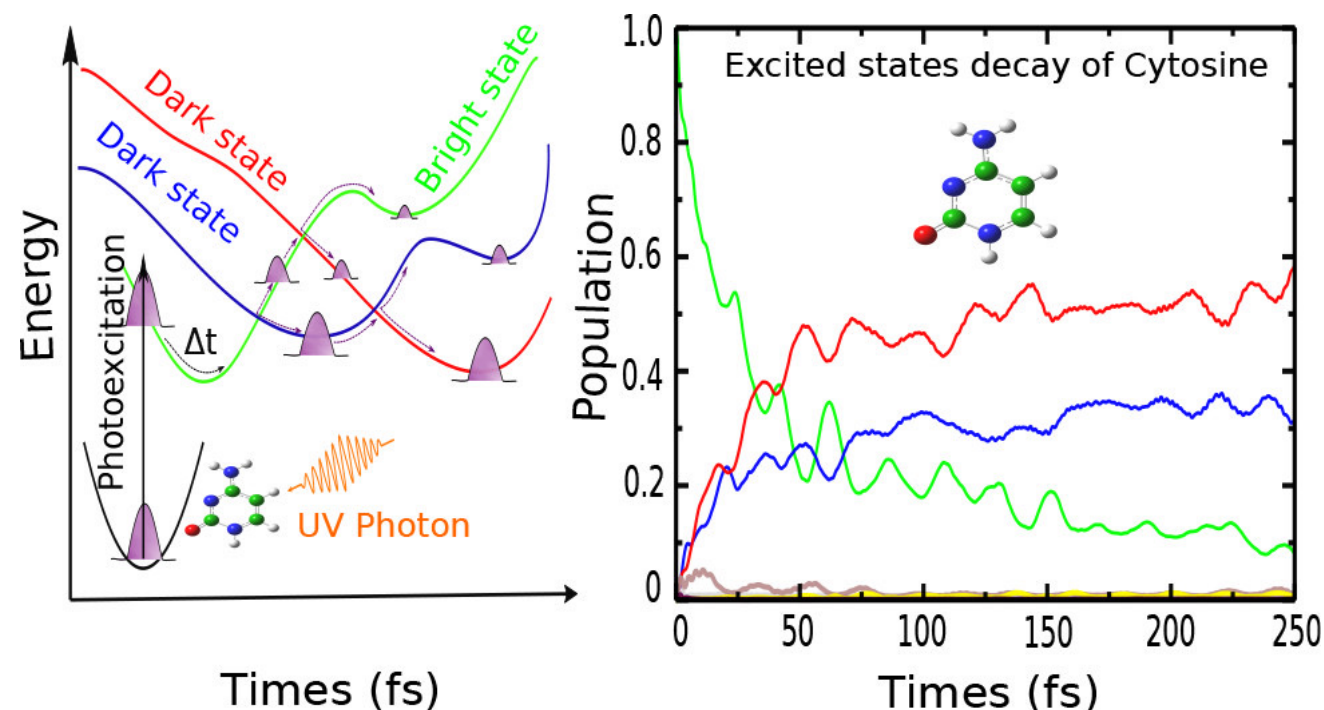


Illustration of the non-adiabatic dynamics process [1]

1. Yaghoubi Jouybari, Martha, et al. *Journal of Chemical Theory and Computation* 16.9 (2020): 5792-5808.

# Application: non-adiabatic nuclear dynamics

$$|\Psi(\tau)\rangle \equiv \sum_{ab} e^{\hat{T}(\tau)} |\Psi(0)\rangle; \hat{T} = \sum_{ab} |a\rangle \langle b| (t_b^a + \sum_i t_b^{ai} \hat{i}^\dagger + \frac{1}{2} \sum_{ij} t_b^{aij} \{\hat{i}^\dagger \hat{j}^\dagger\})$$

- Problem:

1. The exponential ansatz is not unitary:  $(e^{\hat{T}})^\dagger \neq e^{-\hat{T}}$

2. The CC-EOM is not connected:  $\sum_{cd} (e^{-\hat{T}})_{ac} (\hat{H})_{cd} (e^{\hat{T}})_{db} \neq \left( (\hat{H} e^{\hat{T}})_{f.c.} \right)_{ab}$

# Application: non-adiabatic nuclear dynamics

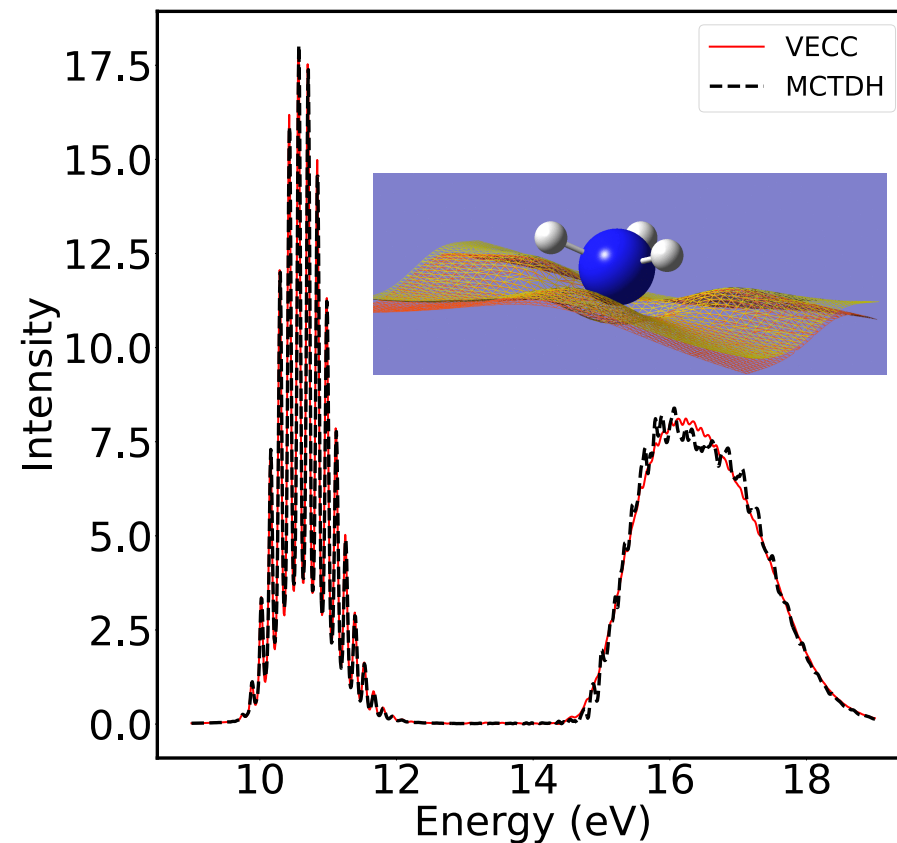
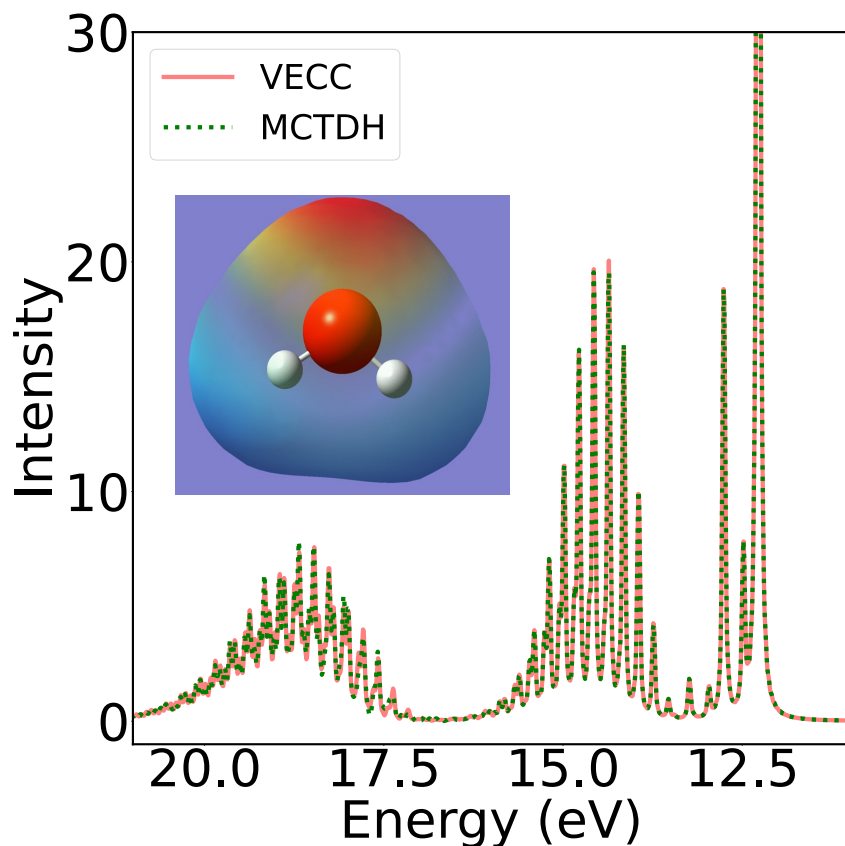
- Solution:

1. Mixed CC/CI ansatz:  $|\Psi(\tau)\rangle \equiv e^{\hat{T}(\tau)} \sum_x \hat{Z}_x(\tau) |0, x\rangle$

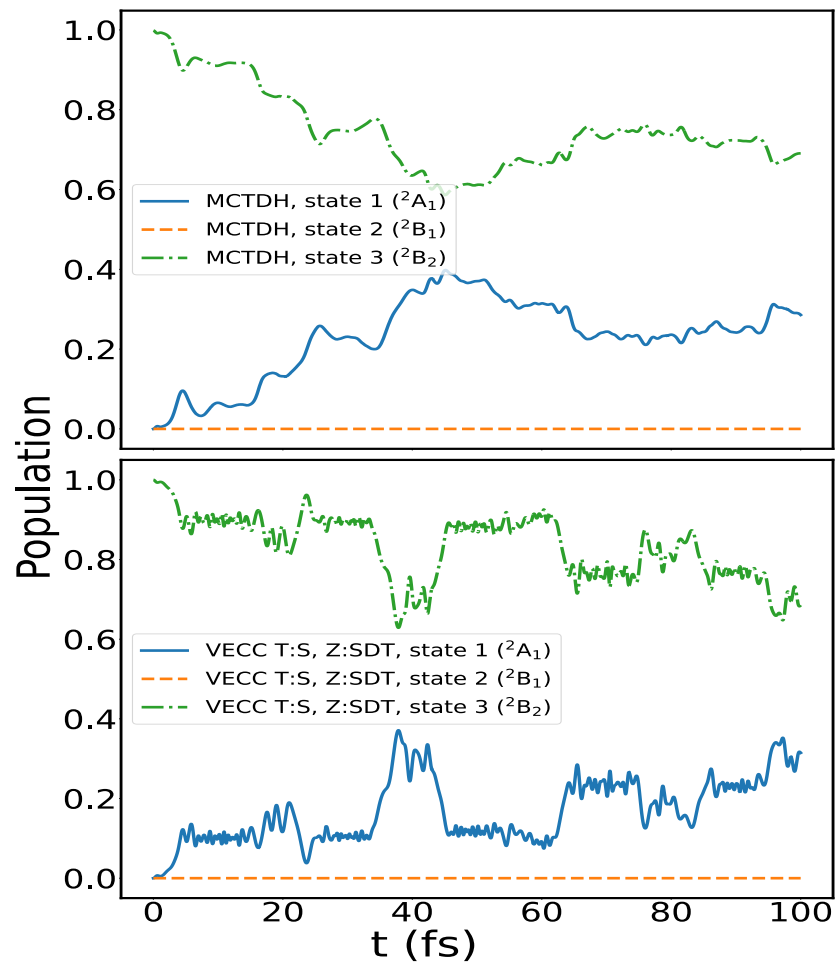
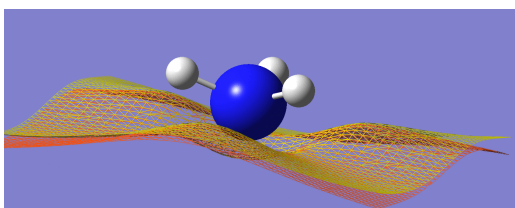
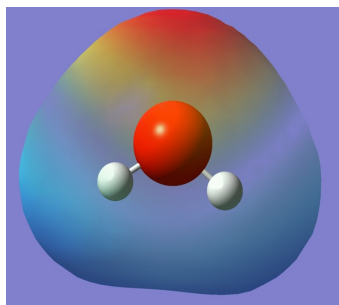
2. Modified projection manifold:  $\langle 0, b | \hat{\Omega}_\mu^\dagger e^{-\hat{T}} \rightarrow \langle 0, b | \hat{\Omega}_\mu^\dagger e^{\hat{T}^\dagger} e^{-\hat{T}}$

3. Ehrenfest parameterization:  $i \frac{dt^i}{d\tau} = \frac{\sum_{xy} (z_y^0)^* \langle y, 0 | \hat{a}_i e^{\hat{T}^\dagger} \bar{H} | x, 0 \rangle z_x^0}{\sum_x (z_x^0)^* z_x^0}$

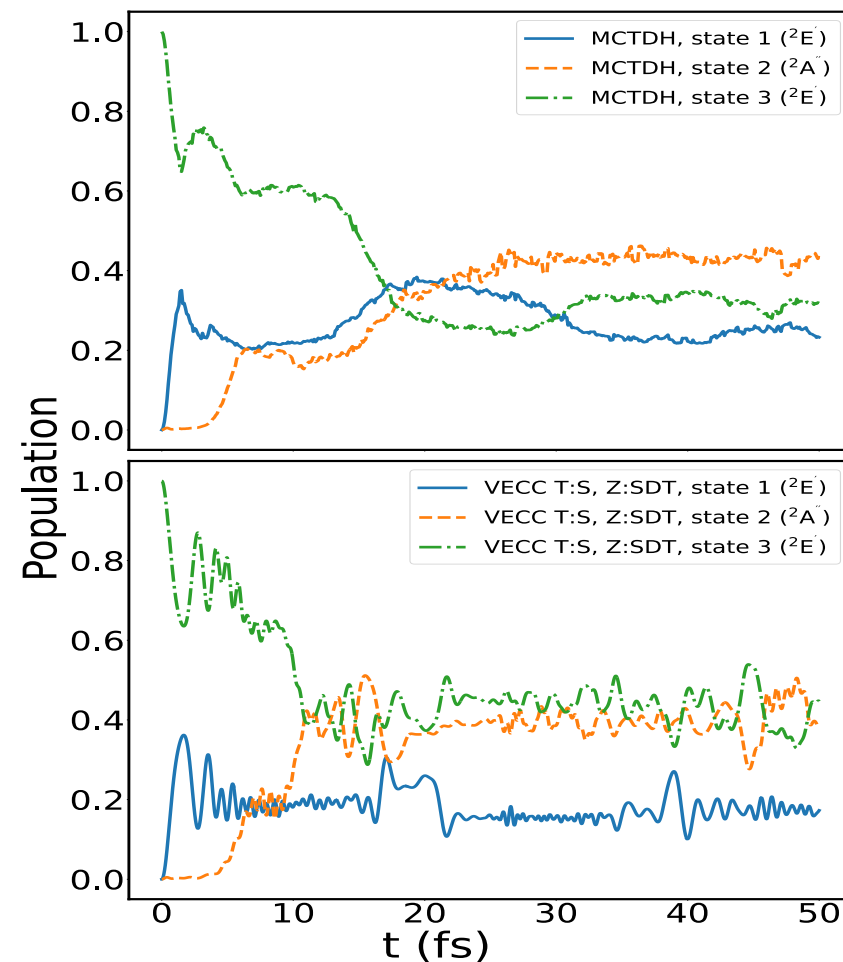
# Application: non-adiabatic nuclear dynamics



# Application: non-adiabatic nuclear dynamics

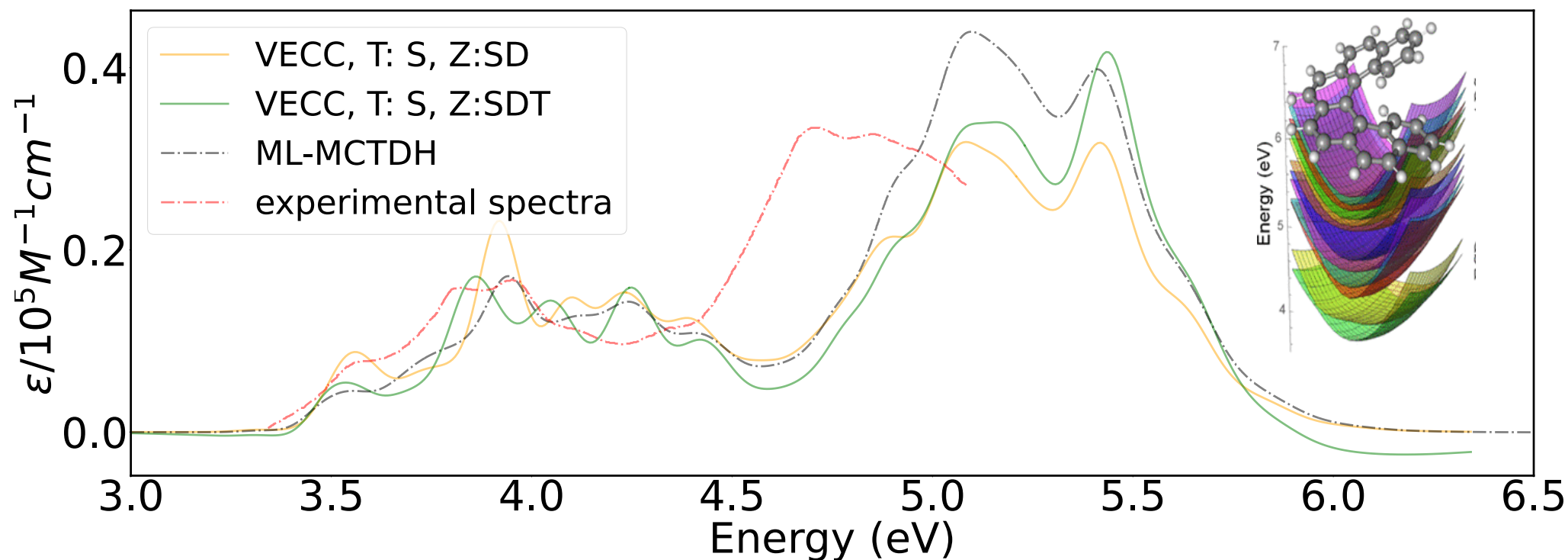


Simulated diabatic state population for water



Simulated diabatic state population for ammonia

# Application: non-adiabatic nuclear dynamics



Experimental and simulation absorption spectra for hexahelicene (14 states, 63 modes)



# Application: thermal properties of vibronic coupling systems

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## Vibrational Electronic-Thermofield Coupled Cluster (VE-TFCC) Theory for Quantum Simulations of Vibronic Coupling Systems at Thermal Equilibrium

Songhao Bao,\* Neil Raymond,\* Tao Zeng,\* and Marcel Nooijen\*



Cite This: *J. Chem. Theory Comput.* 2024, 20, 5882–5900



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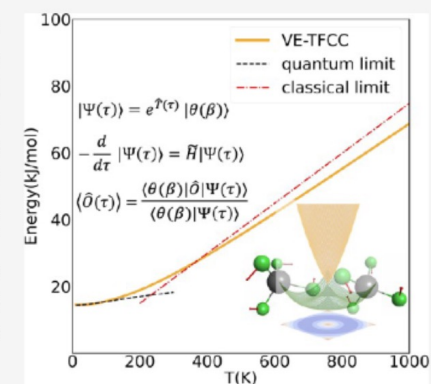
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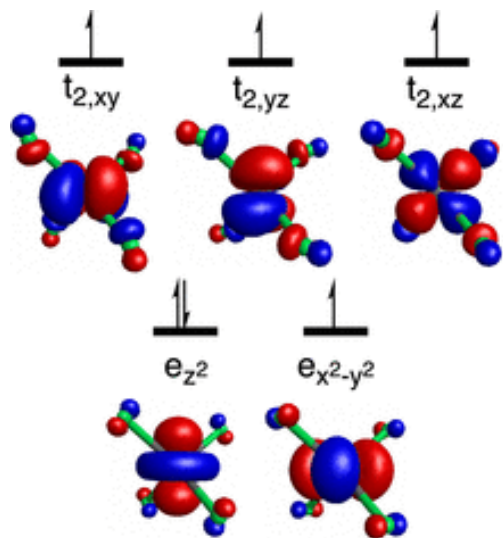
Supporting Information

**ABSTRACT:** A vibrational electronic-thermofield coupled cluster (VE-TFCC) approach is developed to calculate thermal properties of non-adiabatic vibronic coupling systems. The thermofield (TF) theory and a mixed linear exponential ansatz based on second-quantized Bosonic construction operators are introduced to propagate the thermal density operator as a “pure state” in the Bogoliubov representation. Through this compact representation of the thermal density operator, the approach is basis-set-free and scales classically (polynomial) as the number of degrees of freedoms (DoF) in the system increases. The VE-TFCC approach is benchmarked with small test models and a real molecular compound ( $\text{CoF}_4^-$  anion) against the conventional sum over states (SOS) method and applied to calculate thermochemistry properties of a gas-phase reaction:  $\text{CoF}_3 + \text{F}^- \rightarrow \text{CoF}_4^-$ . Results shows that the VE-TFCC approach, in conjunction with vibronic models, provides an effective protocol for calculating thermodynamic properties of vibronic coupling systems.

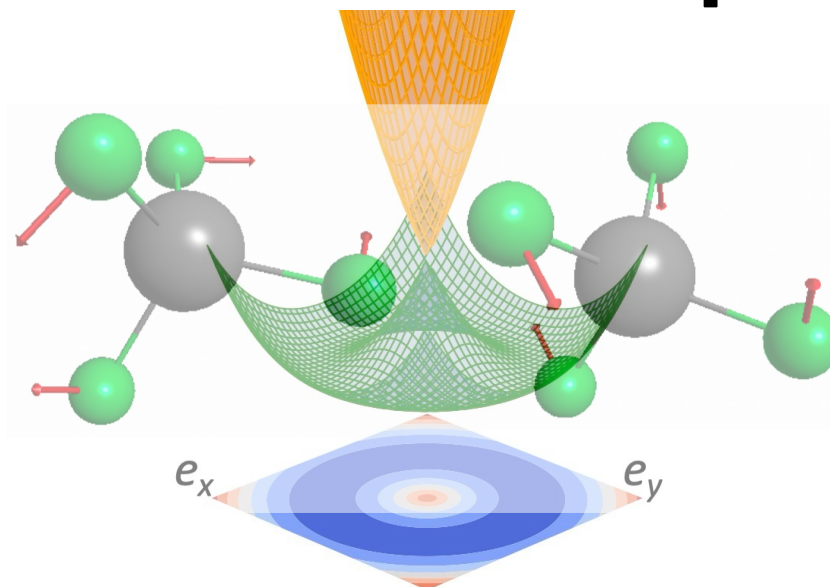


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# Application: thermal properties of vibronic coupling systems



d dominate orbitals of  $\text{CoF}_4^-$  anion



$e \otimes E$  PES of  $\text{CoF}_4^-$  anion

**Table 3. Comparison of Electronic Reaction Energies at 0 K**

method	$\Delta_r E(0 \text{ K})$ (kJ/mol)
CCSD(T)	-392.90
experimental	$-442.0 \pm 25.0$
GMC-QDPT	-479.60

# Application: thermal properties of vibronic coupling systems

- Define the thermal field reference state

$$|\theta\rangle = e^{-\beta\hat{h}_0/2} |u\rangle ; |u\rangle \equiv e^{\hat{u}} |0, \tilde{0}\rangle ; \hat{u} \equiv \sum_i \hat{i}^\dagger \tilde{i}^\dagger ; \hat{h}_0 \equiv \sum_i \omega_i \hat{i}^\dagger \hat{i} + E_0$$

- Bogoliubov transform the Hamiltonian

$$\hat{H} \xrightarrow{\text{Bogoliubov transform}} \tilde{H}$$

$$\begin{bmatrix} \hat{a}_i \\ \hat{b}_i^\dagger \end{bmatrix} = \begin{bmatrix} \cosh\theta & -\sinh\theta \\ -\sinh\theta & \cosh\theta \end{bmatrix} \begin{bmatrix} \hat{i} \\ \tilde{i}^\dagger \end{bmatrix} ; \begin{bmatrix} \hat{a}_i^\dagger \\ \hat{b}_i \end{bmatrix} = \begin{bmatrix} \cosh\theta & -\sinh\theta \\ -\sinh\theta & \cosh\theta \end{bmatrix} \begin{bmatrix} \hat{i}^\dagger \\ \tilde{i} \end{bmatrix}$$

- Map initial cluster amplitudes from the classical limit at high temperature

$$\hat{D}_x \equiv e^{-\beta\hat{H}} |x\rangle \langle x| \equiv e^{\hat{T}} \sum_y \hat{Z}_y |y, \theta\rangle ; Z = \text{Tr}(\hat{D}_x) \approx \prod_i \frac{e^{-\beta(E_x - \sum_i \frac{(\lambda_x^i)^2}{\omega_i})}}{1 - e^{-\beta\omega_i}}$$

$$\hat{T} = \sum_p t^p \hat{p}^\dagger + \frac{1}{2} \sum_{pq} t^{pq} \hat{p}^\dagger \hat{q}^\dagger ; \hat{Z}_y = z_y^0 + \sum_p z_y^p \hat{p}^\dagger + \frac{1}{2} \sum_{pq} z_y^{pq} \hat{p}^\dagger \hat{q}^\dagger$$

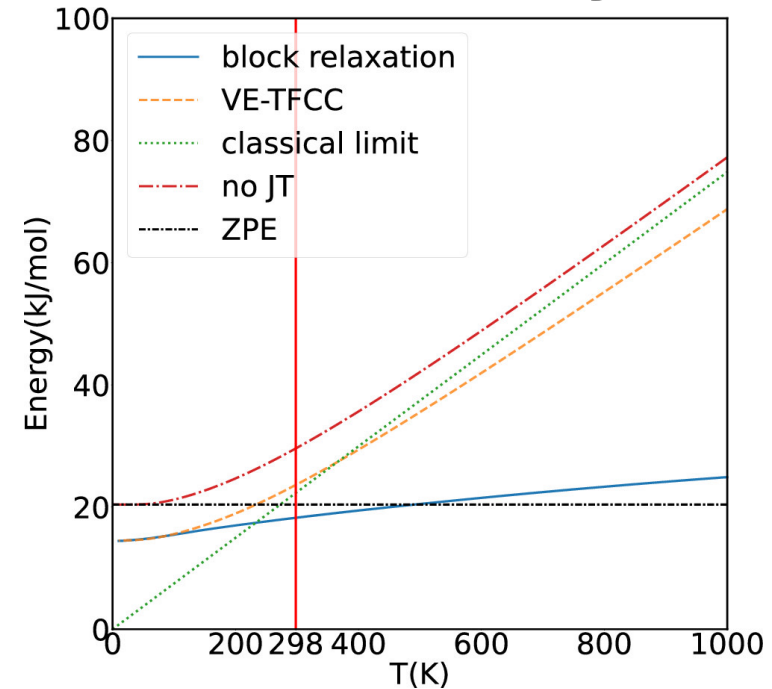
- Solve equation of motion (EOM)

$$-\langle y, \theta | \hat{\Omega}_\nu^\dagger \sum_x \left( \frac{d\hat{T}}{d\beta} \hat{Z}_x + \frac{d\hat{Z}_x}{d\beta} \right) |y, \theta\rangle = \langle y, \theta | \hat{\Omega}_\nu^\dagger \hat{H} \sum_x \hat{Z}_x |x, \theta\rangle$$

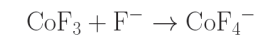
$$-\frac{dt^\nu}{d\beta} = \frac{\sum_{yx}(z^0)_y \langle y, \theta | \hat{\Omega}_\nu^\dagger \hat{H} (z^0)_x |x, \theta\rangle}{\sum_x ((z^0)_x)^2}$$

- Map thermal properties from the cluster amplitudes

$$Z(\beta) = \sum \text{Tr}(\hat{D}_x) = \sum z_x^0 ; E(\beta) = -\frac{d}{d\beta} \ln(Z)$$



We calculate the thermochemistry data for the gas phase chemical reaction:



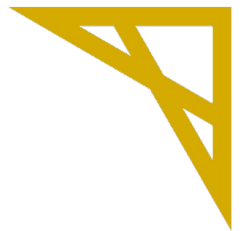
quantity	no JT	static JT	dynamic JT	static – dynamic
$\Delta_r U(0 \text{ K})$	-471.34	-476.34	-477.30	0.96
$\Delta_r U(298 \text{ K})$	-471.18	-475.87	-477.17	1.3
$\Delta_r S(298 \text{ K})$	-0.112	-0.099	-0.109	0.01
$\Delta_r A(298 \text{ K})$	-437.74	-446.40	-444.89	-1.51
$\Delta_r G(298 \text{ K})$	-440.21	-448.88	-447.37	-1.51

Table 1: Summary of the thermochemistry data (Reaction energies and free energies are all in units of kJ/mol and the entropy is in units of kJ/mol/K.)

# Conclusion

- General TNOE and TFCC approaches are developed for stat mech and quantum dynamics simulations in quantum chemistry
- The application of the approach on electronic structure fails to give accurate result due to the N-representability problem.
- The approach with some modifications manage to simulate dynamics and thermal equilibrium properties of vibronic coupling systems with impressive efficiency and accuracy.

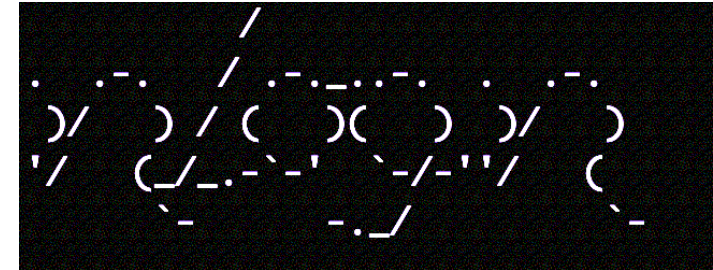
# Acknowledgement



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