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Quantum Coherence in Chemistry: Tackling the Decoherence Challenge  
 Ignacio Franco, University of Rochester  
 Texas Quantum Winter School  
 January 5, 2026

1

**Molecules: highly compact quantum systems with *chemical handles***

Manifolds of transitions in many regions of the electromagnetic spectrum

	Electronic Vibrational Rotational Spin	UV/Vis femtosecond IR 10-100s fs Microwave picoseconds
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Energy levels can be chemically tuned  
**Can be assembled into complex architectures**

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2

## Long standing direction in Chemistry: How can we use quantum coherence to enhance molecular function?

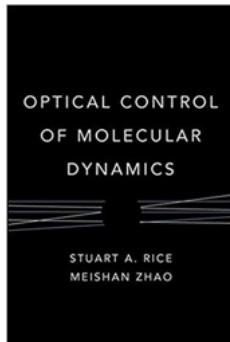
### REVIEW

doi:10.1038/nature21425

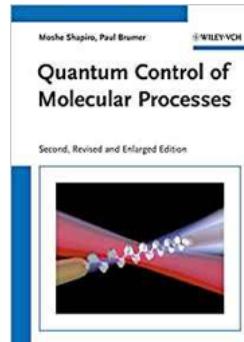
#### Using coherence to enhance function in chemical and biophysical systems

Gregory D. Scholes<sup>1</sup>, Graham R. Fleming<sup>2</sup>, Lin X. Chen<sup>3,4</sup>, Alain Aspuru-Guzik<sup>5</sup>, Andreas Buchleitner<sup>6</sup>, David F. Coker<sup>7</sup>, Gregory S. Engel<sup>8</sup>, Rienk van Grondelle<sup>9</sup>, Akihito Ishizaki<sup>10</sup>, David M. Jonas<sup>11</sup>, Jeff S. Lundeen<sup>12</sup>, James K. McCusker<sup>13</sup>, Shaul Mukamel<sup>14</sup>, Jennifer P. Oglevie<sup>15</sup>, Alexandra Olaya-Castro<sup>16</sup>, Mark A. Ratner<sup>17</sup>, Frank C. Spano<sup>18</sup>, K. Birgitta Whaley<sup>19,20</sup> & Xiaoyang Zhu<sup>21</sup>

30 MARCH 2017 | VOL 543 | NATURE | 647

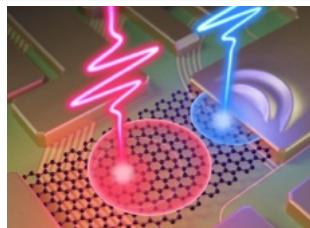


As old as quantum mechanics



3

#### Research in the Franco Group



**Quantum Control of Matter at the Level of Electrons**  
e.g. Nature **605**, 251 (2022)  
PRL **135**, 186901 (2025)

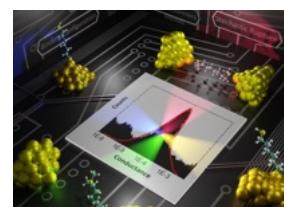


**Quantum Simulation**  
e.g. PRX Quantum **3**, 040308 (2022)



**Protect quantum coherence**  
and you will rule the control and quantum Ren  
world. Coherence is information. foil  
essential for quantum imp

**Quantum Coherence in Matter**  
e.g. PNAS **120**, e2309987120 (2023)  
J. Chem. Phys. **163** 104109 (2025)



**Quantum Transport**  
e.g. Nature Comm. **14**, 7646 (2023)  
JACS **147**, 20310 (2025)

4

## What's the fuzz about quantum coherence



**Coherence is the engine behind all quantum technologies**

**Quantum Control  
Quantum Computation  
Quantum Sensing**



Needed for matter to exhibit interference/controlled entanglement  
Needed for quantum unitary dynamics

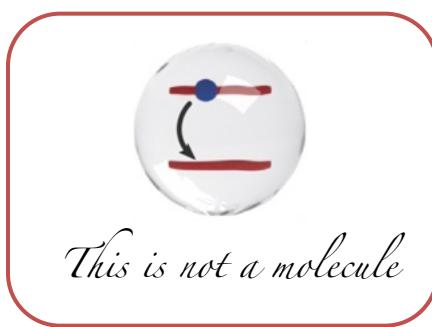
**Enhanced temporal coherence leads to enhanced laser spectroscopy**

**Quantum coherence opens new routes to control reactivity/ electron transfer**

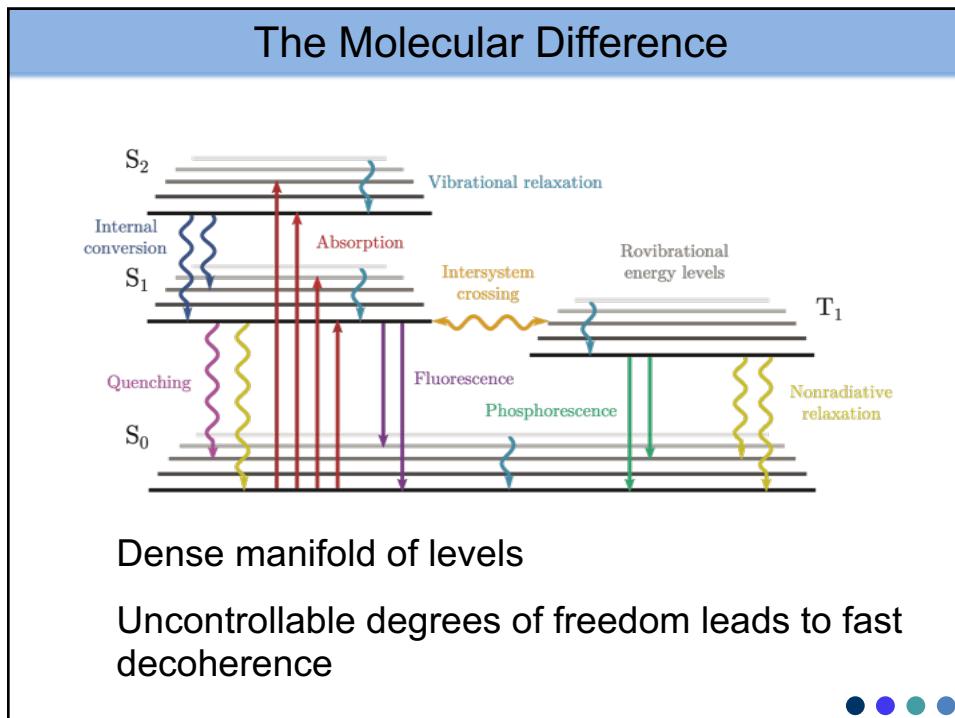


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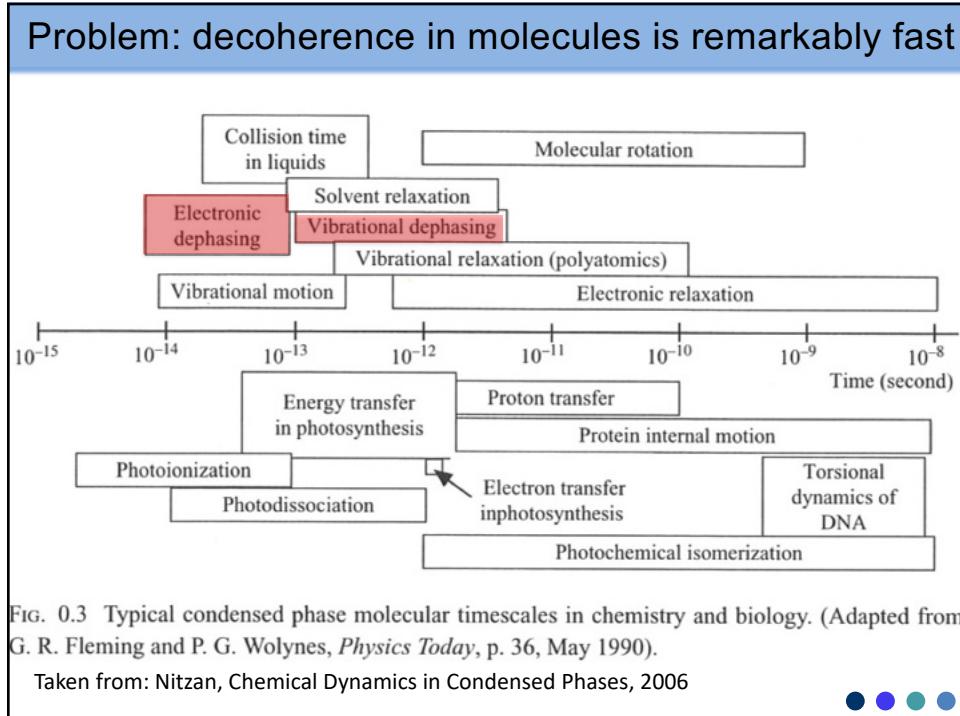
## The Molecular Difference



6



7



8

## Two direction, some common challenges

Molecular Qudits



Quantum technologies

Quantum resources  
(entanglement/coherence)



New Chemistry



9

## Two direction, common challenges

Molecular Qudits



Quantum technologies

Quantum resources  
(entanglement/coherence)



New Chemistry

Dense manifold of levels



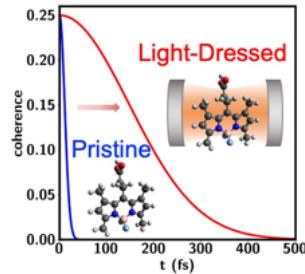
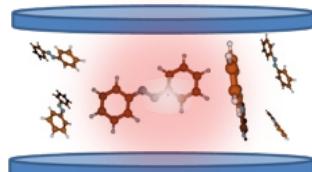
Entanglement-rich, but  
hard to control

Quantum decoherence



10

## Tuning and Enhancing Quantum Decoherence



$$|\sigma_{nm}(t)|^2 = |\sigma_{nm}(0)|^2 \exp(-t^2/\tau_{nm}^2)$$

$$\tau_{nm} = \frac{\hbar}{\sqrt{4\lambda k_B T}} \alpha_{nm}$$

coherence  
enhancement  
due to cavity!

bare molecule

Wu, Gustin, IF, J. Phys. Chem. Lett. **13**, 11503 (2022) (single molecule)  
Herrera, Spano Phys. Rev. Lett. **116**, 238301 (2016) (many molecules)



11

## Long-lived electronic coherences

nature  
chemistry

ARTICLES

<https://doi.org/10.1038/s41557-022-00998-x>

Check for updates

### Functionalizing aromatic compounds with optical cycling centres

Guo-Zhu Zhu <sup>1</sup>, Debayan Mitra <sup>2,3,7</sup>, Benjamin L. Augenbraun <sup>2,3</sup>, Claire E. Dickerson <sup>3,4</sup>, Michael J. Frim <sup>1</sup>, Guanming Lao <sup>3</sup>, Zack D. Lasner <sup>2,3</sup>, Anastassia N. Alexandrova <sup>3,4,5</sup>, Wesley C. Campbell <sup>1,5,6</sup>, Justin R. Caram <sup>4,5</sup>, John M. Doyle <sup>2,3</sup> and Eric R. Hudson <sup>2,3,6,8</sup>

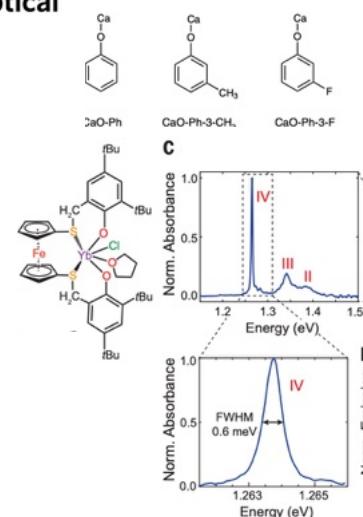
NATURE CHEMISTRY | VOL 14 | SEPTEMBER 2022 | 995–999 |

#### QUANTUM TECHNOLOGY

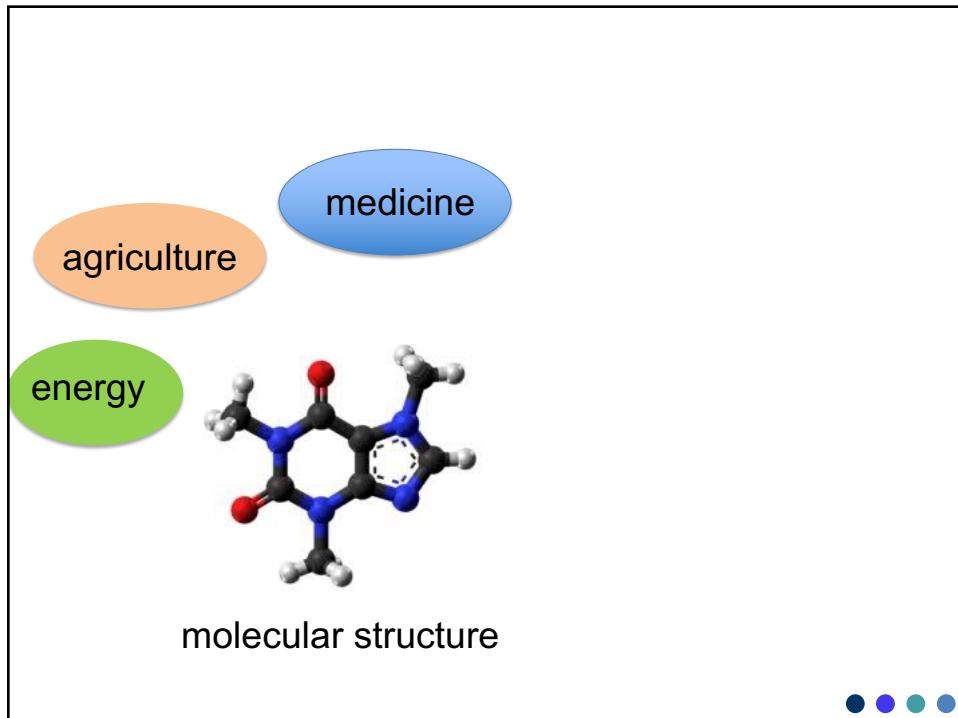
### Toward liquid cell quantum sensing: Ytterbium complexes with ultranarrow absorption

Ashley J. Shin<sup>1†</sup>, Changting Zhao<sup>2†</sup>, Yi Shen<sup>1†</sup>, Claire E. Dickerson<sup>1†</sup>, Barry Li<sup>3</sup>, Hootan Roshandel<sup>4</sup>, Daniel Bim<sup>5</sup>, Timothy L. Atallah<sup>2,3</sup>, Paul H. Oyala<sup>4</sup>, Yongjia He<sup>4</sup>, Lianne K. Olson<sup>1</sup>, Tyler A. Kerr<sup>2</sup>, Anastassia N. Alexandrova<sup>1\*</sup>, Paula L. Diaconescu<sup>3\*</sup>, Wesley C. Campbell<sup>2\*</sup>, Justin R. Caram<sup>1\*</sup>

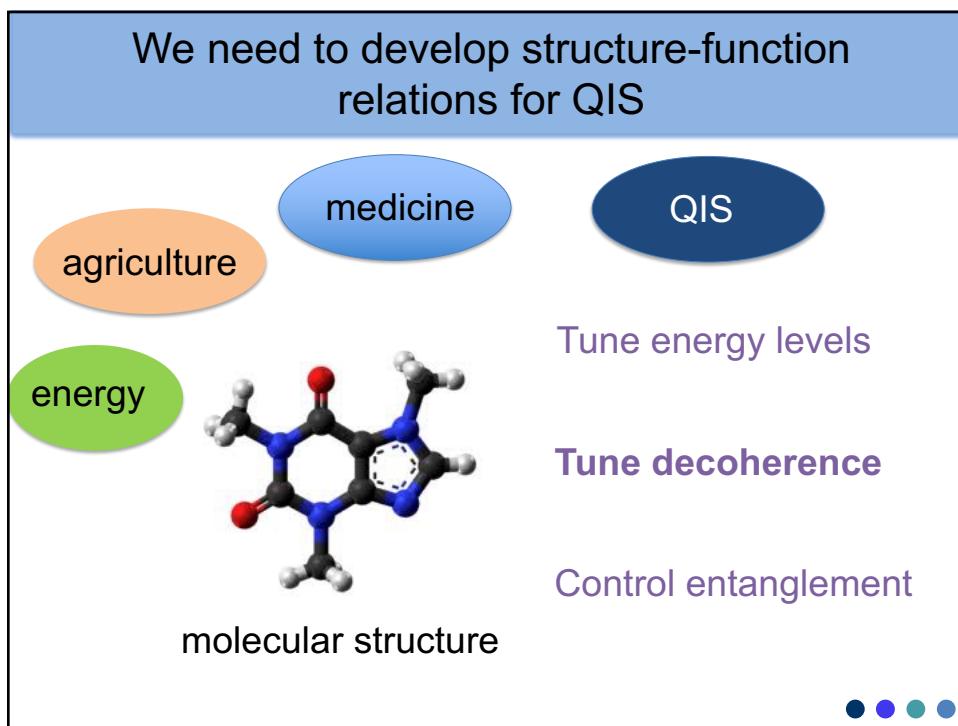
Shin *et al.*, Science **385**, 651–656 (2024)



12



13



14

# The Chemistry of Quantum Decoherence

## How molecular electronic decoherence studies look like right now:



Figure 1. Left-hand side: The pair of interacting chromophores. Right-hand side: the effective light-harvesting two-level system formed from the pair of interacting chromophores.<sup>19,20</sup>

The environment is fully characterized by the spectral density  $J(\omega) = \sum_{\alpha} g_{\alpha}^2 \delta(\omega - \omega_{\alpha})$ , being a quasi-continuous function for typical condensed-phase applications that determines all bath correlations that are relevant for the system.<sup>21,22</sup> For Ohmic dissipation,  $J(\omega) = 2K\omega e^{-\omega/\omega_c}$ , where the dimensionless parameter  $K$  describes the damping strength and  $\omega_c$  is the cutoff frequency.

e.g. J. Phys. Chem. Lett. 2, 2728 (2011)

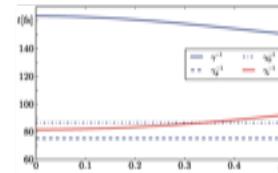
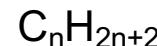
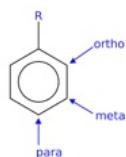


Figure 2. Relaxation time  $\tau^{-1}$  (red line) and decoherence time  $\gamma^{-1}$  (continuous blue line) as functions of  $\epsilon/2\Delta$  for fixed  $\Delta = 35 \text{ cm}^{-1}$  and at  $T = 77 \text{ K}$ . The dashed blue line,  $\gamma_d = 2\pi(4k_B T/\hbar)\lambda/\hbar\omega_{LC}$ , denotes the dephasing rate used in refs 4, 7, and 10, and the dot-dashed blue line denotes the decoherence time  $\tau_D = (\hbar^2/2\lambda k_B T)^{1/2}$  used in refs 3–5. Fixed parameters as in Table 1.

## How I would like them to look like



How does chemical substitution change decoherence?

How does solvent polarity influence coherence loss?

How does decoherence change along a homologous series?

15

# What is decoherence?

Loss of quantum coherence due to entanglement of a system with its environment

$$H = H_S + H_B + H_{SB}$$

Unitary evolution of S + B leads to entanglement

$$|\Omega(0)\rangle \rightarrow |\Omega(t)\rangle$$

$$(c_1|\phi_1\rangle + c_2|\phi_2\rangle)|\chi\rangle \rightarrow c_1|\phi_1\rangle|\chi_1\rangle + c_2|\phi_2\rangle|\chi_2\rangle$$

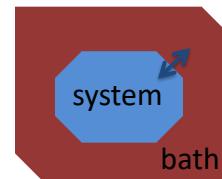
and thus to a decay of the off-diagonal elements of the system's reduced density matrix

$$\sigma(t) = \text{Tr}_B\{\rho(t)\}$$

$$\begin{pmatrix} |c_1|^2 & c_1 c_2^* \\ c_2 c_1^* & |c_2|^2 \end{pmatrix} \rightarrow \begin{pmatrix} |c_1|^2 & c_1 c_2^* \langle \chi_2 | \chi_1 \rangle \\ c_2 c_1^* \langle \chi_1 | \chi_2 \rangle & |c_2|^2 \end{pmatrix}$$

Pure state

→ Mixed state

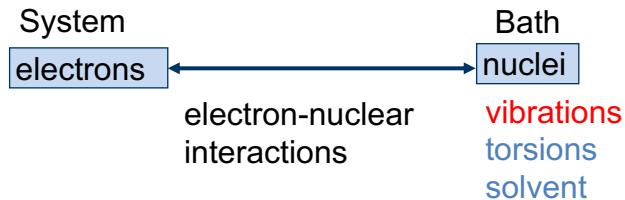


$$|\phi_i\rangle \in \mathcal{S}$$

$$|\chi_i\rangle \in \mathcal{B}$$

16

## Why are we interested in electronic decoherence?



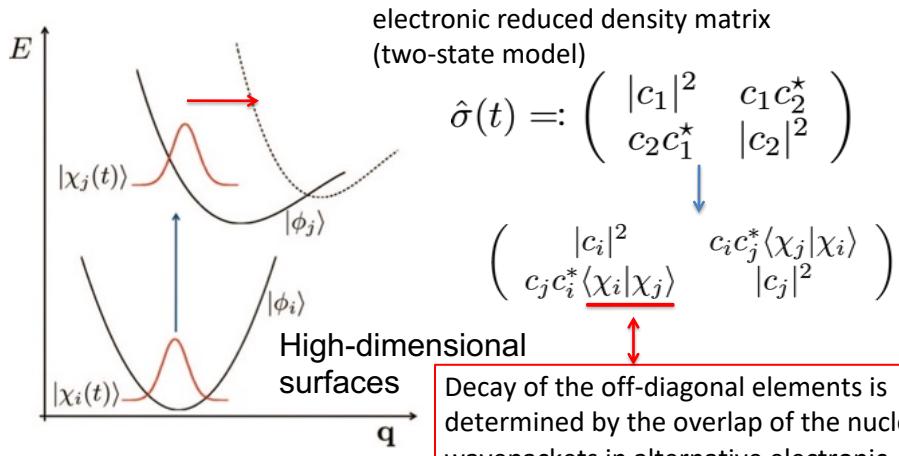
- Protecting the coherence properties of electronic superpositions is desirable for quantum technologies
- Central to our understanding of photosynthesis, vision and electron transfer
- Basic feature of correlated electron-nuclear states
- Important to develop approximate schemes to the electron-vibrational evolution of molecules



17

## Understanding electronic decoherence in molecules

$$(c_1|\phi_1\rangle + c_2|\phi_2\rangle)|\chi\rangle \rightarrow c_1|\phi_1\rangle|\chi_1\rangle + c_2|\phi_2\rangle|\chi_2\rangle$$



E.g. Schwartz, Bittner, Prezhdo and Rossky  
J. Chem. Phys. **104**, 5942 (1996)

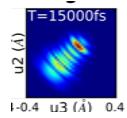
Fiete and Heller, Phys. Rev. A **68**, 022112 (2003)



18

## Our work on decoherence

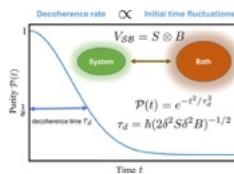
**Basic questions:** How fast?      Basic mechanisms?      How to overcome it?  
 How to quantify it?      How to model it?



**Modeling decoherence dynamics explicitly**  
 Hu, Gu, IF, J. Chem. Phys., **148**, 134304 (2018)  
 Gu and IF, J. Chem. Phys. **146**, 194104 (2017)



Wenxiang Hu  
(now at Amazon)



### Theory of decoherence time scales

Gu and IF, J. Phys. Chem. Lett., **9**, 773 (2018)  
 J. Phys. Chem. Lett., **8**, 4289 (2017)



Bing Gu  
(now Prof@Westlake)



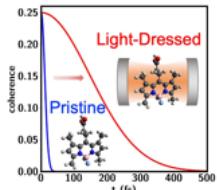
**Validity of classical noise models**  
 Gu and IF, J. Chem. Phys. **151**, 014109 (2019)



19

## Our recent work on decoherence

**Basic questions:** How fast?      Basic mechanisms?      How to overcome it?  
 How to quantify it?      How to model it?

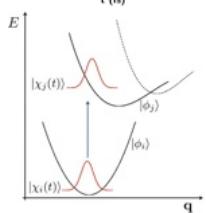


### Tuning and enhancing coherence with quantum and classical light

Hu, Gu and IF, J. Chem. Phys. **152**, 184305 (2020)  
 Hu, Gustin, Krauss and IF, J. Phys. Chem. Lett. **13**, 11503 (2022)



Wenxiang Hu  
(now at Amazon)



### Connection between electronic interactions and decoherence

Gu and IF, J. Chem. Phys. **149**, 174115 (2018)  
 Kar, Chen and IF, J. Phys. Chem. Lett., **7**, 1616 (2016)



Arnab Kar  
(now at Intel)



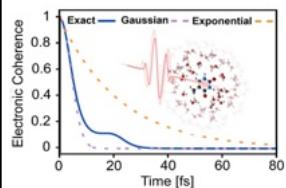
20

## Our recent work on decoherence

**Basic questions:** How fast?  
How to quantify it?

**Basic mechanisms?**  
How to model it?

How to overcome it?



### Basic temporal patterns of coherence loss

Gustin, Chen, IF J. Chem. Phys. **162**, 064106 (2025)



Ignacio Gustin  
(now at Toronto)



### High-Frequency Tails in Spectral Densities

Korol, Chen and IF J. Phys. Chem. A **129**, 15, 3587 (2025)



Roman Korol  
(now Prof@Sherbrooke)

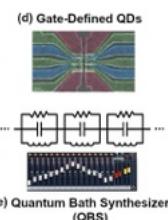
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## Our recent work on decoherence

**Basic questions:** How fast?  
How to quantify it?

**Basic mechanisms?**  
How to model it?

How to overcome it?

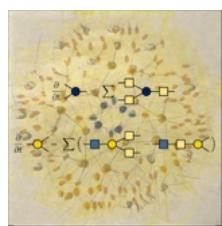


### Analog Quantum Simulation of Open Quantum Systems

Kim, Nichol, Jordan and IF, PRX Quantum **3**, 040308 (2022)



Chang Woo Kim  
(now Prof@Chonnam)



### Numerically Exact Methods and their Efficient Computational Implementation using Tensor Networks

Chen and IF J. Chem. Phys. **160**, 204116 (2024)  
Chen and IF J. Chem. Phys. **163**, 104109 (2025)

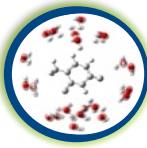


Xinxian Chen  
(now at Huawei)

22

## Our recent work on decoherence

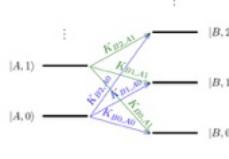
**Basic questions:** How fast?      Basic mechanisms?      How to overcome it?  
 How to quantify it?      How to model it?



**Mapping Electronic Dephasing Pathways in Molecules**  
 Gustin, Kim, McCamant and IF PNAS **120**, e2309987120 (2023)



Ignacio Gustin



**Mapping dissipation pathways in Molecules**  
 Kim and IF, J. Chem. Phys. **154**, 084103 (2021)  
*J. Chem. Phys.* **160**, 214111 (2024)  
*J. Chem. Phys.* **160**, 214112 (2024)  
 Gustin, Kim and IF  
*J. Phys. Chem. Lett.* **16**, 13093 (2025)  
*J. Chem. Phys.* (in press, arXiv:2510.04372)



Chang Woo Kim

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23

## Generalized theory of electronic decoherence

Gu, Franco J. Phys. Chem. Lett, **9**, 773 (2018)      Bing Gu 

Separable initial state       $|\Psi_0\rangle = (c_g|g\rangle + c_e|e\rangle) \otimes |\chi_0(\mathbf{R})\rangle$

$$\tau_d^{-2} = 2\hbar^{-2} \left( |c_g|^2 |c_e|^2 \langle \delta^2 \mathcal{E}_{eg} \rangle \quad \text{pure dephasing} \right.$$

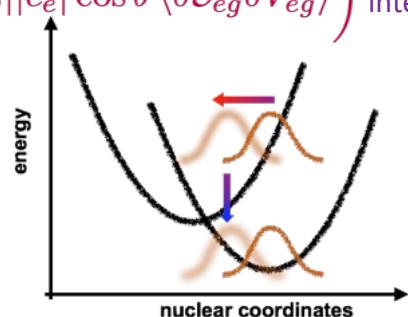
$$+ (1 - 4|c_g|^2 |c_e|^2 \cos^2 \theta) \langle \delta^2 V_{eg} \rangle \quad \text{electronic transitions}$$

$$\left. + 2(|c_g|^2 - |c_e|^2) |c_g| |c_e| \cos \theta \langle \delta \mathcal{E}_{eg} \delta V_{eg} \rangle \right) \text{interference}$$

$\mathcal{E}_{eg}(\mathbf{R}) \equiv \mathcal{H}_e - \mathcal{H}_g$   
 energy gap operator

$$\delta^2 A = \langle A^2 \rangle - \langle A \rangle^2$$

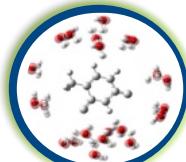
$$c_g c_e^* = |c_g| |c_e| e^{i\theta}$$



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25

## The Plan for 2 lectures:



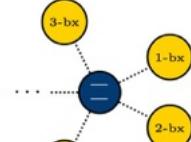
Mapping Electronic Dephasing Pathways in Molecules

PNAS **120**, e2309987120 (2023)

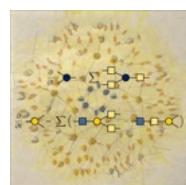
with Ignacio Gustin, David McCamant and Chang Woo Kim



Ignacio Gustin



TTN-HEOM: Tree tensor network hierarchical equations of motion for efficient numerically exact open quantum dynamics



Chen and IF J. Chem. Phys. **160**, 204116 (2024)  
Chen and IF J. Chem. Phys. **163**, 104109 (2025)



Xinxian Chen

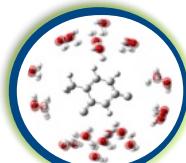
TENSO tutorial

Rodríguez, Anderson, Niu, Chen and IF (upcoming)



26

## The Plan for 2 lectures:



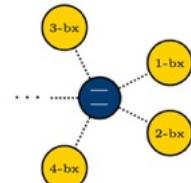
Mapping Electronic Dephasing Pathways in Molecules

PNAS **120**, e2309987120 (2023)

with Ignacio Gustin, David McCamant and Chang Woo Kim



Ignacio Gustin

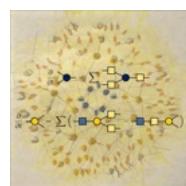


How does dephasing

really happen?

The Bexcitonic generalization of the Hi

How can we exactly model the decoherence?

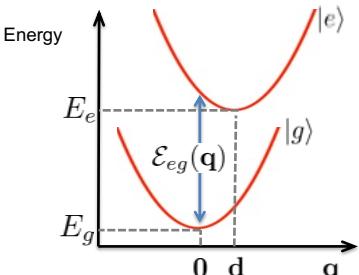


Xinxian Chen



27

**“Pure Dephasing” Electronic Decoherence in Molecules**

<b>System: Electrons</b> 	<b>Bath: Vibrations/Solvent</b> <b>“Early time” coherence decay</b> $ \sigma_{eg}(t) ^2 =  \sigma_{eg}(0) ^2 \exp(-t^2/\tau_{eg}^2)$ $\tau_{eg} = \frac{\hbar}{\sqrt{\langle \delta^2 \mathcal{E}_{eg}(\mathbf{q}) \rangle}} \approx \frac{\hbar}{\sqrt{4\lambda k_B T}}$ $\lambda = \sum_k \frac{1}{2} m_k \omega_k d_k^2 \quad \text{Reorganization energy (half the Stokes shift)}$
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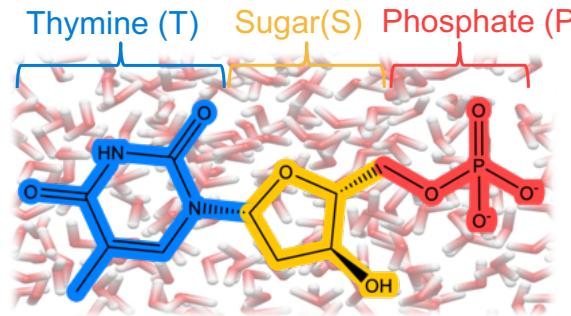
E.g. Schwartz, Bittner, Prezhdo and Rossky, J. Chem. Phys. **104**, 5942 (1996)  
Fiete and Heller, Phys. Rev. A **68**, 022112 (2003)  
Gu and IF, J. Phys. Chem. Lett., **9**, 773 (2018)

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28

*How does electronic dephasing *really* occur for a molecule in solvent?*

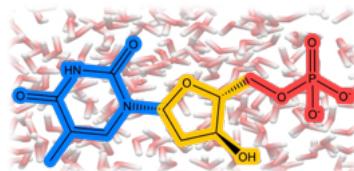
Thymine (T)   Sugar(S)   Phosphate (P)



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29

## The Challenge: Structure-Function Relations for Quantum Decoherence



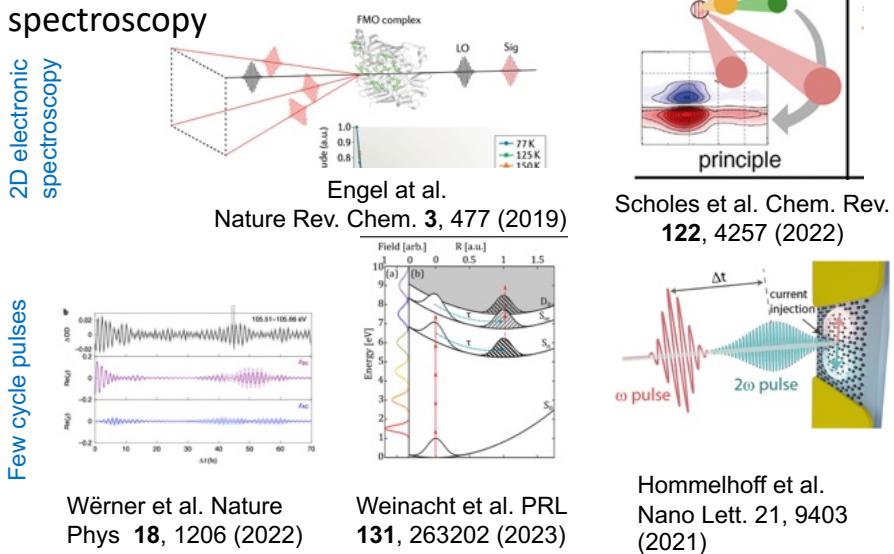
### Theory:

Accurate fully quantum method to capture the interactions of molecules with their environment and the resulting quantum dynamics. #manybodyproblem



30

### Experiments: Optical Absorption, Photon-Echo, 2D spectroscopy



Need systematic way to decompose the overall signal into contributions by individual chemical groups #itishard!



31

## Harmonic Environments

### Useful model of the environment: Collection of harmonic oscillators

- Any environment can be mapped into an effective harmonic environment to second order in perturbation theory
- Dominant behavior in the thermodynamic limit
- The reason why the displaced harmonic oscillator model is so successful in spectroscopy

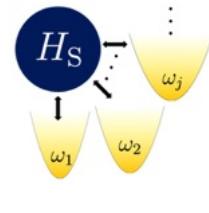
### Hamiltonian

$$H = H_S + H_{SB} + H_B,$$

$$H_B = \sum_{j=1}^{\infty} \omega_j a_j^\dagger a_j$$

$$H_{SB} = Q_S \otimes X_B$$

$$X_B = \sum_{j=1}^{\infty} (g_j a_j^\dagger + g_j^* a_j)$$



Feynman and Vernon. Ann. Phys. 24 118–173 (1963)

Caldeira and Leggett. Ann. Phys. 149 374–456 (1983)

Suárez and Silbey, J Chem. Phys. 95, 9115 (1991)

Makri J. Phys. Chem. B 103, 2823–2829 (1999)



32

## Dynamical Map for Harmonic Environments

### Hamiltonian

$$H = H_S + H_{SB} + H_B,$$

$$H_B = \sum_{j=1}^{\infty} \omega_j a_j^\dagger a_j$$

$$H_{SB} = Q_S \otimes X_B$$

$$X_B = \sum_{j=1}^{\infty} (g_j a_j^\dagger + g_j^* a_j)$$

### Initially separable state

$$\rho(0) = \rho_S(0) \otimes \rho_B^{eq}$$

### Exact dynamical map in interaction picture

$$\tilde{\rho}_S(t) = \mathcal{T} \tilde{\mathcal{F}}(t, 0) \rho_S(0) \equiv \mathcal{T} \exp \left( - \int_0^t dt_2 \tilde{Q}_S^\times(t_2) \int_0^{t_2} dt_1 [\mathbf{C}(t_2 - t_1) \tilde{Q}_S(t_1)]^\times \right) \rho_S(0)$$

### Notation

$$A^\times B = AB - BA^\dagger$$

### Correlation Function

$$C(t) = \langle X_B(t) X_B(0) \rangle_B.$$

### Spectral Density

$$C(t) = \int_{-\infty}^{\infty} \mathcal{J}(\omega) (1 + n_{BE}(\omega, T)) e^{-i\omega t} d\omega.$$

$$J(\omega) = \sum_j |g_j|^2 \delta(\omega - \omega_j) \quad (\omega > 0)$$

$$\mathcal{J}(\omega) = J(\omega) - J(-\omega) \quad \text{odd extension}$$

Ishizaki and Fleming, J. Chem. Phys. 130, 234111 (2009)

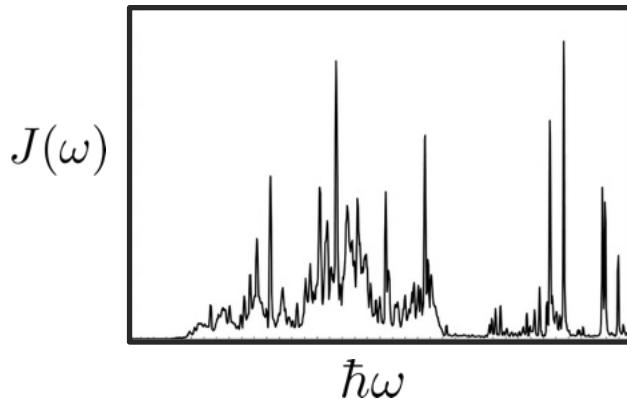
Molinari, arXiv:1710.09248 (2017)

Isserlis, Biometrika 12, 134 (1918)



33

## Spectral Density: characterizes system-bath interaction



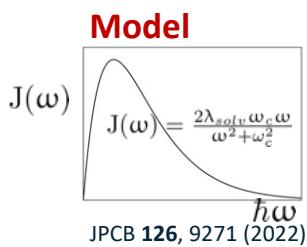
Summarizes frequencies of the bath and interaction strength with the system



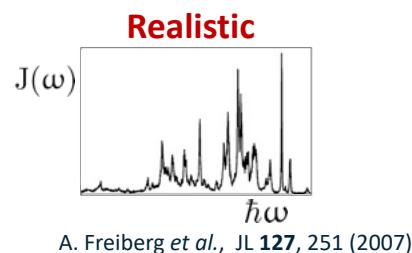
34

## What we need:

### 1. Method to reconstruct spectral densities in chemically complex environments



FMO  
vs.



#### How to obtain it?

##### QM/MM

Expensive + Challenging to be accurate  
Kleinekathöfer et al. Photosynthesis Res. 157, 147 82023 (2023)

Mennucci et al. JCP 156, 120901 (2022)  
Coker et al. JCP 155, 014108 (2021)  
Montoya-Castillo et al. JCP 159, 244114 (2023)

##### Experiments ( $\Delta$ FLN)

Fluorescent Molecules  
Cryogenic Temperatures  
Glassy matrices  
Jankowiak, Reppert et al. JPC-B 117, 7323 (2013)



35

## Resonance Raman Spectroscopy

Fitting of resonance Raman excitation profile yields:

Vibrational frequencies  
Huang-Rhys factors  
Solvent effects

Shreve and Mathies J. Phys. Chem. **99**, 7285 (1995)  
Mukamel, Principles of Nonlinear Optical Spectroscopy  
Myers, Anne B. J. Raman Spectrosc. 389-401 (1997)  
McCamant *et al.* Annu. Rev. Phys. Chem. **58**, 461-488 (2007)

36

### Our observation: Spectral Densities can be reconstructed from Resonance Raman Experiments

**Decomposition of the spectral density**

$$J(\omega) = \sum_{\alpha=0}^N J_{\alpha}(\omega)$$

$$J_0(\omega) = \frac{2}{\pi} \lambda_0 \frac{\omega \Lambda}{\omega^2 + \Lambda^2} \quad \text{solvent}$$

$$J_{\alpha}(\omega) = \frac{2}{\pi} \lambda_{\alpha} \omega_{\alpha}^2 \frac{\omega \gamma_{\alpha}}{(\omega_{\alpha}^2 - \omega^2)^2 + \omega^2 \gamma_{\alpha}^2} \quad \text{vibrations}$$

Vibrational frequencies  
Huang-Rhys factors  
Solvent effects

Reconstruct spectral density with experimental complexity!

Shreve and Mathies J. Phys. Chem. **99**, 7285 (1995)  
Mukamel, Principles of Nonlinear Optical Spectroscopy

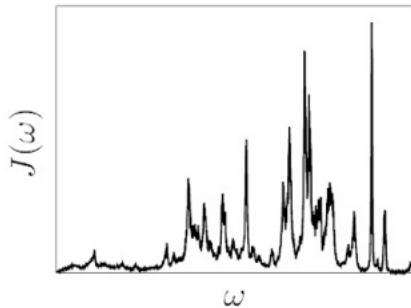
37

## What we need

### 2. Method to propagate the quantum dynamics in highly structured environments

Challenge: Computational cost of quantum dynamics grows exponentially with the complexity of the spectral density

(details will follow)



38

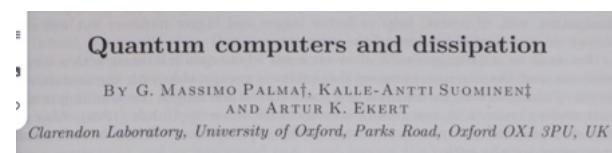
## Pure dephasing dynamics can be propagated analytically

### 2. Method to propagate the quantum dynamics in highly structured environments

Maintaining coherence in quantum computers

W. G. Unruh

Phys. Rev. A **51**, 992 – Published 1 February 1995



$$|\sigma_{eg}(t)| = |\sigma_{eg}(0)| \exp[-\Gamma(t)]$$

$$\Gamma(t) = \frac{1}{\hbar} \int_0^{\infty} d\omega J(\omega) \coth\left(\frac{\beta\hbar\omega}{2}\right) \frac{1 - \cos(\omega t)}{\omega^2}$$



39

## Decoherence Pathways

**3. Method to decompose the overall decoherence into contributions from solvent and vibrational modes**

Decomposition of the spectral density

$$J(\omega) = \sum_{\alpha=0}^N J_{\alpha}(\omega) \quad J_0(\omega) = \frac{2}{\pi} \lambda_0 \frac{\omega \Lambda}{\omega^2 + \Lambda^2} \quad \text{solvent}$$

$$J_{\alpha}(\omega) = \frac{2}{\pi} \lambda_{\alpha} \omega_{\alpha}^2 \frac{\omega \gamma_{\alpha}}{(\omega_{\alpha}^2 - \omega^2)^2 + \omega^2 \gamma_{\alpha}^2} \quad \text{vibrations}$$

Decomposition of the decoherence function

$$|\sigma_{eg}(t)| = |\sigma_{eg}(0)| \exp[-\Gamma(t)]$$

$$\Gamma(t) = \sum_{\alpha=0}^N \Gamma_{\alpha}(t)$$

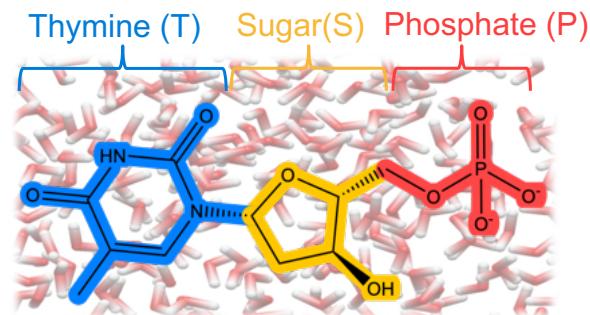
$$\Gamma_{\alpha}(t) = \frac{1}{\hbar} \int_0^{\infty} d\omega J_{\alpha}(\omega) \coth\left(\frac{\beta \hbar \omega}{2}\right) \frac{1 - \cos(\omega t)}{\omega^2}.$$

Contribution to the  
decoherence by a  
particular nuclear mode!

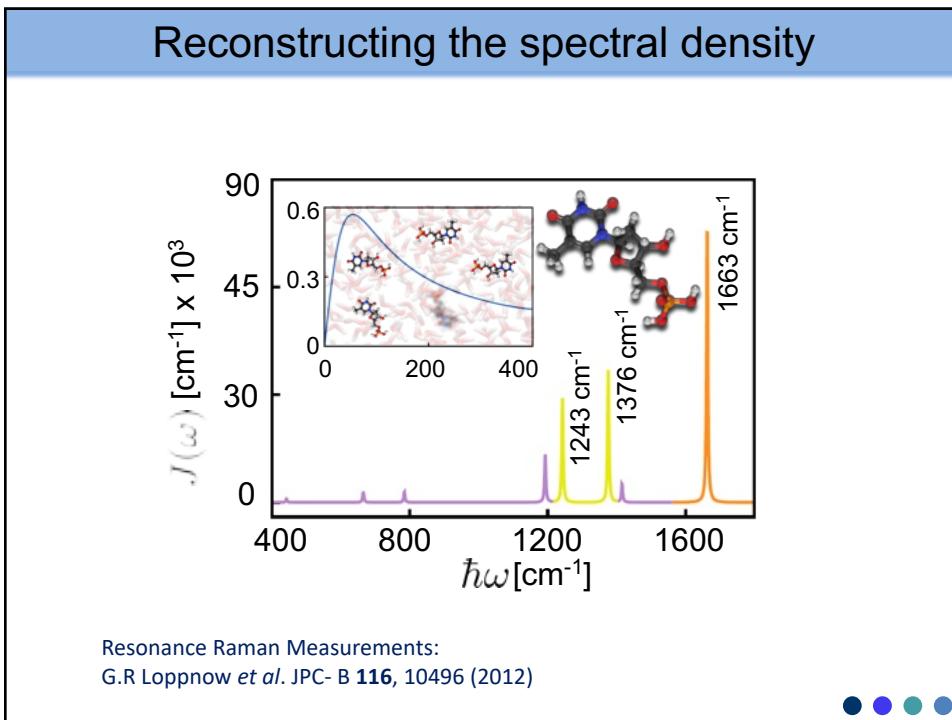


40

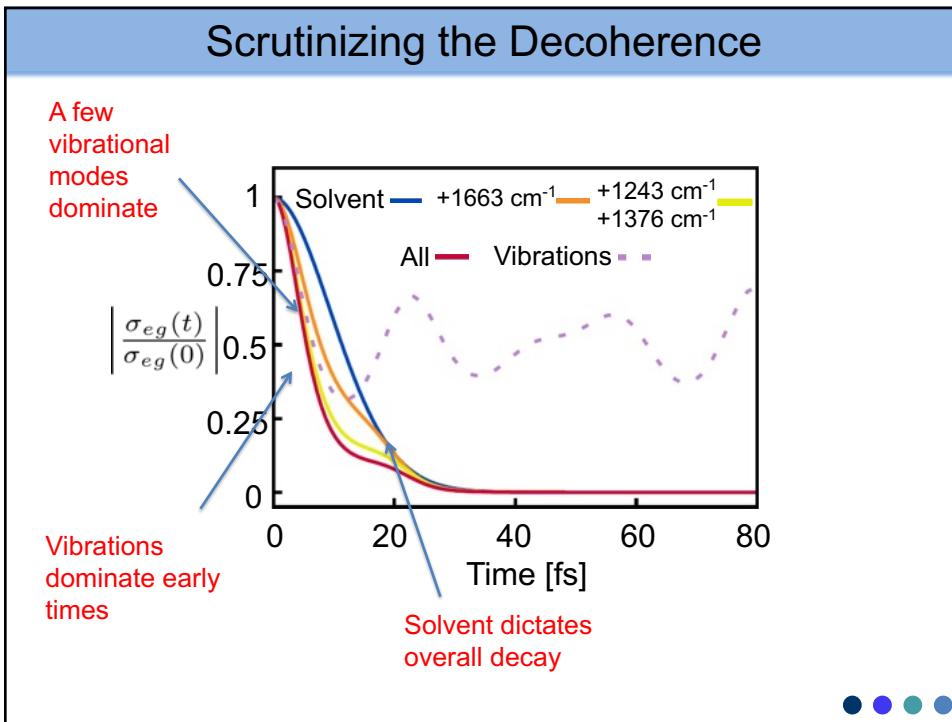
Finally! How does electronic dephasing occur for a molecule in solvent?



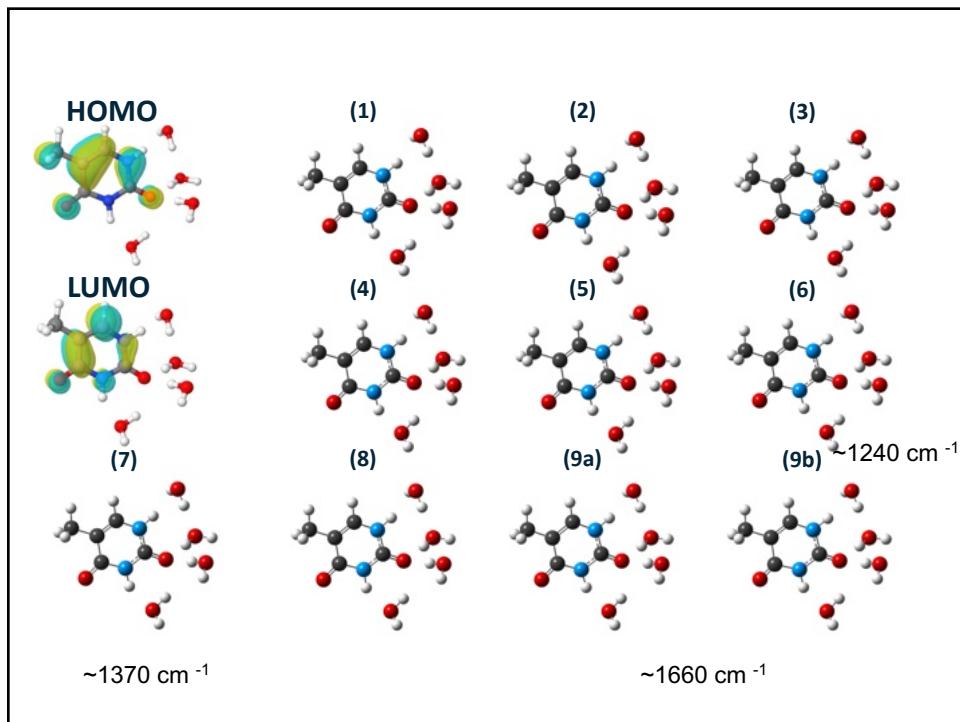
41



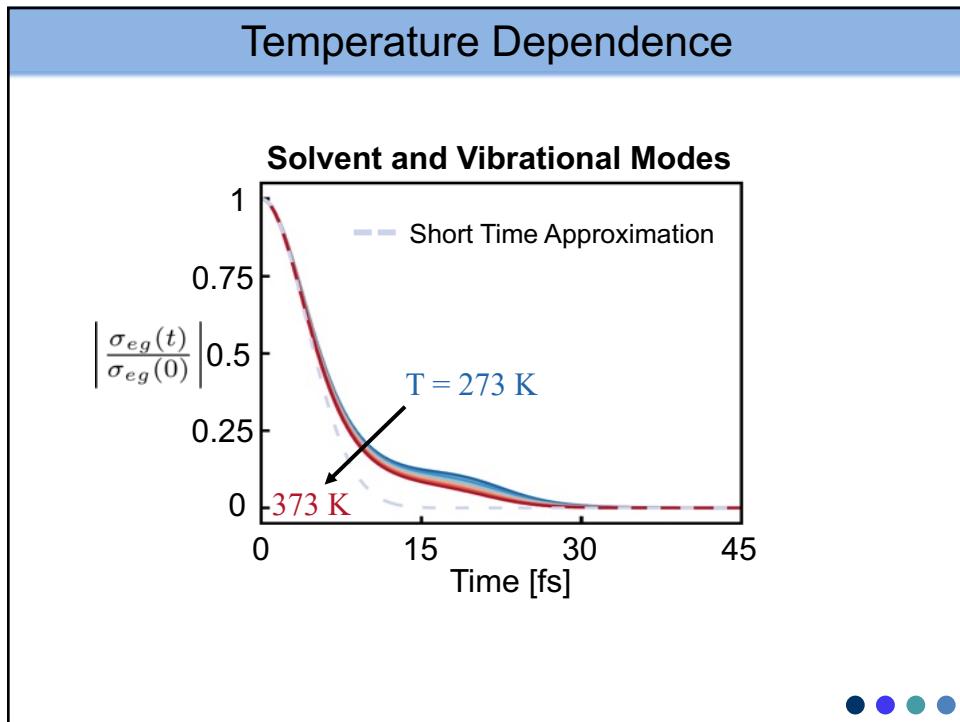
42



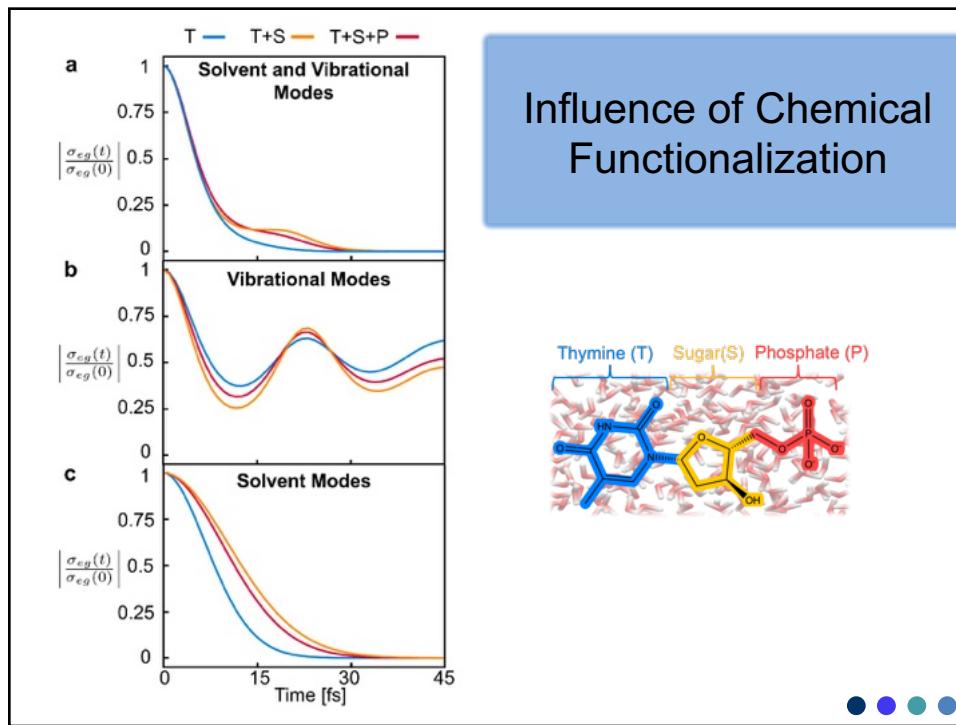
43



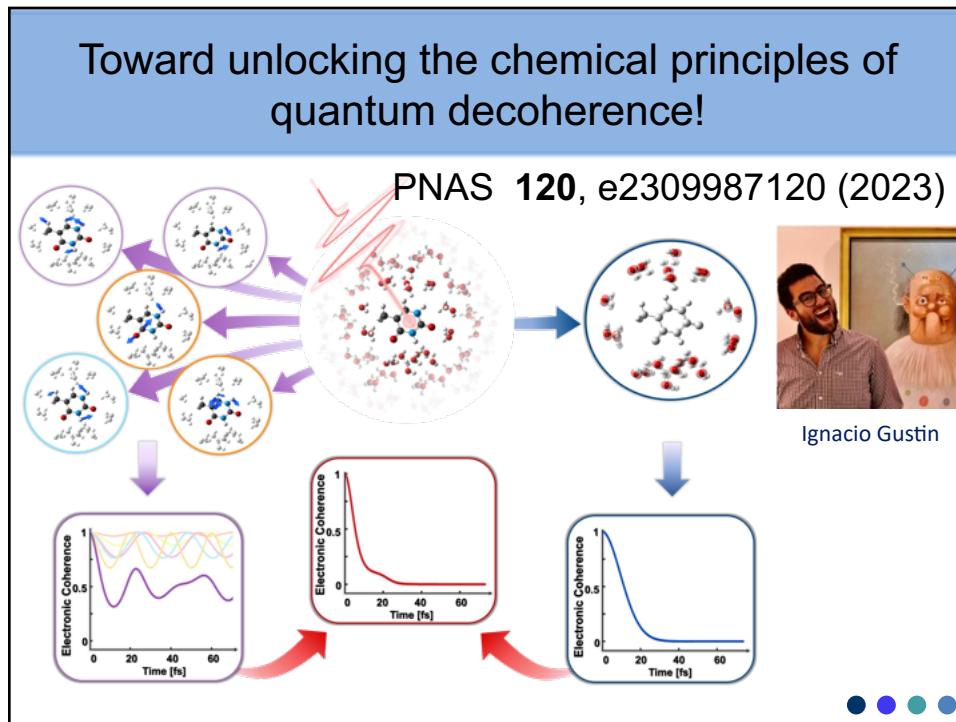
44



45

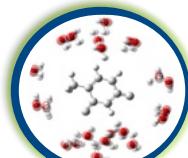


46



47

## The Plan for 2 lectures:



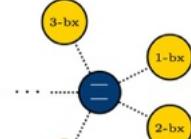
Mapping Electronic Dephasing Pathways in Molecules

PNAS **120**, e2309987120 (2023)

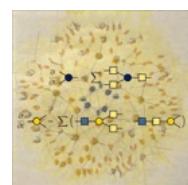
with Ignacio Gustin, David McCamant and Chang Woo Kim



Ignacio Gustin



TTN-HEOM: Tree tensor network hierarchical equations of motion for efficient numerically exact open quantum dynamics



Chen and IF J. Chem. Phys. **160**, 204116 (2024)  
Chen and IF J. Chem. Phys. **163**, 104109 (2025)



Xinxian Chen

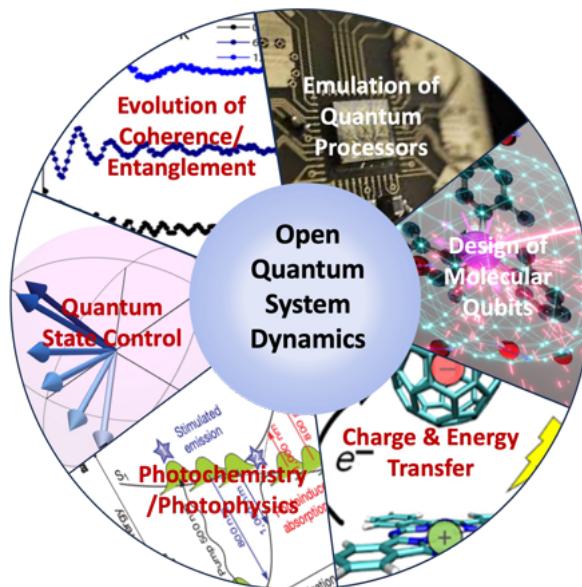
TENSO tutorial

Rodríguez, Anderson, Niu, Chen and IF  
(upcoming)



48

## Open Quantum Dynamics



49

## Methods in Open Quantum Dynamics

- H.-P. Breuer and F. Petruccione, *The Theory of Open Quantum Systems* (Oxford University Press, 2007).  
 M. Schlosshauer, *Decoherence and the Quantum-To-Classical Transition* (Springer, 2007).  
 E. Joos, H. D. Zeh, C. Kiefer, J. C. Gellini, J. Kupsch, and I.-O. Stamatescu, *Decoherence and the Appearance of a Classical World in Quantum Theory*  
 D. A. Lidar, Lecture notes on the theory of open quantum systems (2020), arXiv:1902.00967 [quant-ph].  
 A. G. Redfield, IBM Journal of Research and Development 1, 19 (1957).223  
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 A. Ishizaki and G. R. Fleming, The Journal of Chemical Physics 130, 234111 (2009).  
 T. Ikeda and G. D. Scholes, The Journal of Chemical Physics 152, 204104 (2020).  
 M. Xu, Y. Yan, Q. Shi, J. Ankerhold, and J. T. Stockburger, Physical Review Letters 129, 230601 (2022).  
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 N. Lambert, S. Ahmed, M. Cirio, and F. Nori, Nature Communications 10, 3721 (2019).  
 G. Park, Z. Huang, Y. Zhu, C. Yang, G. K.-L. Chan, and L. Lin, Physical Review B 110, 195148 (2024).  
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 X. Zheng, J. Jin, S. Welack, M. Luo, and Y. Yan, The Journal of Chemical Physics 130, 164708 (2009).  
 J. Hu, R.-X. Xu, and Y. Yan, The Journal of Chemical Physics 133, 101106 (2010).  
 J. Hu, M. Luo, F. Jiang, R.-X. Xu, and Y. Yan, The Journal of Chemical Physics 134, 244106 (2011). 

50

## The Hierarchical Equation of Motion (HEOM)

- System agnostic
- Admits driven systems
- Numerically exact for harmonic environments
- Admits non-commuting system-bath interactions
- Goes beyond Lindblad/Redfield Markovian models
- Memory hungry
- Computational cost scales exponentially with size of system and complexity of the environment

Ishizaki and Tanimura, JCP 125 084501 (2006)  
 Tanaka and Tanimura, JCP 132 214502 (2010)  
 Tanimura JCP 141 044114 (2014)  
 Ikeda and Scholes, JCP, 152, 204101 (2020)  
 Tanimura, JCP 153, 020901 (2020)  
 Yan, Xu, Li, and Shi, JCP 154, 194104 (2021)  
 Chen and Franco, JCP 160, 204116 (2024)



51

## Dynamical Map for Harmonic Environments

**Hamiltonian**  $H = H_S + H_{SB} + H_B$ ,

$$H_B = \sum_{j=1}^{\infty} \omega_j a_j^\dagger a_j \quad H_{SB} = Q_S \otimes X_B \quad X_B = \sum_{j=1}^{\infty} (g_j a_j^\dagger + g_j^* a_j)$$

**Initially separable state**  $\rho(0) = \rho_S(0) \otimes \rho_B^{eq}$

**Exact dynamical map in interaction picture**

$$\tilde{\rho}_S(t) = \mathcal{T} \tilde{\mathcal{F}}(t, 0) \rho_S(0) \equiv \mathcal{T} \exp \left( - \int_0^t dt_2 \tilde{Q}_S^\times(t_2) \int_0^{t_2} dt_1 [\mathbf{C}(t_2 - t_1) \tilde{Q}_S(t_1)]^\times \right) \rho_S(0)$$

**Notation**

$$A^\times B = AB - BA^\dagger$$

**Correlation Function**

$$C(t) = \langle X_B(t) X_B(0) \rangle_B$$

**Spectral Density**

$$C(t) = \int_{-\infty}^{\infty} \mathcal{J}(\omega) (1 + n_{BE}(\omega, T)) e^{-i\omega t} d\omega.$$

$$J(\omega) = \sum_j |g_j|^2 \delta(\omega - \omega_j) \quad (\omega > 0)$$

$$\mathcal{J}(\omega) = J(\omega) - J(-\omega) \quad \text{odd extension}$$

Ishizaki and Fleming, J. Chem. Phys. **130**, 234111 (2009)  
Molinari, arXiv:1710.09248 (2017)

Isserlis, Biometrika **12**, 134 (1918)



52

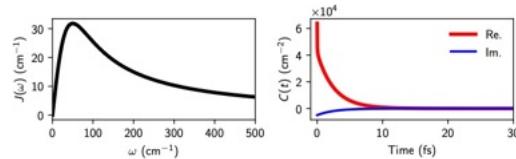
## The HEOM way

**Spectral Density**  $C(t) = \int_{-\infty}^{\infty} \mathcal{J}(\omega) (1 + n_{BE}(\omega, T)) e^{-i\omega t} d\omega.$

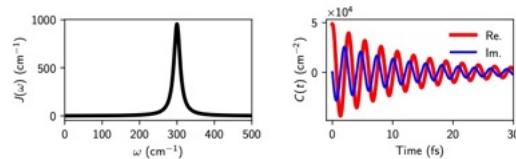
**Decomposition the BCF into complex exponentials or features**

$$C^*(t) = \sum_{k=1}^K \bar{c}_k e^{\gamma_k t}. \quad C(t) = \sum_{k=1}^K c_k e^{\gamma_k t}$$

▪ Solvent: Drude–Lorentz model



▪ Intramolecular vibrations: Brownian oscillators



53

## The HEOM way

Decomposition the BCF into complex exponentials or features is exact

$$C^*(t) = \sum_{k=1}^K \bar{c}_k e^{\gamma_k t}. \quad C(t) = \sum_{k=1}^K c_k e^{\gamma_k t}$$

From residue theorem/Padé or Matsubara expansions

$$C(t) = -2\pi i \sum_i \text{Res}_{z=\zeta_i} [\mathcal{J}(z)] f_{\text{BE}}(\beta \zeta_i) e^{-i\zeta_i t} - 2\pi i \sum_j \text{Res}_{z=\xi_j} [f_{\text{BE}}(z)] \mathcal{J}(\xi_j/\beta) e^{-i(\xi_j/\beta)t},$$

$\{\zeta_i\}$  First order poles of  $\mathcal{J}(\omega)$  in the lower half  
 $\{\xi_i/\beta\}$   $f_{\text{BE}}(\beta\omega) = (1 - e^{-\beta\omega})^{-1}$   
 complex plane (guarantees that  $C(t) \rightarrow 0$  as  $t \rightarrow \infty$ )

Several available methods:

- JCP 130, 164708 (2009)
- JCP 133, 101106 (2010)
- JCP 151, 024110 (2019)
- JCP 152, 064107 (2020)
- PRL 129, 230601 (2022)
- JCP 160, 204105 (2024)



54

## The HEOM way

BCF decomposition

$$C^*(t) = \sum_{k=1}^K \bar{c}_k e^{\gamma_k t}. \quad C(t) = \sum_{k=1}^K c_k e^{\gamma_k t}$$

Common Cases

Drude-Lorentz  $J(\omega) = \frac{2}{\pi} \frac{\lambda \omega \omega_c}{\omega_c^2 + \omega^2}$  - leads to one decaying real exponential with characteristic rate  $\omega_c$  (one feature)

Brownian  $J(\omega) = \frac{4}{\pi} \lambda_b \omega_b^2 \frac{\omega \gamma_b}{(\omega^2 - \omega_b^2)^2 + 4\omega^2 \gamma_b^2}$  - leads to two oscillatory decaying exponentials (two features)

Low temperature corrections - Poles of thermal factor are purely imaginary - Each leads to a decaying exponentials (one feature per correction)



55

## The HEOM way

Decomposition the BCF into complex exponentials or features is exact

$$C^*(t) = \sum_{k=1}^K \bar{c}_k e^{\gamma_k t}, \quad C(t) = \sum_{k=1}^K c_k e^{\gamma_k t}$$

From residue theorem/Padé or Matsubara expansions

$$C(t) = -2\pi i \sum_i \text{Res}_{z=\zeta_i} [\mathcal{J}(z)] f_{\text{BE}}(\beta \zeta_i) e^{-i\zeta_i t} - 2\pi i \sum_j \text{Res}_{z=\xi_j} [f_{\text{BE}}(z)] \mathcal{J}(\xi_j/\beta) e^{-i(\xi_j/\beta)t},$$

Use this decomposition to decompose the dynamical map

Introduce auxiliary density matrix (ADM) to keep bath information

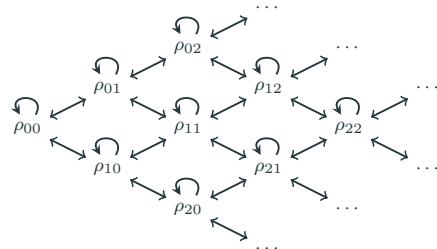
$$\rho_{\vec{n}} = \rho_{n_1, \dots, n_K} \quad n_k = 0, 1, 2, \dots, N$$



56

## The HEOM way

$$\frac{\partial}{\partial t} \rho_{\vec{n}}(t) = -iH_S^\times + \sum_k (n_k \gamma_k \rho_{\vec{n}}(t) - i n_k (c_k q_S^> - \bar{c}_k q_S^<) \rho_{\vec{n}-\hat{1}_k}(t) - i q_S^\times \rho_{\vec{n}+\hat{1}_k}(t))$$



Curse of dimensionality: The hierarchy generate an infinite K-dimensional grid

Tanimura and Kubo. J. Phys. Soc. Jpn. **58**, 101–114 (1989)  
 Tanimura. J. Chem. Phys. **153**, 020901 (2020)



57

## Bexcitonic generalization of the HEOM

X. Chen and I. Franco, J. Chem. Phys. **160**, 204116 (2024)

### Decomposition of the BCF into $K$ features

$$C(t) = \sum_{k=1}^K c_k \psi_k(t) \quad C^*(t) = \sum_{k=1}^K \bar{c}_k \psi_k(t) \quad \frac{d}{dt} \psi_k(t) = \sum_{k'=1}^K \gamma_{kk'} \psi_{k'}(t)$$

$$\psi_k(0) = 1$$

$$\tilde{\rho}_S(t) = \mathcal{T} \tilde{\mathcal{F}}(t, 0) \rho_S(0) \equiv \mathcal{T} \exp \left( - \int_0^t dt_2 \tilde{Q}_S^\times(t_2) \int_0^{t_2} dt_1 [C(t_2 - t_1) \tilde{Q}_S(t_1)]^\times \right) \rho_S(0)$$

### Define Auxiliary Density Matrices (ADMs)

$$\tilde{\varrho}_{\vec{n}}(t) \equiv \mathcal{T} \left( \prod_{k=1}^K \frac{\tilde{f}_k^{n_k}(t, 0)}{Z_k(n_k) \sqrt{n_k!}} \right) \tilde{\mathcal{F}}(t, 0) \rho_S(0) \quad \vec{n} \equiv (n_1, \dots, n_K)$$

$$\tilde{f}_k(t, 0) = c_k \tilde{\theta}_k^>(t, 0) - \bar{c}_k \tilde{\theta}_k^<(t, 0) \quad \tilde{\theta}_k(s, 0) = \int_0^s \tilde{Q}_S(u) \psi_k(s-u) du$$

$Z_k$  is a non-zero c-number: metric



58

## Bexcitonic generalization of HEOM

X. Chen and I. Franco, J. Chem. Phys. **160**, 204116 (2024)

Put all the ADMs in a vector

$$|\Omega(t)\rangle \equiv \sum_{\vec{n}} \varrho_{\vec{n}}(t) |\vec{n}\rangle$$

$$|\vec{n}\rangle \equiv |n_1\rangle \otimes \cdots \otimes |n_k\rangle$$

Equations of motion

$$\frac{d}{dt} |\Omega(t)\rangle = \left( -iH_S^\times(t) + \sum_{k=1}^K \mathcal{D}_k \right) |\Omega(t)\rangle \quad |\Omega(0)\rangle = \rho_S(0) |0\rangle \otimes \cdots \otimes |0\rangle$$

$$\mathcal{D}_k = \gamma_{kk} \hat{n}_k + \sum_{k' \neq k} \gamma_{kk'} \hat{z}_k^{-1} \hat{\alpha}_k^\dagger \hat{\alpha}_{k'} \hat{z}_{k'} + (c_k Q_S^> - \bar{c}_k Q_S^<) \hat{z}_k^{-1} \hat{\alpha}_k^\dagger - Q_S^\times \hat{\alpha}_k \hat{z}_k$$

$$\hat{\alpha}_k^\dagger |n_k\rangle = \sqrt{n_k + 1} |n_k + 1\rangle \quad \hat{\alpha}_k |n_k\rangle = \sqrt{n_k} |n_k - 1\rangle$$

$$\hat{n}_k = \hat{\alpha}_k^\dagger \hat{\alpha}_k$$

Bexciton  
raising/lowering  
operators

$\hat{z}_k$  metric operator (needs to commute with  $n_k$ )

Varying BCF decomposition, metric, representation leads to various HEOM variants



59

## Bexcitonic picture

X. Chen and I. Franco, J. Chem. Phys. **160**, 204116 (2024)

$$\frac{d}{dt}|\Omega(t)\rangle = \left(-iH_S^\times(t) + \sum_{k=1}^K \mathcal{D}_k\right)|\Omega(t)\rangle$$

$$\mathcal{D}_k = \gamma_{kk}\hat{n}_k + \sum_{k' \neq k} \gamma_{kk'}\hat{z}_k^{-1}\hat{\alpha}_k^\dagger\hat{\alpha}_{k'}\hat{z}_{k'} + (c_k Q_S^> - \bar{c}_k Q_S^<) \hat{z}_k^{-1}\hat{\alpha}_k^\dagger - Q_S^\times \hat{\alpha}_k \hat{z}_k$$

**Open Quantum Dynamics = Dynamics of the System + Bexcitons**  
(fictitious bosonic quasiparticles)

Depth of HEOM  $N$  = Number of bexcitonic levels

60



## Develop many HEOM variants

$$\frac{d}{dt}|\Omega(t)\rangle = \left(-iH_S^\times(t) + \sum_{k=1}^K \mathcal{D}_k\right)|\Omega(t)\rangle$$

$$\mathcal{D}_k = \gamma_{kk}\hat{n}_k + \sum_{k' \neq k} \gamma_{kk'}\hat{z}_k^{-1}\hat{\alpha}_k^\dagger\hat{\alpha}_{k'}\hat{z}_{k'} + (c_k Q_S^> - \bar{c}_k Q_S^<) \hat{z}_k^{-1}\hat{\alpha}_k^\dagger - Q_S^\times \hat{\alpha}_k \hat{z}_k$$

**Flexibility:**

- Varying BCF decomposition
- Bexciton representation: position, momentum, number, etc
- Metric

Q. Shi, et al., J. Chem. Phys. **130**, 84105 (2009)  
T. Ikeda and A. Nakayama, J. Chem. Phys. **156**, 104104 (2022)

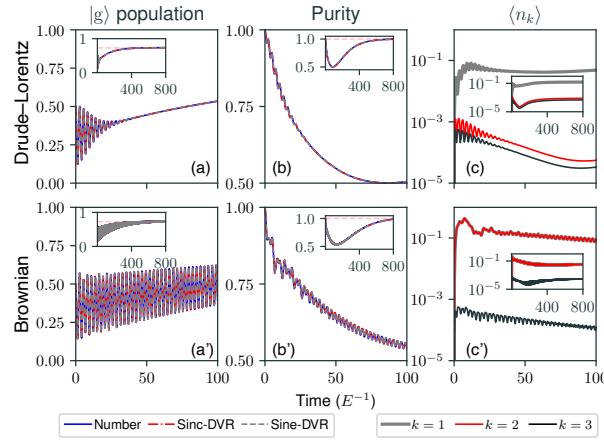
61



## Numerical verification

$$\sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad \sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$$

- Qubit model  $\{|e\rangle, |g\rangle\}$ :  
 $H_S = (E/2)\sigma_z + E\sigma_x$
- $Q_S = \sigma_z$
- Starts from a pure state  
 $|\psi\rangle = (|g\rangle + |e\rangle)/\sqrt{2}$ .
- Purity:  $\text{Trs}\{\rho_S^2(t)\}$



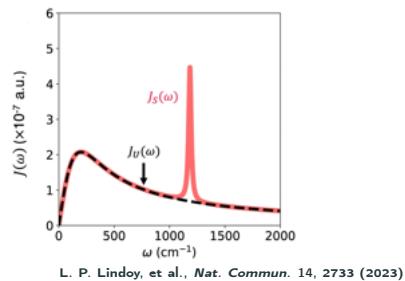
62

## The curse of dimensionality in HEOM

Memory needs grow exponentially with number of features

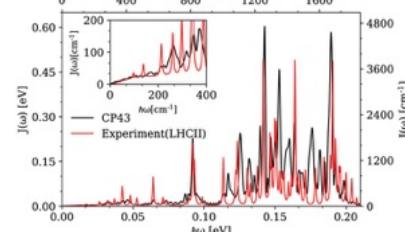
$$\mathcal{O}(N^K)$$

Model spectral density



L. P. Lindoy, et al., Nat. Commun. 14, 2733 (2023)

Realistic spectral density



$K$ : 10s to 100s.

$K$ : typically 1 ~ 5.



63

## Approaches to curb the curse of dimensionality

More efficient BCF decomposition schemes, e.g.

Dé, Jaouadi, Mangaud, Chin and Desouter-Lecomte,  
JCP **160**, 244102 (2024)

Filter out near-zero ADMs

Q. Shi, L. Chen, G. Nan, R.-X. Xu, and Y. Yan,  
JCP **130**, 084105 (2009)



64

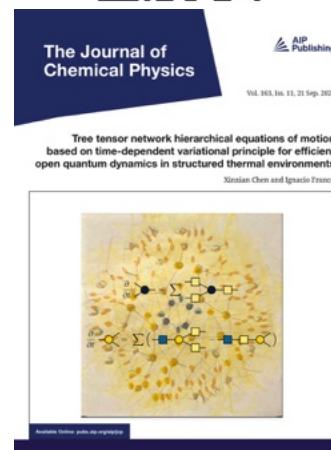
## Tree Tensor Network HEOM and TENSO

Chen and Franco J. Chem. Phys. **163**, 104109 (2025)

**Editor's Pick!**  
**Cover Article!**

<https://github.com/ifgroup/pytenso>

- Enables HEOM computations with highly structured environments
- Implements tensor trains and tensor trees
- Three propagation strategies (Direct, PS1 and PS2)
- Fixed and variable rank propagation strategies
- Allows for time-dependent driving and non-commuting fluctuations
- Open-source code TENSO



65

## Other HEOM Tensor Network Efforts

Tensor Train Y. Yan, M. Xu, T. Li, and Q. Shi, JCP **154**, 194104 (2021)

Tensor Tree Y. Ke, R. Borrelli, and M. Thoss, JCP **156**, 194102 (2022)

Y. Ke JCP **158**, 211102 (2023)

Fixed Rank + Propagator based on Trotter Splitting  
No need for master equations for core tensors

**Our Work** Chen and Franco JCP **163**, 104109 (2025)

Tensor Trees + Trains

Master equation for core tensors

Arbitrary Tree Geometry

Arbitrary Order for Tensors

Fixed and Variable Rank

Three Propagation Strategies



66

## Singular Value Decomposition (SVD)

$$A_{ij} = \sum_{k=1}^R U_{ik} s_k V_{jk}^* \quad U^\dagger U = V^\dagger V = \hat{1}$$

semi-unitary matrices

$s_k$  : singular values ( $s_1 \geq s_2 \geq s_K \geq 0$ )

Keep the  $R$  largest singular values to compress redundant information in an array

Raw ( $R = 587$ )



$R = 5$



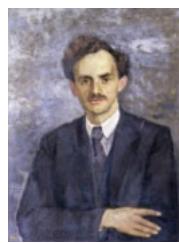
$R = 10$



$R = 20$



$R = 50$



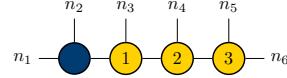
67

## From SVD to Tree Tensor Network (TTN)

TTN: repeated SVDs of a high-order tensor

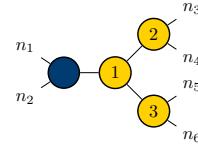
Tensor Train

$$A_{n_1 \dots n_6} = \sum_{a_1 a_2 a_3} C_{n_1 n_2 a_1} U_{a_2 n_3 a_1}^{(1)} U_{a_3 n_4 a_2}^{(2)} U_{n_5 n_6 a_3}^{(3)}$$



Tensor Tree

$$A_{n_1 \dots n_6} = \sum_{a_1 a_2 a_3} C_{n_1 n_2 a_1} U_{a_2 a_3 a_1}^{(1)} U_{n_3 n_4 a_2}^{(2)} U_{n_5 n_6 a_3}^{(3)}$$



Root Tensor

Semi-Unitary Tensors

$$\sum_{\alpha \beta} U_{\alpha \beta \gamma}^* U_{\alpha \beta \gamma'} = \delta_{\gamma \gamma'}$$



68

## TTN decomposition of the extended density operator

**Hypothesis:** There is significant redundancy in the bexcitonic space that can be compressed

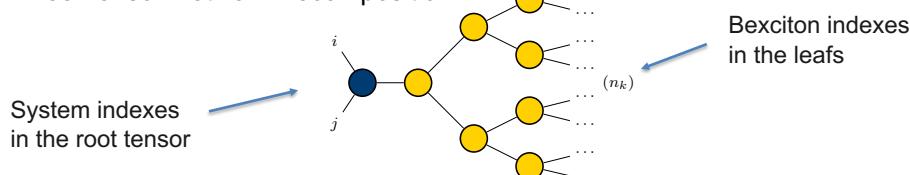
Extended Density Operator

$$|\Omega(t)\rangle \equiv \sum_{\vec{n}} \varrho_{\vec{n}}(t) |\vec{n}\rangle$$

Put all ADMs in a high-order tensor

$$\Omega_{ij n_1 \dots n_K} = (\rho_{\vec{n}})_{ij}$$

Tree-Tensor Network Decomposition



Polynomial space complexity with  $K$  (!)

$$\mathcal{O}((M^2 + N^2)R + K R^2 N)$$



69

## Sum of product form for the generator of the dynamics

$$\frac{d}{dt}\Omega(t) = \mathcal{L}(t)\Omega(t)$$

$$\mathcal{L}(t) = -iH_S^\times(t) + \sum_{k=1}^K \mathcal{D}_k = \sum_m h_m^>(t) \otimes h_m^<(t) \otimes h_m^{(1)} \otimes \cdots \otimes h_m^{(K)}.$$

$m$	$h_m^>(t)$	$h_m^<(t)$	$h_m^{(k)}$
1	$-iH_S(t)$	$\hat{1}$	$\hat{1}$
2	$\hat{1}$	$iH_S(t)$	$\hat{1}$
$5k-2$	$\hat{1}$	$\hat{1}$	$\gamma_{kk}\hat{n}_k$
$5k-1$	$c_k Q_S$	$\hat{1}$	$\hat{z}_k^{-1}\hat{\alpha}_k^\dagger$
$5k$	$\hat{1}$	$-\bar{c}_k Q_S$	$\hat{z}_k^{-1}\hat{\alpha}_k^\dagger$
$5k+1$	$-Q_S$	$\hat{1}$	$\hat{\alpha}_k\hat{z}_k$
$5k+2$	$\hat{1}$	$Q_S$	$\hat{\alpha}_k\hat{z}_k$

Parallel to Multi-configurational time-dependent Hartree

H. Wang and M. Thoss, JCP **119**, 1289 (2003)



70

## Master Equation for Core Tensors

Time Dependent Variational Principle

$$\sum_{ijn_1 \dots n_K} [\delta\Omega(t)]_{ijn_1 \dots n_K}^* \left[ \left( \mathcal{L} - \frac{d}{dt} \right) \Omega(t) \right]_{ijn_1 \dots n_K} = 0$$

Root Tensor – Simpler Dynamics

$$\left[ \frac{\partial}{\partial t} \begin{array}{c} i \\ j \end{array} \bullet a_1 \right] = \sum_m \begin{array}{c} i - h_m^> \\ j - h_m^< \end{array} \bullet \begin{array}{c} f_m^{(1)} \\ a_1 \end{array}$$

$$\frac{\partial}{\partial t} A_{i'j'a'_1}^{(0)} = \sum_m \sum_{ija_1} [h_m^>]_{i'i} [h_m^<]_{j'j} [f_m^{(1)}]_{a'_1 a_1} A_{ij a_1}^{(0)}$$

Non-Root Tensors – Requires Regularization

$$\frac{\partial}{\partial t} U_{a''s\beta'\gamma'}^{(s)} = \sum_m \sum_{a'_s a_s \beta \gamma} [\mathcal{C}_m^{(s)}]_{a'_s a''_s} \left( [f_m^{(\beta)}]_{\beta' \beta} [f_m^{(\gamma)}]_{\gamma' \gamma} U_{a'_s \beta \gamma}^{(s)} - U_{a_s \beta' \gamma'}^{(s)} [f_m^{(s)}]_{a_s a'_s} \right)$$

$$\left[ \frac{\partial}{\partial t} \begin{array}{c} a_s \\ \gamma \end{array} \bullet \begin{array}{c} \beta \\ \gamma \end{array} \right] = \sum_m \left( \begin{array}{c} a_s - \mathcal{C}_m^{(s)} \bullet \begin{array}{c} f_m^{(\beta)} \\ f_m^{(\gamma)} \end{array} \bullet \begin{array}{c} \beta \\ \gamma \end{array} \\ - a_s - \mathcal{C}_m^{(s)} \bullet \begin{array}{c} f_m^{(s)} \\ f_m^{(s)} \end{array} \bullet \begin{array}{c} \beta \\ \gamma \end{array} \end{array} \right)$$



71

## Propagation Strategies

Adapt propagation strategies from MCTDH to the TTN-HEOM

### Projector Splitting 1

- Trotterization algorithm. Errors determined by split time step
- Challenging to parallelize
- Fixed rank
- Also adapted by Ke in JCP 158, 211102 (2023)

### Projector Splitting 2

- Similar features to PS1
- Two-site algorithm
- Adaptive rank

### Direct Propagation of Master Equation for Core Tensors

- Admits high-order numerical propagation schemes (e.g. Runge-Kutta) and their parallelization
- Requires regularization like in MCTDH (specially at early times)
- Fixed rank

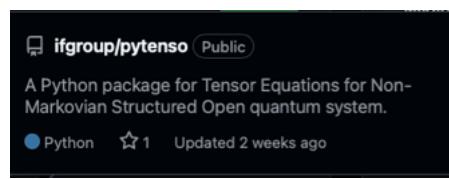
THIS WORK



72

## TENSO

- Implemented in Python with NumPy and PyTorch
- Supports HEOM/ML-MCDTH/etc in a unified framework
- Supports direct integration, PS1, PS2 and mixed strategies for propagation
- Can handle structured baths for molecular systems
- Arbitrary tensor trees and tensor order
- Open source and available on GitHub



<https://github.com/ifgroup/pytenso>



73

## Example: Two-surface molecule

$$H_S = \frac{E}{2}\sigma_z + V\sigma_x \quad Q_S = \sigma_z \quad |\psi\rangle = \frac{1}{\sqrt{2}}(|0\rangle + |1\rangle)$$

Spectral density for thymine in 300 K water

**Bath Features  $K = 20$**

- 1 from Drude-Lorentz solvent
- 16 from Brownian Oscillators
- 3 from low temperature corrections (Padé)

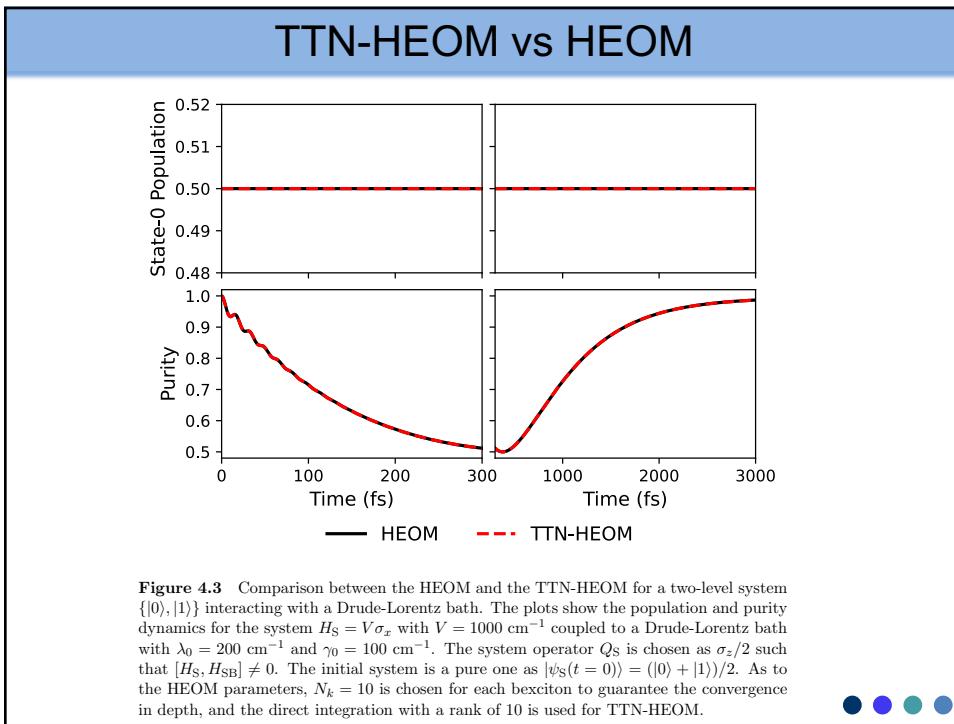
**Impossible for other HEOM implementations**

Gustin, McCamant, Franco PNAS **120**, e2309987120 (2023)

	Balanced Tree			Train			Dense HEOM
Rank	40	60	80	40	60	80	—
Size ( $\times 10^6$ )	0.7	2.2	4.9	0.6	1.3	2.3	$4.2 \times 10^{20}$

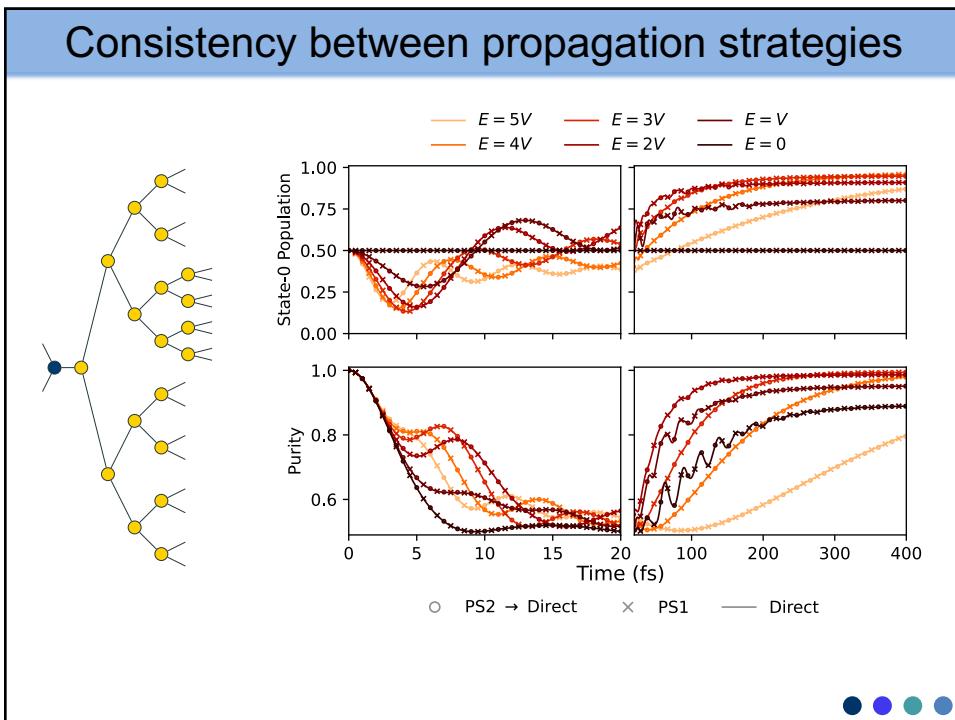
**Table 4.2** The size (overall number of core tensor elements) of TTN for a bath described by 20 features and a depth of 20 for each  $N_k$ . The memory usage of a dense high-order EDO tensor in HEOM is also showed for comparison.

74

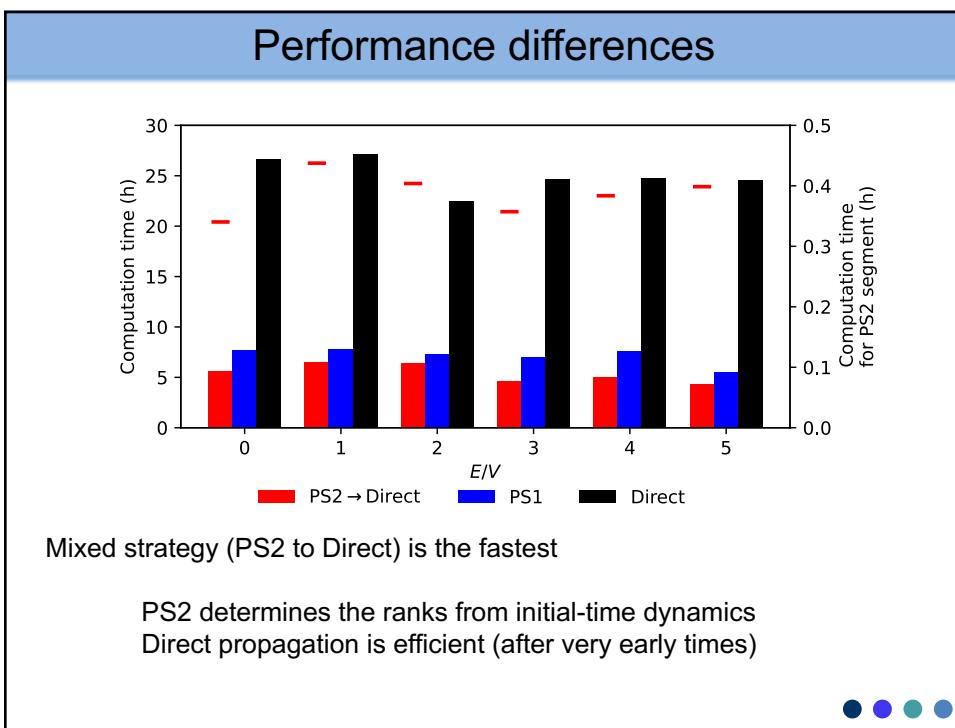


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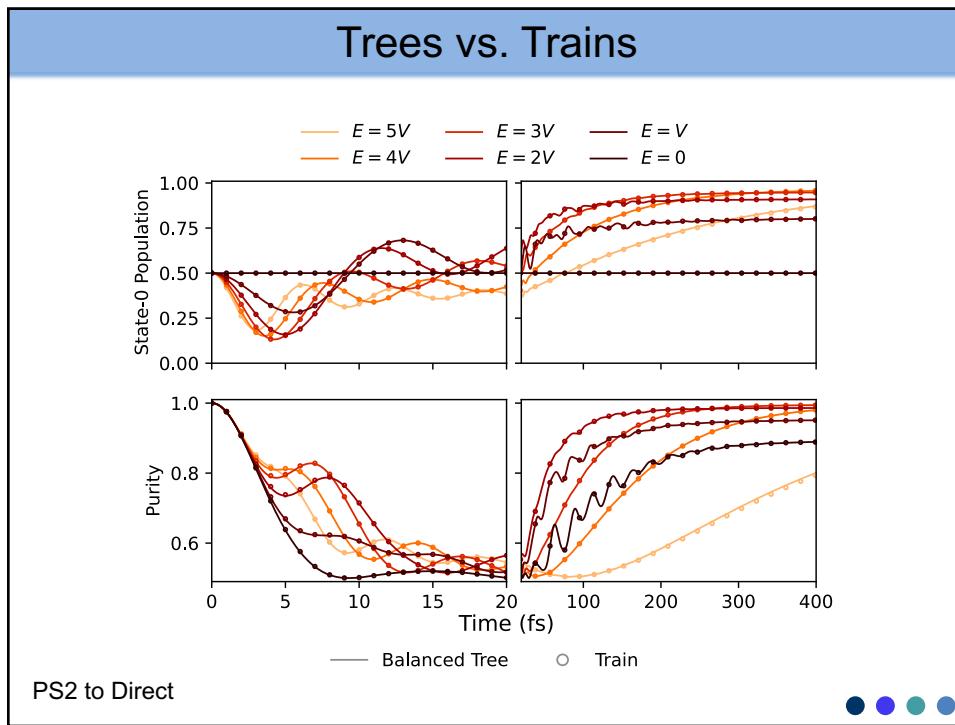




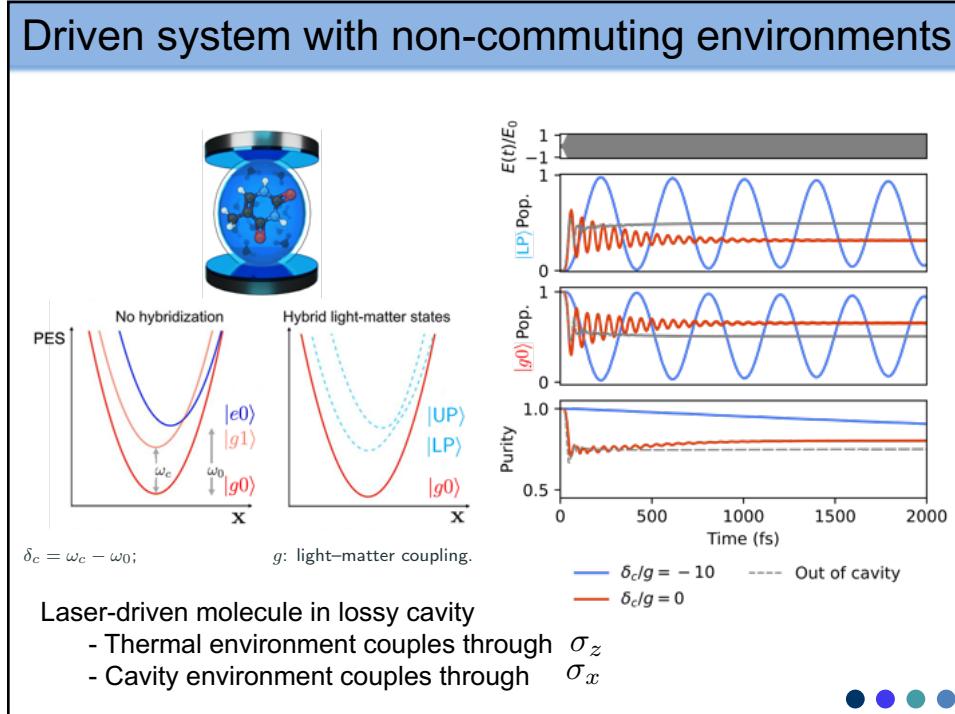
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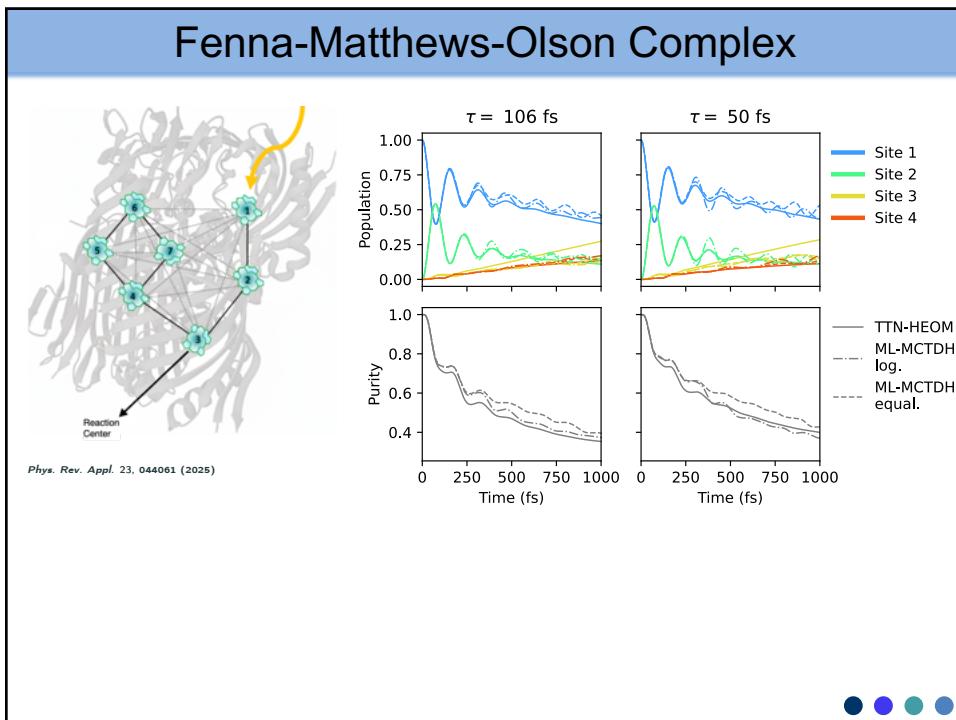
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78



79



80



### Tree Tensor Network HEOM and TENSO

Xinxian Chen and IF, *J. Chem. Phys.* **160**, 204116 (2024)  
*J. Chem. Phys.* **163**, 104109 (2025)

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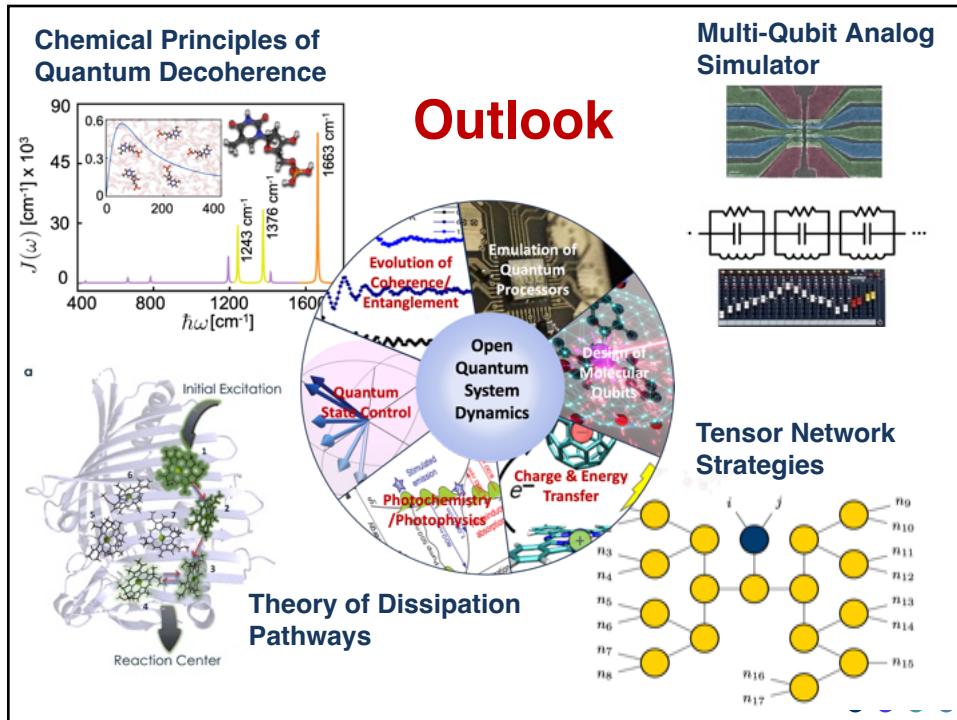
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81



82



83