Virtual International Seminar on Theoretical Advancements

Quantum dissipative dynamics approach to many-body open quantum systems

Xiao Zheng （郑 晓）

Email: xzheng@fudan.edu.cn

Department of Chemistry, Fudan University

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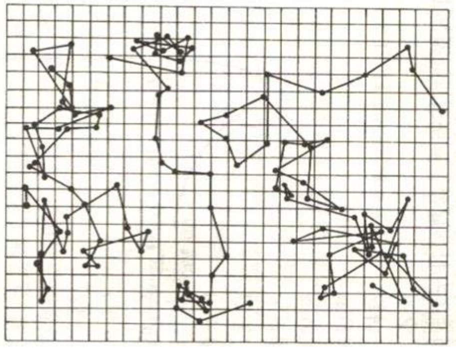
Outline

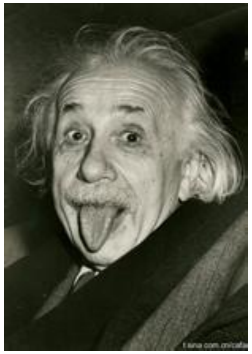
1. **Background and motivation**
2. Fermionic HEOM & SEOM methods
3. Application to molecules on surfaces
4. Summary

Classical dissipative system

Brownian motion

Experiment
(1827)





Theory
(Einstein 1905)

- **Langevin Equation (1908)**

$$m\frac{d^2\boldsymbol{x}}{dt^2} = -\lambda\frac{d\boldsymbol{x}}{dt} + \boldsymbol{\eta}(t)$$

Friction (dissipation)

Random driving (fluctuation)

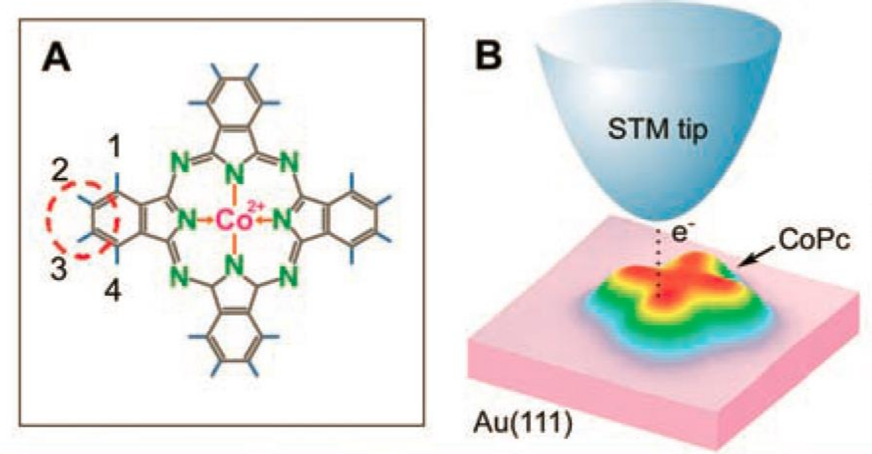
- **Fokker-Planck Equation (1914)**

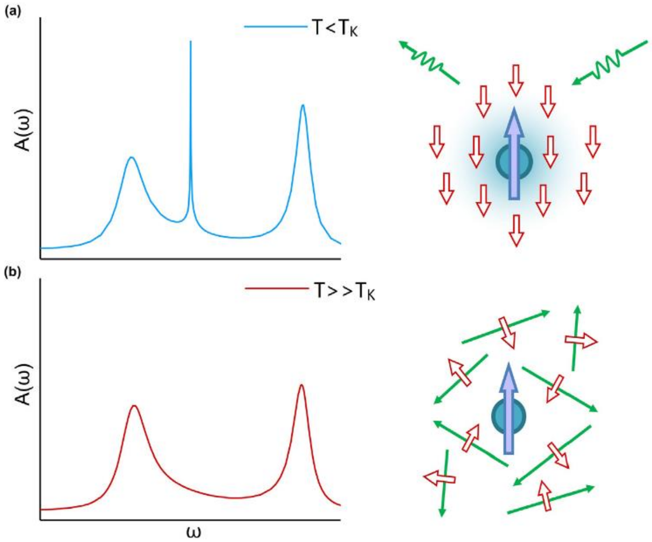
$$\frac{\partial p(x,t)}{\partial t} = -\frac{\partial[\mu(x,t)p]}{\partial x} + \frac{\partial^2[D(x,t)p]}{\partial x^2}$$

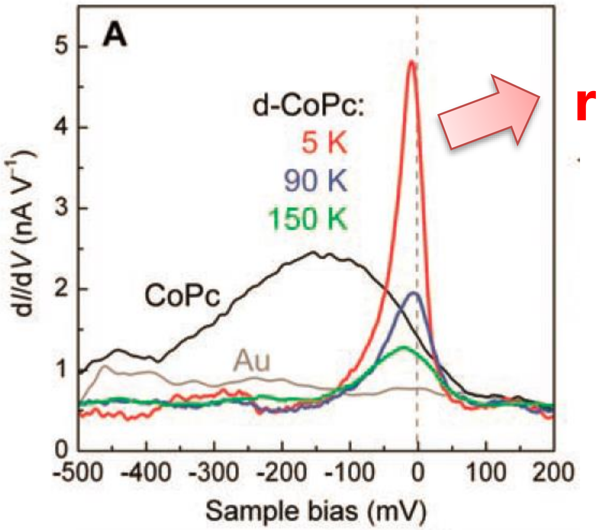
Particles' drift

Diffusion

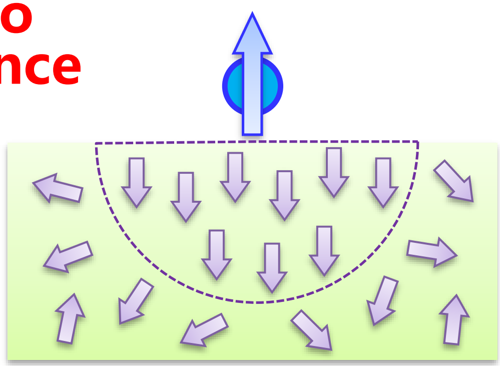
Kondo state in molecule/metal composite







Kondo resonance



Kondo state

Jun Kondo

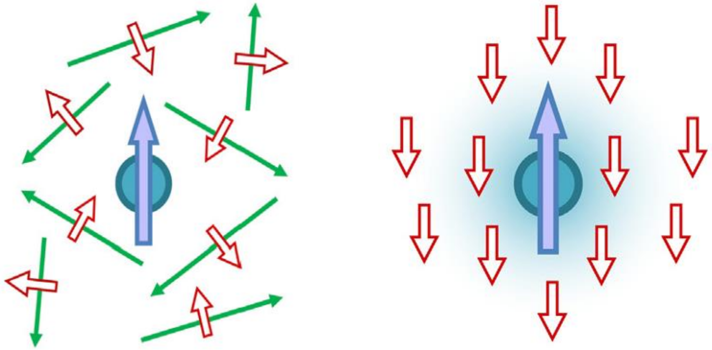
Zhao, Yang, and Hou et al., **Science** 309, 1542 (2005)

Classical *vs* quantum environment

➢ Brownian motion

fluctuation & dissipation

➢ Kondo screening



High *T* **Low *T***

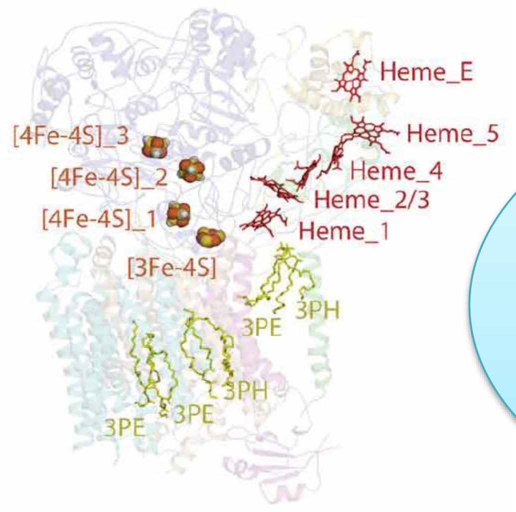
quantum coherence & correlation

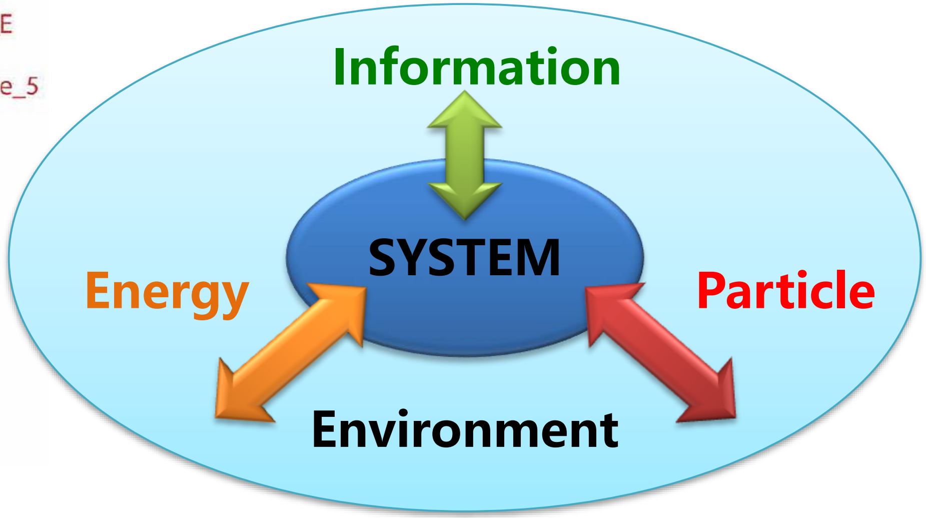
➢ Active roles of environment

- Enable formation of unconventional quantum states
- Mediate or screen long-range many-body interaction
- Provide new channels for tuning system properties

Open quantum systems

Electron transfer in enzymes





Information

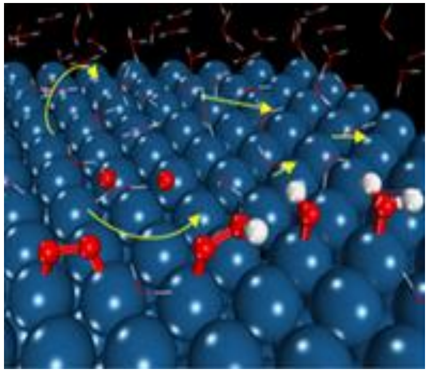
SYSTEM

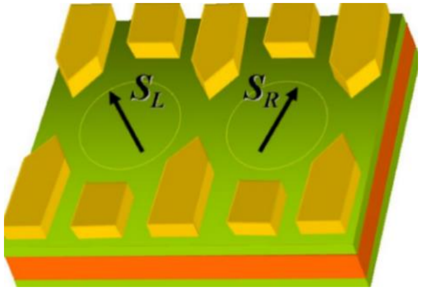
Energy

Particle

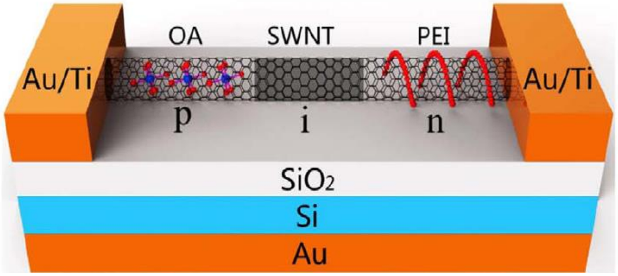
Environment

Electrochemical interfaces

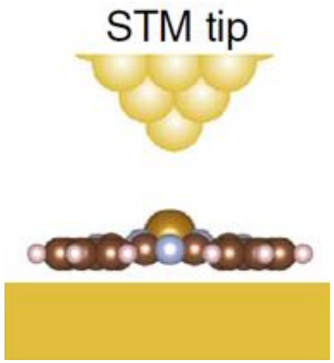




Solid-state qubits

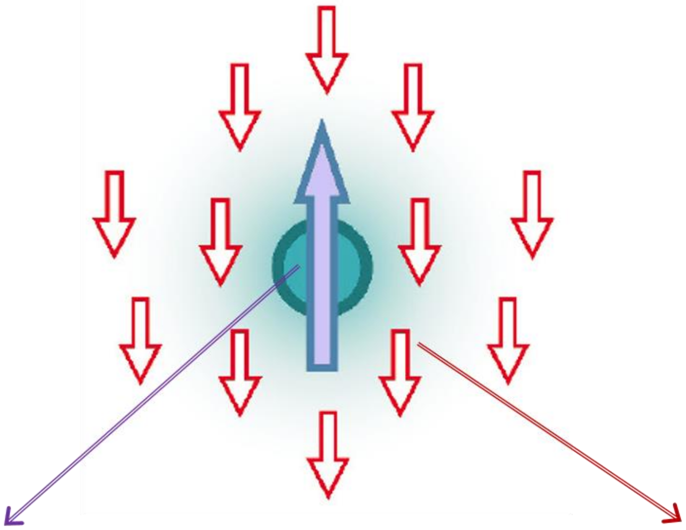


Nanoelectronic devices



Molecular junctions

An open-system perspective



System $(\mathrm{DoF} = 1)$:
Highly accurate *quantum mechanical* description

Environment $\left(\mathrm{DoF} \approx 10^{23}\right)$:
Highly accurate *quantum statistical* description

- **Simulate real complex systems**
- **Reproduce and predict experimental observations**
- **Reveal mechanisms behind exotic quantum phenomena**

Methods for many-body open quantum systems

- Numerical renormalization group (NRG)

Wilson (1975), Costi (1997), Weichselbaum and von Delft (2007)

- Quantum Monte Carlo (QMC)

Hirsch and Fye (1986), Gull et al. (2011), Cohen et al. (2015)

- Density matrix renormalization group (DMRG)

White (1992), Xiang (1996), Shuai (1997), White and Feiguin (2004), Vidal (2004)

- Single- and many-body Green function (GF)

Kadanoff and Baym (1962), Myohanen et al. (2008), Thygesen and Rubio (2008)

- Exact diagonalization (ED)

Dagotto (1994), Caffarel and Krauth (1994), Si et al. (1994)

- Real-time path-integral

Muhlbacher and Rabani (2008), Weiss and Egger (2008), Segal, Millis, and Reichman (2010)

- Many others

Quantum dissipation theories

- **Isolated system: Schrödinger/Liouville equation**

$$\dot{\rho}_{\mathrm{T}}(t) = -i\left[H_{\mathrm{T}}, \rho_{\mathrm{T}}\right]$$

- **Open system**

$$H_{\mathrm{T}} = H_{\mathrm{sys}} + H_{\mathrm{bath}} + H_{\mathrm{sb}}$$

Reduced density matrix ⇦

$$\rho(t) \equiv \mathrm{tr}_{\mathrm{B}}\left[\rho_{\mathrm{T}}(t)\right]$$

$$\dot{\rho}(t) = -i\left[H_{\mathrm{sys}}, \rho(t)\right] - \underline{\mathcal{R}\,\rho}$$

dissipation

- **Problem: What is the exact form of $\mathcal{R}$?**

An overview of theories

- **Quantum master equation (Mori-Zwanzig projection)**

$$\dot{\rho}(t) = -i[H_{\text{sys}}, \rho(t)] - \int_{-\infty}^{t} d\tau\, \underline{C(t,\tau)}\rho(\tau)$$

Memory effect

- **Perturbative approximation: weak system-bath coupling**

☐ Lindblad master equation

$$\dot{\hat{\rho}} = \mathcal{L}\hat{\rho} = -i[\hat{H}, \hat{\rho}] + \sum_j \frac{\gamma_j}{2}[2\hat{L}_j\hat{\rho}\hat{L}_j^\dagger - \{\hat{L}_j^\dagger\hat{L}_j, \hat{\rho}\}]$$

- **Markovian approximation:** $C(t,\tau) \sim \delta(t-\tau)$

✓ **Preserves positivity of reduced density matrix**

Breuer and Petruccione, **The Theory of Open Quantum Systems** (Oxford University Press, 2007)

An overview of theories

➢ Exact theories

☐ Hierarchical equations of motion (HEOM)

$$\begin{aligned}\frac{\partial}{\partial t}\hat{\rho}^{(n)}_{j_1,\ldots,j_K}(t) = &-\left[i\hat{L}_A + n\gamma + \sum_{k=1}^{K} j_k\nu_k + \hat{\Xi}\right]\hat{\rho}^{(n)}_{j_1,\ldots,j_K}(t) \\ &+ \hat{\Phi}\left[\hat{\rho}^{(n+1)}_{j_1,\ldots,j_K}(t) + \sum_{k=1}^{K}\hat{\rho}^{(n)}_{j_1,\ldots,j_k+1,\ldots,j_K}(t)\right] \\ &+ n\hat{\Theta}_0\hat{\rho}^{(n-1)}_{j_1,\ldots,j_K}(t) + \sum_{k=1}^{K} j_k\hat{\Theta}_k\hat{\rho}^{(n)}_{j_1,\ldots,j_k-1,\ldots,j_K}(t)\end{aligned}$$

Ryogo Kubo

Tanimura and Kubo (1989), Yan and Shao et al. (2004), Xu and Yan (2005), Jin, Zheng and Yan (2008), Shi et al. (2009), Wu (2015)

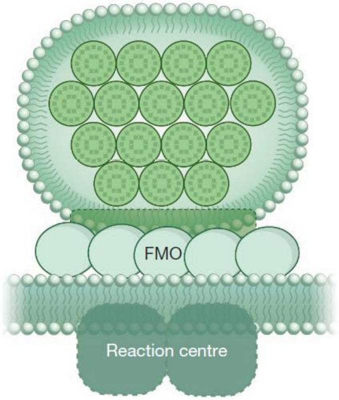
☐ Stochastic equation of motion (SEOM)

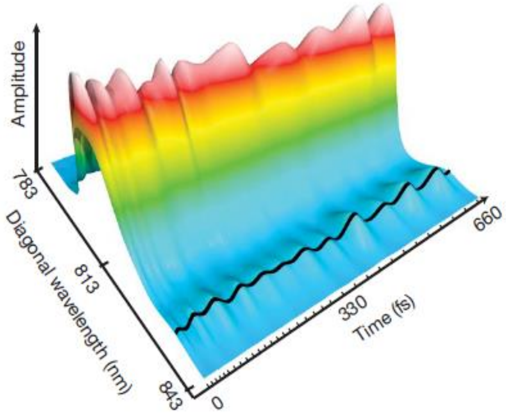
$$i\hbar\dot{\rho} = [H_0,\rho] + \frac{\mu}{2}[q^2,\rho] - \xi[q,\rho] - \frac{\hbar}{2}\nu\{q,\rho\}$$

Stockburger and Mak (1998), Stockburger and Grabert (2002), Shao (2004), Moix and Cao (2013), Zhu, Liu and Shi (2013), Han and Zheng et al. (2019)

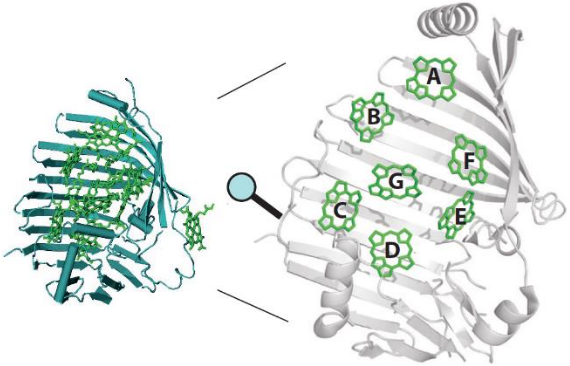
Quantum coherence in living systems

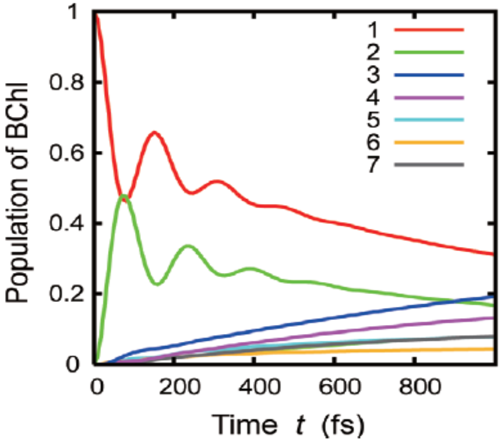
- **Fenna-Matthews-Olson (FMO) complex in photosystem**





Experiment
(2D spectrum)





Simulation
(HEOM method)

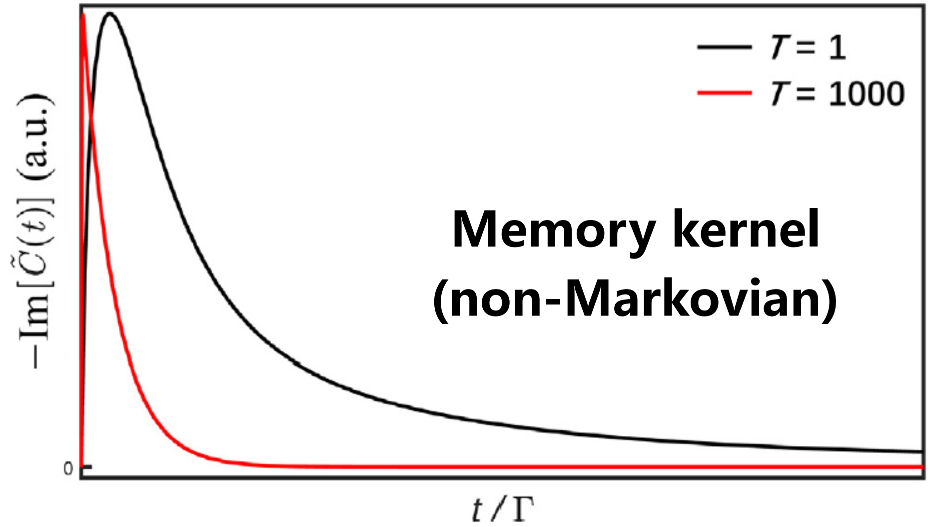
Flemming et al., **Nature** 446, 782 (2007); Ishizaki and Flemming, **PNAS** 106, 17255 (2009)

Challenges

➢ Limitations of existing theoretical methods

- Bosonic environment
- High temperature
- Weak coupling regime
- Simple model systems

- Fermionic environment
- Low temperature
- Strong coupling regime
- Real complex systems



Memory kernel
(non-Markovian)

Significant advancements in experiments

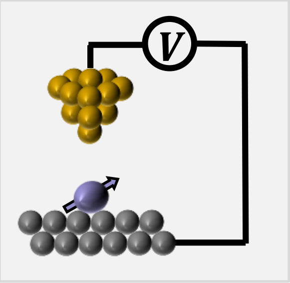
- **Theoretical challenge: unprecedentedly high energy resolution**

Energy resolution (eV)

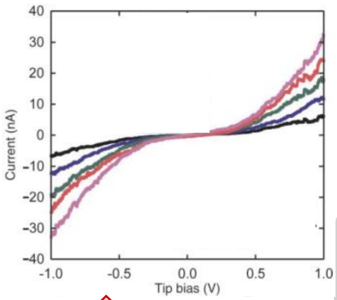
10^{-6}

10^{-3}

10^{0}

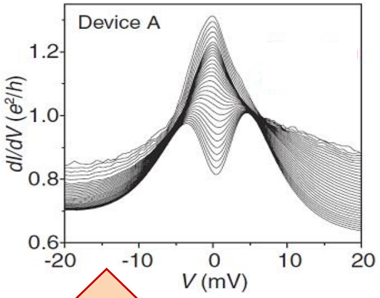


Cui et al., **Science** 294, 571 (2001)



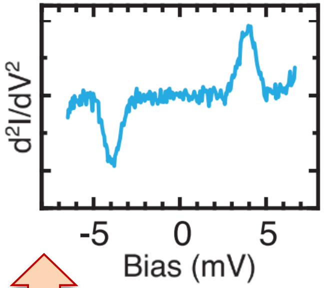
STM
Charge-state excitation

Parks et al., **Science** 328, 1370 (2010)



STM
Local spin excitation

Czap et al., **Science** 364, 670 (2019)



SP-STM
Enhanced spin sensing

~ 1 meV

2010

2020

Year

Outline

1. Background and motivation
2. **Fermionic HEOM & SEOM methods**
3. Application to molecules on surfaces
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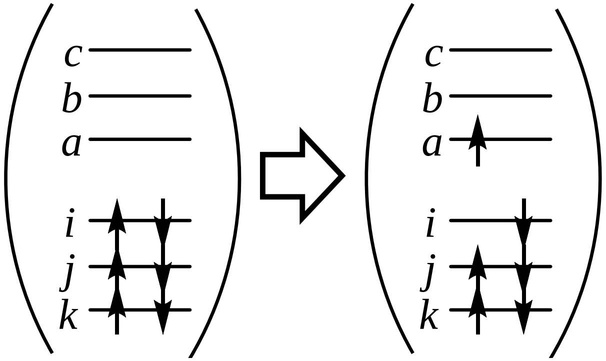
Coupled cluster (CC) theory

- **CC expansion of electron excitations**

$$|\Psi\rangle = e^{\hat{T}}\underline{|\Phi_0\rangle} \Rightarrow$$

Reference state



$$T = T_1 + T_2 + T_3 + \cdots$$

$$T_n = \frac{1}{(n!)^2} \sum_{i_1,i_2,\ldots,i_n} \sum_{a_1,a_2,\ldots,a_n} \underbrace{t^{i_1,i_2,\ldots,i_n}_{a_1,a_2,\ldots,a_n}}_{\text{Amplitudes of excitations}} \hat{a}^{a_1}\hat{a}^{a_2}\ldots\hat{a}^{a_n}\hat{a}_{i_n}\ldots\hat{a}_{i_2}\hat{a}_{i_1}$$

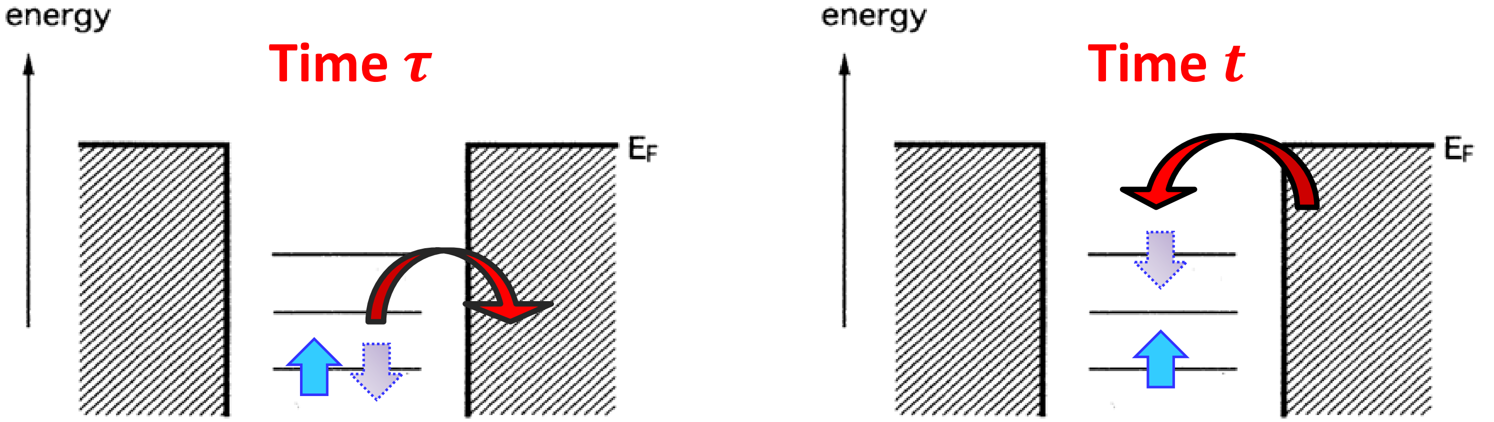
$\hat{a}^a = \hat{a}_a^\dagger$ and $\hat{a}_i$ denote the creation and annihilation operators

Path integral formulation

- **CC-like expansion for impurity-reservoir coupling**

$$\rho = \mathcal{U}(t,t_0)\rho_0 \quad \Rightarrow \quad \rho = \int e^{-\int_{t_0}^{t}\mathcal{R}(\tau)d\tau}\rho_0$$

$$\mathcal{R}(t) = \sum_{\sigma=\pm}\left(\psi_t^{\bar{\sigma}} + \psi_t'^{\bar{\sigma}}\right)\int_{t_0}^{t} d\tau \left\{C^{\sigma}(t-\tau)\psi_\tau^{\sigma} - \left[C^{\bar{\sigma}}(t-\tau)\right]^{*}\psi_\tau'^{\sigma}\right\}$$



Environment-mediated excitations

Construction of fermionic HEOM

- **Decomposition of memory kernel: elementary process**

$$C^{\sigma}(t) = \sum_{m=1}^{M} B_m^{\sigma} e^{-\gamma_m^{\sigma} t}$$

- **Excitations with characteristic memory times** $\{1/\gamma_m^{\sigma}\}$

$$\mathcal{R}(t) = \sum_{\sigma=\pm} \mathcal{R}^{\sigma}(t) = \sum_{\sigma=\pm} \sum_{m=1}^{M} \mathcal{R}_m^{\sigma}(t)$$

$$\partial_t \mathcal{R}_m^{\sigma}(t) \propto -\gamma_m^{\sigma} \mathcal{R}_m^{\sigma} + B_m^{\sigma} \psi_t$$

- **Auxiliary density operators (ADOs) as amplitudes of excitations**

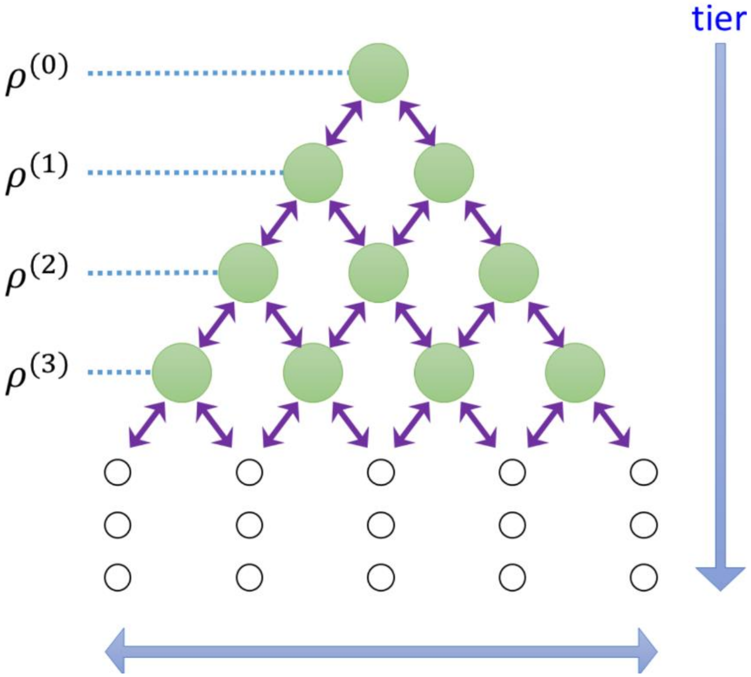
$$\rho_{m_1 \cdots m_I n_1 \cdots n_J}^{(- \cdots - + \cdots +)} \propto (-i)^{I+J} \mathcal{F} \mathcal{R}_{m_I}^{-} \cdots \mathcal{R}_{m_1}^{-} \mathcal{R}_{n_J}^{+} \cdots \mathcal{R}_{n_1}^{+} \rho_0$$

Construction of fermionic HEOM

$$\dot{\rho}^{(n)}_{j_1\cdots j_n} = \left(-i\mathcal{L}_s + \sum_{r=1}^{n}\gamma_{j_r}\right)\rho^{(n)}_{j_1\cdots j_n} + \sum_{j=1}^{N_j}\mathcal{A}_j\,\rho^{(n+1)}_{j_1\cdots j_n j} + \sum_{r=1}^{n}\mathcal{C}_{j_r}\,\rho^{(n-1)}_{j_1\cdots j_{r-1}j_{r+1}\cdots j_n}$$

✓ Formally exact

- Computational cost scales exponentially with M and L
- Careful handling of truncation error



Depth L: Strength of many-body correlation

Width M: Memory time (temperature)

Jin, Zheng and Yan, **J. Chem. Phys.** 128, 234703 (2008)

Roadmap for fermionic HEOM method

Enhanced efficiency & extensive applications

2007

- Matsubara spectrum decomposition
- Time-dependent electron transport
- Steady-state properties
- Quantum resonances

2012

- Padé spectrum decomposition
- Kondo phenomena
- Dynamic response properties
- HEOM-space Linear response theory

2014

- DMFT-HEOM for 1D Hubbard model
- Mott metal-insulator transition
- Thermoelectric properties

2016

- Sparse matrix technique
- Derivative-based terminator
- DFT+HEOM for realistic systems

2019

- Fano spectrum decomposition
- Competition between Kondo and spin excitation
- Local temperatures out of equilibrium

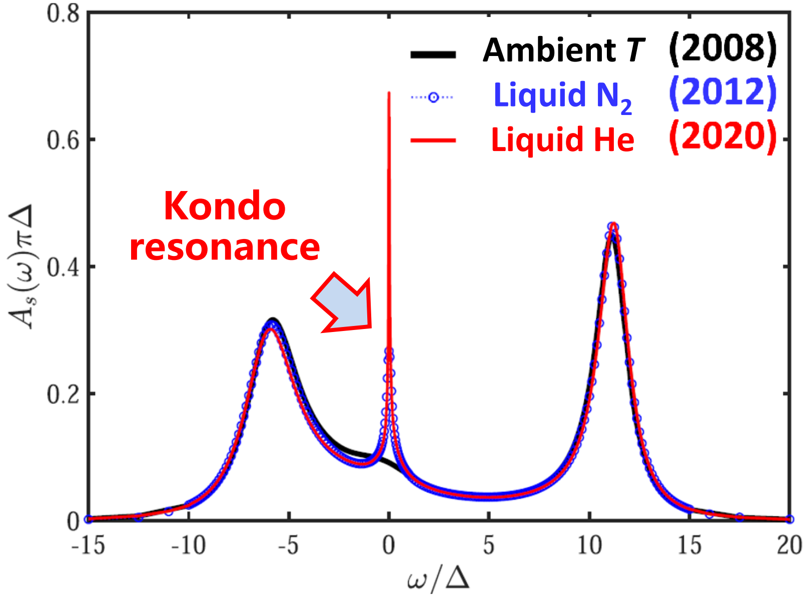
2021

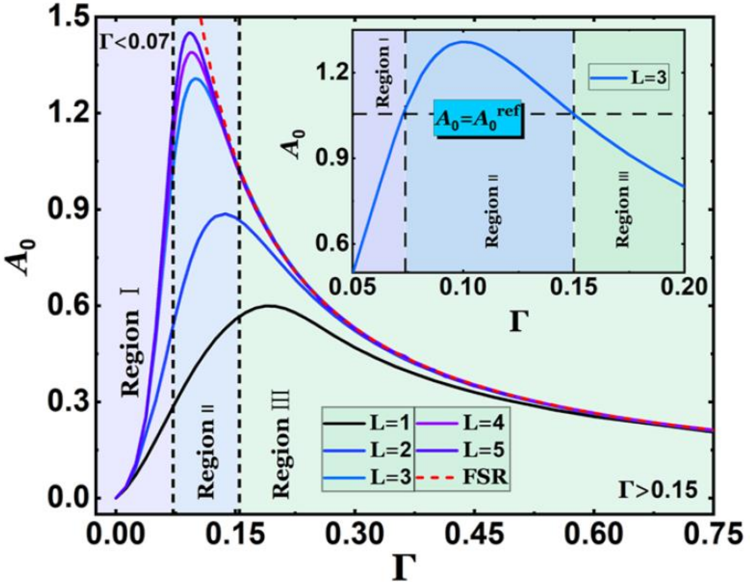
- Adiabatic terminator
- Projector for subsystem HEOM
- Prony fitting decomposition
- Spin excitation
- Long-time dynamics

Numerical performance of HEOM

- **Single-impurity Anderson model**

$$A_s(\omega) = \frac{1}{2\pi}\int_{-\infty}^{+\infty} dt\, e^{i\omega t}\langle\{\hat{d}_s(t), \hat{d}_s^{\dagger}\}\rangle$$





Highly accurate results achieved in low-T and strong-Γ regimes

Li, Zheng, and Yan et al., **Phys. Rev. Lett.** 109, 266403 (2012)
Zhang and Zheng et al., **J. Chem. Phys.** 152, 064107 (2020)
Ding and Zheng et al., **J. Chem. Phys.** 157, 224107 (2022)

Stochastic theories for boson bath

- **Non-Markovian quantum state diffusion (NMQSD)**

$$\frac{d}{dt}\psi_t = -iH\psi_t + L\psi_t z_t - L^\dagger \int_0^t \alpha(t,s)\frac{\delta\psi_t}{\delta z_s}ds$$

$\{z_t\}$: complex Gaussian white noises

Gisin and Percival (1992), Diósi and Strunz (1997), Jing and Yu (2010), Zhao et al. (2015)

- **Stochastic equation of motion (SEOM) method**

$$i\hbar\dot{\rho} = [H_0,\rho] + \frac{\mu}{2}[q^2,\rho] - \xi[q,\rho] - \frac{\hbar}{2}\nu\{q,\rho\}$$

$\{\xi, \upsilon\}$: complex Gaussian colored noises

Stockburger and Mak (1998), Stockburger and Grabert (2002), Shao (2004)

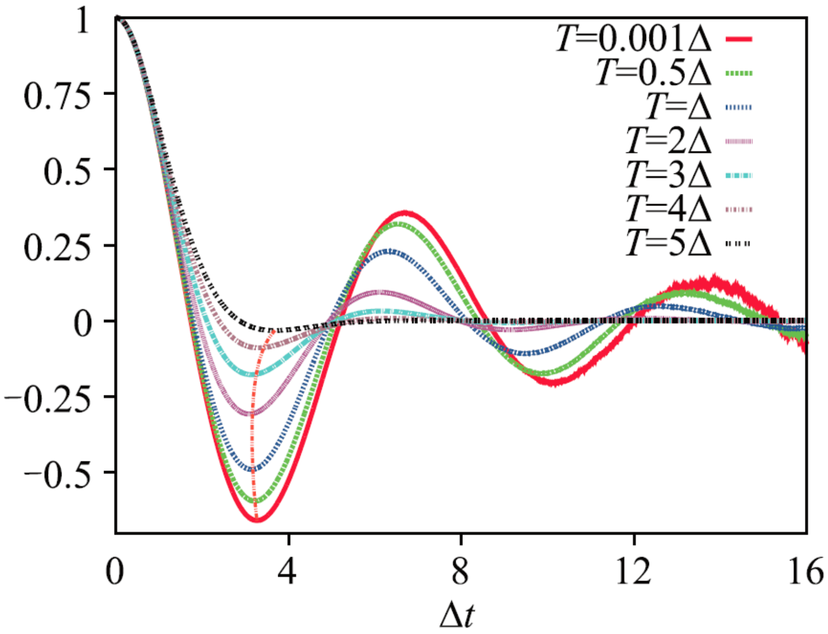
A single equation yields exact dissipative dynamics

Bosonic stochastic EOM

- Dissipative two-level system (spin-boson model)

☐ **decoupled initial state**

☐ **40 million trajectories**



Yan and **Shao**, **Front. Phys. China** (2016)

Evolution of population

$$\sigma_z(t) = \langle \hat{\sigma}_z \, \rho(t) \rangle = \mathcal{M}\{\mathrm{tr}(\hat{\sigma}_z \rho)\}$$

SEOM can easily access low-temperature regime

Fermionic stochastic EOM?

- **Analytic formulation of fermion Brownian motion was proposed as early as in 1980s**

Barnett, Streater and Wilder (1982), Applebaum and Hudson (1984), Rogers (1987)

- **Both NMQSD and SEOM were formally extended to fermionic open systems**

Zhao and Yu et al. (2012), Chen and You (2013), Suess, Strunz and Eisfeld (2015)

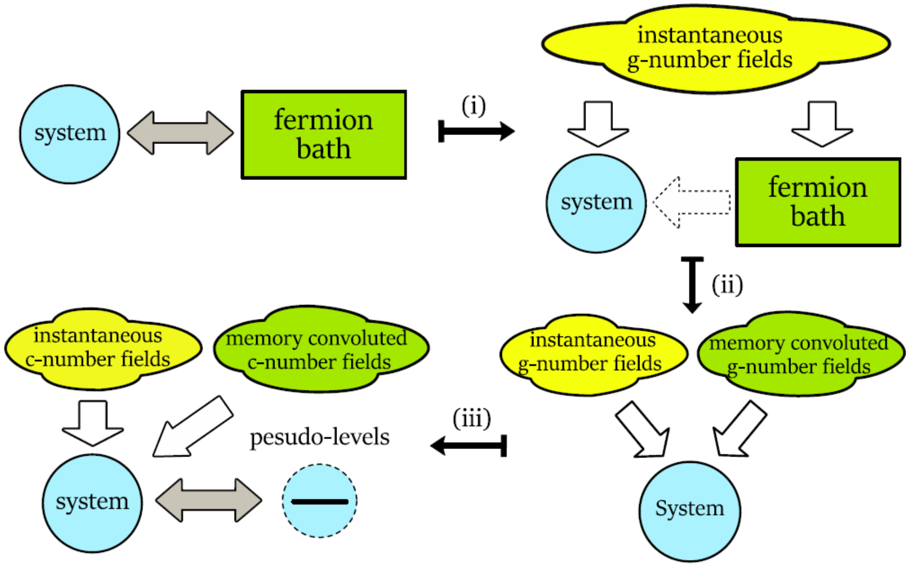
- **No direct stochastic numerical calculation**

Grassmann fields (g-fields) ⇨ $\eta_t\eta_\tau = -\eta_\tau\eta_t$ ⇨ **Need N matrices of size $2^N \times 2^N$**

Hsieh and **Cao**, ***J. Chem. Phys.*** 148, 014103 (2018)

A numerically feasible SEOM

- **The minimal-auxiliary-space mapping**



- **A numerically feasible fermionic SEOM**

$$\eta_t \mapsto v_t X^- \qquad \bar{\eta}_t \mapsto v_t X^+$$

$$\begin{aligned}\dot{\tilde{\rho}}_{\mathrm{S}} = -i[H_{\mathrm{S}}, \tilde{\rho}_{\mathrm{S}}] + e^{-i\pi/4}(\hat{c}^\dagger Y_1 + Y_2\,\hat{c})\tilde{\rho}_{\mathrm{S}} \\ + e^{i\pi/4}\tilde{\rho}_{\mathrm{S}}(\hat{c}^\dagger Y_3 + Y_4\,\hat{c})\end{aligned}$$

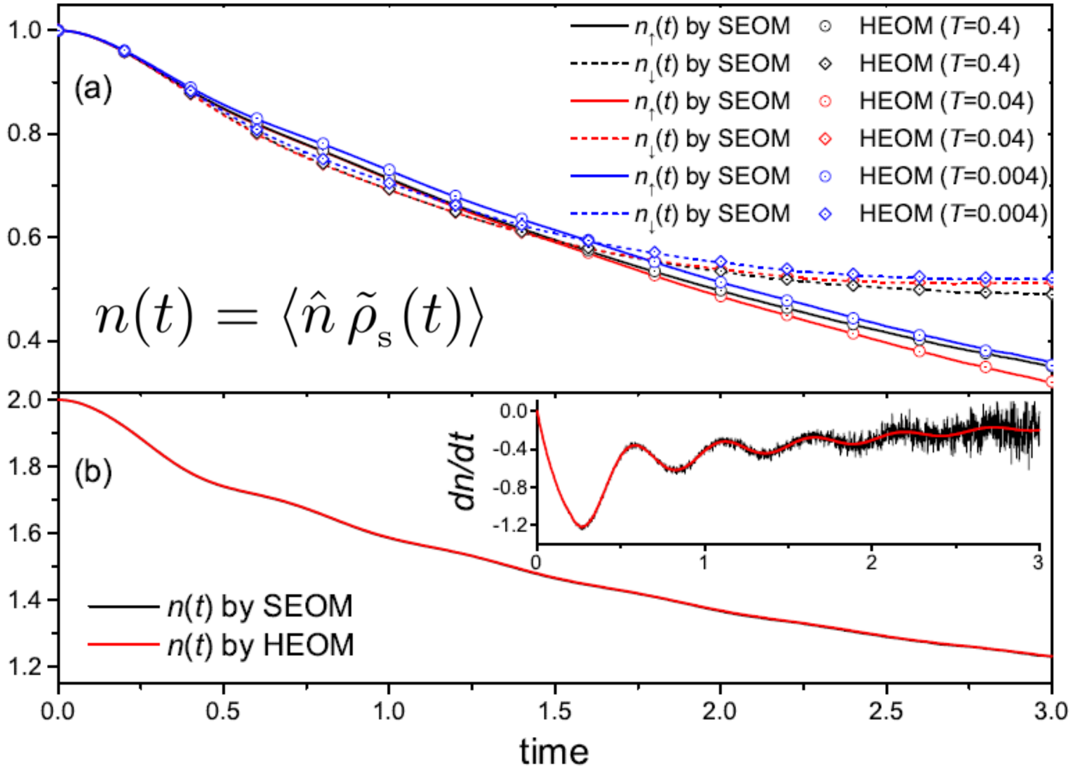
(CIS-like treatment)

Han and Zheng et al. **Phys. Rev. Lett.** 123, 050601 (2019)

Performance of fermionic SEOM

➢ Interacting single-impurity Anderson model

- **decoupled initial state**
- **5 million trajectories**



SEOM is highly accurate in the short-time regime

Han and **Zheng** et al., **Phys. Rev. Lett.** 123, 050601 (2019)
Zheng et al., **J. Chem. Phys.** 152, 204105 (2020); 152, 204106 (2020)

Fermionic HEOM versus SEOM

➢ Summary of current status

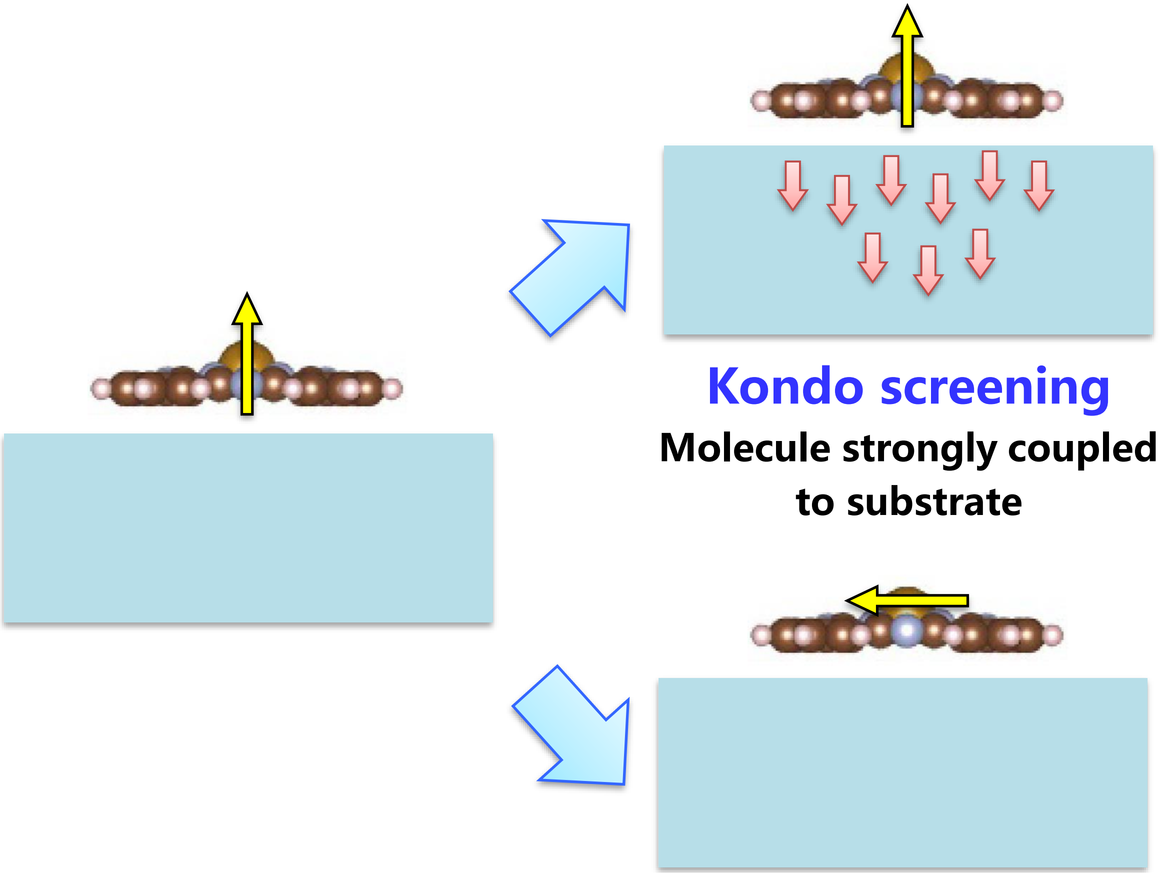
	HEOM	SEOM
Short-time dynamics	✓	✓
Long-time dynamics	✓	working
Stationary state	✓	✘
Correlated initial state	✓	✘
Numerically "exact" $(U = 0)$	✓	✓
Numerically "exact" $(U \neq 0)$	✓	✘
Low temperature	✓	✓
Strong sys-env coupling	✓	working
Massive parallelization	working	✓

Outline

1. Background and motivation
2. Fermionic HEOM & SEOM methods
3. **Application to molecules on surfaces**
4. Summary

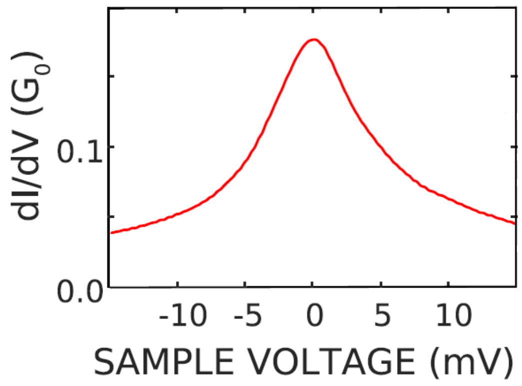
Control of molecular spin state

- **Kondo screening versus spin excitation**



Kondo screening

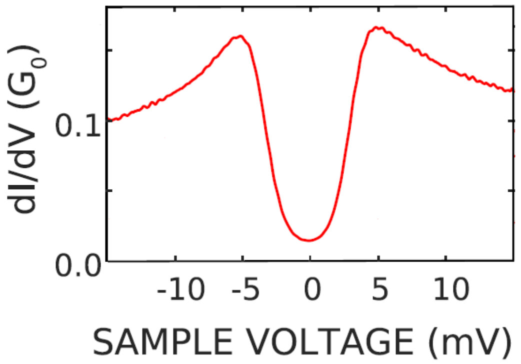
Molecule strongly coupled to substrate



Energy scale: ~meV

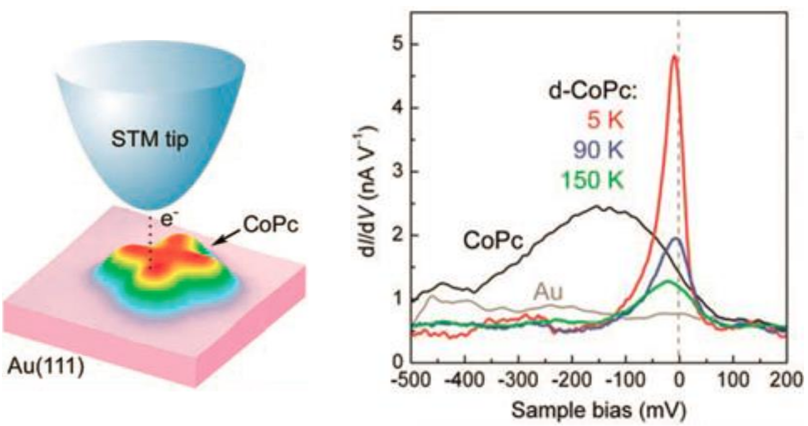
Spin-orbit coupling

Molecule weakly coupled to substrate

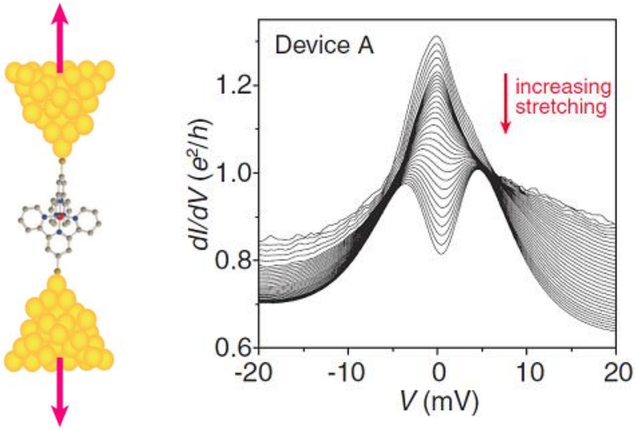


Control of molecular spin state

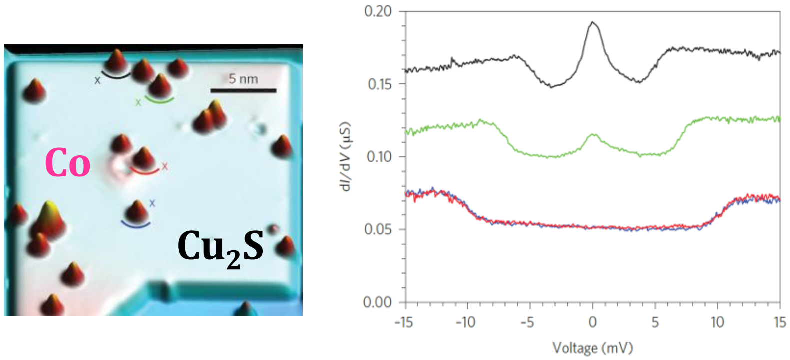
- **Kondo screening versus spin excitation**



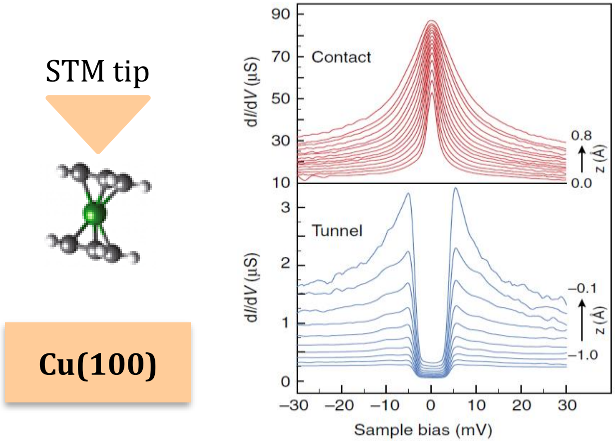
Zhao, **Yang** & **Hou** et al., **Science** 309, 1542 (2005)



Ralph et al., **Science** 328, 1370 (2010)



Hirjibehedin et al., **Nat. Nanotechnol.** 9, 64 (2014)



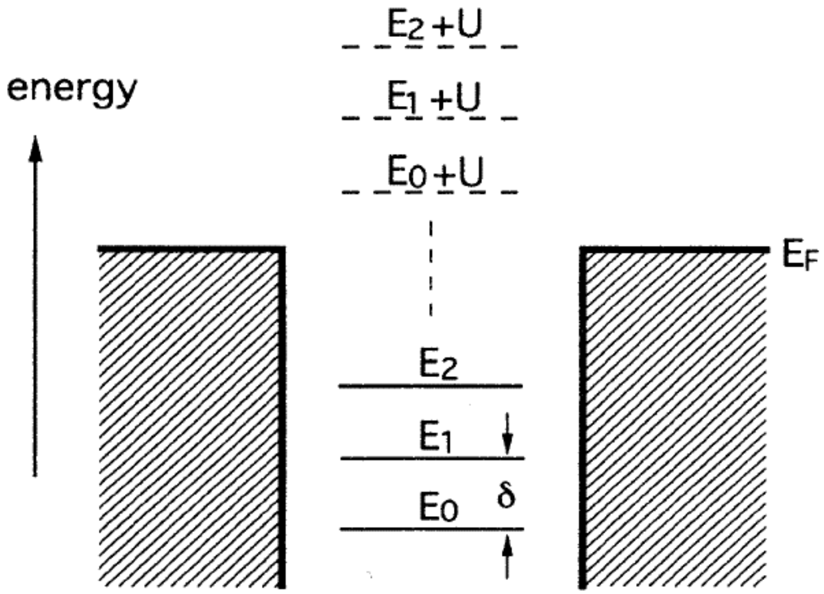
Ormaza et al., **Nat. Commun.** 8, 1974 (2017)

Many-body open quantum systems

- **Anderson impurity model (with extensions)**

$$H_{\text{total}} = H_{\text{impurity}} + H_{\text{reservoir}} + H_{\text{coupling}}$$

$$H_{\text{impurity}} = \sum_{is} \epsilon_{is}\, \hat{n}_{is} + U \sum_{i} \hat{n}_{i\uparrow}\, \hat{n}_{i\downarrow} + H_{\text{spin-field}} + H_{\text{spin-spin}}$$



$$H_{\text{reservoir}} = \sum_{\alpha} \sum_{ks} \epsilon_{k\alpha}\, \hat{d}^{\dagger}_{\alpha ks}\, \hat{d}_{\alpha ks}$$

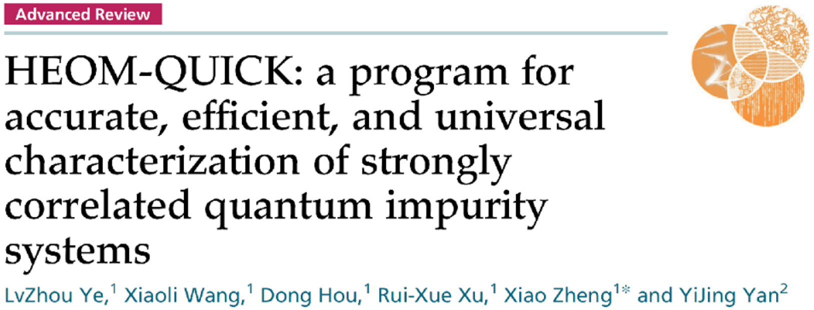
$$H_{\text{coupling}} = \sum_{\alpha iks} t_{\alpha ik}\, \hat{d}^{\dagger}_{\alpha ks}\, \hat{a}_{is} + \text{h.c.}$$

Gaussian statistics

Reservoir hybridization function

$$J_{\alpha,ij}(\omega) = \pi \sum_{\alpha k} t_{\alpha ik} t^{*}_{\alpha jk} \delta(\omega - \epsilon_{k\alpha})$$

HEOM for QUantum Impurity with a Correlated Kernel



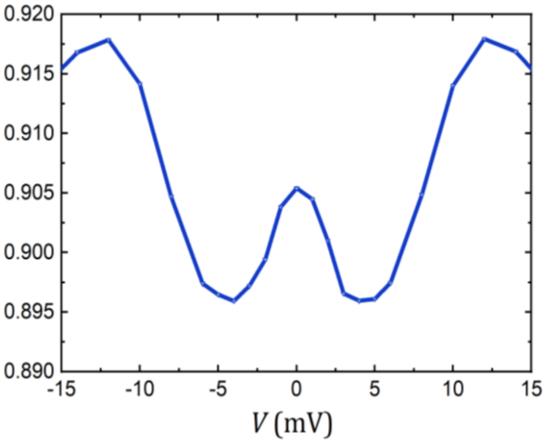
Advanced Review

HEOM-QUICK: a program for accurate, efficient, and universal characterization of strongly correlated quantum impurity systems

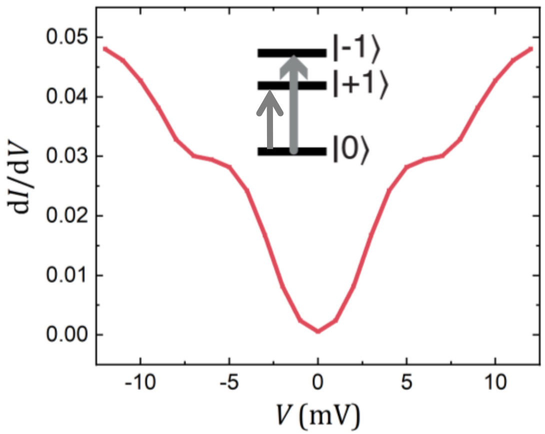
LvZhou Ye,[1] Xiaoli Wang,[1] Dong Hou,[1] Rui-Xue Xu,[1] Xiao Zheng[1]* and YiJing Yan[2]

WIREs Comput. Mol. Sci. 6, 608 (2016)

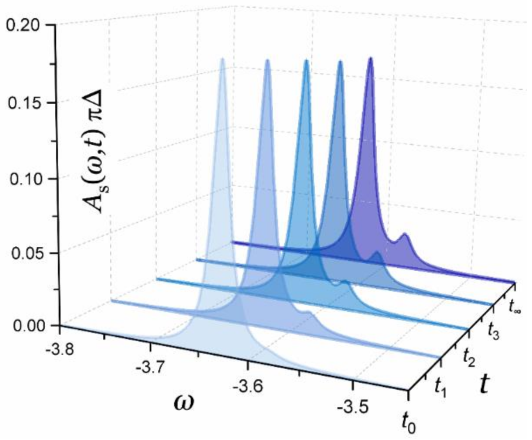
- **V1.0** **(2016): Accurate characterization of Kondo state**
- **V2.0** **(2023): Accurate characterization of spin excitation**



Kondo + spin excitation



Multiple spin excitations

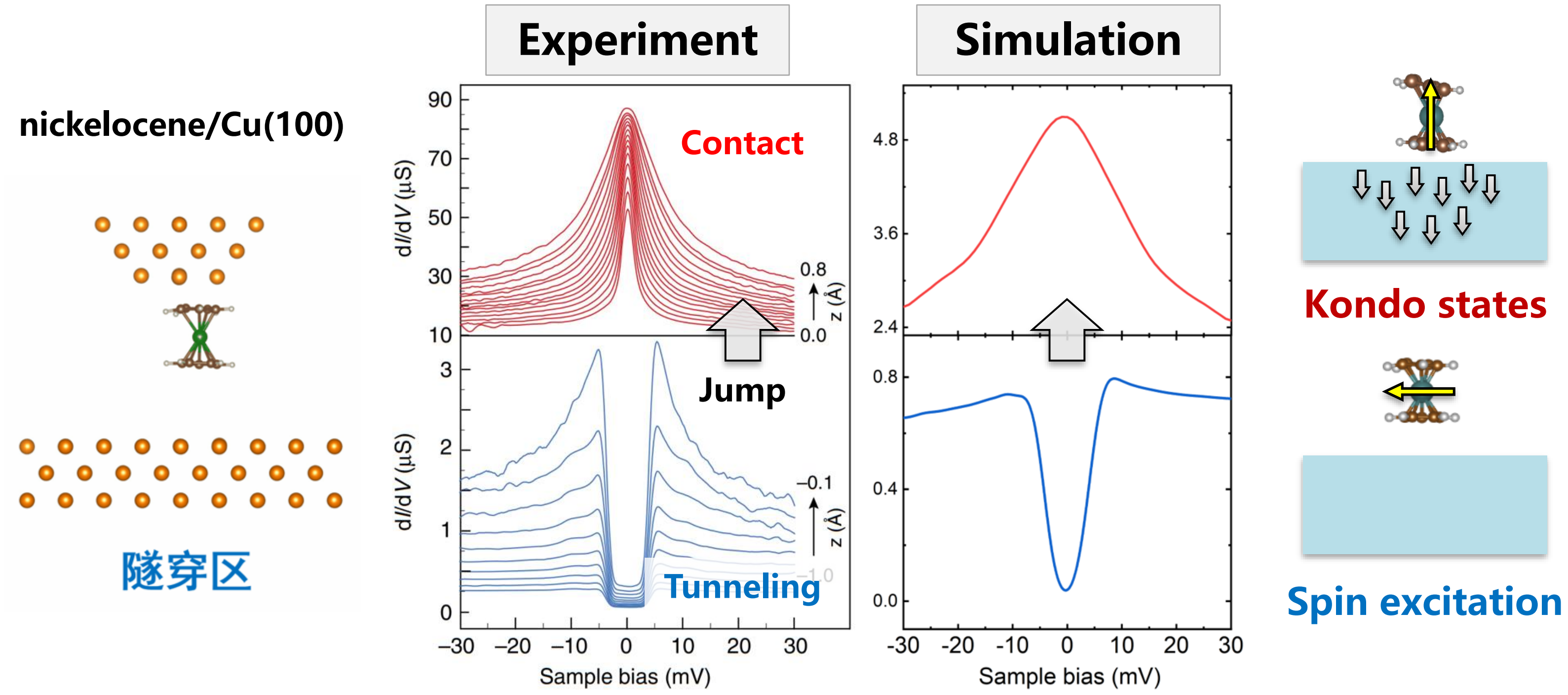


Dynamic spin excitation

Zhang and **Zheng** et al., **unpublished**

Competition between Kondo and spin excitation

- **Abrupt jump in the $\mathrm{d}I/\mathrm{d}V$ spectral lineshape: why?**



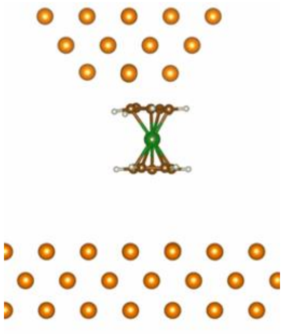
- **Uncover the decisive factor for the jump:**

Strength of hybridization between Ni d orbitals and surface bands

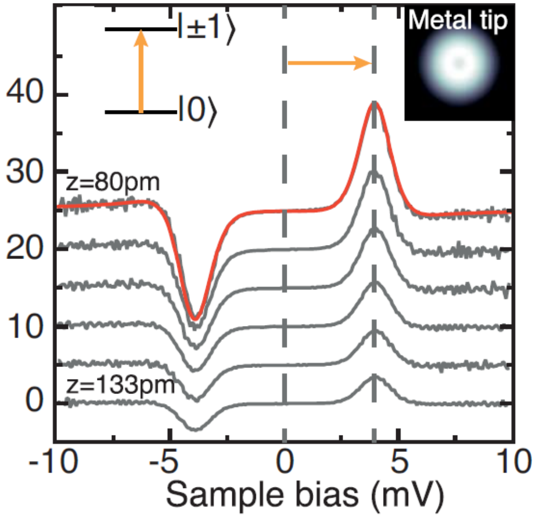
Zuo et al., **J. Phys. Chem. Lett.** 13, 11262 (2022)

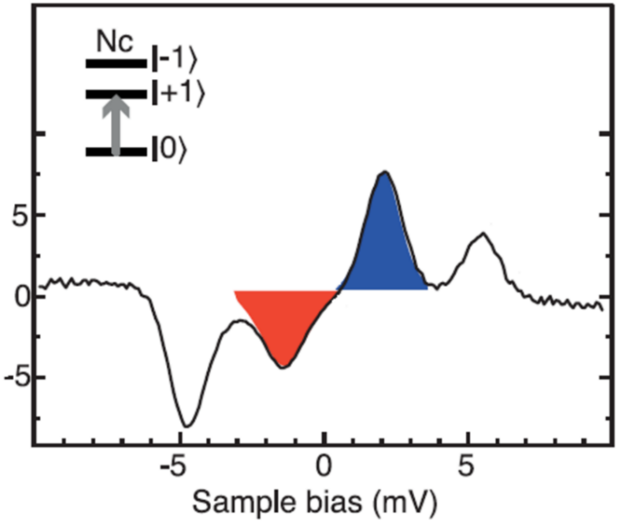
Enhanced spin sensing with SP-STM

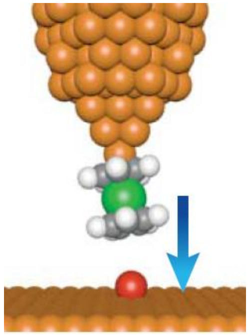
- **Experiment:** $\mathrm{d}^2 I/\mathrm{d}V^2$ **spectra (resolution < 1 meV)**



Cu(100)







Fe/Cu(100)

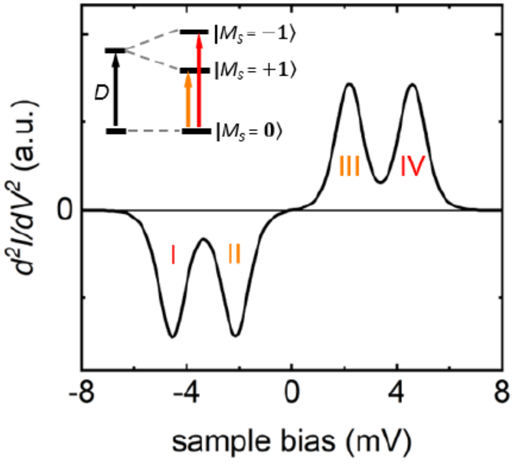
Verlhac and **Limot** et al., **Science** 366, 623 (2019)

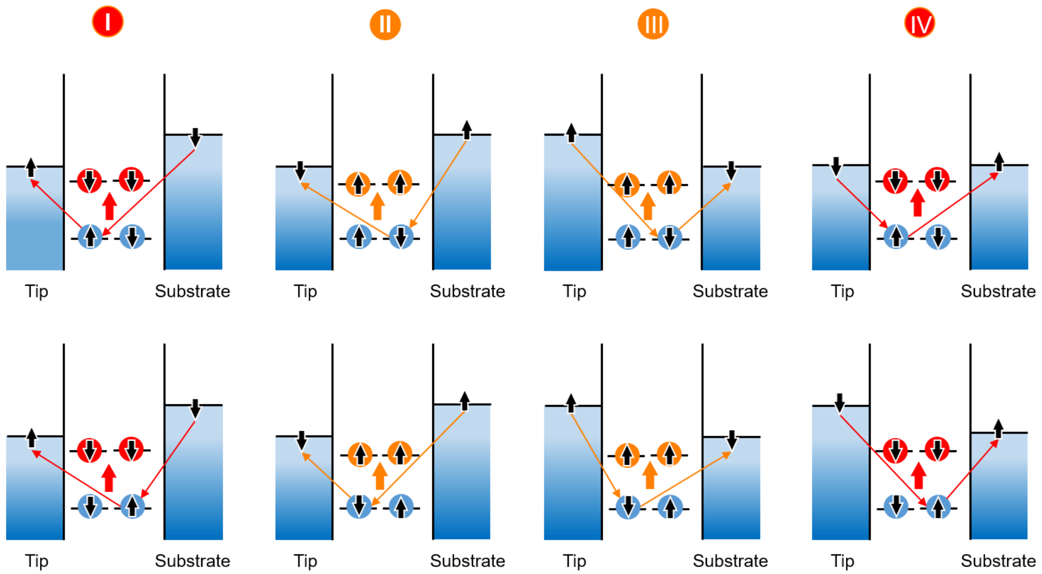
What do the peaks tell about the probed spin?

- **Theoretical study: an open-system approach**
  - **System:** d_{xz} & d_{yz} **orbitals on Ni-ion**
  - **Environment: Cu-tip** & **Fe/Cu(100)**

Enhanced spin sensing with SP-STM

➢ Analytic formulas by electron cotunneling theory





$$\eta = \frac{\Gamma_\uparrow - \Gamma_\downarrow}{\Gamma_\uparrow + \Gamma_\downarrow}$$

Spin polarization

$$\lambda = \frac{\Gamma_1 - \Gamma_2}{\Gamma_1 + \Gamma_2}$$

Orbital polarization

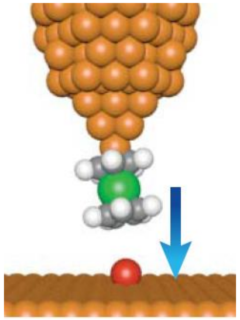
Peak area

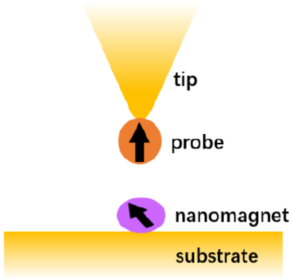
$$\begin{cases} T_{\mathrm{I}} = (1+\lambda)(1-\eta)\,\Gamma_s\Gamma_t \\ T_{\mathrm{II}} = (1-\lambda)(1+\eta)\,\Gamma_s\Gamma_t \\ T_{\mathrm{III}} = (1-\lambda)(1-\eta)\,\Gamma_s\Gamma_t \\ T_{\mathrm{IV}} = (1+\lambda)(1+\eta)\,\Gamma_s\Gamma_t \end{cases}$$

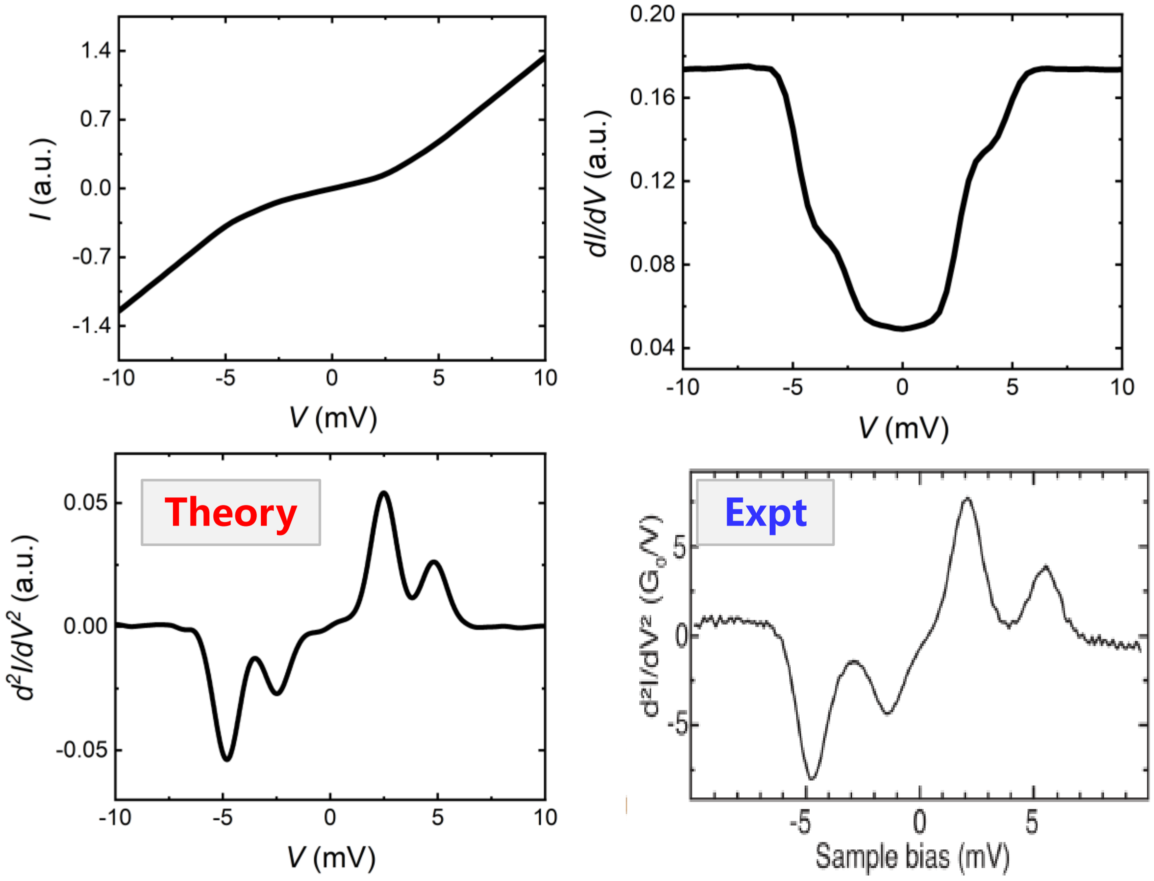
Zuo and **Zheng** et al., unpublished

Enhanced spin sensing with SP-STM

- Simulation (by HEOM-QUICK) versus experiment





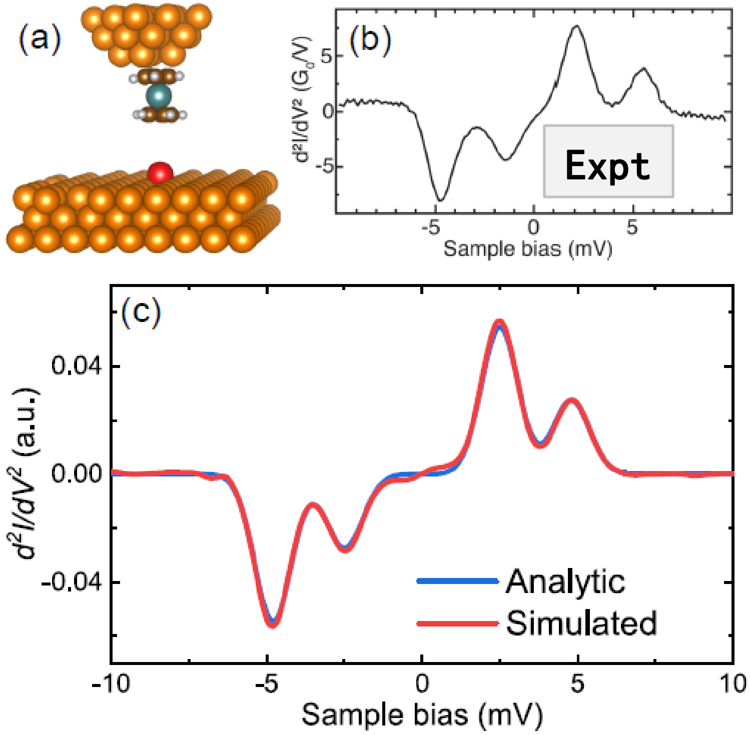


- **Peak position: probe-nanomagnet spin-exchange energy**
- **Peak area: rate of inelastic electron cotunneling process**

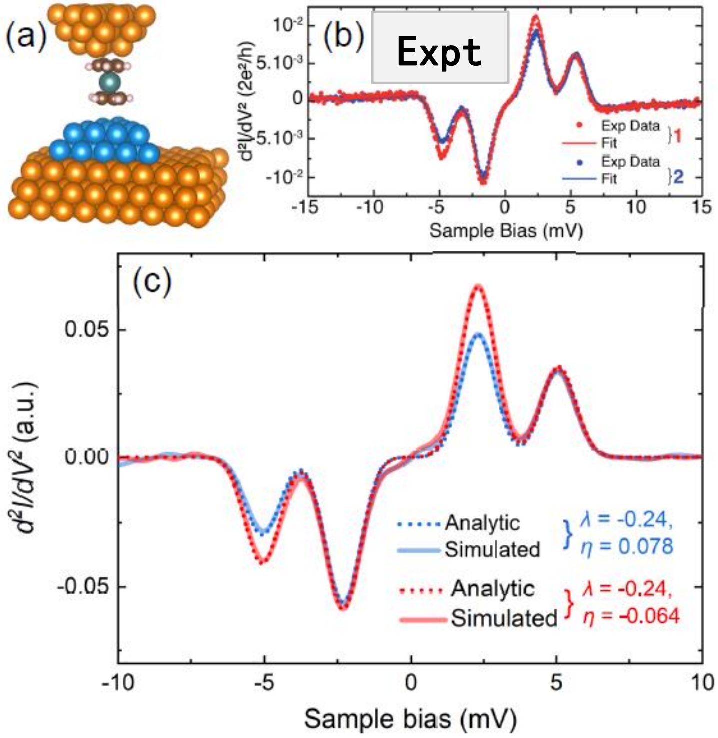
Enhanced spin sensing with SP-STM

- **Theory, simulation and experiment**

Cu-tip/Nc/Fe/Cu(100)



Cu-tip/Nc/Co island/Cu

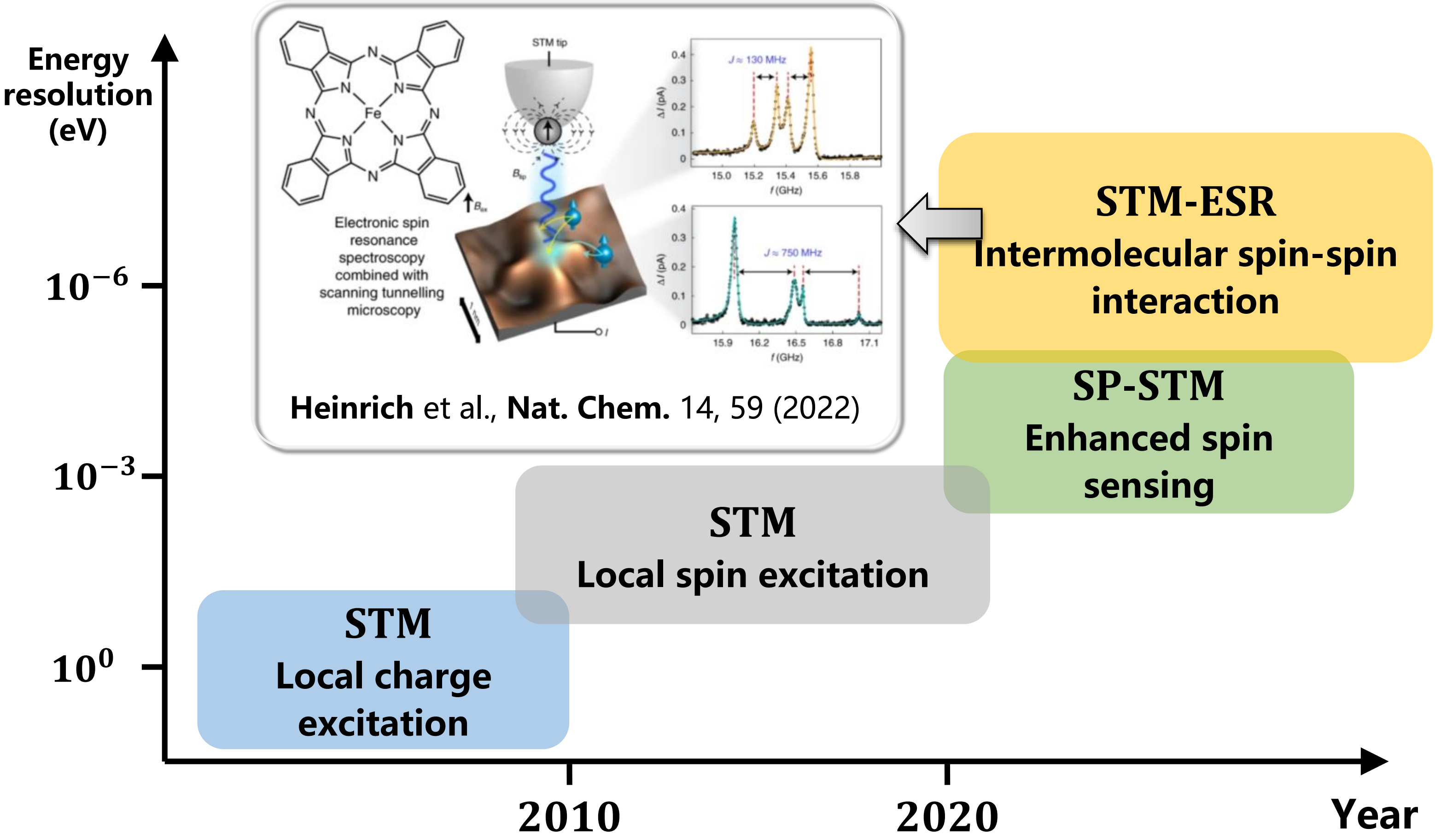


- **Uncover the decisive factor for the spectral lineshape:**

Spin- & orbital-polarization of probe-nanomagnet hybridization

Significant advancements in experiments

- ➢ **Theoretical challenge: unprecedentedly high energy resolution**



Heinrich et al., **Nat. Chem.** 14, 59 (2022)

STM-ESR
Intermolecular spin-spin interaction

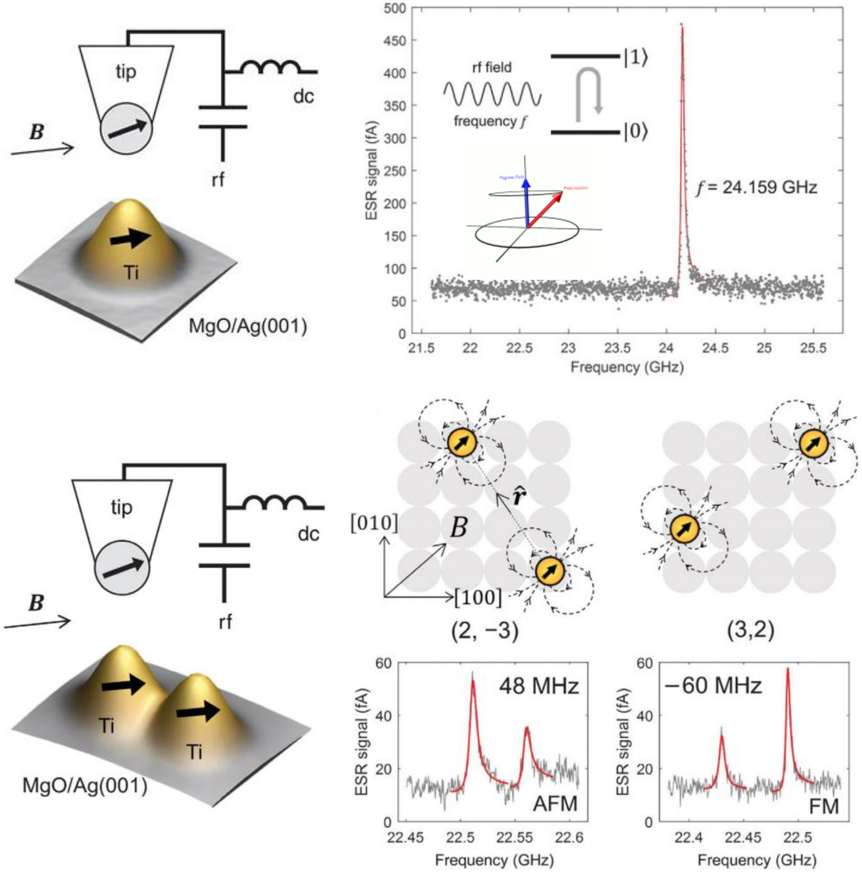
SP-STM
Enhanced spin sensing

STM
Local spin excitation

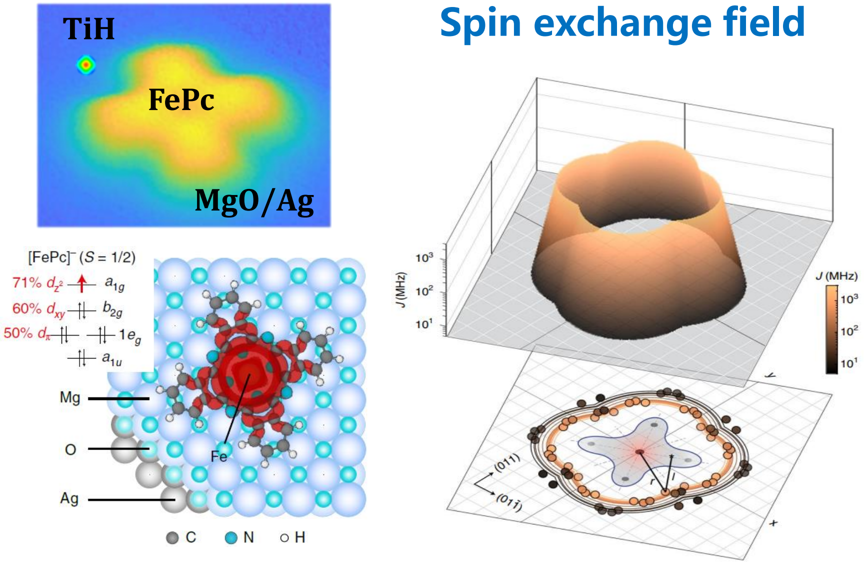
STM
Local charge excitation

Probing weak spin-spin interactions

- **Electron spin resonance (ESR) based on STM setup**



Baumann et al., **Science** 350, 6259 (2015)
Heinrich et al., **Phys. Rev. Lett.** 119, 227206 (2017)
Heinrich et al., **Nat. Chem.** 14, 59 (2022)

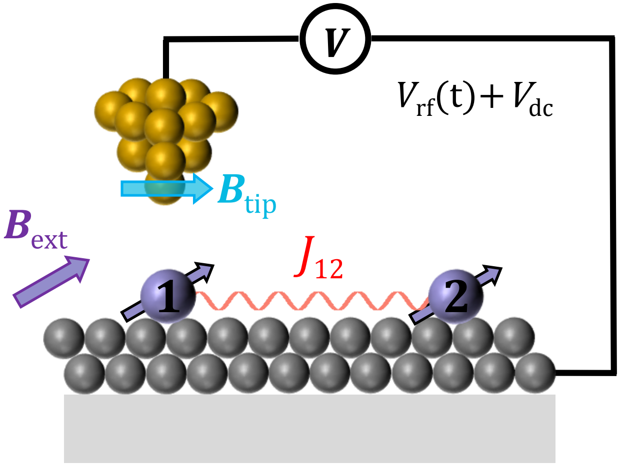


Heinrich et al., **Nat. Chem.** 14, 59 (2022)

- **Puzzle: origin of signal?**
  - **Piezoelectric effect**
  - **Spin-phonon coupling**
  - **Electron co-tunneling**
  - **Spin transfer torque**

Probing weak spin-spin interactions

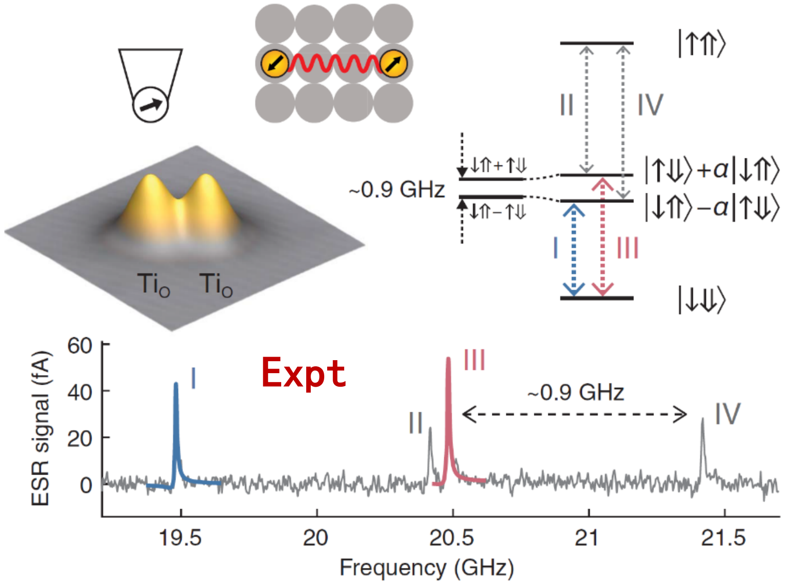
➢ Simulation with HEOM：TiH dimer/MgO/Ag



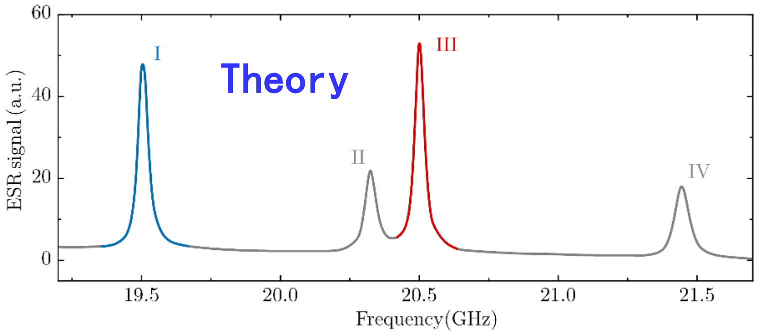
$$\hat{H}_{\text{TIAM}} = \hat{H}_{\text{imp}} + \hat{H}_{\text{env}} + \hat{H}_{\text{int}}$$

$$\hat{H}_{\text{imp}} = \sum_{i=1,2} \left(\epsilon_i \hat{n}_i + U\hat{n}_{i\uparrow}\hat{n}_{i\downarrow} + g_i\mu_B \boldsymbol{B}_{\text{ext}} \cdot \hat{\boldsymbol{S}}_i\right) + J_{12}\hat{\boldsymbol{S}}_1 \cdot \hat{\boldsymbol{S}}_2 + D\left(3\hat{S}_{1z}\hat{S}_{2z} - \hat{\boldsymbol{S}}_1 \cdot \hat{\boldsymbol{S}}_2\right)$$

$$\hat{H}_{\text{env}} = \sum_{\alpha k s} [\epsilon_{\alpha k s} - V_\alpha(t)]\, \hat{n}_{\alpha k s}$$



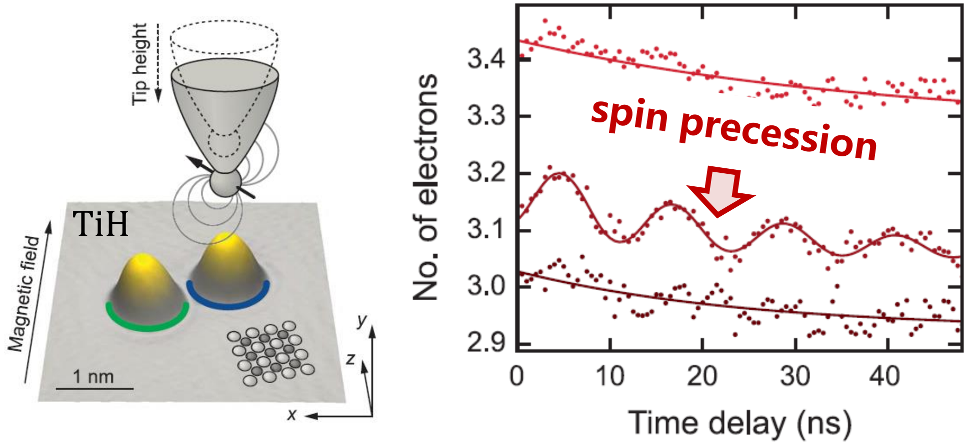
Heinrich et al., **Science** 366, 509 (2019)



Cao et al., **unpublished**

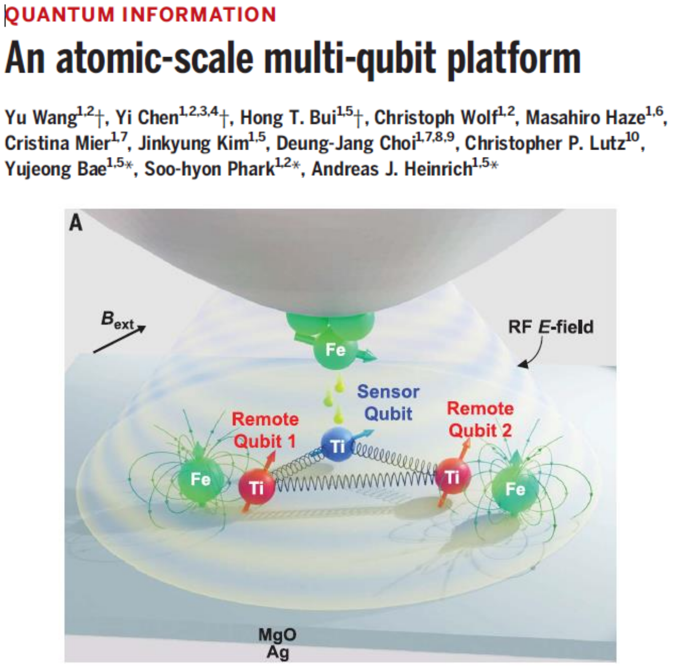
Probing weak spin-spin interactions

- **Prediction and novel design based on simulation**



spin precession

Otte et al., **Science** 372, 964 (2021)



QUANTUM INFORMATION

An atomic-scale multi-qubit platform

Yu Wang[1,2]†, Yi Chen[1,2,3,4]†, Hong T. Bui[1,5]†, Christoph Wolf[1,2], Masahiro Haze[1,6], Cristina Mier[1,7], Jinkyung Kim[1,5], Deung-Jang Choi[1,7,8,9], Christopher P. Lutz[10], Yujeong Bae[1,5]*, Soo-hyon Phark[1,2]*, Andreas J. Heinrich[1,5]*

Wang et al., **Science** 382, 87 (2023)

- **Challenge for coherent control**
  - **Longer coherence time (presently several hundred *ns*)**
  - **Accurate prediction of non-Markovian dissipative dynamics**

Summary

- **The HEOM method offers accurate, efficient, and versatile tools for the simulation of spin-related phenomena in realistic open systems**

  - ✓ Kondo spin-screening effect
  - ✓ Magnetic anisotropy
  - ✓ Long-range superexchange interaction
  - ✓ Precise manipulation of molecular magnets
  - ✓ Precise measurement of spin interactions
  - ✓ Spin-boosted heterogeneous catalysis
  - More to discover …

- **Quantum environment has crucial influence on local spin states and strongly correlated states**

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Prof. Bing Wang

Dr. Lu Han
Dr. Lyuzhou Ye
Dr. Yao Wang
Dr. Xiangyang Li
Dr. Houdao Zhang
Dr. Arif Ullah

Mr. Daochi Zhang
Ms. Lijun Zuo
Ms. Xu Ding
Mr. Xiang Li
Mr. Jiaan Cao
…

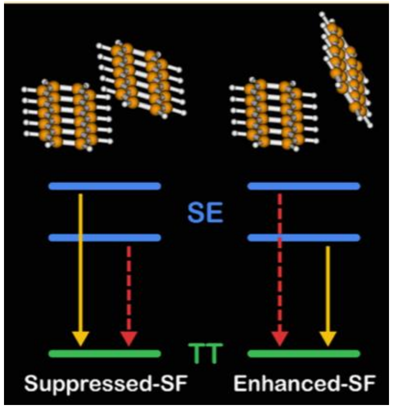
➢ Collaborators

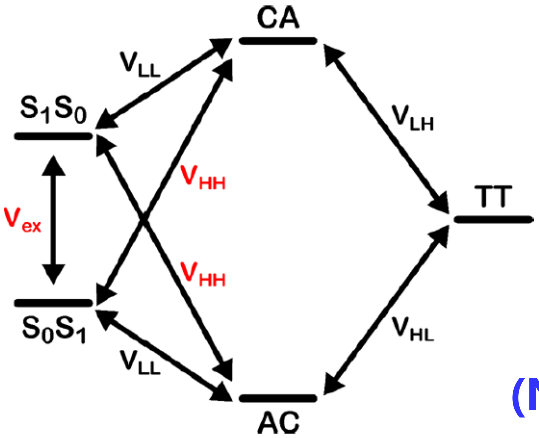
Prof. GuanHua Chen (HKU)
Prof. Weitao Yang (Duke)
Prof. Yun-An Yan (LuDong Univ)
Prof. JianHua Wei (RUC)

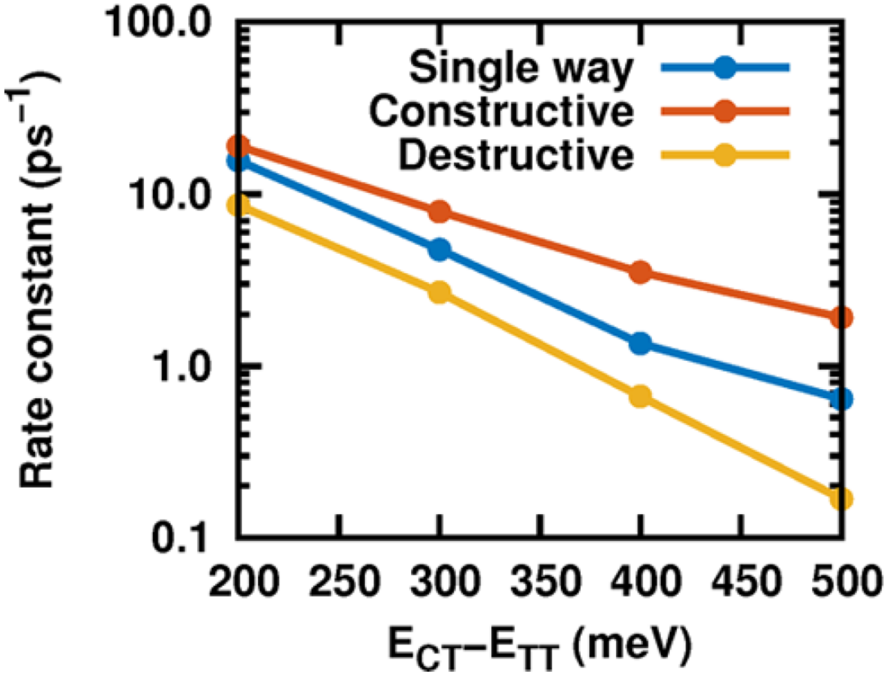
Prof. M. Di Ventra (UCSD)
Prof. V. Chernyak (WSU)
Prof. Jinshuang Jin (HZNU)
Prof. NingHua Tong (RUC)

Quantum interference in organic materials

- **Charge and excitation energy transfer in molecular aggregates**







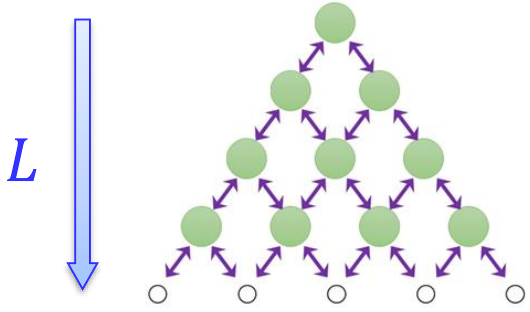
Simulation by a stochastic QDT method

(Non-Markovian Stochastic Schrödinger Equation)

Zhao and Liang et al., **J. Phys. Chem. Lett.** 8, 5105 (2017); 12, 1032 (2021)

Exact termination of fermionic hierarchy

- **Zero-value terminator (L^{th}-tier truncation)**



$$\rho^{(L+1)}_{j_1 \cdots j_{L+1}} = 0$$

- **Theorem: existence of a rigorous finite-tier termination**

L	$n_\uparrow = n_\downarrow$	$\rho_{\uparrow\uparrow} = \rho_{\downarrow\downarrow}$
1	0.530 091 197 209	0.283 567 930 856
2	0.460 675 469 887	0.306 745 231 635
3	0.490 952 014 924	0.270 358 283 528
4	0.490 675 288 339	0.269 359 794 471
5	0.490 526 324 607	0.269 327 938 933
6	0.490 540 350 968	0.269 327 915 854
7	0.490 540 484 313	0.269 328 203 985
8	0.490 540 476 338	0.269 328 185 419
9	0.490 540 476 338	0.269 328 185 419
10	0.490 540 476 338	0.269 328 185 419

Convergence test on a single-level system

L = 4 (CCSDTQ-like) yields accurate ρ

L = 8 yields exact ρ

Han and Zheng et al., **J. Chem. Phys.** 148, 234108 (2018)

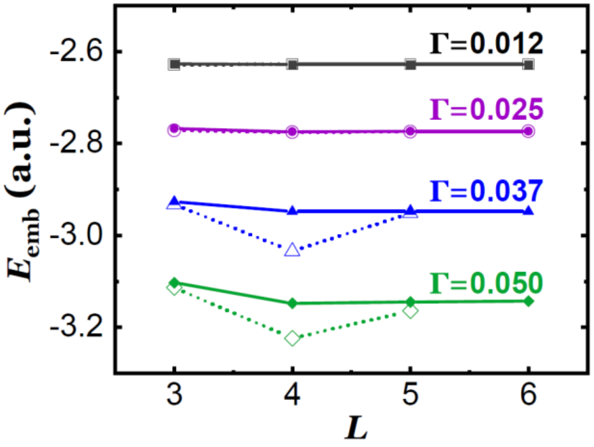
Efficient termination of the hierarchy

- **A new terminator: adiabatic terminator**

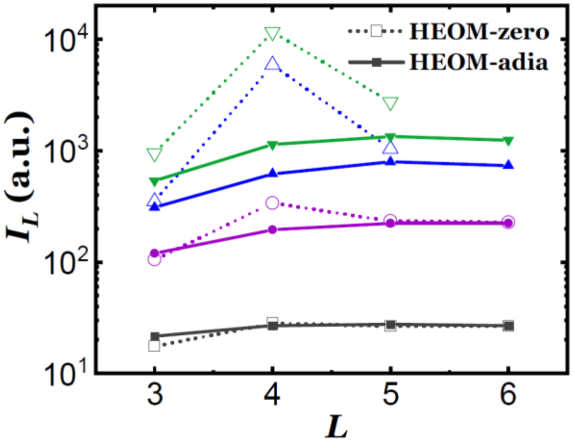
$$\rho^{(L+1)}_{j_1\cdots j_{L+1}} \simeq -i \sum_{\nu'} \Big[\underline{\mathcal{W}_{j_r\nu'}}\, \hat{c}^{\sigma}_{\nu'}\, \rho^{(L)}_{j_1\cdots j_{r-1}j_{r+1}\cdots j_{L+1}} - \underline{\mathcal{W}^{\dagger}_{\bar{j}_r\nu'}}\, \rho^{(L)}_{j_1\cdots j_{r-1}j_{r+1}\cdots j_{L+1}}\, \hat{c}^{\sigma}_{\nu'} \Big]$$

Decoupling the fastest dissipative mode from other modes (BO-like)

$E_{\mathrm{emb}} = \langle \hat{H}_{\mathrm{SB}} \rangle$



Electric current

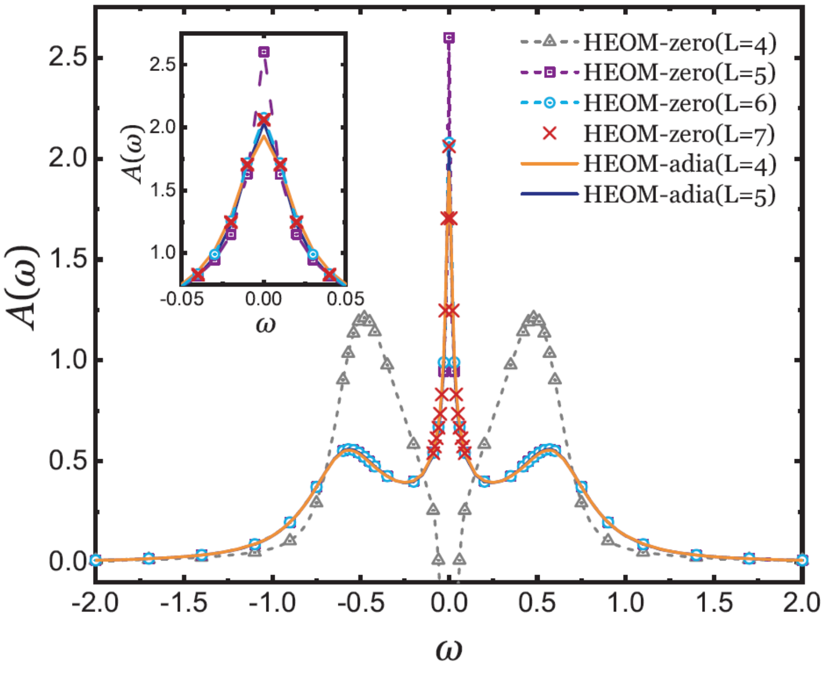


Zhang and Zheng et al., **Chin. J. Chem. Phys.** 34, 905 (2021)

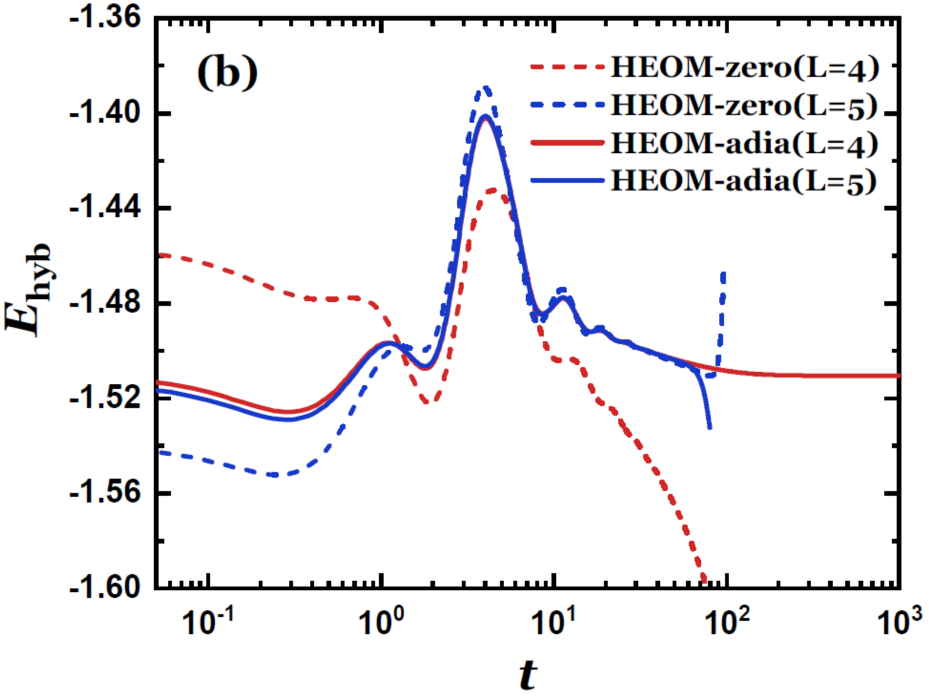
Efficient termination of the hierarchy

- **Performance test for adiabatic terminator: dynamics**

Spectral function



Real-time dynamics



Adiabatic terminator greatly improves the efficiency and stability

Zhang and Zheng et al., **Chin. J. Chem. Phys.** 34, 905 (2021)