CSRC Summer School on *Quantum Non-Equilibrium Phenomena: Methods and Applications*, Beijing, 17-21 June 2019

Dissipaton Equation of Motion Theory

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Intended Learning Outcomes

Get familiar with the DEOM theory, an exact and universal method in quantum mechanics of open systems

- **DEOM : Quasi-particle generalization to the widely used hierarchical equations of motion (HEOM) formalism**

  DEOM = HEOM + dissipaton algebra

- **DEOM construction = Schrödinger eq. + dissipaton algebra**

- **DEOM evaluations of measurable quantities & illustrations**

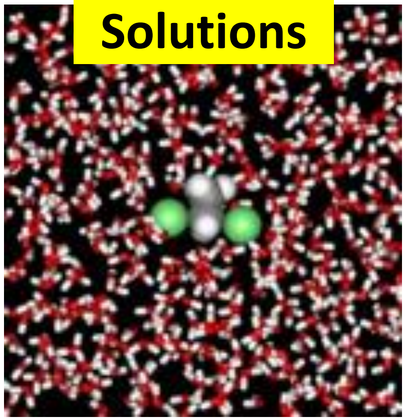
- **Prospects of further developments and applications**

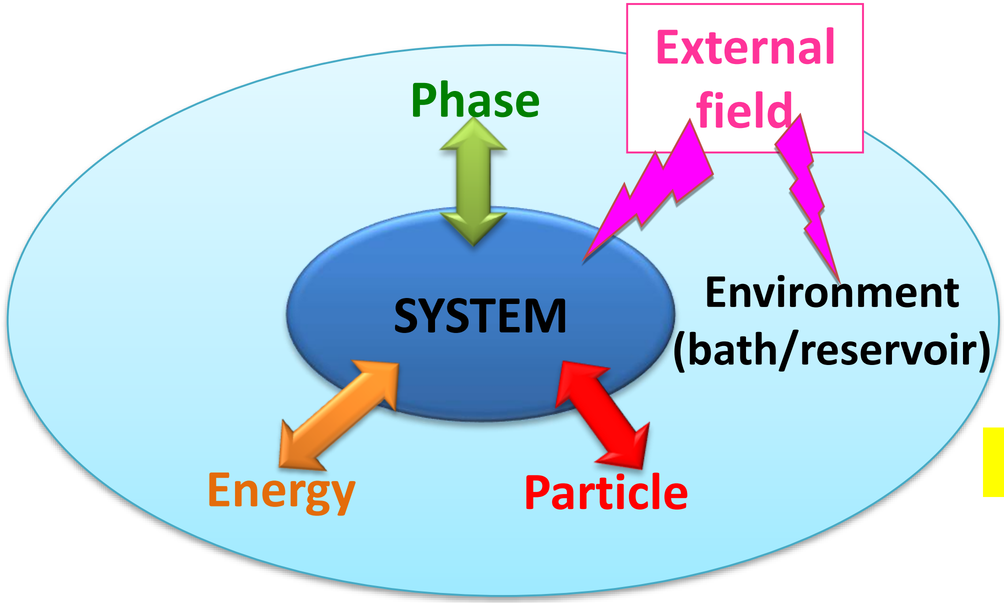
Outline

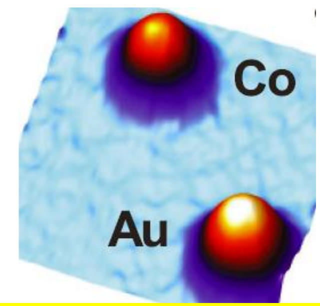
- **Quantum mechanics of open systems: Background**
- **The HEOM formalism: Machineries & applications**
- **HEOM-QUICK package**
- **The DEOM theory and applications**
- **Prospects**

Open Quantum Systems

Solutions

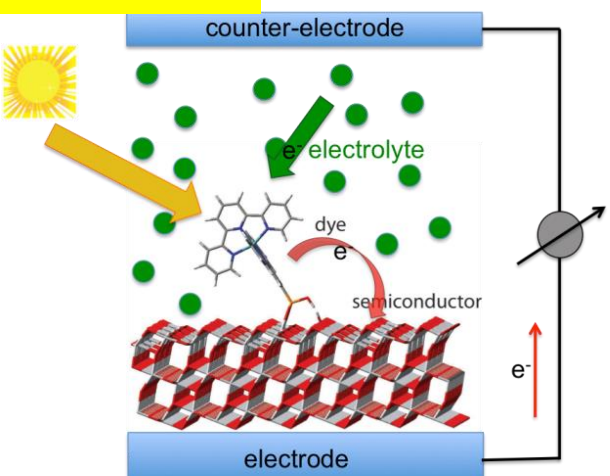




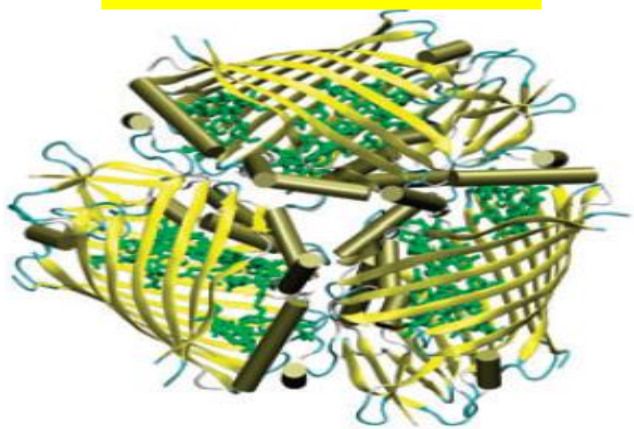


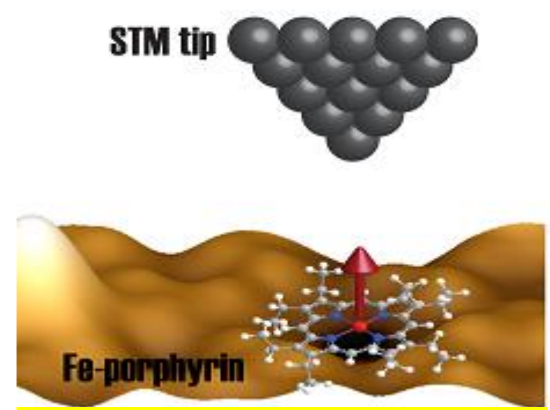
Adsorbed atoms

Photocells



EET in biosystems



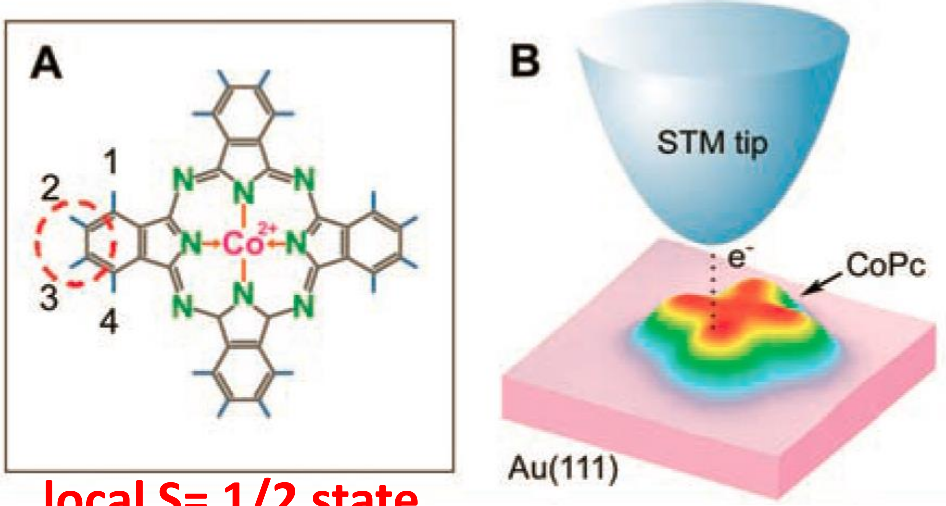


Molecular spintronics

Control of local quantum states

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

dehydrogenated-CoPc/Au(111)

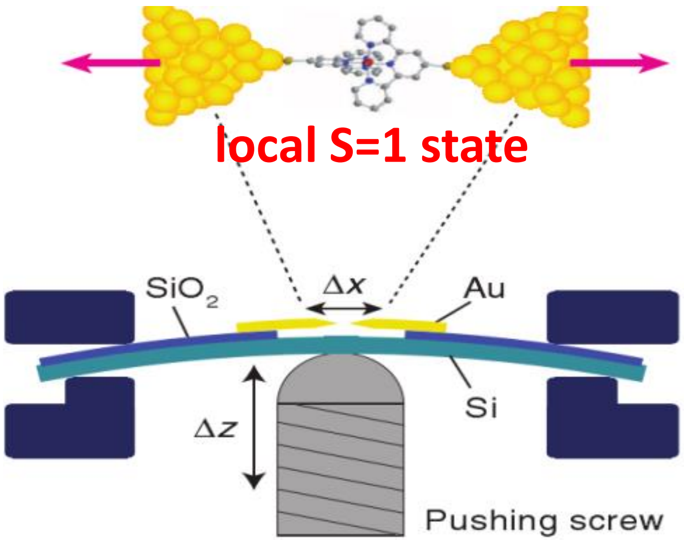


local S= 1/2 state

Pc = phthalocyanine

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

$Co(tpy\text{-}SH)_2$

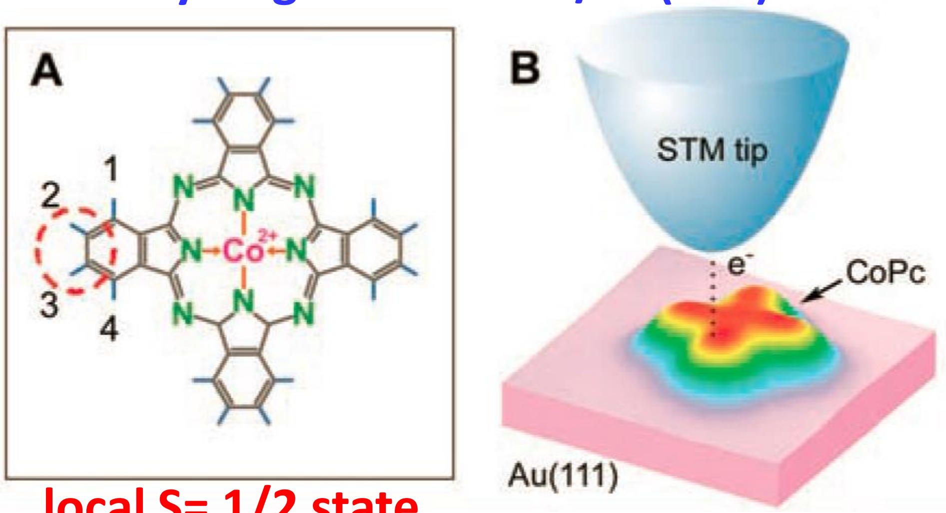


embedded in break junction

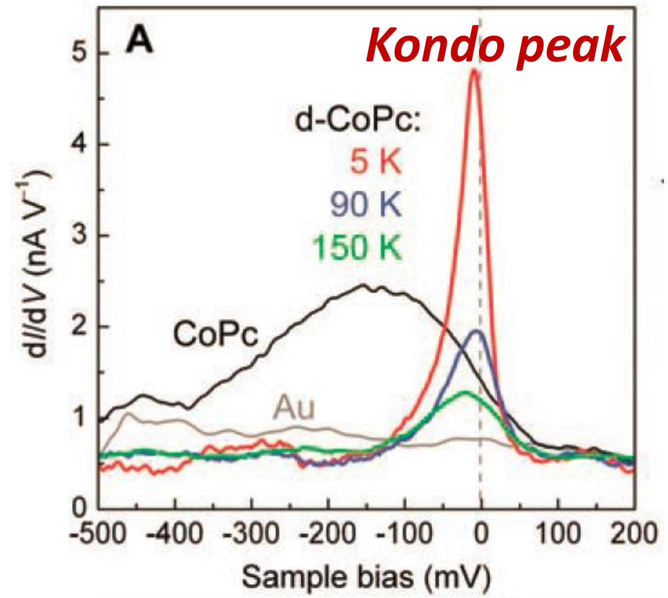
Control of local quantum states

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

dehydrogenated-CoPc/Au(111)

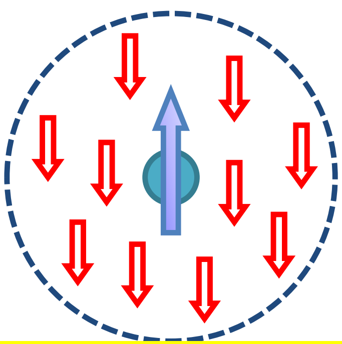


local S= 1/2 state



Kondo physics: Requirements

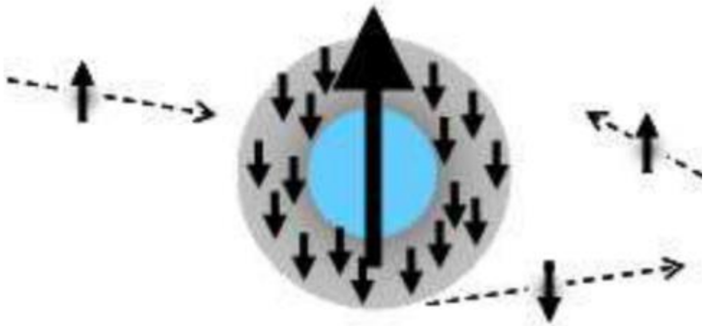
- Local magnetic moment (spin-unpaired *d*-electron)
- Strong e-e Coulomb interaction
- Screening of local spin by surrounding free electrons
- Low temperature (suppressing thermal fluctuations)



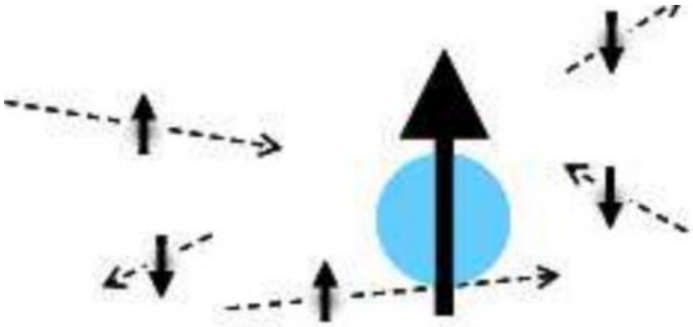
Kondo Singlet

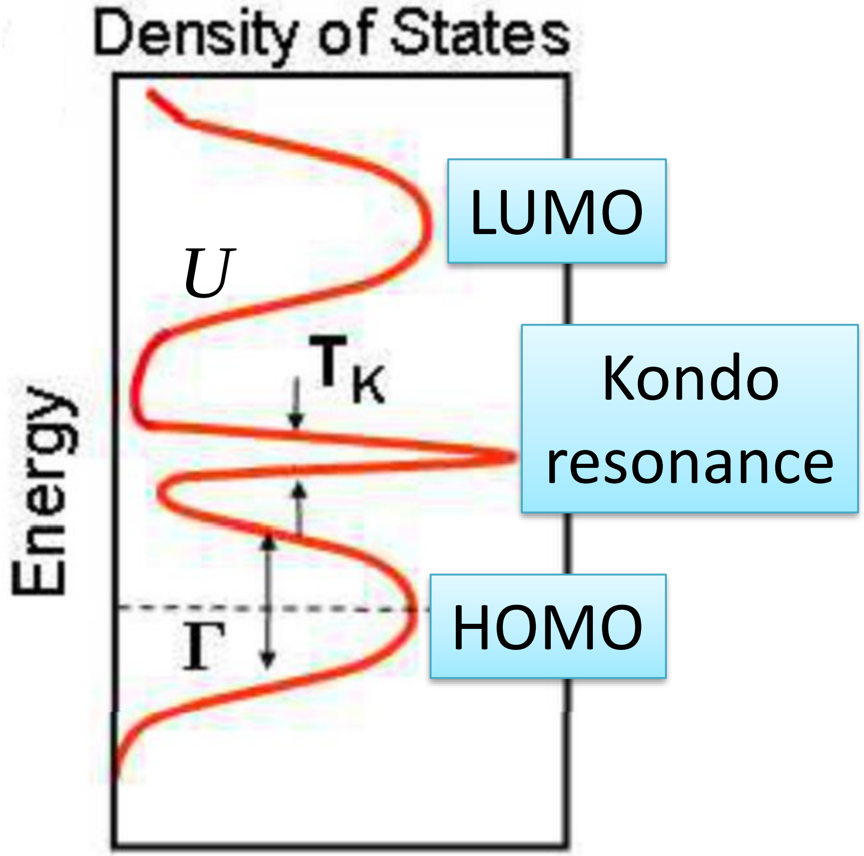
Control of local quantum states

$T < T_K$: Local magnetic moment screened by free electrons, forming a Kondo singlet



$T > T_K$: No Kondo





Control of local quantum states

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

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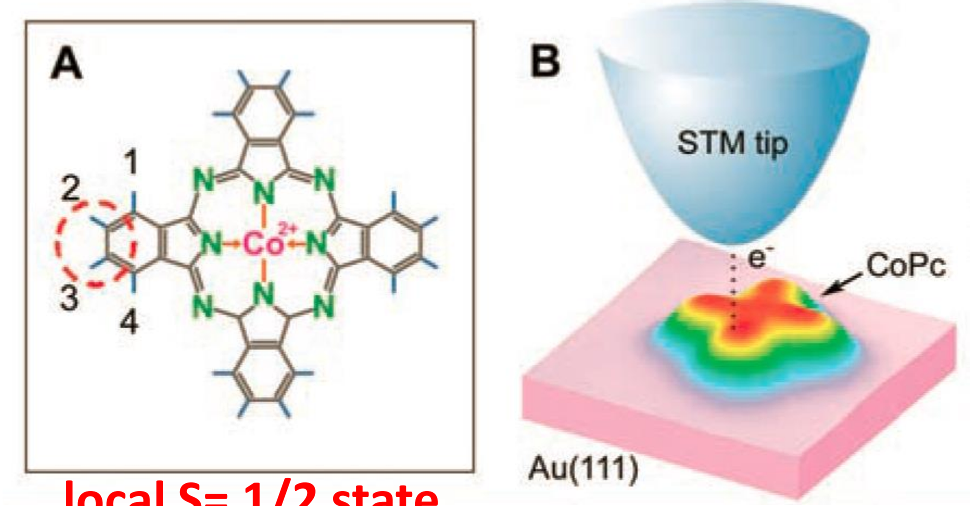
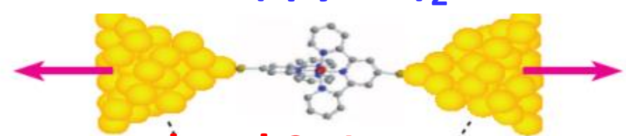


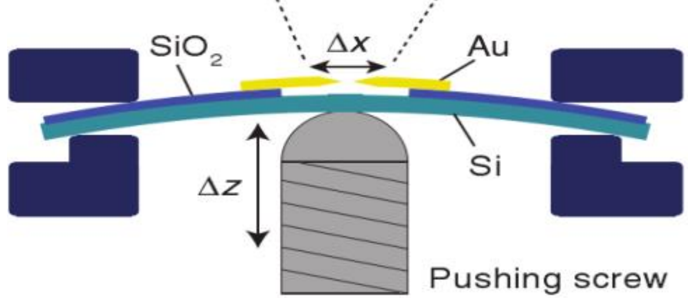
local S= 1/2 state

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

$Co(tpy\text{-}SH)_2$



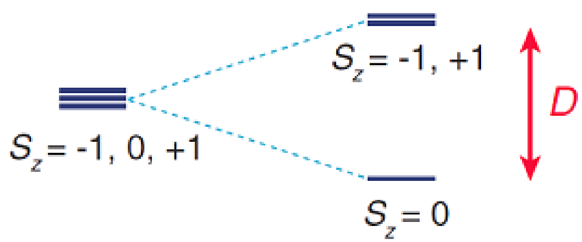
local S=1 state



embedded in break junction

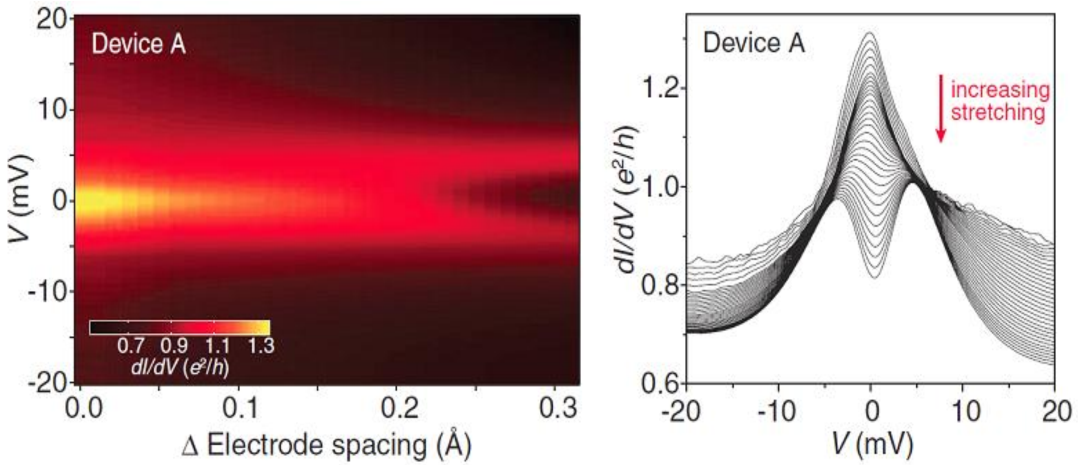
Control of local quantum states

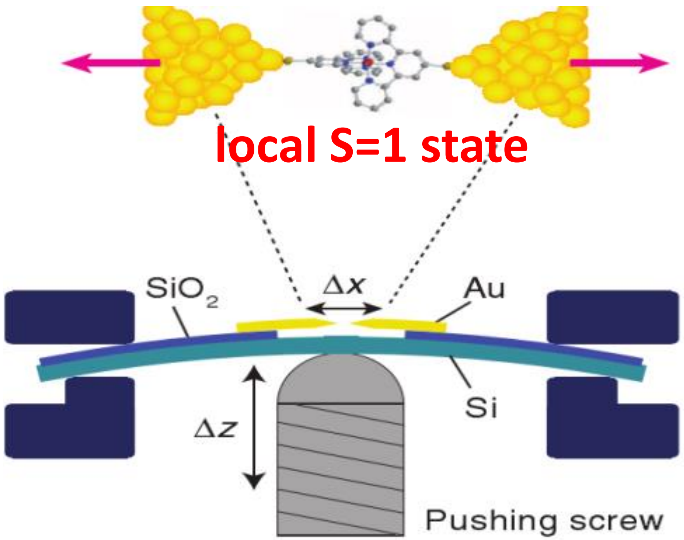
Competition between Kondo resonance and spin-orbit coupling



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

$Co(tpy\text{-}SH)_2$





Split of Kondo peak by magnetic anisotropy energy *D*

embedded in break junction

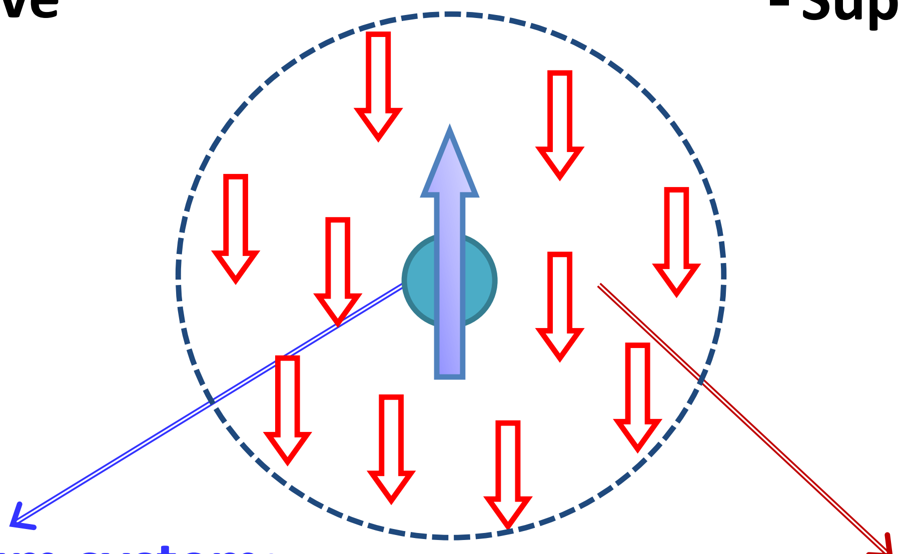
Challenges for theoretical study

Strong correlation:

- **Large DoF ($\sim 10^{23}$)**
- **High degeneracy**
- **Nonperturbative**

Related properties:

- **Mott metal-insulator transition**
- **Superconductivity; …**



Local quantum system:
Highly accurate quantum mechanical methods

Environment (DoF $\sim 10^{23}$):
Thermodynamics limit

Challenges for theoretical study

- Large composite systems with surface/interface
- Crucial roles of material environment
- Strong electron correlation (multi-reference nature)
- Computation of nonequilibrium response properties

A first-principles based approach

- DFT/post-DFT methods for geometric/electronic structure
- Quantum impurity model involving explicit e-e interaction and impurity-environment couplings
- On demand of accurate, universal & efficient solver/methods for strongly correlated impurity systems

Quantum impurity model

$$H_{\text{total}} = H_{\text{impurity}} + h_{\text{env}} + H_{\text{sys-env}}$$

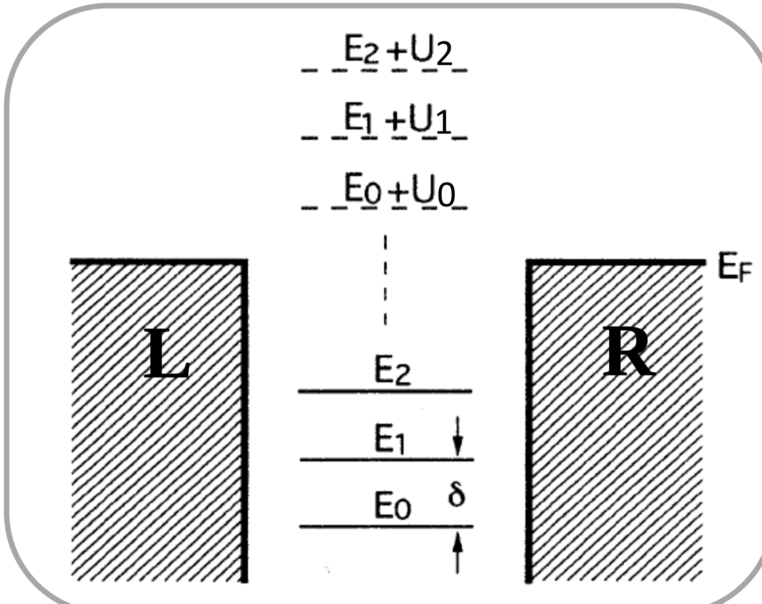
Arbitrary · Noninteracting · Linear

Multi-level Anderson impurity model

$$H_{\text{impurity}} = \sum_{us} E_{us}\hat{n}_{us} + \sum_{u} U_u \hat{n}_{u\uparrow}\hat{n}_{u\downarrow} + \sum_{u>v}\sum_{ss'} U_{uv}\hat{n}_{us}\hat{n}_{vs'}$$

$$h_{\text{env}} = \sum_{\alpha=\text{L,R}}\sum_{ks} \epsilon_{\alpha ks}\hat{d}^{\dagger}_{\alpha ks}\hat{d}_{\alpha ks}$$

$$H_{\text{sys-env}} = \sum_{\alpha uks} t_{\alpha uks}\hat{d}^{\dagger}_{\alpha ks}\hat{a}_{us} + \text{H.c.}$$



What else needed?

- **Temperature(s):** via Fermi func.
- Applied voltage/external field

Quantum impurity model

$$H_{\text{total}} = H_{\text{impurity}} + h_{\text{env}} + H_{\text{sys-env}}$$

Arbitrary — Noninteracting — Linear

Gaussian-Wick's bath, completely characterized by

$$\langle \hat{F}^{\sigma}_{\alpha u s}(t)\hat{F}^{\bar{\sigma}}_{\alpha v s}(0)\rangle^{\text{eq}}_{\text{B}} = \frac{1}{\pi}\int_{-\infty}^{\infty} \mathrm{d}\omega \frac{e^{\sigma i\omega t} J^{\sigma}_{\alpha u v s}(\omega)}{1+e^{\sigma\beta_\alpha \omega}}$$

where $\sigma = +, -$ and $\bar{\sigma} \equiv -\sigma$

Fluctuation-dissipation theorem

$$H_{\text{sys-env}} = \sum_{\alpha u k s} t_{\alpha u k s}\hat{d}^{\dagger}_{\alpha k s}\hat{a}_{u s} + \text{H.c.} = \sum_{\alpha u s}(\hat{F}^{+}_{\alpha u s}\hat{a}^{-}_{u s} + \hat{a}^{+}_{u s}\hat{F}^{-}_{\alpha u s})$$

where $\hat{a}^{+}_{us} \equiv \hat{a}^{\dagger}_{us} \equiv (\hat{a}^{-}_{us})^{\dagger}$ and $\hat{F}^{+}_{\alpha u s} \equiv \sum_{k} t_{\alpha u k s}\hat{d}^{\dagger}_{\alpha k s} \equiv (\hat{F}^{-}_{\alpha u s})^{\dagger}$

hybridizing bath environment modes

Existing Methods

- **Numerical renormalization group (NRG) :** Wilson (1975); Costi (1997); Weichselbaum and von Delft (2007)
- **Single- and many-body Green functions:** Kadanoff & Baym (1962); Myohanen et al. (2008); Thygesen & Rubio (2008)
- **Quantum Monte Carlo**: Hirsch & Fye (1986); Gull et al. (2011)
- **Real-time path-integral:** Muhlbacher & Rabani (2008); Weiss & Egger (2008); Segal, Millis & Reichman (2010)
- **Multi-layer-multi-configuration time-dependent Hartree:** Meyer (1990); Wang & Thoss 20(03)
- **Time-dependent density functional theory:** Kurth & Gross et al. (2010); Stefanucci & Kurth (2011)
- **Exact diagonalization:** Dagotto (1994); Caffarel & Krauth (1994); Si et al. (1994)

Quantum dissipation theories

➢ Let $\rho(t) \equiv \mathrm{tr}_{\mathrm{B}}[\rho_{\mathrm{T}}(t)]$ (reduced system density operator)

Total composite one satisfies **Schrödinger equation**:

$$\dot{\rho}_{\mathrm{T}}(t) = -i[H_{\mathrm{S}} + h_{\mathrm{B}} + H_{\mathrm{SB}}, \rho_{\mathrm{T}}(t)]$$ (Liouville-von Neumann eq.)

- **Quantum master equations to open system: Problems**

$$\dot{\rho}(t) = -(i\mathcal{L}_{\mathrm{S}} + \mathcal{R}_t)\rho(t)$$

(Nonperturb. & time-dep $\mathcal{R}$???)

dissipation superoperator

- **Feynman-Vernon path integral functional formalism (1963)** for the reduced system propagator:

$$\rho(t) = \mathcal{U}(t, t_0)\rho(t_0)$$

(Numerically very expensive!!!)

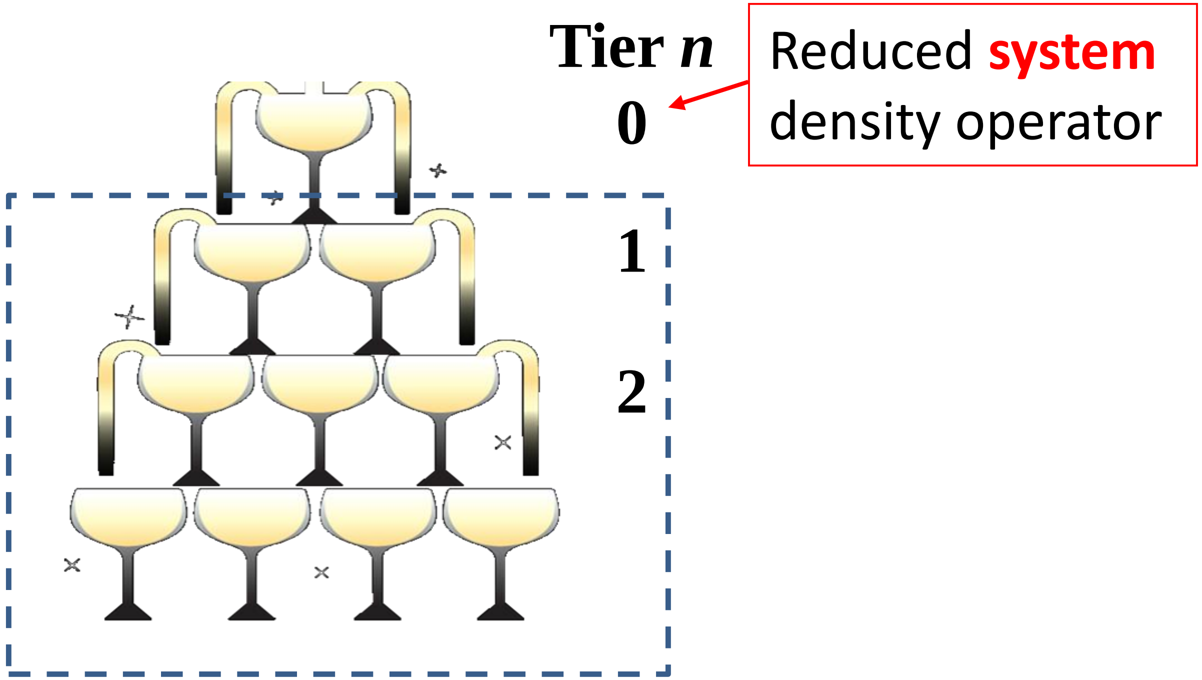
- **Hierarchical equations of motion method: Exact & tractable**

Outline

- Quantum mechanics of open systems: Background
- **The HEOM formalism: Machineries & applications**
- HEOM-QUICK package
- The DEOM theory and applications
- Prospects

Hierarchical equations of motion (HEOM)

$$\dot{\rho}_{\mathbf{j}}^{(n)} = -\Big(i\mathcal{L}_{\mathrm{S}} + \sum_{r=1}^{n} \gamma_{j_r}\Big)\rho_{\mathbf{j}}^{(n)} - i\sum_{j} \mathcal{A}_{\bar{j}}\rho_{\mathbf{j}j}^{(n+1)} - i\sum_{r=1}^{n} \mathcal{C}_{j_r}\rho_{\mathbf{j}_r^-}^{(n-1)}$$



What do we obtain from HEOM?

$$\dot{\rho}_{\mathbf{j}}^{(n)} = -\Big(i\mathcal{L}_{\rm S} + \sum_{r=1}^{n} \gamma_{j_r}\Big)\rho_{\mathbf{j}}^{(n)} - i\sum_{j} \mathcal{A}_{\bar{j}}\,\rho_{\mathbf{j}j}^{(n+1)} - i\sum_{r=1}^{n} \mathcal{C}_{j_r}\,\rho_{\mathbf{j}_r^-}^{(n-1)}$$

- **Electronic structure:**

$$\boldsymbol{\rho}^{\rm st} \equiv \big\{\rho^{(0)};\rho_{\mathbf{j}}^{(n>0)}\big\}^{\rm st}$$ **(steady-state solutions)**

- **Expectation values:**

$$A(t) = {\rm tr}[\hat{A}\rho(t)] = {\rm tr}\big[\hat{A}\,\rho^{(0)}(t)\big]$$ **(system properties)**

Electric current (hybrid system-reservoir property):

$$I_\alpha(t) = -2\,{\rm Im}\sum_{j\in\alpha} {\rm tr}\big[\hat{a}_\mu\,\rho_j^{(1)}(t)\big]$$

What do we obtain from HEOM?

$$\dot{\rho}_{\mathbf{j}}^{(n)} = -\Big(i\mathcal{L}_{\mathrm{S}} + \sum_{r=1}^{n} \gamma_{j_r}\Big)\rho_{\mathbf{j}}^{(n)} - i\sum_{j} \mathcal{A}_{\bar{j}}\rho_{\mathbf{j}j}^{(n+1)} - i\sum_{r=1}^{n} \mathcal{C}_{j_r}\rho_{\mathbf{j}_r^-}^{(n-1)}$$

- **Correlation functions:** $\langle \hat{A}(t)\hat{B}(0)\rangle = \langle\!\langle \boldsymbol{A}|\boldsymbol{\mathcal{G}}(t)|\boldsymbol{B}\boldsymbol{\rho}^{\mathrm{st}}\rangle\!\rangle$

Note also the **time-reversal identity**: $\langle \hat{B}^\dagger(0)\hat{A}(t)\rangle = \langle \hat{A}^\dagger(t)\hat{B}(0)\rangle^*$

- **Nonequilibrium Green functions (nGFs) and spectrums**

$$G^{>}_{uv}(t) \equiv \langle \hat{a}_u^\dagger(t)\hat{a}_u(0)\rangle$$

$$G^{<}_{uv}(t) \equiv \langle \hat{a}_u(0)\hat{a}_u^\dagger(t)\rangle$$

and $G^{r}_{uv}(t) \equiv -i\theta(t)\langle\{\hat{a}_v^\dagger(t), \hat{a}_u(0)\}\rangle$

- **Electric and heat currents versus nGFs**

$$I_\alpha = \frac{ie}{h}\int d\epsilon\, 2\Delta_\alpha(\epsilon)\Big\{G^{<}(\epsilon) + 2\,i f_\alpha(\epsilon)\,\mathrm{Im}\,[G^{r}(\epsilon)]\Big\}$$

$$J_\alpha^{\mathrm{H}} = \frac{i}{h}\int d\epsilon\, (\epsilon - \mu_\alpha)\, 2\Delta_\alpha(\epsilon)\Big\{G^{<}(\epsilon) + 2\,i f_\alpha(\epsilon)\,\mathrm{Im}\,[G^{r}(\epsilon)]\Big\}$$

HEOM formalism (path integral based)

- **Bosonic: Tanimura & Kubo (1989); Shao & Yan (2004); YJY et al (2005)**

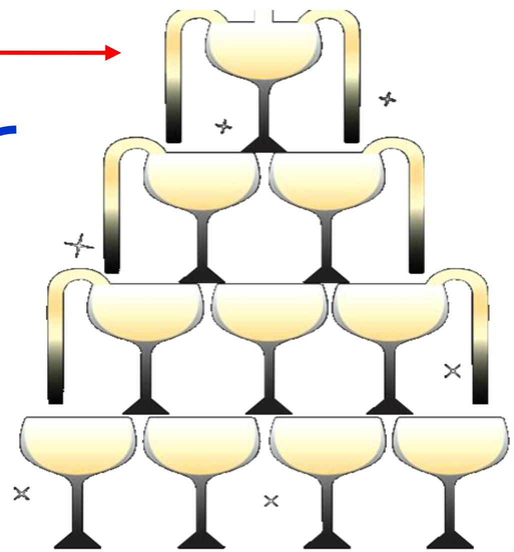
Reduced **system** density operator

Tier

0

1

2

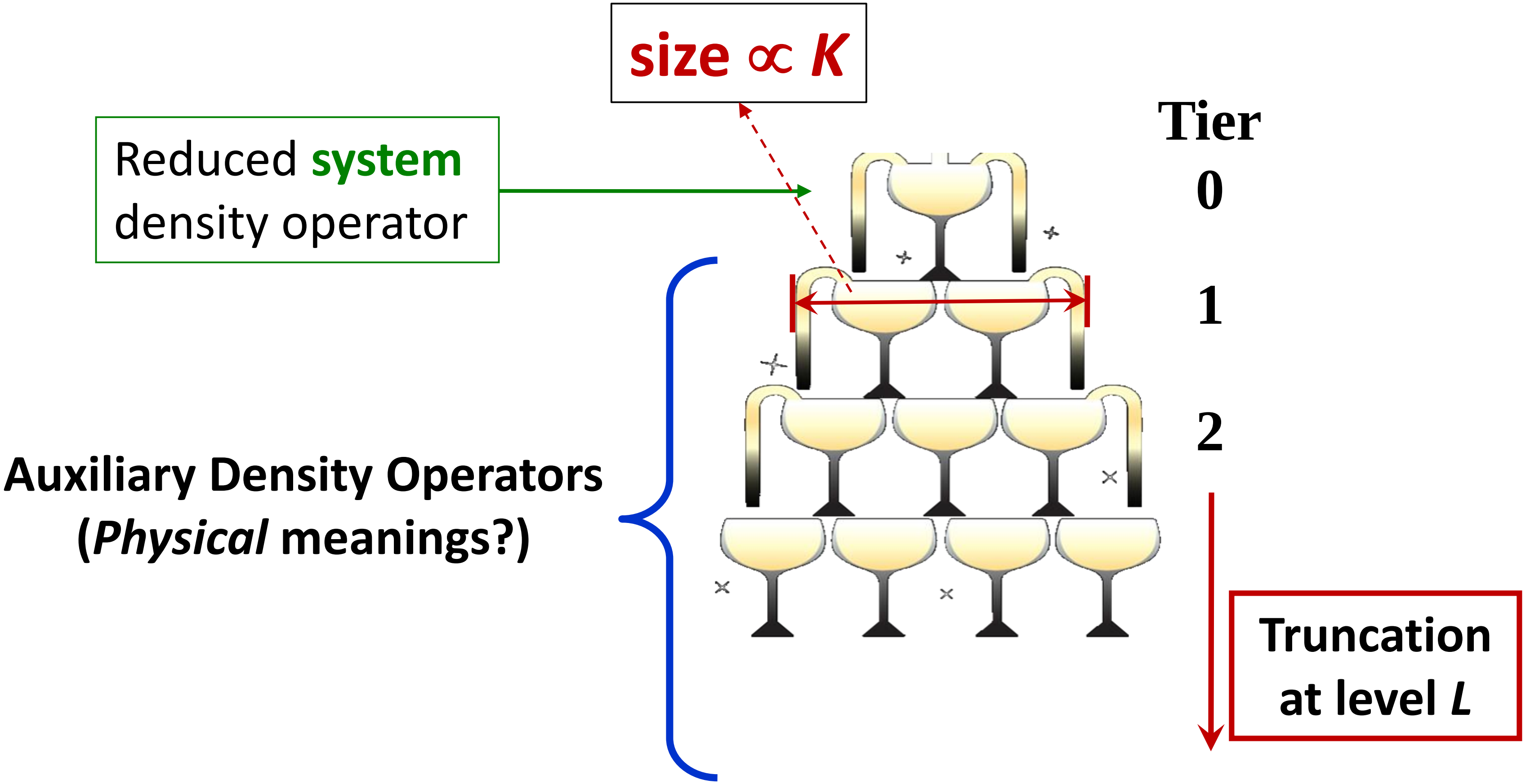


Auxiliary Density Operators (*Physical* meanings?)

- **Fermionic: J. S. Jin, X. Zheng, YJY (2008), J. Chem. Phys., 128: 234703**

Grassmann numbers: xy = – yx (rather than c-numbers)

HEOM formalism (path integral based)



- ***K* & *L* determine the size (computational cost) of HEOM**
- ***K*-dissipatons are used to unravel reservoir memory**
- ***K* increases exponentially as $T \to 0$**

HEOM formalism: Machineries (since 2009)

2009: **Efficient propagator with on-the-fly numerical filter algorithm**

2010: **Padé spectrum decomposition of Bose/Fermi function**

2011: **Mixed Heisenberg-Schrödinger dynamics for multiple-dimensional spectroscopy evaluations**

2015: Derivative hierarchy truncation scheme (**prescription-invariance**)

2015: **Symmetry-determined pre-screening sparse-matrix method**

2017: **Efficient steady-state solver: Self-consistent iteration method**

2019: **Fano spectrum decomposition of Bose/Fermi function**

- **Q Shi (2017-): Matrix-product and clustered ADOs methods**
- **JS Shao/JS Cao & JL Wu/Y Zhao: Stochastic + HEOM**
- **JS Cao/A Aspuru-Guzik: Machine Learning + HEOM**
- **Kreisbeck et al (2011)/Strümpfer & Schulten (2012): Parallel/GPU codes**

Reducing the horizontal K-dimension

Unravel reservoir bath memory into K components

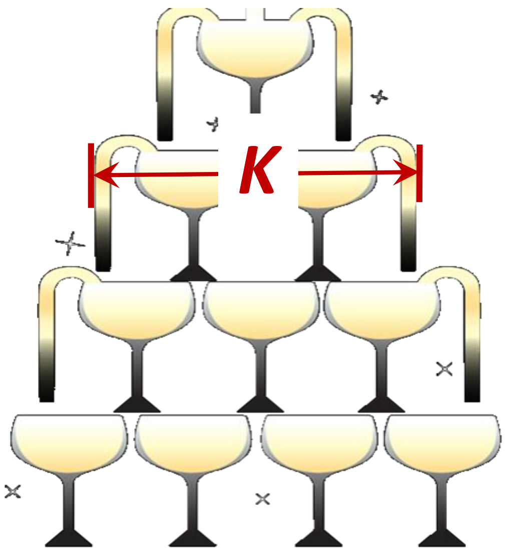
$$\langle \hat{F}^{+}_{\alpha u s}(t)\hat{F}^{-}_{\alpha v s}(0)\rangle^{\rm eq}_{\rm B} \propto \int_{-\infty}^{\infty} \mathrm{d}\omega\, e^{i\omega t} f^{\rm Fermi}(\omega;T) J_{\alpha u v s}(\omega)$$

$$\simeq \sum_{k=1}^{K} \eta_{\alpha k u v s} e^{-\gamma^{\alpha}_{k} t}$$

$K = N + N'$

Sum-over-poles (SOP)

HEOM construction basis set



Tier
0
1
2

Reducing the horizontal K-dimension

Search for the best SOP schemes for Fermi/Bose function

e.g. Bose function: $(x = \beta\omega)$

$$\frac{1}{1-e^{-x}} = \frac{1}{2} + \frac{1}{2}\frac{\cosh(x/2)}{\sinh(x/2)}$$

- **MSD (Matsubara spectrum decomposition) -- Textbook**

$$\frac{1}{1-e^{-x}} \approx \frac{1}{2} + \frac{1}{x} + \sum_{m=1}^{N}\left(\frac{1}{x+i2\pi m} + \frac{1}{x-i2\pi m}\right)$$

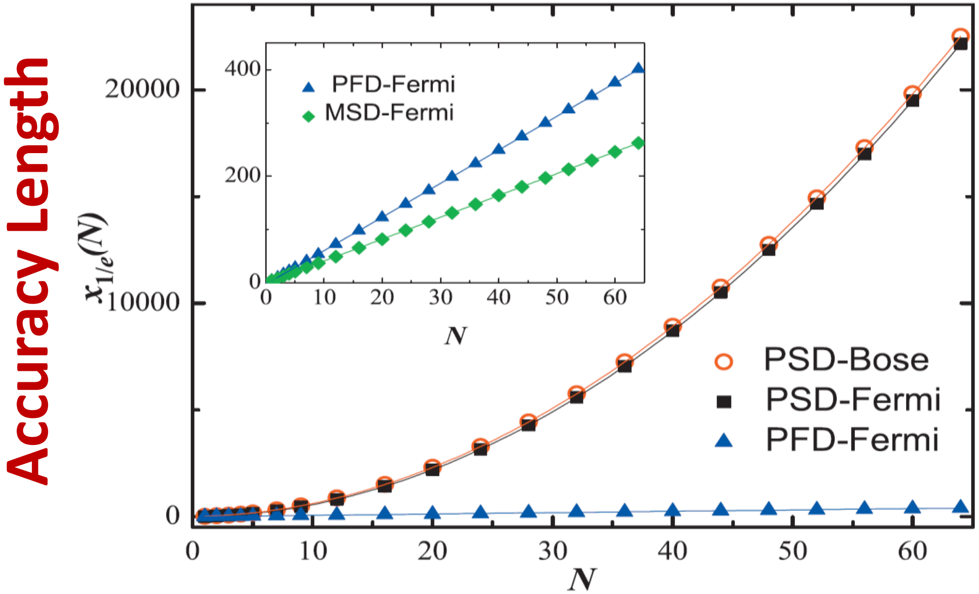
- **PSD (Pade spectrum decomposition) – Numerical standard now**

$$\frac{1}{1-e^{-x}} \approx \frac{1}{2} + \frac{1}{x} + \sum_{j=1}^{N}\left(\frac{\eta_j}{x+i\xi_j} + \frac{\eta_j}{x-i\xi_j}\right)$$

$\{\xi_j\}>0$ & $\{\eta_j\}>0$: **Machine-precision !**

- T. Ozaki, Phys. Rev. B **75**, 035123 2007
- J Hu, RX Xu, & YJY, *JCP* **133** (2010) 101106; **134**, 244106 (2011)

Superiority: PSD >> PFD > MSD

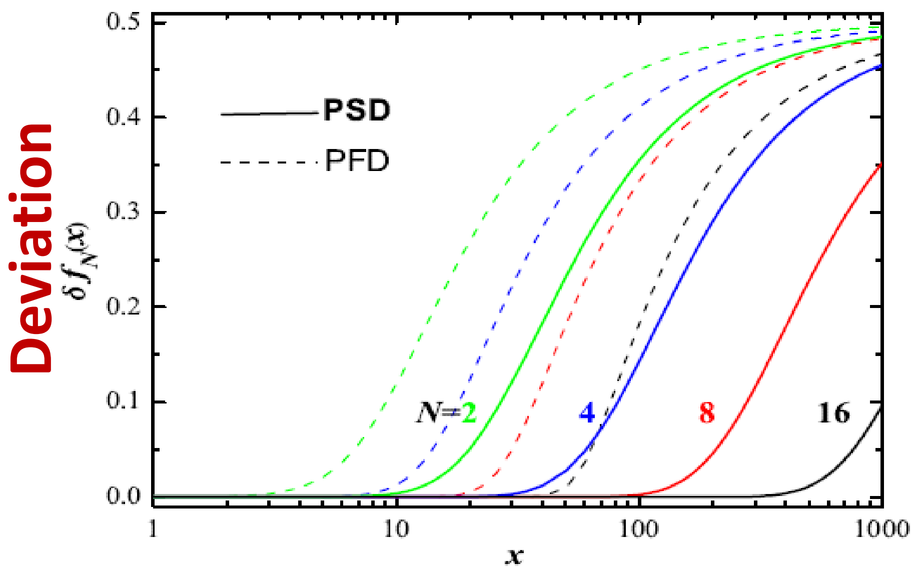


MSD (tradition method)

PFD (partial fraction decom.)

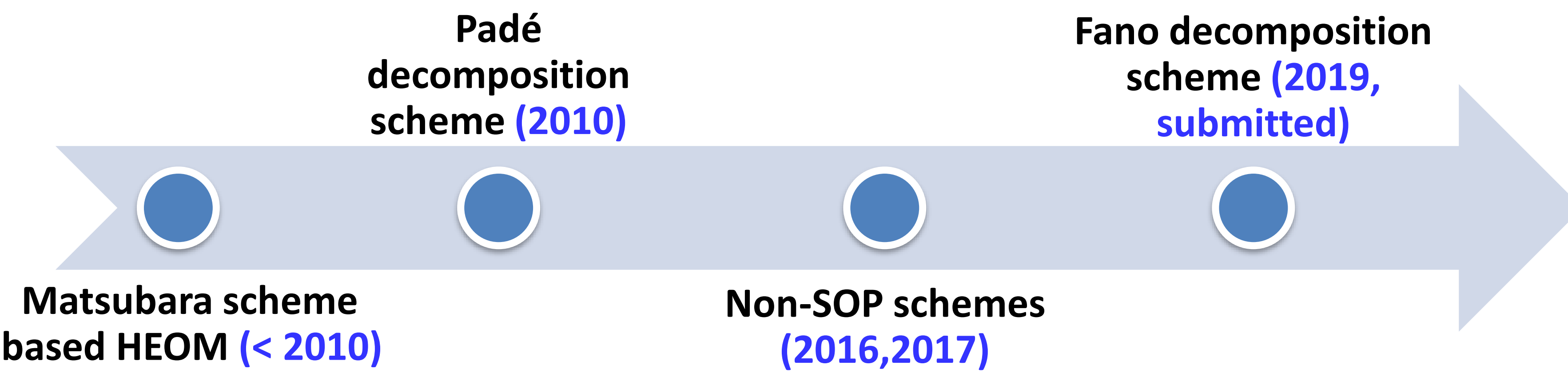
Croy & Saalmann, *Phys. Rev.* B 80, 073102 (2009) ; J Xu, RX Xu, YJY, *Chem. Phys.* 370, 109 (2010)

PSD (standard now)



Reducing the horizontal K-dimension

Search for the best SOP schemes for Fermi/Bose function



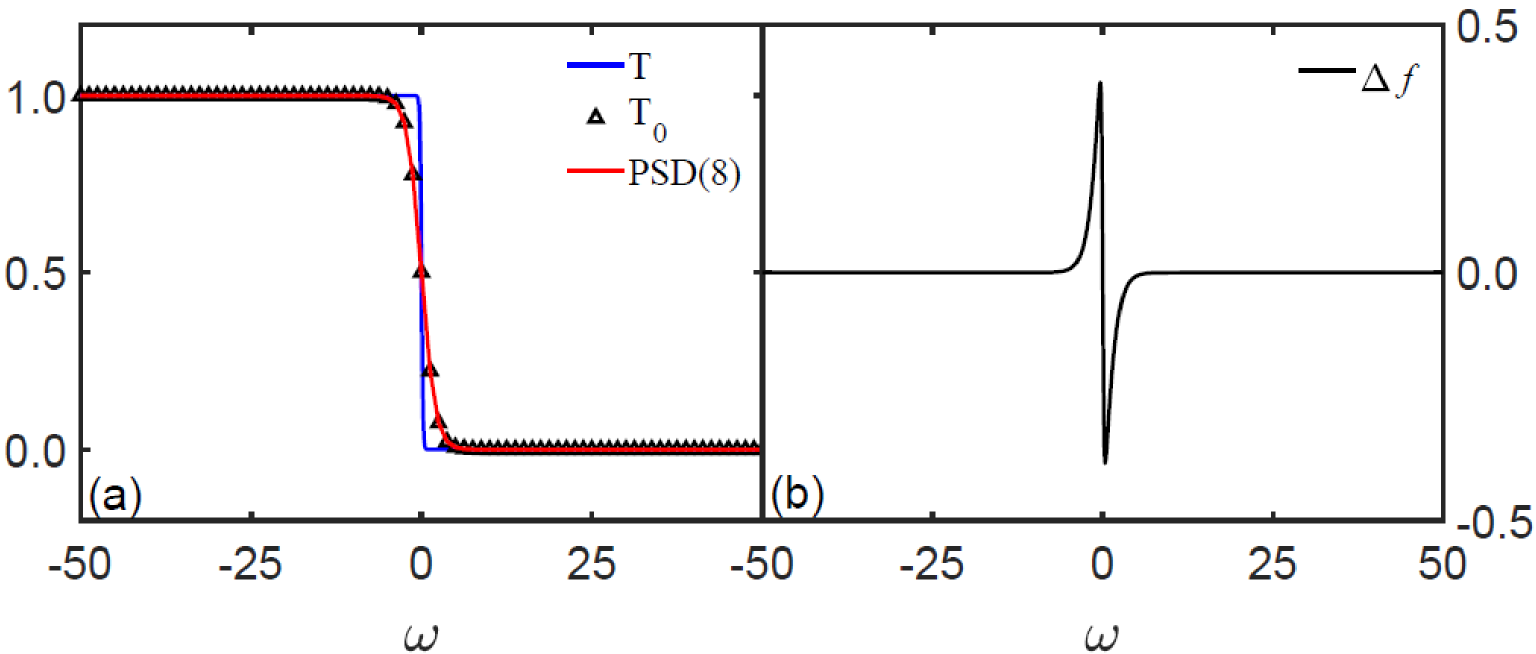
J. Chem. Phys. **145**, 204110 (2016); **146**, 024104 (2017); **147**, 074111 (2017).

Reducing the horizontal K-dimension

Search for the best SOP schemes for Fermi/Bose function

- **Focusing on the low-*T* domain w.r.t. a reference high T_0**

$$\Delta f(\omega, T; T_0) \equiv f^{\mathrm{Fermi}}(\omega, T) - f^{\mathrm{Fermi}}(\omega, T_0)$$



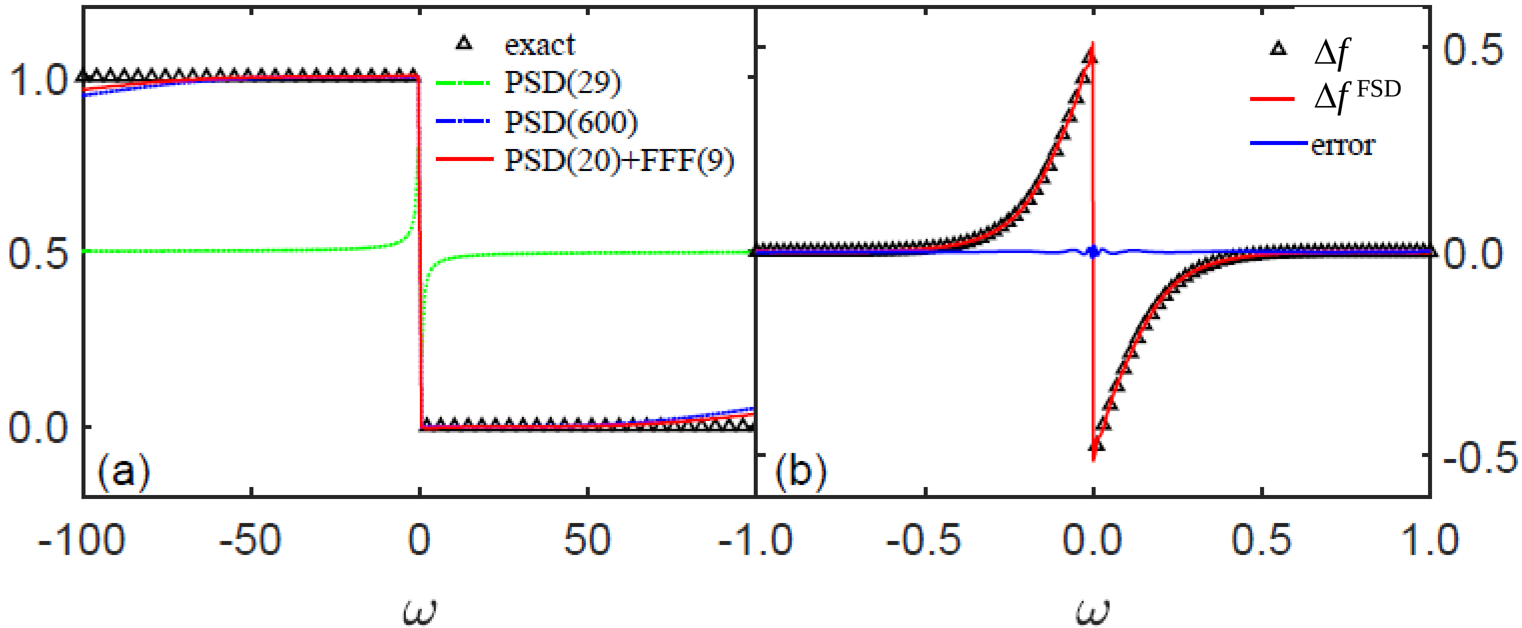
Reducing the horizontal K-dimension

Search for the best SOP schemes for Fermi/Bose function

- **Focusing on the low-*T* domain w.r.t. a reference high T_0**

$$\Delta f(\omega, T; T_0) \approx \sum_{d=1}^{D} \frac{b_d \omega}{[1+(a_d\omega)^2]^{j_d}}$$

Fano spectrum decomposition

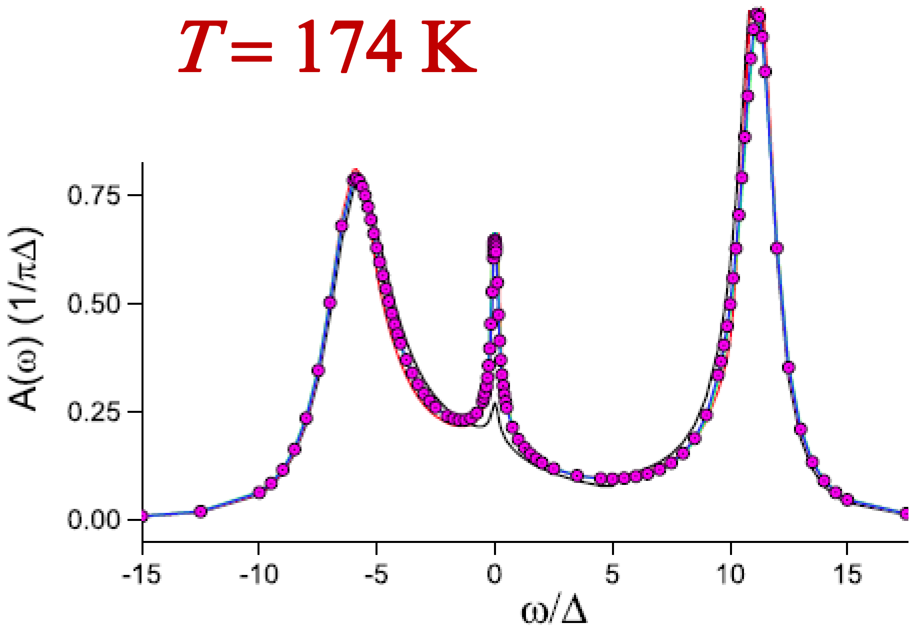


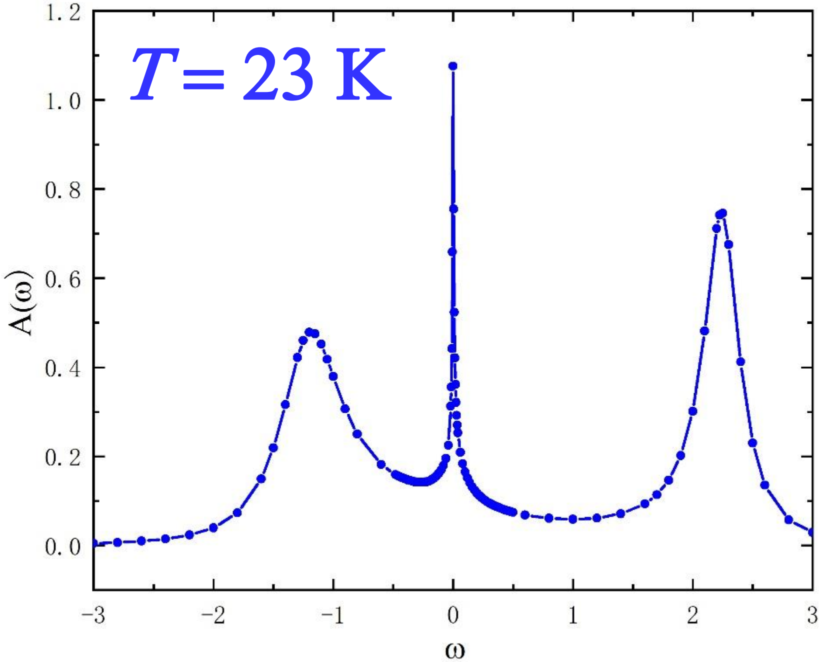
Superiority: FSD >> PSD for extremely low-*T* cases

Toward Experimental Low-T Regimes

Liquid N_2: 77 K; Liquid He: 4 K

HEOM evaluation on SIAM:
Spectrum in Kondo regime





PSD scheme

Li, Zheng, YJY et al. *PRL* 109, 266403 (2012)

FSD scheme

Zhang, Zheng et al (unpublished)

HEOM: Nonperturbative in Nature

Existence of an exact and finite hierarchy level truncation

- **For fermion HEOM** $\rho^{(n>n_{\max})}_{j_1\cdots j_n} = 0; \qquad n_{\max} = N_\sigma N_u N_\alpha K$

$N_\sigma = 2$:	Parity of fermions
N_υ :	# of hybridization system modes
N_α :	# of baths (α = L,R)
K :	Size of basis set (a large number)

- **For the exact $\rho^{(0)}$:** $\rho^{(n>n^{(0)}_{\max})}_{j_1\cdots j_n} = 0; \qquad n^{(0)}_{\max} = 2N_\sigma N_u$

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

HEOM: Nonperturbative in Nature

Existence of an exact and finite hierarchy level truncation

TABLE I. $n_\uparrow$, $n_\downarrow$, and $\rho_{\uparrow\uparrow}$ of an SIAM calculated at different truncation tiers. The converged (unconverged) digits are marked by normal (italic) font. See the main text for the values of parameters.

L	$n_\uparrow$	$n_\downarrow$	$\rho_{\uparrow\uparrow}$
1	0.5*62 479 725 093*	0.*399 843 457 389*	0.*349 149 952 492*
2	0.*499 440 108 806*	0.4*61 089 036 198*	0.*283 947 704 486*
3	0.50*3 648 803 692*	0.45*4 958 233 447*	0.28*7 476 336 354*
4	0.502 9*13 018 977*	0.456 *307 175 157*	0.286 6*20 580 229*
5	0.502 9*53 417 487*	0.456 2*24 386 764*	0.286 6*84 865 267*
6	0.502 949 *750 959*	0.456 23*5 095 328*	0.286 678 0*62 145*
7	0.502 949 7*06 728*	0.456 235 1*82 013*	0.286 678 0*50 832*
8	0.502 949 709 239	0.456 235 179 35*5*	0.286 678 049 92*6*
9	0.502 949 709 239	0.456 235 179 356	0.286 678 049 925
10	0.502 949 709 239	0.456 235 179 356	0.286 678 049 925

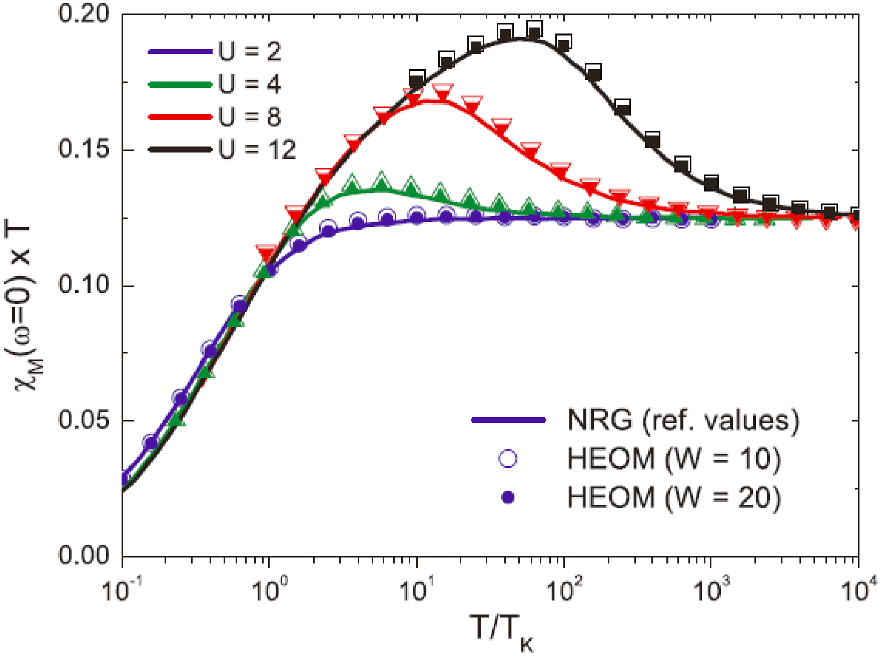
Accurate (L = 4)

Exact (L = 8)

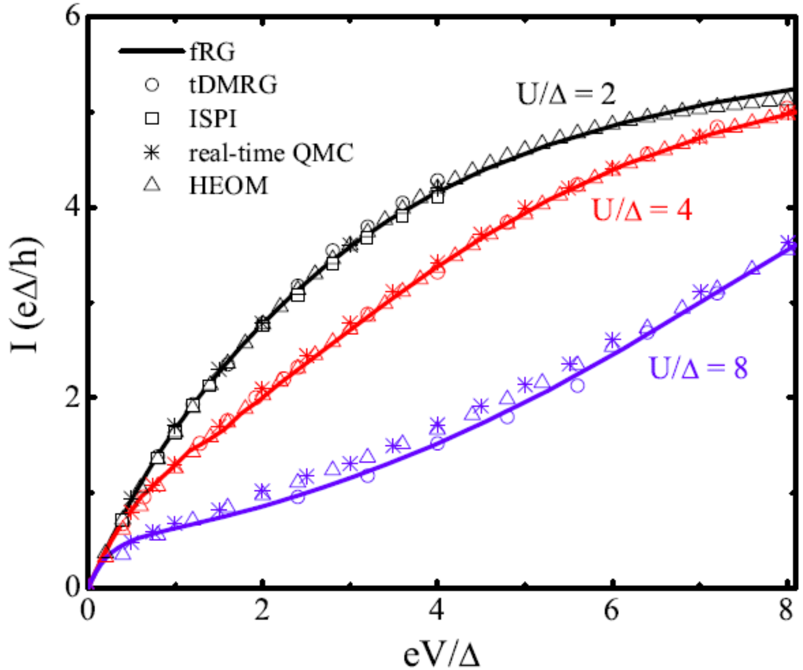
Han, Zheng, YJY et al, *J. Chem. Phys.* 148, 234108 (2018)

HEOM: Numerical Accuracy

Local magnetic susceptibility



Electric current

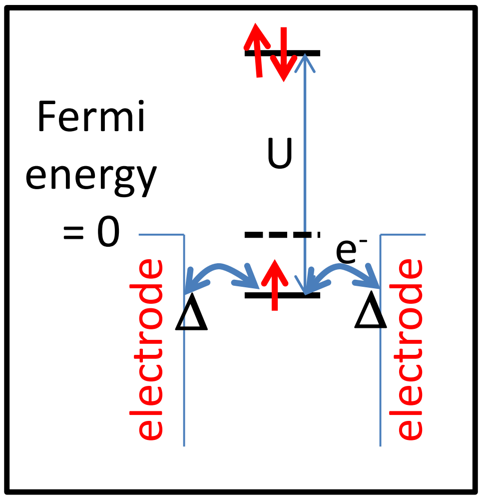


HEOM agree well with the standard methods such as NRG

J. Eckel et al., *New J. Phys.* 12, 043042 (2010)
Wang and Zheng et al., *Phys. Rev. B* 88, 035129 (2013)
Zheng, Yan, and Di Ventra, *Phys. Rev. Lett.* 111, 086601 (2013)

HEOM: Numerical Accuracy

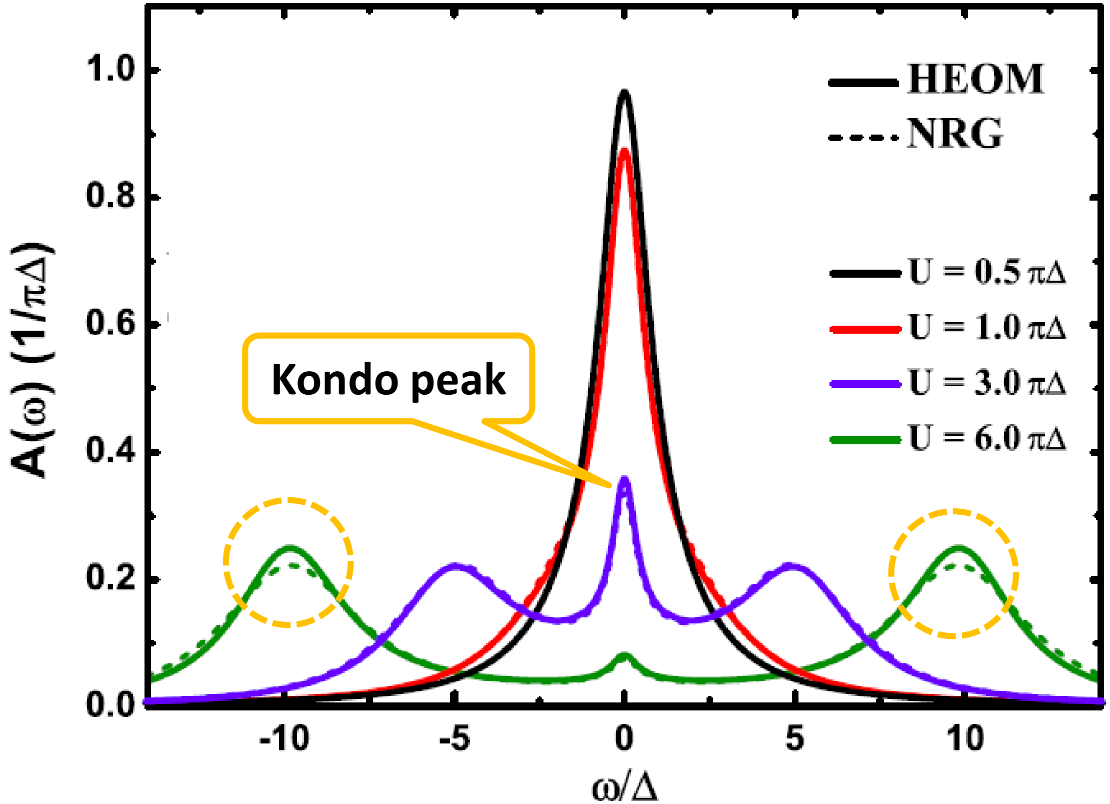
Single Impurity Anderson Model



Δ: s-b coupling

U: Coulomb energy

Comparison to NRG evaluation on symmetric SIAM at a finite *T*

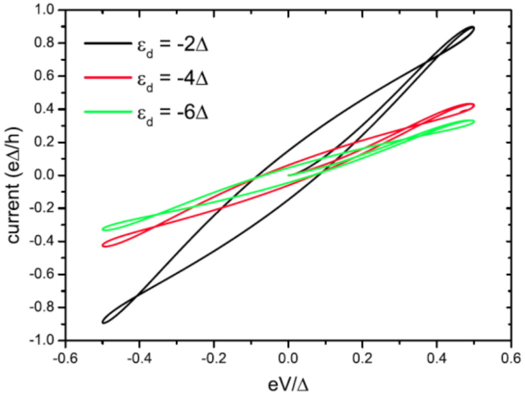


HEOM often more accurate & efficient than the "standard" methods

Z Li, NH Tong, X Zheng, D Hou, JH Wei, J Hu, YJY, *Phys. Rev. Lett.* (2012) **109**:266403

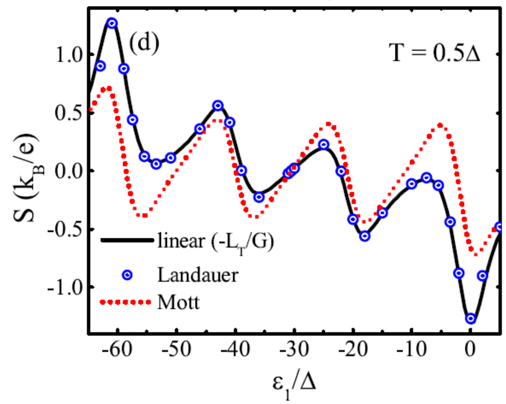
HEOM: Applications

Memristive system



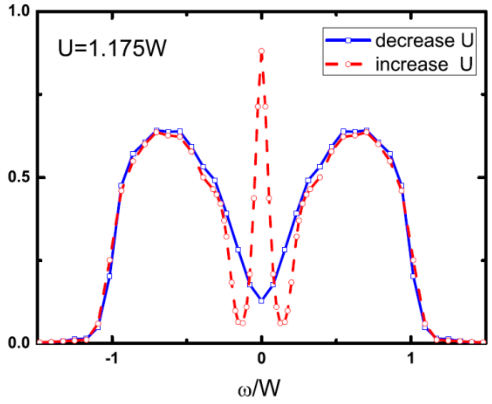
Phys. Rev. Lett. 111, 086601 (2013)

Thermopower



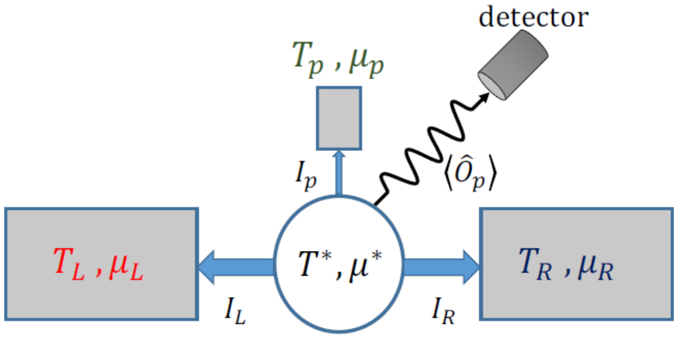
Phys. Rev. B 90, 165116 (2014)

Impurity solver for DMFT



Phys. Rev. B 90, 045141 (2014)

Measurement of local *T*



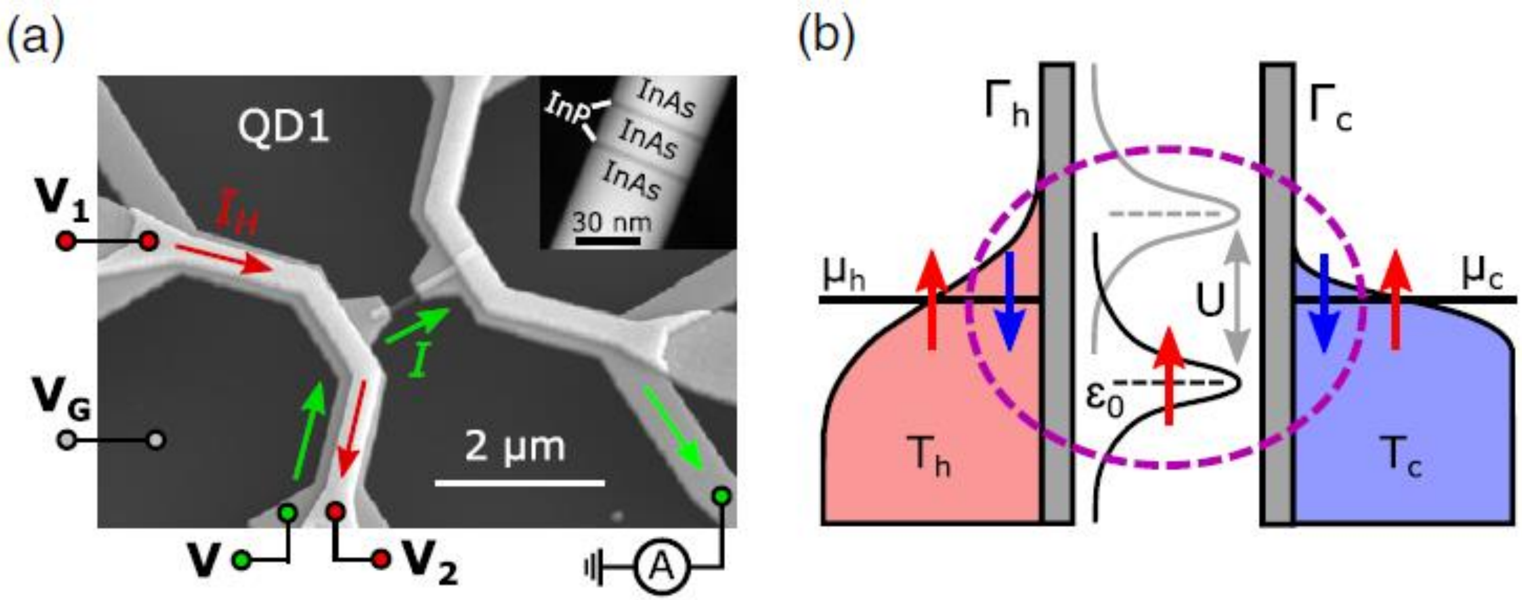
Phys. Rev. B 91, 205106 (2015)

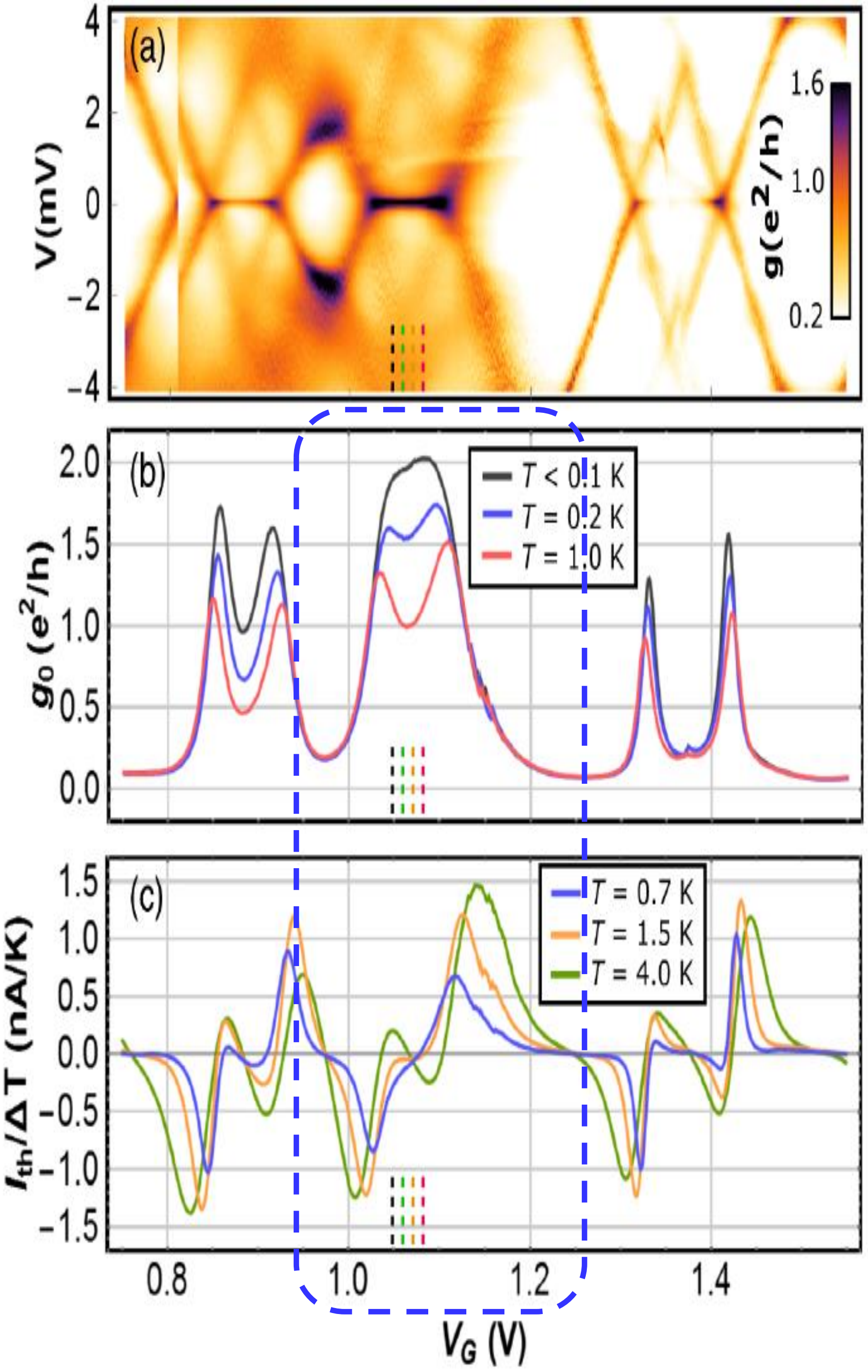
PHYSICAL REVIEW LETTERS **121,** 206801 (2018)

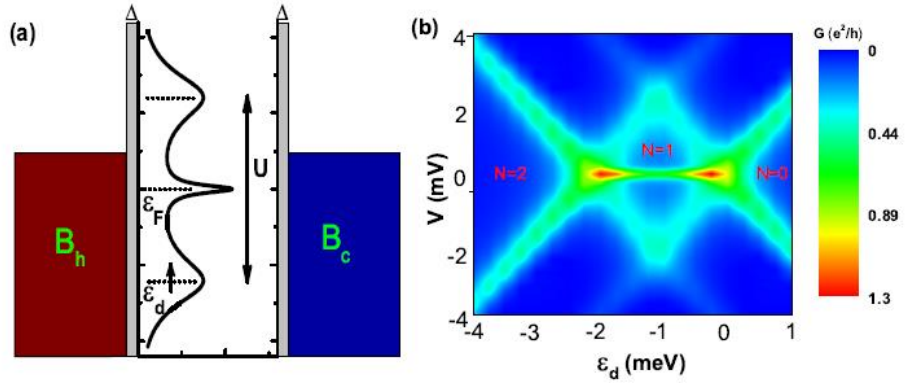
Thermoelectric Characterization of the Kondo Resonance in Nanowire Quantum Dots

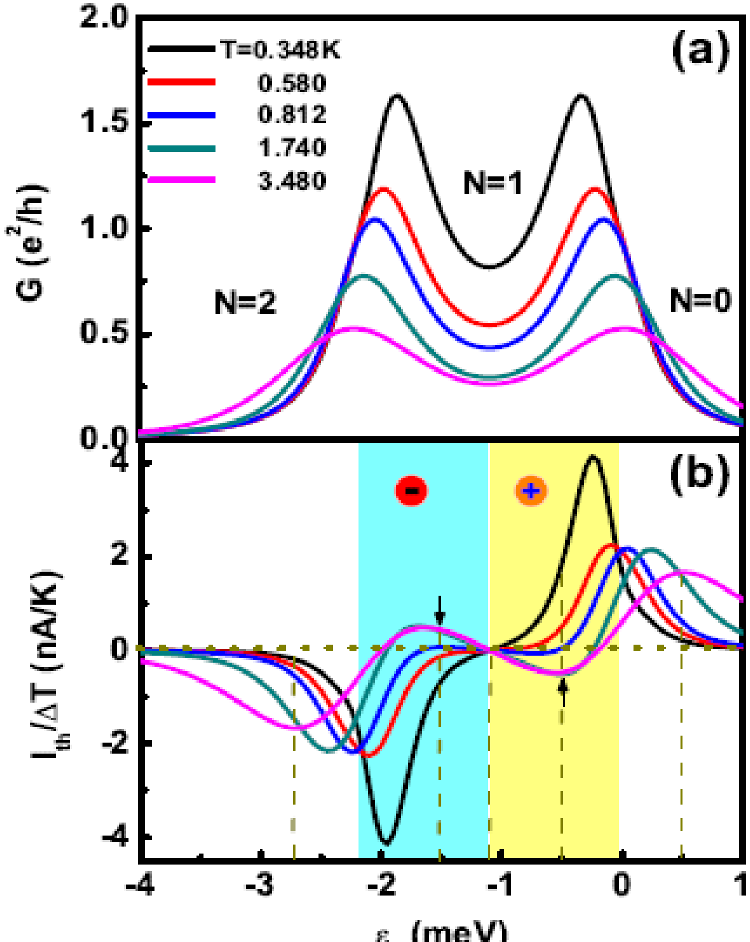
Artis Svilans,* Martin Josefsson, Adam M. Burke, Sofia Fahlvik, Claes Thelander,
Heiner Linke, and Martin Leijnse†
Division of Solid State Physics and NanoLund, Lund University, Box 118, S-221 00 Lund, Sweden

(Received 19 July 2018; published 16 November 2018)

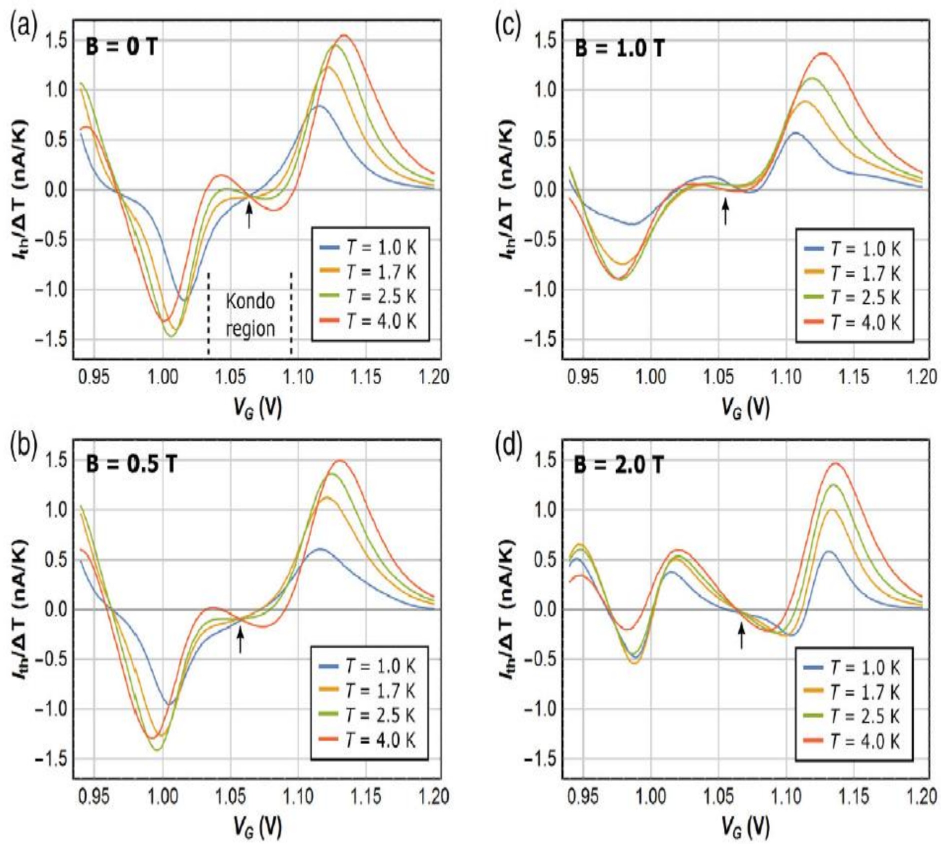


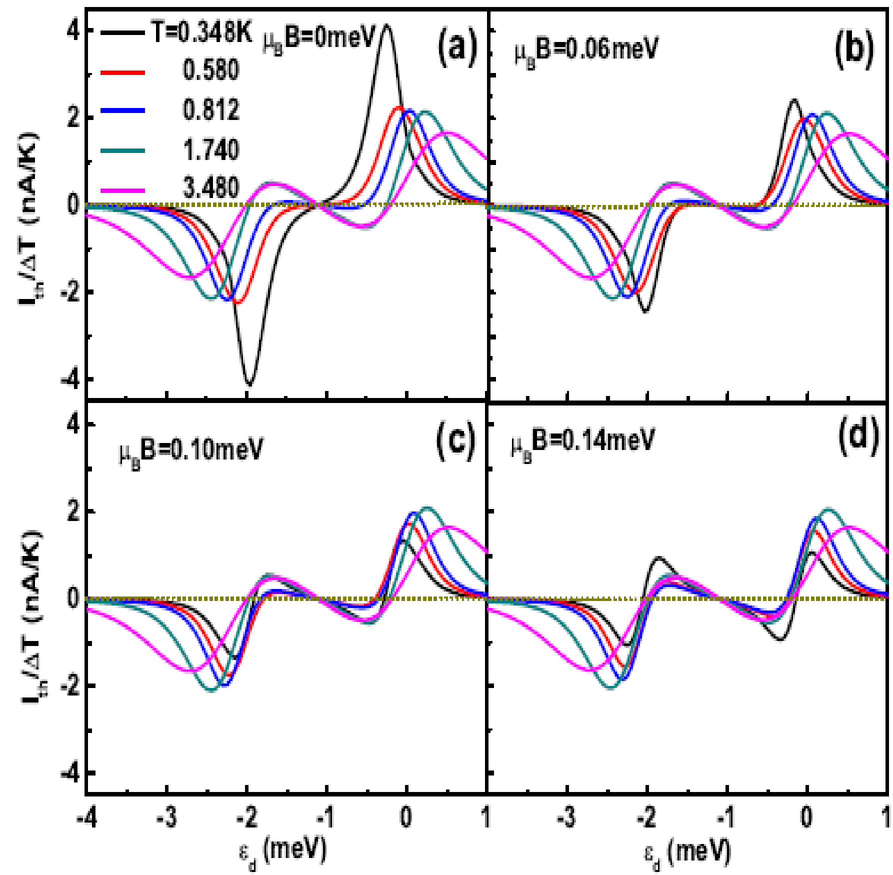






CSRC: YX Cheng et al (in preparation)





CSRC: YX Cheng et al (in preparation)

Outline

- **Quantum mechanics of open systems: Background**
- **The HEOM formalism: Machineries & applications**
- **HEOM-QUICK package**
- **The DEOM theory and applications**
- **Prospects**

Outline

- **HEOM-QUICK package**

WIREs Comput. Mol. Sci. **6**, 608-638 (2016)

QUICK: QUantum Impurity with a Correlated Kernel

Combined DFT+HEOM approach for reality systems/processes

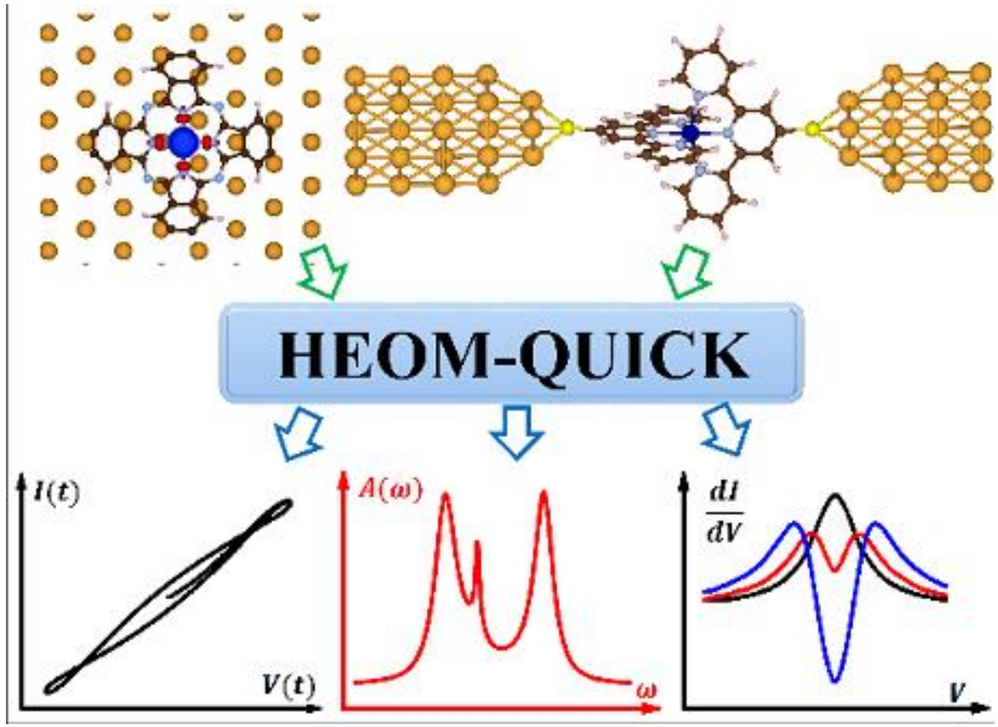
geometric and electronic structure (DFT) → **parameters** → **strongly correlated quantum impurity model (HEOM)**

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 2016, 6:608–638. doi: 10.1002/wcms.1269



Advanced Review

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

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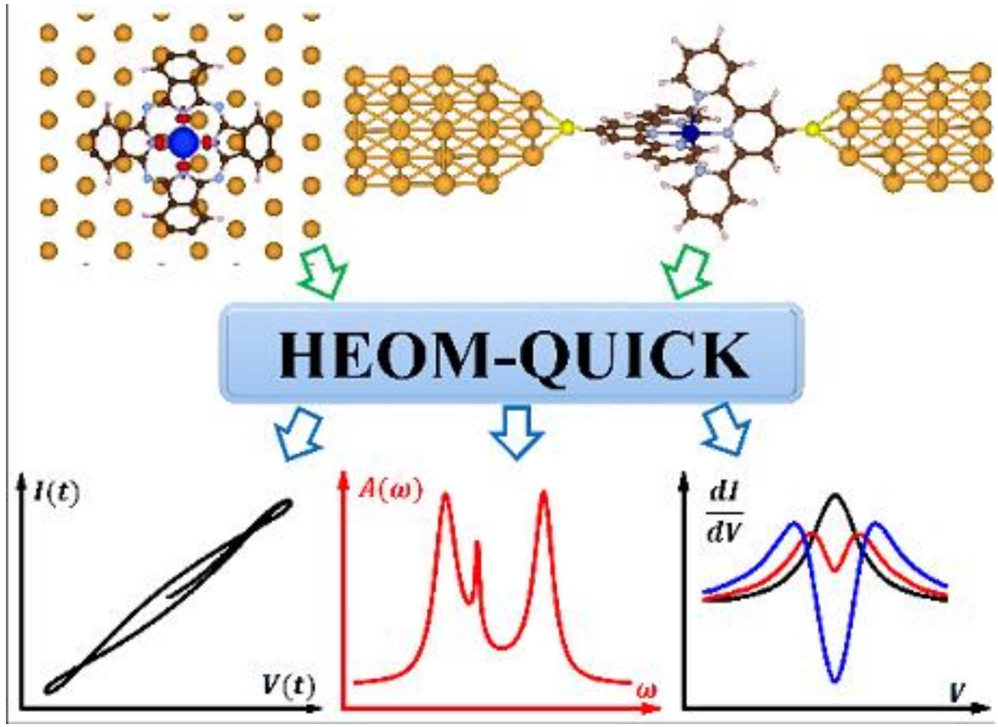
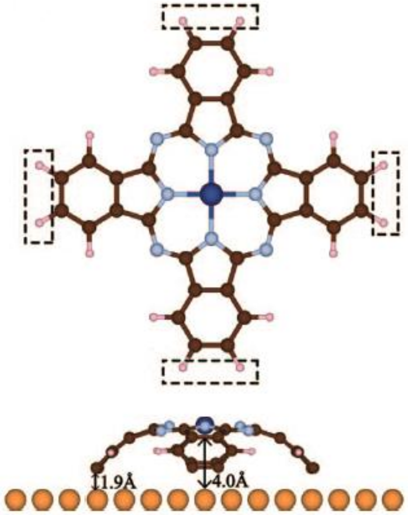


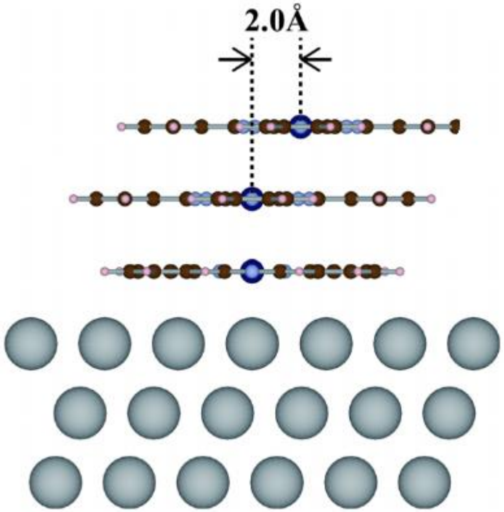
HEOM-QUICK Evaluations

d-CoPc/Au(111)



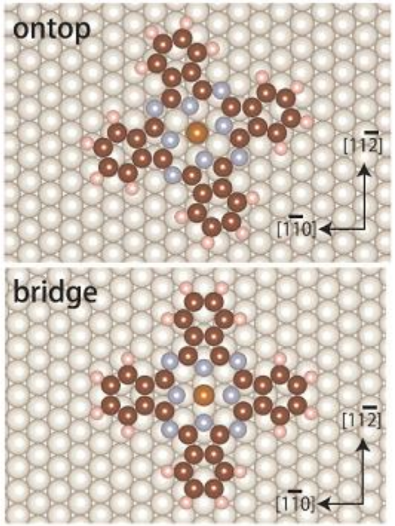
J. Chem. Phys. 141, 084713 (2014)

few-layer CoPc/Pb(111)



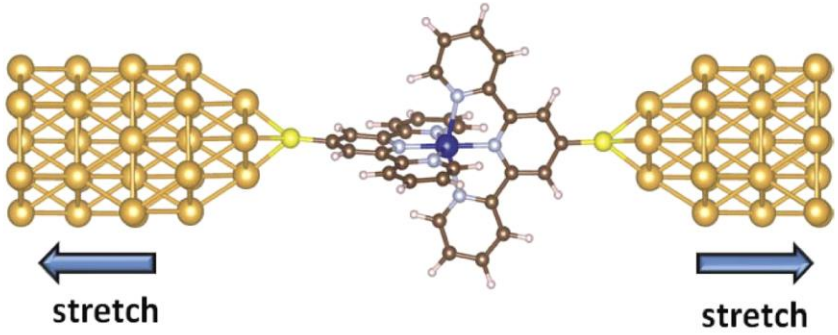
J. Chem. Phys. 145, 154301 (2016)

FePc/Au(111)



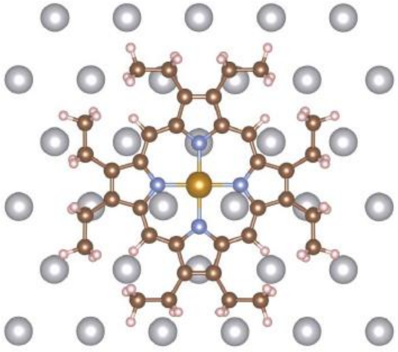
Phys. Rev. B 93, 125114 (2016)

Au—Co(tpy-S)$_2$—Au



J. Chem. Phys. 144, 034101 (2016)

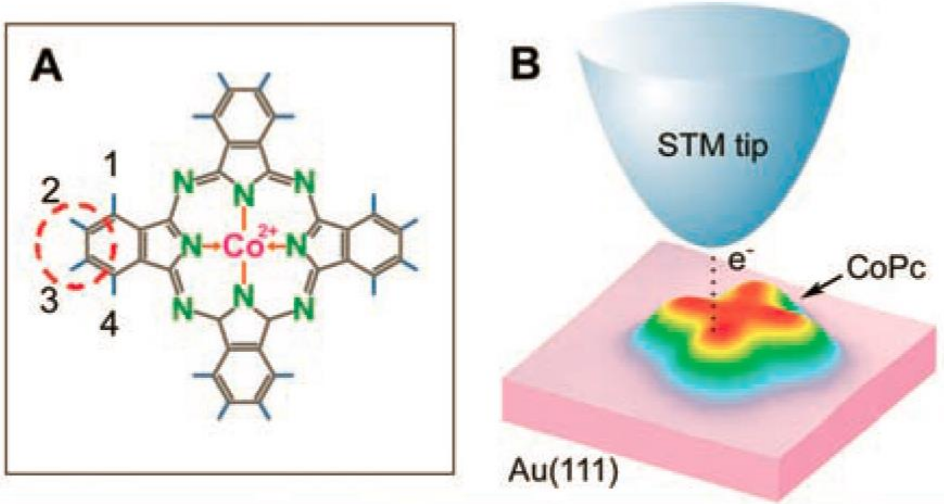
FeOEP/Pb(111)



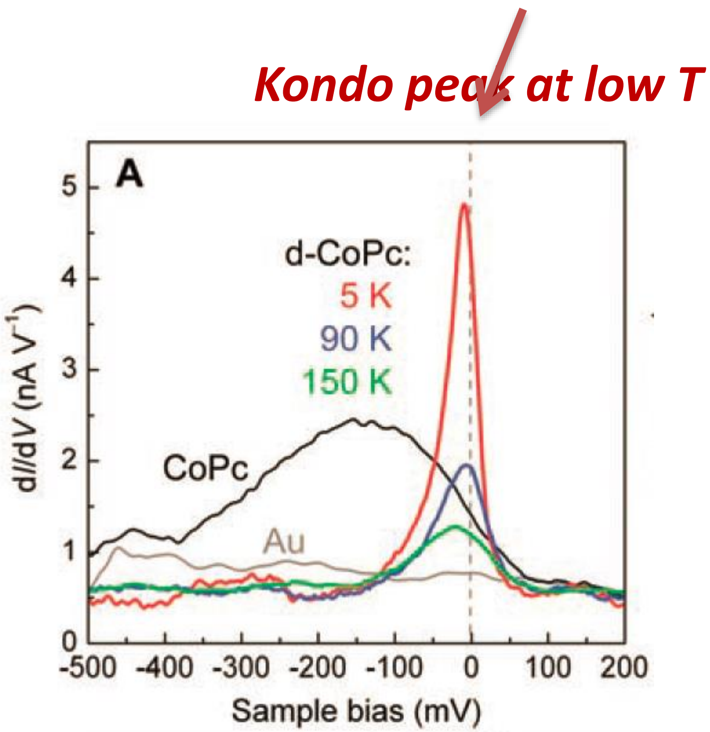
J. Phys. Chem. Lett. 9, 2418 (2018)

A. Kondo effect in d-CoPc/Au(111) composite

Experiment



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



A. Kondo effect in d-CoPc/Au(111) composite

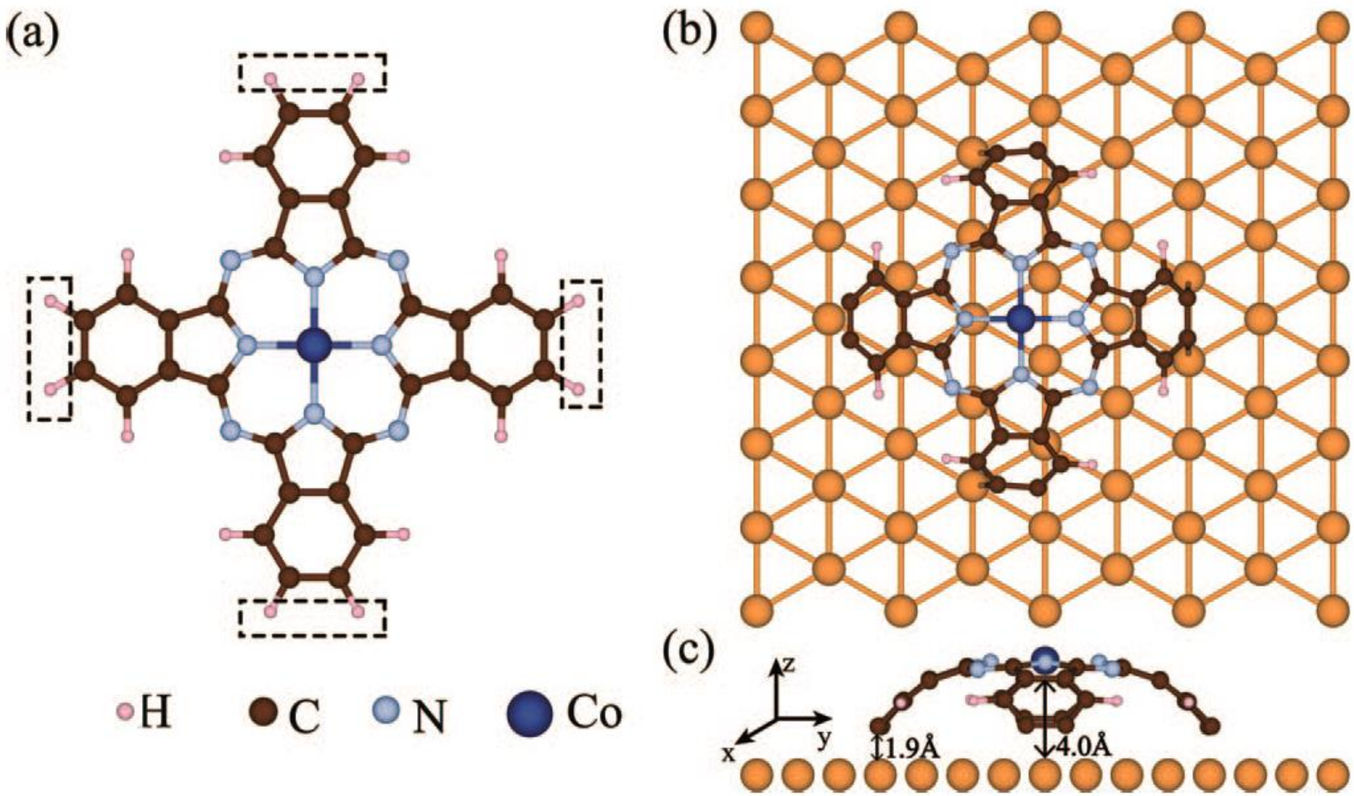
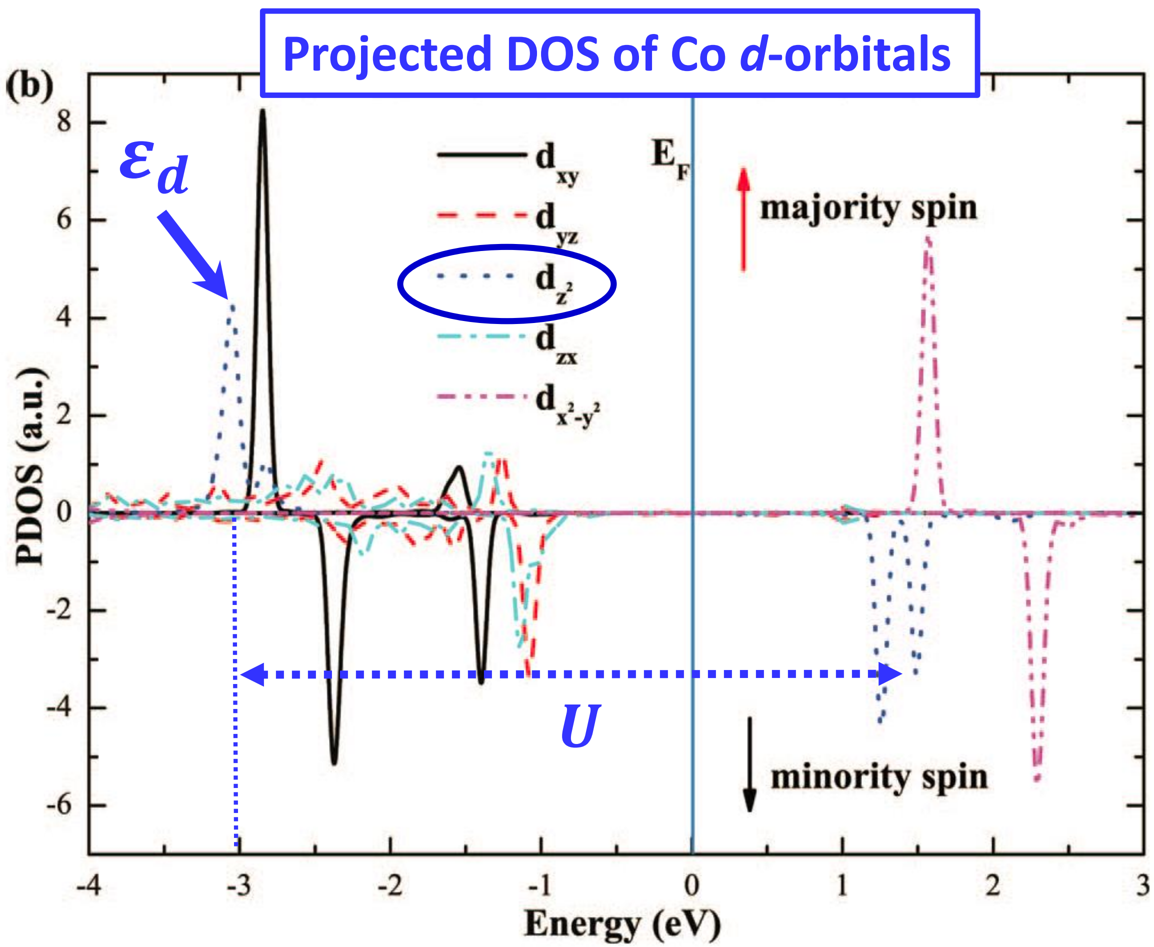


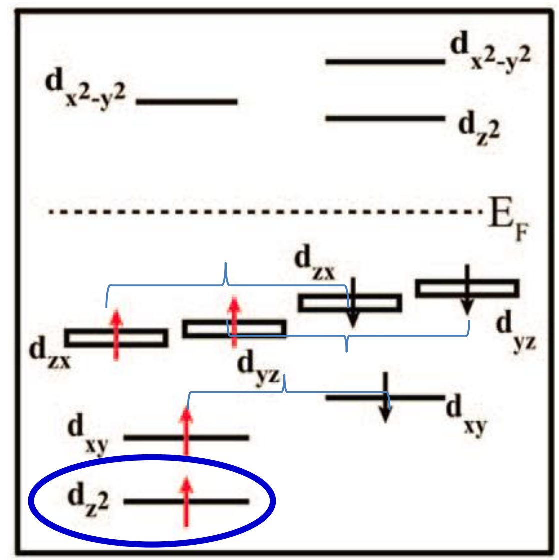
FIG. 2. (a) The molecular structure of the isolated CoPc. For the d-CoPc, the eight hydrogen atoms in the dashed squares are dissociated. (b) and (c) depict the top and side views of the optimized geometry of the composite d-CoPc/Au(111) adsorption system, respectively.

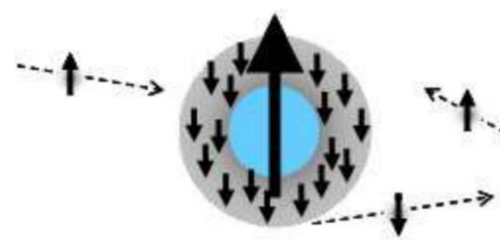
Yu, Zheng, and Yang et al. *J. Chem. Phys.* 141, 084713 (2014)

A. Kondo effect in d-CoPc/Au(111) composite

Construct Anderson impurity model (AIM) from DFT+U result



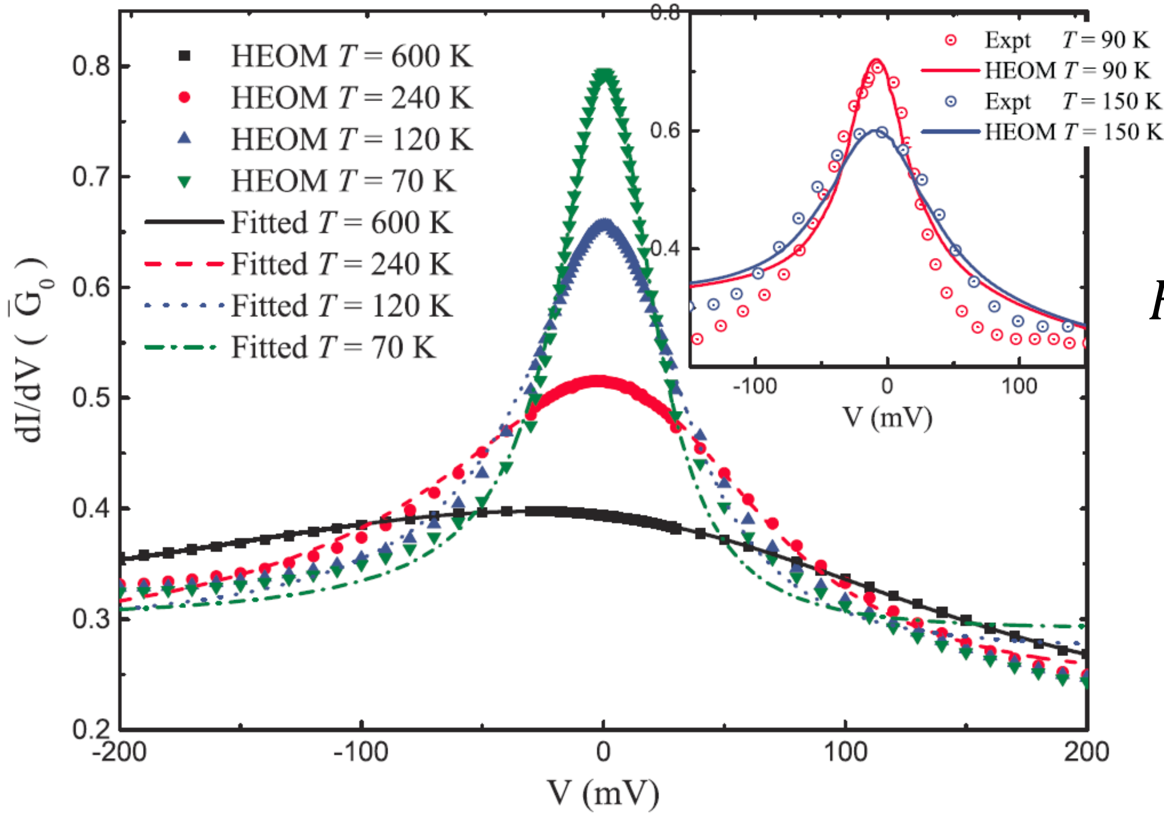




Yu, Zheng, and Yang et al. *J. Chem. Phys.* 141, 084713 (2014)

A. Kondo effect in d-CoPc/Au(111) composite

dI/dV spectra calculated by HEOM



impurity Hamiltonian

$$H_{imp} = \varepsilon_d(\hat{n}_\uparrow + \hat{n}_\downarrow) + U\hat{n}_\uparrow\hat{n}_\downarrow$$

reservoir spectral func

$$\Delta(\omega) = \frac{\Delta W^2}{(\omega-\mu)^2 + W^2}$$

Kondo temperature $T_K = 200.2 \pm 2.5$ K (*theo*) vs 208 K (*expt*)

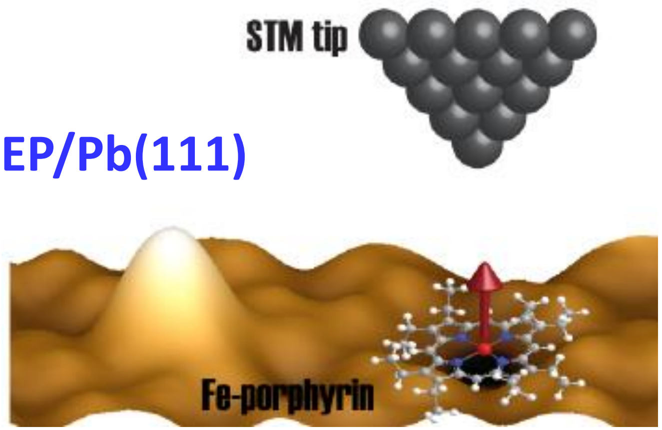
High T_K ⇐ strong coupling btw Co d_{z^2} orbital and Au states

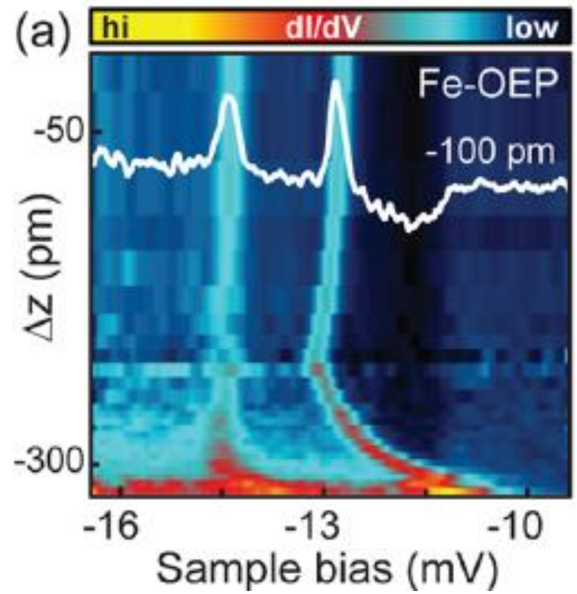
Yu, Zheng, and Yang et al. *J. Chem. Phys.* 141, 084713 (2014)

B. STM tip controlled magnetic anisotropy

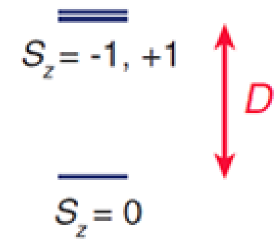
Experiment

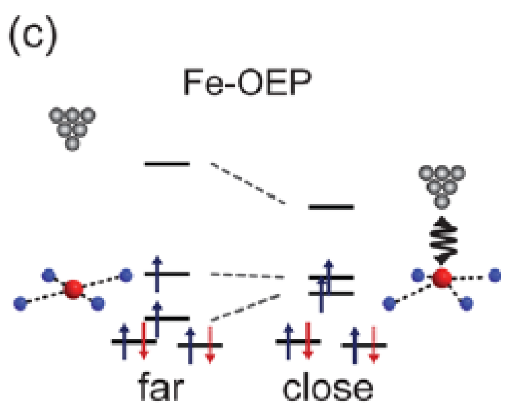
FeOEP/Pb(111)



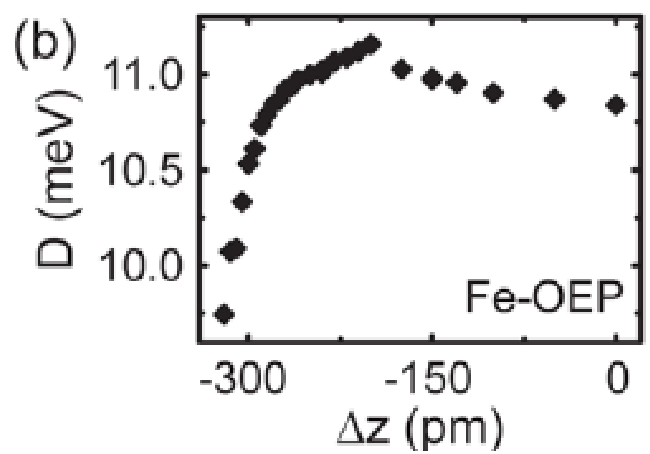


Magnetic anisotropy (*D*)





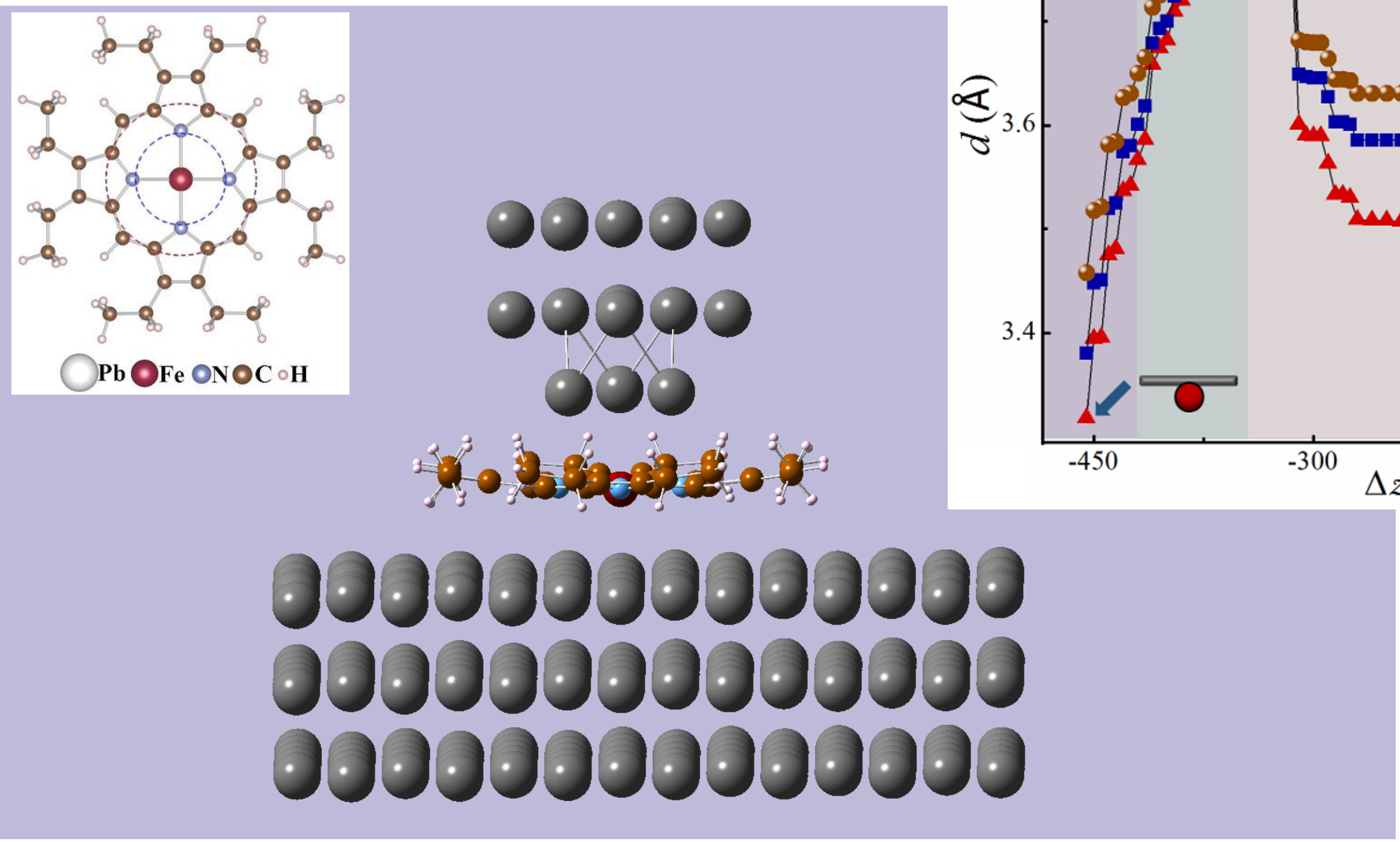
shifting of Fe 3*d* levels

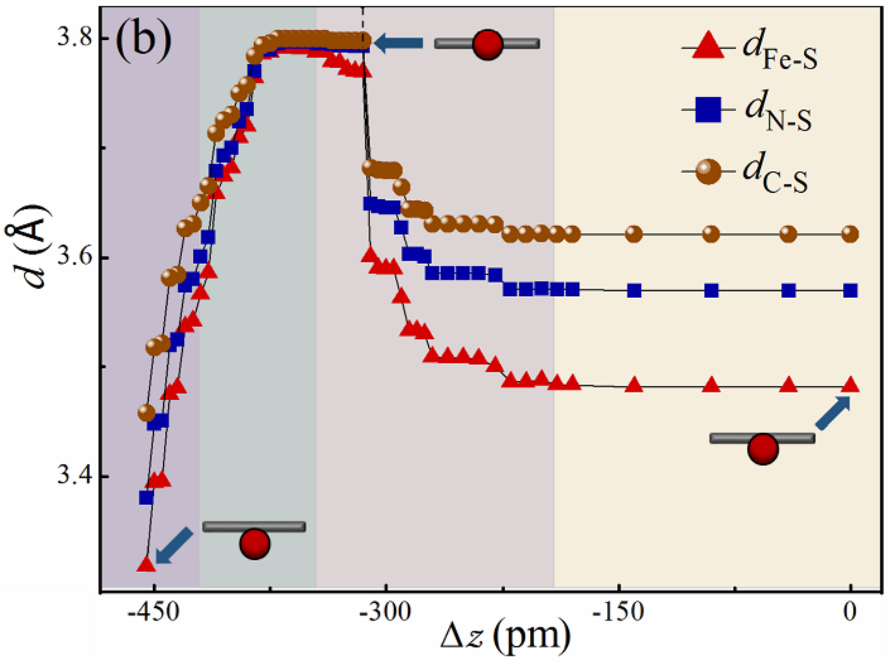


Benjamin et al. *Nano Lett.* 15, 4024 (2015)

B. STM tip controlled magnetic anisotropy

- **Evolution of geometric structure**



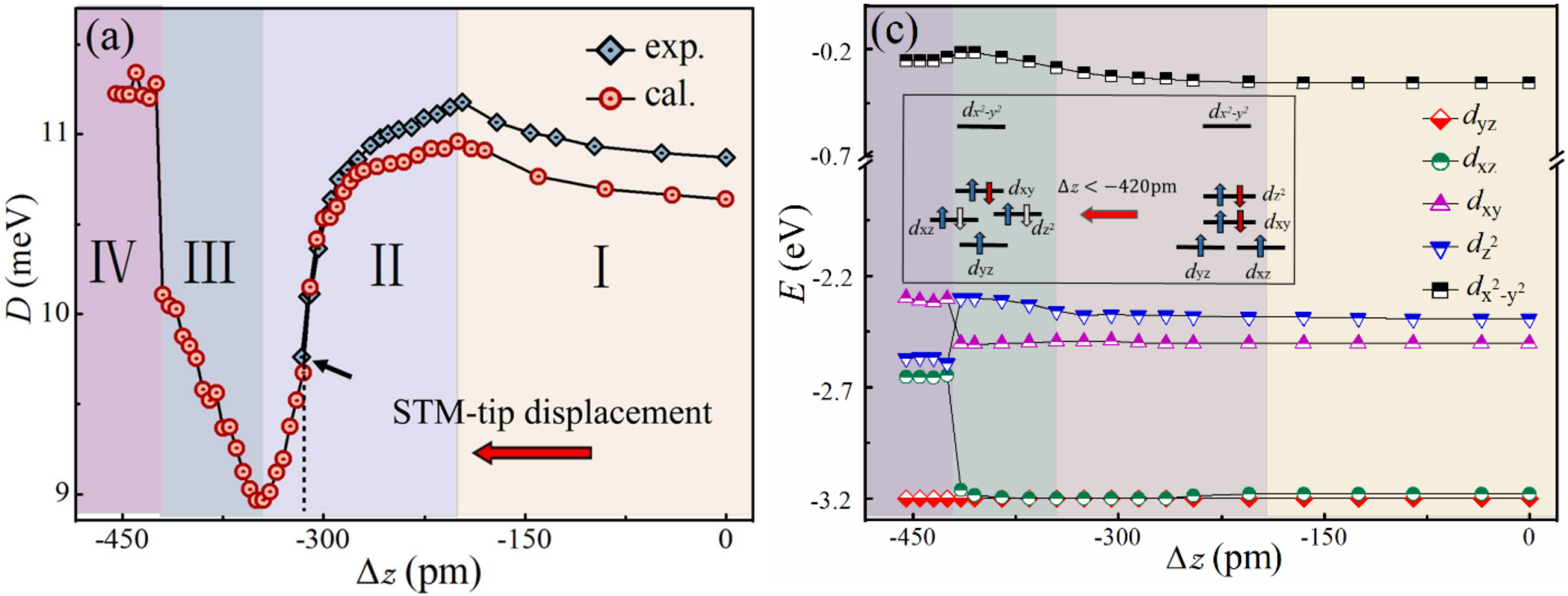


XL Wang, L. Yang, LZ Ye, X. Zheng, YJY. J. Phys. Chem. Lett. 9, 2418 (2018)

B. STM tip controlled magnetic anisotropy

Tuning of MA as tip approaches towards Pb(111) surface

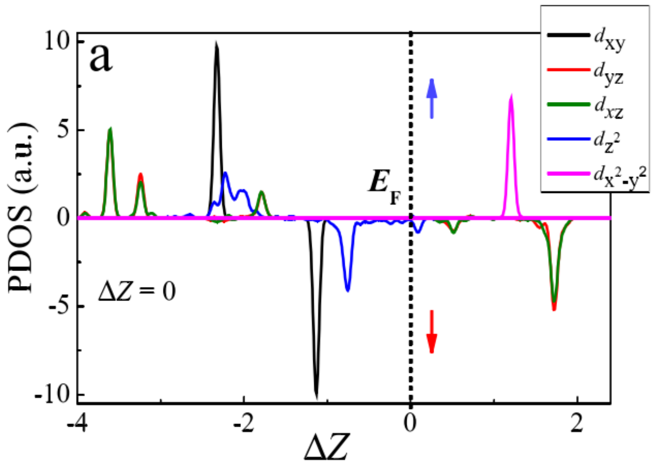
$$D = D_{\text{FeOEP}}^{\text{CASSCF}} + \left(D_{\text{tip/FeOEP/Pb(111)}}^{\text{DFT}} - D_{\text{FeOEP}}^{\text{DFT}} \right)$$



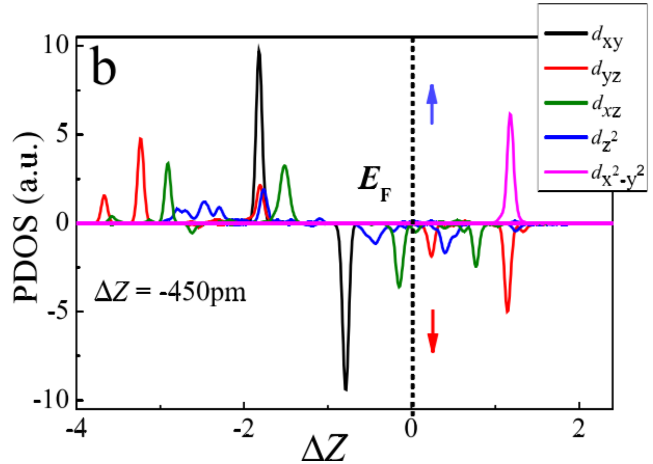
XL Wang, L. Yang, LZ Ye, X. Zheng, YJY. J. Phys. Chem. Lett. 9, 2418 (2018)

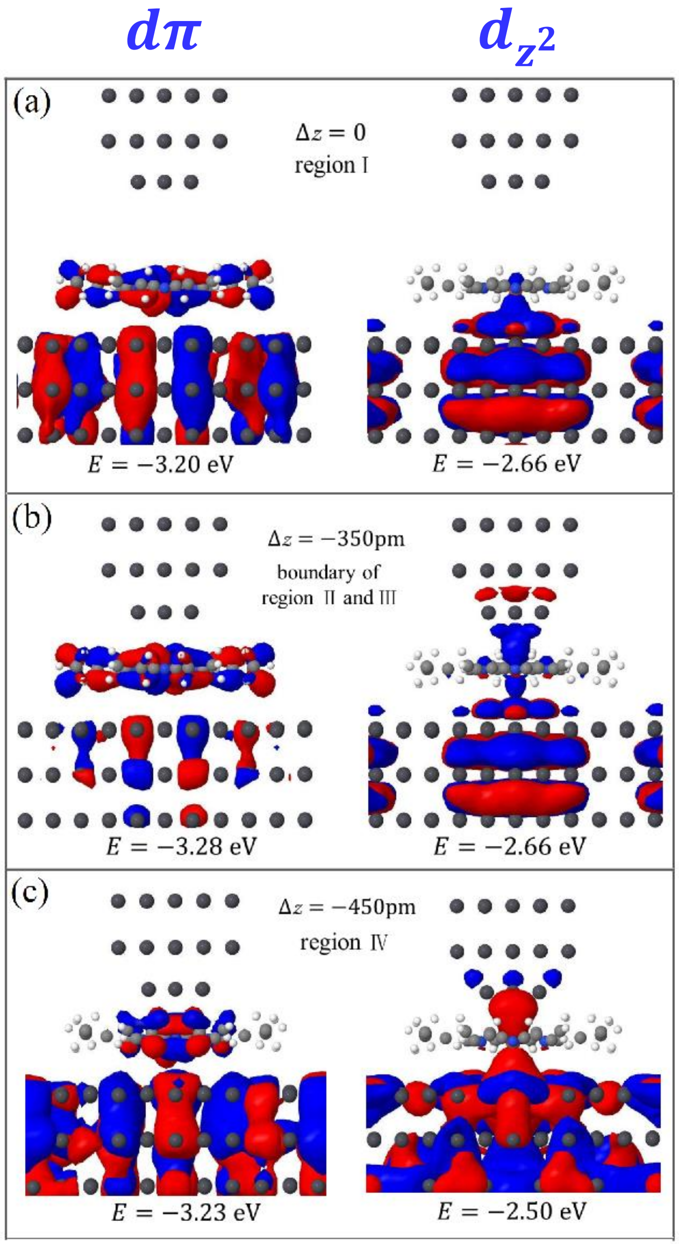
B. STM tip controlled magnetic anisotropy

tip is far $(dxy)^2(dz^2)^2 (dxz)^1 (dyz)^1$



tip is near $(dxy)^2(dz^2)^{1.3} (dyz)^1 (dxz)^{1.4}$





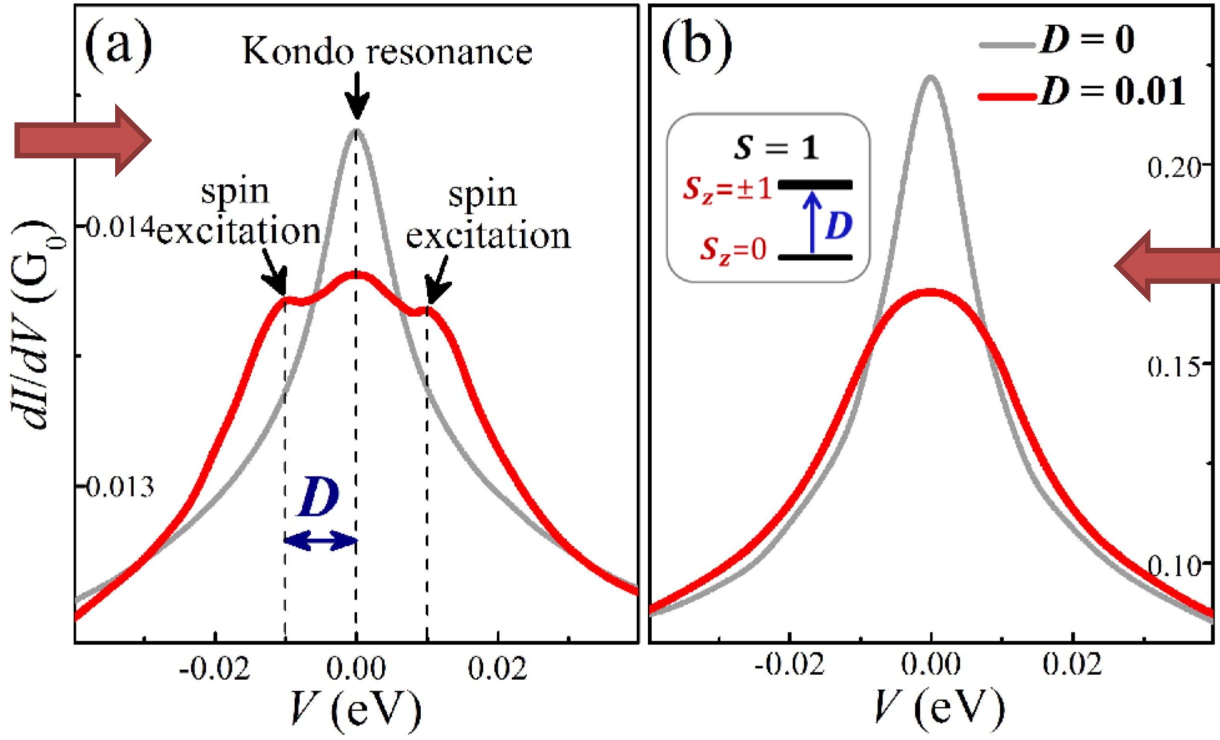
B. STM tip controlled magnetic anisotropy

Two-level Anderson impurity model

magnetic impurity

$$H_{\mathrm{imp}} = \epsilon_{\mathrm{a}}(\hat{n}_{\mathrm{a}\uparrow} + \hat{n}_{\mathrm{a}\downarrow}) + U_{\mathrm{a}}\hat{n}_{\mathrm{a}\uparrow}\hat{n}_{\mathrm{a}\downarrow} + \epsilon_{\mathrm{b}}(\hat{n}_{\mathrm{b}\uparrow} + \hat{n}_{\mathrm{b}\downarrow}) + U_{\mathrm{b}}\hat{n}_{\mathrm{b}\uparrow}\hat{n}_{\mathrm{b}\downarrow} + DS_z^2.$$

maximal $d_{\mathrm{Fe-S}}$

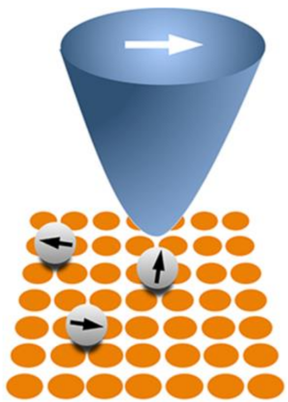


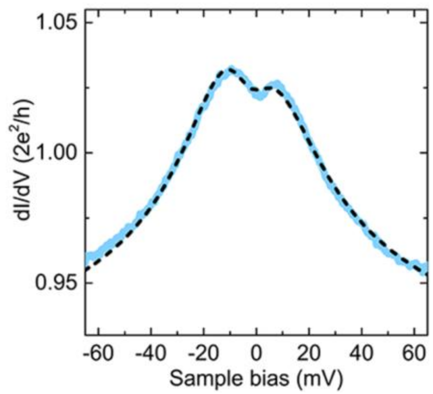
minimal $d_{\mathrm{Fe-S}}$

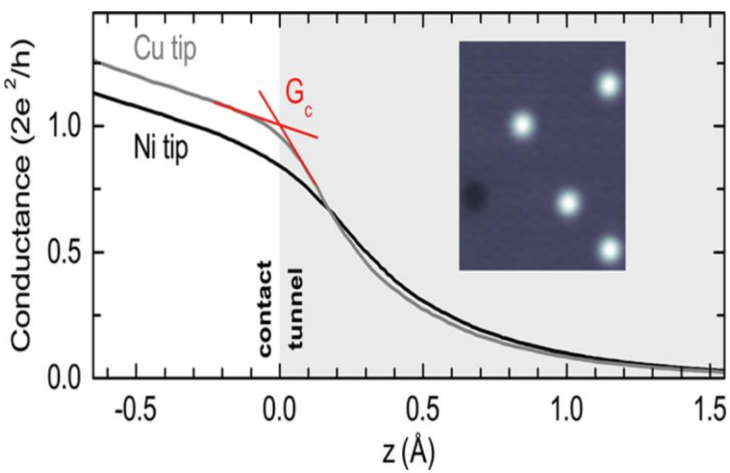
Spin excitations are suppressed by strong Kondo resonance

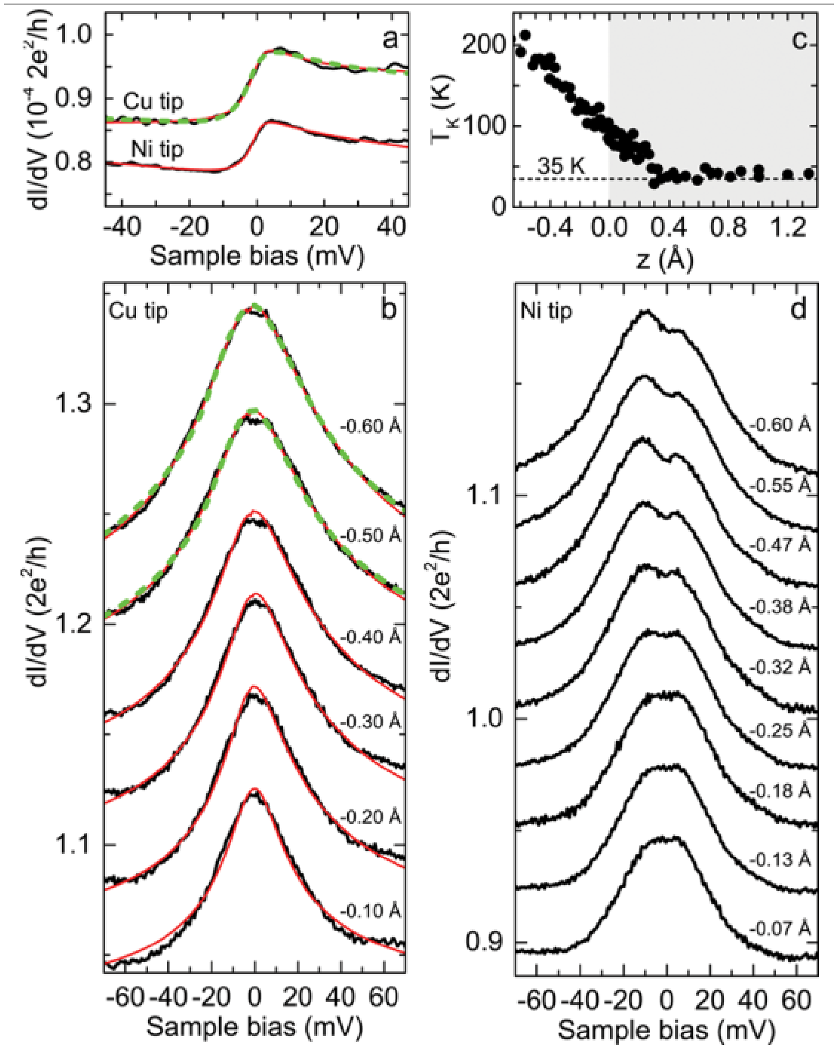
C. Control with spin-polarized STM tip

Experiment





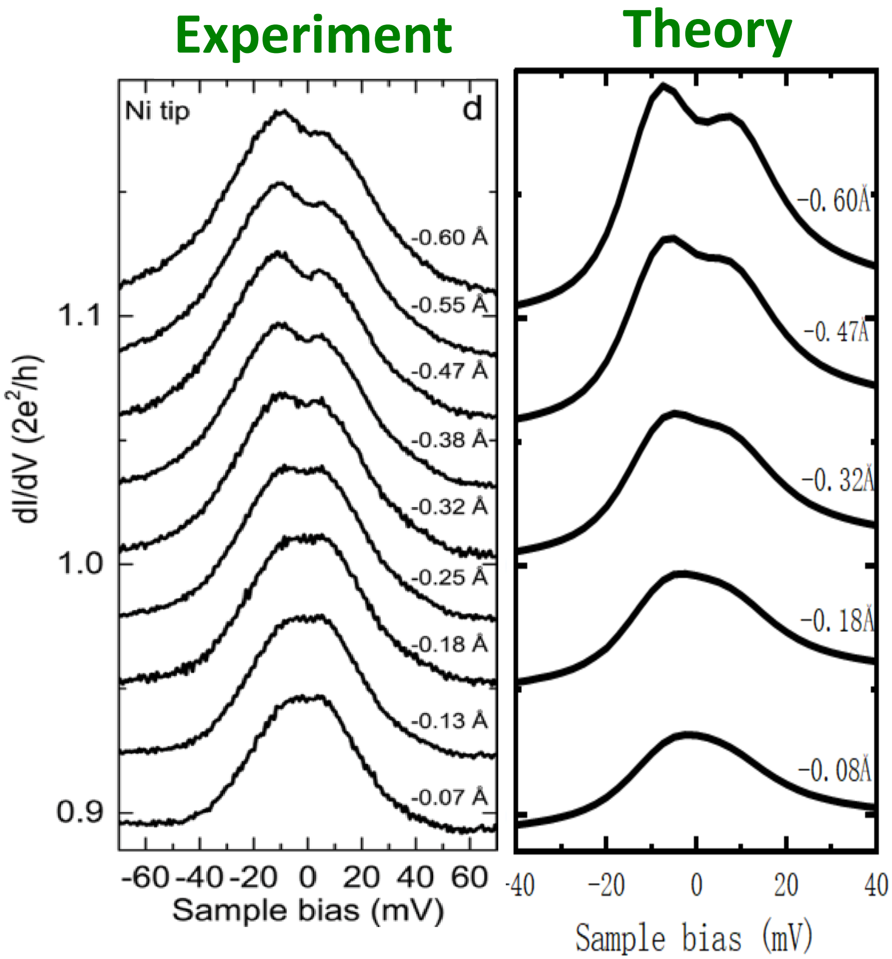




Kondo resonance of a Co Atom Exchange coupled to a Ferromagnetic tip

Choi et al. *Nano Lett* 16,6298 (2016)

C. Control with spin-polarized STM tip



Zhuang, Wang and Zheng et al. unpublished

Outline

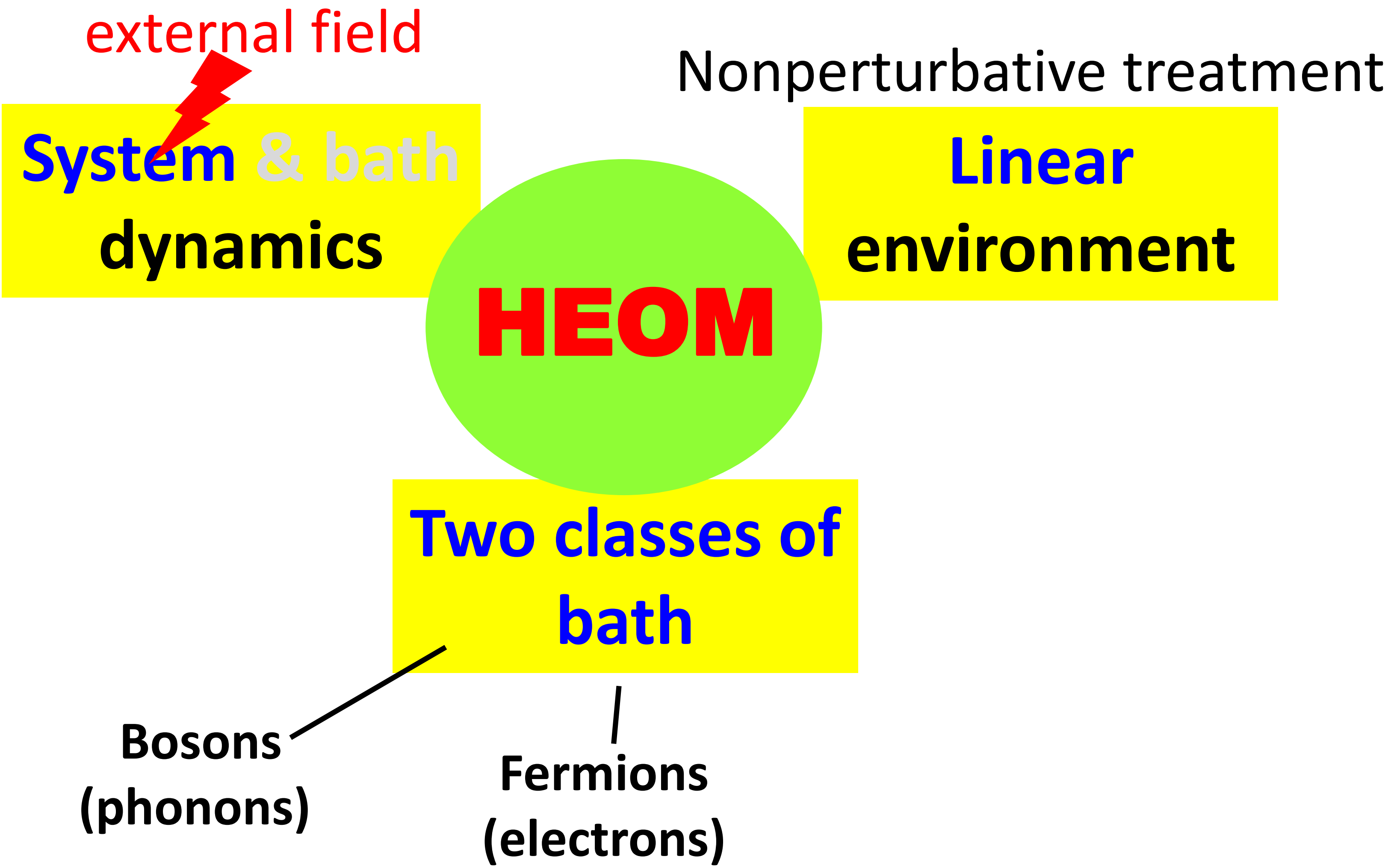
- Quantum mechanics of open systems: Background
- The HEOM formalism: Machineries & applications
- HEOM-QUICK package
- **The DEOM theory and applications**
- Prospects

DEOM: Statistical quasi-particle generalization of HEOM

HEOM Formalism

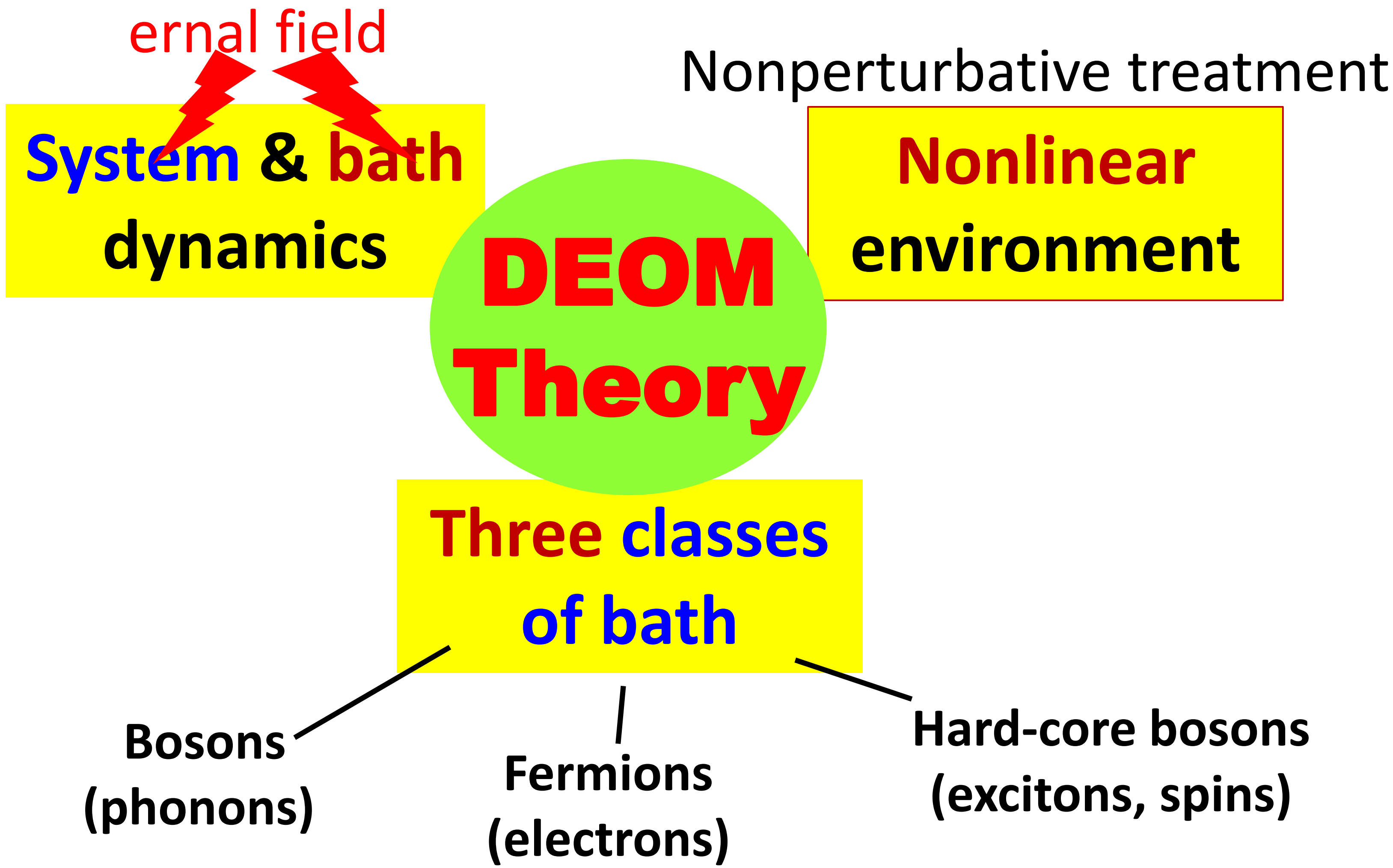
Bosonic: Tanimura (1990); YA Yan, JS Shao (2004); RX Xu, …, YJ Yan (2005)

Fermionic: JS Jin, Xiao Zheng, YJ Yan (2008)



DEOM Theory

YJ Yan, *J. Chem. Phys.* **140** (2014) 054105; YJ Yan et al, *Front. Phys.* **11** (2016) 110306;
HD Zhang et al., *Mol. Phys*. **116** (2018) 780-812



DEOM Theory: Construction

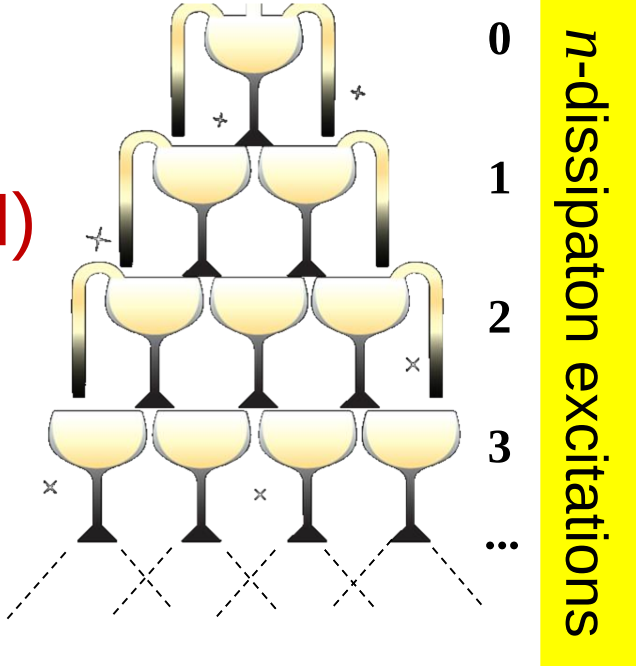
DEOM = Schrödinger Eq. + Dissipaton Algebra

1. Basic Features

Dissipaton Density Operators (DDOs)

$$\rho_{\mathbf{n}}^{(n)}(t) \equiv \mathrm{tr}_{\mathrm{B}}\left[\left(\hat{f}_K^{n_K}\cdots\hat{f}_1^{n_1}\right)^{\circ}\rho_{\mathrm{total}}(t)\right]$$

(HEOM)



- $n = n_1 + \ldots + n_K$
- $\mathbf{n} = \{n_1 \ldots n_K\}$: configuration
- $(\ldots)^{\mathrm{o}}$: **irreducibility**; *i.e.*, (c-number)$^{\mathrm{o}}$ = 0

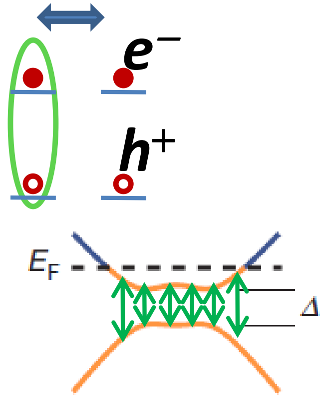
Environment effects are characterized with **dissipatons**, $\{\hat{f}_1, \ldots, \hat{f}_K\}$, **statistical quasi-particles**

1. Basic Features

$$\rho_{\mathbf{n}}^{(n)}(t) \equiv \mathrm{tr}_{\mathrm{B}}\left[\left(\hat{f}_K^{n_K}\cdots\hat{f}_1^{n_1}\right)^{\circ}\rho_{\mathrm{total}}(t)\right]$$

Environment

Dissipatons $\{\hat{f}_j\}$	Bosonic	Fermionic	Hard-core bosonic
Occupation n_j	0, 1, 2, …	0 or 1	0 or 1
Particle Permutation	Symmetric	Anti-Sym.	Symmetric



1. Basic Features

$$\rho_{\mathbf{n}}^{(n)}(t) \equiv \mathrm{tr}_{\mathrm{B}}\left[\left(\hat{f}_K^{n_K}\cdots\hat{f}_1^{n_1}\right)^{\circ}\rho_{\mathrm{total}}(t)\right]$$

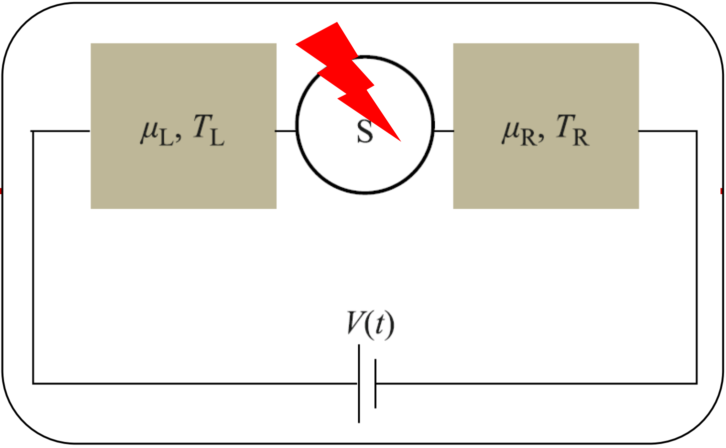
Environment

Dissipatons $\{\hat{f}_j\}$	Bosonic	Fermionic	Hard-core bosonic
Occupation n_j	0, 1, 2, …	0 or 1	0 or 1
Particle Permutation	Symmetric	Anti-Sym.	Symmetric

- Bosonic : $\left(\hat{f}_j\hat{f}_{j'}\right)^{\circ} = \left(\hat{f}_{j'}\hat{f}_j\right)^{\circ}$
- Fermionic : $\left(\hat{f}_j\hat{f}_{j'}\right)^{\circ} = -\left(\hat{f}_{j'}\hat{f}_j\right)^{\circ}$
- Hard-core bosonic: $\left(\hat{f}_j\hat{f}_{j'}\right)^{\circ} = (1-\delta_{jj'})\left(\hat{f}_{j'}\hat{f}_j\right)^{\circ}$

(c-number) $^{\circ}$ = 0

1. Basic Features



$$H_T(t) = H(t) + \sum_{\alpha=L,R} \hat{h}^{\text{eff}}_\alpha(t) + H_{SB}$$

$$H_{SB} = \sum_{\alpha u} (\hat{a}^+_u \hat{F}^-_{\alpha u} + \hat{F}^+_{\alpha u} \hat{a}^-_u)$$

$$\hat{F}^+_{\alpha u} \equiv \sum_k t_{\alpha k u} \hat{d}^+_{\alpha k} = (\hat{F}^-_{\alpha u})^\dagger$$

fermionic

Electrode

$$\hat{h}^{\text{eff}}_\alpha(t) = \sum_k [\epsilon_{\alpha k} + \mu_\alpha(t)] \hat{d}^+_{\alpha k} \hat{d}^-_{\alpha k}$$

Current operator

$$\hat{I}_\alpha \equiv -\frac{d}{dt}\hat{N}_\alpha = -\mathrm{i}[H_{SB}, \hat{N}_\alpha]$$

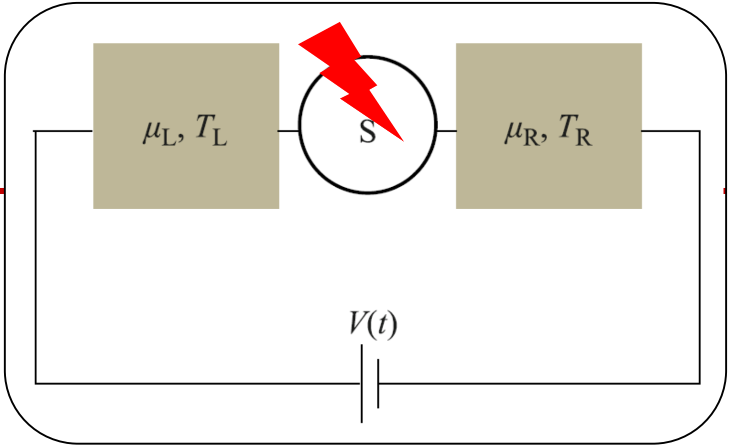
$$= -\mathrm{i} \sum_u (\hat{a}^+_u \hat{F}^-_{\alpha u} - \hat{F}^+_{\alpha u} \hat{a}^-_u)$$

$\bar{\sigma}$: opposite sign of

$\sigma = +, -$

$$\langle \hat{F}^\sigma_{\alpha u}(t) \hat{F}^{\bar{\sigma}}_{\alpha v}(0) \rangle^{\text{eq}}_B = \frac{1}{\pi} \int_{-\infty}^{\infty} \mathrm{d}\omega\, \mathrm{e}^{\sigma \mathrm{i}\omega t} \frac{J^\sigma_{\alpha u v}(\omega)}{1 + e^{\sigma \beta_\alpha \omega}}$$

1. Basic Features



$$H_T(t) = H(t) + \sum_{\alpha=\mathrm{L,R}} \hat{h}^{\mathrm{eff}}_{\alpha}(t) + H_{\mathrm{SB}}$$

$$H_{\mathrm{SB}} = \sum_{\alpha u} \left(\hat{a}^{+}_{u} \hat{F}^{-}_{\alpha u} + \hat{F}^{+}_{\alpha u} \hat{a}^{-}_{u} \right)$$

$$\widetilde{F}^{\sigma}_{\alpha u} \equiv -\sigma \hat{F}^{\sigma}_{\alpha u} \equiv \sum_{\kappa=1}^{K} \hat{f}^{\sigma}_{\alpha\kappa u}$$

$\bar{\sigma}$: opposite sign of
$\sigma = +\,,\ -$

$$\left\langle \hat{F}^{\sigma}_{\alpha u}(t) \hat{F}^{\bar{\sigma}}_{\alpha v}(0) \right\rangle^{\mathrm{eq}}_{\mathrm{B}} = \frac{1}{\pi} \int_{-\infty}^{\infty} \mathrm{d}\omega\, \mathrm{e}^{\sigma \mathrm{i}\omega t} \frac{J^{\sigma}_{\alpha uv}(\omega)}{1 + e^{\sigma\beta_\alpha \omega}} = \sum_{\kappa=1}^{K} \eta^{\sigma}_{\alpha\kappa uv} \mathrm{e}^{-\gamma^{\sigma}_{\alpha\kappa} t}$$

1. Basic Features

Fermionic DDOs

$$\rho_{\boldsymbol{j}}^{(n)}(t) \equiv \mathrm{tr}_{\mathrm{B}}\Big[\big(\hat{f}_{j_n}\cdots\hat{f}_{j_1}\big)^{\circ}\rho_{\mathrm{total}}(t)\Big]$$

dissipaton's index

$$j \equiv (\sigma\alpha\kappa u)$$

$$H_{\mathrm{T}}(t) = H(t) + \sum_{\alpha=\mathrm{L,R}} \hat{h}_{\alpha}^{\mathrm{eff}}(t) + \sum_{\sigma\alpha\kappa u} \hat{a}_u^{\bar{\sigma}} \hat{f}_{\alpha\kappa u}^{\sigma}$$

$$H_{\mathrm{SB}} = \sum_{\alpha u}\big(\hat{a}_u^{+}\hat{F}_{\alpha u}^{-} + \hat{F}_{\alpha u}^{+}\hat{a}_u^{-}\big) = \sum_{\sigma\alpha\kappa u} \hat{a}_u^{\bar{\sigma}} \hat{f}_{\alpha\kappa u}^{\sigma}$$

$$\widetilde{F}_{\alpha u}^{\sigma} \equiv -\sigma \hat{F}_{\alpha u}^{\sigma} \equiv \sum_{\kappa=1}^{K} \hat{f}_{\alpha\kappa u}^{\sigma}$$

$\bar{\sigma}$: opposite sign of $\sigma = +, -$

$$\big\langle \hat{F}_{\alpha u}^{\sigma}(t)\hat{F}_{\alpha v}^{\bar{\sigma}}(0)\big\rangle_{\mathrm{B}}^{\mathrm{eq}} = \frac{1}{\pi}\int_{-\infty}^{\infty} \mathrm{d}\omega\, \mathrm{e}^{\sigma \mathrm{i}\omega t}\frac{J_{\alpha uv}^{\sigma}(\omega)}{1+e^{\sigma\beta_{\alpha}\omega}} = \sum_{\kappa=1}^{K}\eta_{\alpha\kappa uv}^{\sigma}\mathrm{e}^{-\gamma_{\alpha\kappa}^{\sigma}t}$$

1. Basic Features

$$\rho_{\boldsymbol{j}}^{(n)}(t) \equiv \mathrm{tr}_{\mathrm{B}}\left[\left(\hat{f}_{j_n}\cdots\hat{f}_{j_1}\right)^{\circ}\rho_{\mathrm{total}}(t)\right]$$

$$H_{\mathrm{T}}(t) = H(t) + \sum_{\alpha=\mathrm{L,R}} \hat{h}_{\alpha}^{\mathrm{eff}}(t) + \sum_{\sigma\alpha\kappa u} \hat{a}_u^{\bar{\sigma}} \hat{f}_{\alpha\kappa u}^{\sigma}$$

$$\widetilde{F}_{\alpha u}^{\sigma} \equiv -\sigma \hat{F}_{\alpha u}^{\sigma} \equiv \sum_{\kappa=1}^{K} \hat{f}_{\alpha\kappa u}^{\sigma}$$

$$\left\langle \hat{f}_{\alpha\kappa u}^{\sigma}(t)\hat{f}_{\alpha'\kappa' v}^{\sigma'}(0)\right\rangle_{\mathrm{B}} = -\delta_{\alpha\kappa,\alpha'\kappa'}^{\sigma,\bar{\sigma}'}\eta_{\alpha\kappa uv}^{\sigma} e^{-\gamma_{\alpha\kappa}^{\sigma} t}$$

$$\left\langle \hat{f}_{\alpha'\kappa' v}^{\sigma'}(0)\hat{f}_{\alpha\kappa u}^{\sigma}(t)\right\rangle_{\mathrm{B}} = -\delta_{\alpha\kappa,\alpha'\kappa'}^{\sigma,\bar{\sigma}'}\eta_{\alpha\kappa uv}^{\bar{\sigma}*} e^{-\gamma_{\alpha\kappa}^{\sigma} t}$$

$$\left\langle \hat{B}(0)\hat{A}^{\dagger}(t)\right\rangle = \left\langle \hat{A}(t)\hat{B}^{\dagger}(0)\right\rangle^{*}$$

$\bar{\sigma}$: opposite sign of $\sigma = +\,,\ -$

$$\left\langle \hat{F}_{\alpha u}^{\sigma}(t)\hat{F}_{\alpha v}^{\bar{\sigma}}(0)\right\rangle_{\mathrm{B}}^{\mathrm{eq}} = \frac{1}{\pi}\int_{-\infty}^{\infty} \mathrm{d}\omega\, \mathrm{e}^{\sigma \mathrm{i}\omega t} \frac{J_{\alpha uv}^{\sigma}(\omega)}{1+e^{\sigma\beta_{\alpha}\omega}} = \sum_{\kappa=1}^{K} \eta_{\alpha\kappa uv}^{\sigma} \mathrm{e}^{-\gamma_{\alpha\kappa}^{\sigma} t}$$

1. Basic Features

$$\rho_{\boldsymbol{j}}^{(n)}(t) \equiv \mathrm{tr}_{\mathrm{B}}\left[\left(\hat{f}_{j_n}\cdots\hat{f}_{j_1}\right)^{\circ}\rho_{\mathrm{total}}(t)\right]$$

$$H_{\mathrm{T}}(t) = H(t) + \sum_{\alpha=\mathrm{L,R}} \hat{h}_{\alpha}^{\mathrm{eff}}(t) + \sum_{\sigma\alpha\kappa u} \hat{a}_u^{\bar{\sigma}} \hat{f}_{\alpha\kappa u}^{\sigma}$$

Dissipatons:

Statistically independent quasi-particles

$$\left\langle \hat{f}_{\alpha\kappa u}^{\sigma}(t)\hat{f}_{\alpha'\kappa' v}^{\sigma'}(0)\right\rangle_{\mathrm{B}} = -\delta_{\alpha\kappa,\alpha'\kappa'}^{\sigma,\bar{\sigma}'}\eta_{\alpha\kappa uv}^{\sigma}e^{-\gamma_{\alpha\kappa}^{\sigma}t}$$

$$\left\langle \hat{f}_{\alpha'\kappa' v}^{\sigma'}(0)\hat{f}_{\alpha\kappa u}^{\sigma}(t)\right\rangle_{\mathrm{B}} = -\delta_{\alpha\kappa,\alpha'\kappa'}^{\sigma,\bar{\sigma}'}\eta_{\alpha\kappa uv}^{\bar{\sigma}*}e^{-\gamma_{\alpha\kappa}^{\sigma}t}$$

2. Dissipaton Algebra

$$\rho_{\boldsymbol{j}}^{(n)}(t) \equiv \mathrm{tr}_{\mathrm{B}}\left[\left(\hat{f}_{j_n}\cdots\hat{f}_{j_1}\right)^{\circ}\rho_{\mathrm{total}}(t)\right]$$

$$H_{\mathrm{T}}(t) = H(t) + \sum_{\alpha=\mathrm{L,R}} \hat{h}_{\alpha}^{\mathrm{eff}}(t) + \sum_{\sigma\alpha\kappa u} \hat{a}_u^{\bar{\sigma}} \hat{f}_{\alpha\kappa u}^{\sigma}$$

$$\left\langle \hat{f}_{\alpha\kappa u}^{\sigma}(t)\hat{f}_{\alpha'\kappa' v}^{\sigma'}(0)\right\rangle_{\mathrm{B}} = -\delta_{\alpha\kappa,\alpha'\kappa'}^{\sigma,\bar{\sigma}'}\eta_{\alpha\kappa uv}^{\sigma} e^{-\gamma_{\alpha\kappa}^{\sigma}t}$$

$$\left\langle \hat{f}_{\alpha'\kappa' v}^{\sigma'}(0)\hat{f}_{\alpha\kappa u}^{\sigma}(t)\right\rangle_{\mathrm{B}} = -\delta_{\alpha\kappa,\alpha'\kappa'}^{\sigma,\bar{\sigma}'}\eta_{\alpha\kappa uv}^{\bar{\sigma}*} e^{-\gamma_{\alpha\kappa}^{\sigma}t}$$

2.1 Generalized diffusion equation

$$\mathrm{tr}_{\mathrm{B}}\left[\left(\frac{\partial \hat{f}_{\alpha\kappa u}^{\sigma}}{\partial t}\right)_{\mathrm{B}}\rho_{\mathrm{total}}(t)\right] = -\gamma_{\alpha\kappa}^{\sigma}\,\mathrm{tr}_{\mathrm{B}}\left[\hat{f}_{\alpha\kappa u}^{\sigma}\rho_{\mathrm{total}}(t)\right]$$

$$i\,\mathrm{tr}_{\mathrm{B}}\left\{\left(\hat{f}_{j_n}\cdots\hat{f}_{j_1}\right)^{\circ}\left[h_{\mathrm{B}}^{\mathrm{eff}}(t),\rho_{\mathrm{T}}\right]\right\} = \gamma_{\boldsymbol{j}}^{(n)}(t)\rho_{\boldsymbol{j}}^{(n)}$$

2. Dissipaton Algebra

$$\rho_{\boldsymbol{j}}^{(n)}(t) \equiv \mathrm{tr}_{\mathrm{B}}\left[\left(\hat{f}_{j_n}\cdots\hat{f}_{j_1}\right)^{\circ}\rho_{\mathrm{total}}(t)\right]$$

$$H_{\mathrm{T}}(t) = H(t) + \sum_{\alpha=\mathrm{L,R}} \hat{h}^{\mathrm{eff}}_{\alpha}(t) + \sum_{\sigma\alpha\kappa u} \hat{a}_u^{\bar{\sigma}}\hat{f}^{\sigma}_{\alpha\kappa u}$$

2.2 Generalized Wick's Theorem

$$\mathrm{tr}_{\mathrm{B}}\left[\left(\hat{f}_{j_n}\cdots\hat{f}_{j_1}\right)^{\circ}\hat{f}_j\rho_{\mathrm{T}}(t)\right] = \sum_{r=1}^{n}(-)^{r-1}\langle\hat{f}_{j_r}\hat{f}_j\rangle^{>}_{\mathrm{B}}\rho^{(n-1)}_{\boldsymbol{j}_r^-} + \rho^{(n+1)}_{\boldsymbol{j}j}$$

$$\mathrm{tr}_{\mathrm{B}}\left[\left(\hat{f}_{j_n}\cdots\hat{f}_{j_1}\right)^{\circ}\rho_{\mathrm{T}}(t)\hat{f}_j\right] = (-)^n\left[\sum_{r=1}^{n}(-)^{n-r}\langle\hat{f}_j\hat{f}_{j_r}\rangle^{<}_{\mathrm{B}}\rho^{(n-1)}_{\boldsymbol{j}_r^-} + \rho^{(n+1)}_{\boldsymbol{j}j}\right]$$

$$\langle\hat{f}^{\sigma}_{\alpha\kappa u}\hat{f}^{\sigma'}_{\alpha'\kappa' v}\rangle^{>}_{\mathrm{B}} = -\delta^{\sigma,\bar{\sigma}'}_{\alpha\kappa,\alpha'\kappa'}\eta^{\sigma}_{\alpha\kappa uv}, \qquad \langle\hat{f}^{\sigma'}_{\alpha'\kappa' v}\hat{f}^{\sigma}_{\alpha\kappa u}\rangle^{<}_{\mathrm{B}} = -\delta^{\sigma,\bar{\sigma}'}_{\alpha\kappa,\alpha'\kappa'}\eta^{\bar{\sigma}*}_{\alpha\kappa uv}$$

$$\mathrm{tr}_{\mathrm{B}}\left[\left(\hat{f}_{j_n}\cdots\hat{f}_{j_1}\right)^{\circ}\hat{a}_{\bar{j}}\hat{f}_j\rho_{\mathrm{T}}(t)\right] = (-)^n\hat{a}_{\bar{j}}\mathrm{tr}_{\mathrm{B}}\left[\left(\hat{f}_{j_n}\cdots\hat{f}_{j_1}\right)^{\circ}\hat{f}_j\rho_{\mathrm{T}}(t)\right]$$

3. DEOM Dynamics

$$\rho_{\boldsymbol{j}}^{(n)}(t) \equiv \mathrm{tr}_{\mathrm{B}}\left[\left(\hat f_{j_n}\cdots \hat f_{j_1}\right)^{\circ}\rho_{\mathrm{total}}(t)\right]$$

$$H_{\mathrm{T}}(t) = H(t) + \sum_{\alpha=\mathrm{L,R}} \hat h_{\alpha}^{\mathrm{eff}}(t) + \sum_{\sigma\alpha\kappa u} \hat a_u^{\bar\sigma}\hat f_{\alpha\kappa u}^{\sigma}$$

$$\dot\rho_{\mathrm{total}} = -i[H_{\mathrm{T}}(t), \rho_{\mathrm{total}}]$$

Generalized

Diffusion Equation & Wick's Theorem

$$\dot\rho_{\mathbf{j}}^{(n)} = -\left(i\mathcal{L}_{\mathrm{S}} + \sum_{r=1}^{n}\gamma_{j_r}\right)\rho_{\mathbf{j}}^{(n)} - i\sum_{j}\mathcal{A}_{\bar j}\rho_{\mathbf{j}j}^{(n+1)} - i\sum_{r=1}^{n}\mathcal{C}_{j_r}\rho_{\mathbf{j}_r^-}^{(n-1)}$$

4. DEOM Steady States

$$\rho^{(n)}_{\mathbf{j};\mathrm{st}}(\not{t}) \equiv \mathrm{tr}_{\mathrm{B}}\left[\left(\hat{f}_{j_n}\cdots\hat{f}_{j_1}\right)^{\circ}\rho^{\mathrm{st}}_{\mathrm{total}}(\not{t})\right]$$

$$H_{\mathrm{T}}(t) = H(t) + \sum_{\alpha=\mathrm{L,R}} \hat{h}^{\mathrm{eff}}_{\alpha}(t) + \sum_{\sigma\alpha\kappa u} \hat{a}^{\bar{\sigma}}_{u}\hat{f}^{\sigma}_{\alpha\kappa u}$$

$$\dot{\rho}^{(n)}_{\mathbf{j}} = -\left(i\mathcal{L}_{\mathrm{S}} + \sum_{r=1}^{n}\gamma_{j_r}\right)\rho^{(n)}_{\mathbf{j}} - i\sum_{j}\mathcal{A}_{\bar{j}}\rho^{(n+1)}_{\mathbf{j}j} - i\sum_{r=1}^{n}\mathcal{C}_{j_r}\rho^{(n-1)}_{\mathbf{j}_r^-}$$

Steady States

$$0 = -\left(i\mathcal{L}_{\mathrm{S}} + \sum_{r=1}^{n}\gamma_{j_r}\right)\rho^{(n)}_{\mathbf{j};\mathrm{st}} - i\sum_{j}\mathcal{A}_{\bar{j}}\rho^{(n+1)}_{\mathbf{j}j;\mathrm{st}} - i\sum_{r=1}^{n}\mathcal{C}_{j_r}\rho^{(n-1)}_{\mathbf{j}_r^-;\mathrm{st}}$$

5. Evaluation of Experimental Observables

$$H_{\mathrm{T}}(t) = H(t) + \sum_{\alpha=\mathrm{L,R}} \hat{h}^{\mathrm{eff}}_{\alpha}(t) + \sum_{\sigma\alpha\kappa u} \hat{a}^{\bar{\sigma}}_{u} \hat{f}^{\sigma}_{\alpha\kappa u}$$

Experimental observables such as transient transport current, nonequilibrium many-particle Green's functions, & so on can be *accurately* evaluated

$$\dot{\rho}^{(n)}_{\mathbf{j}} = -\Big(i\mathcal{L}_{\mathrm{S}} + \sum_{r=1}^{n} \gamma_{j_r}\Big)\rho^{(n)}_{\mathbf{j}} - i\sum_{j} \mathcal{A}_{\bar{j}}\rho^{(n+1)}_{\mathbf{j}j} - i\sum_{r=1}^{n} \mathcal{C}_{j_r}\rho^{(n-1)}_{\mathbf{j}_r^-}$$

Steady States

$$0 = -\Big(i\mathcal{L}_{\mathrm{S}} + \sum_{r=1}^{n} \gamma_{j_r}\Big)\rho^{(n)}_{\mathbf{j};\mathrm{st}} - i\sum_{j} \mathcal{A}_{\bar{j}}\rho^{(n+1)}_{\mathbf{j}j;\mathrm{st}} - i\sum_{r=1}^{n} \mathcal{C}_{j_r}\rho^{(n-1)}_{\mathbf{j}_r^-;\mathrm{st}}$$

H. D. Zhang, Qin Qiao, R. X. Xu, X. Zheng, and YJY, *J. Chem. Phys.* **147**, 044105 (2017)

Dissipaton algebra, especially the generalized Wick's theory, enables DEOM/HEOM evaluation of not only system properties, but also hybridizing bath dynamics

2. Dissipaton Algebra

$$\rho_{\boldsymbol{j}}^{(n)}(t) \equiv \mathrm{tr}_{\mathrm{B}}\left[\left(\hat{f}_{j_n}\cdots\hat{f}_{j_1}\right)^{\circ}\rho_{\mathrm{total}}(t)\right]$$

$$H_{\mathrm{T}}(t) = H(t) + \sum_{\alpha=\mathrm{L,R}} \hat{h}_{\alpha}^{\mathrm{eff}}(t) + \sum_{\sigma\alpha\kappa u} \hat{a}_{u}^{\bar{\sigma}} \hat{f}_{\alpha\kappa u}^{\sigma}$$

2.2 Generalized Wick's Theorem

$$\mathrm{tr}_{\mathrm{B}}\left[\left(\hat{f}_{j_n}\cdots\hat{f}_{j_1}\right)^{\circ}\hat{f}_{j}\rho_{\mathrm{T}}(t)\right] = \sum_{r=1}^{n}(-)^{r-1}\langle\hat{f}_{j_r}\hat{f}_{j}\rangle_{\mathrm{B}}^{>}\rho_{\boldsymbol{j}_r^-}^{(n-1)} + \rho_{\boldsymbol{j}j}^{(n+1)}$$

$$\mathrm{tr}_{\mathrm{B}}\left[\left(\hat{f}_{j_n}\cdots\hat{f}_{j_1}\right)^{\circ}\rho_{\mathrm{T}}(t)\hat{f}_{j}\right] = (-)^{n}\left[\sum_{r=1}^{n}(-)^{n-r}\langle\hat{f}_{j}\hat{f}_{j_r}\rangle_{\mathrm{B}}^{<}\rho_{\boldsymbol{j}_r^-}^{(n-1)} + \rho_{\boldsymbol{j}j}^{(n+1)}\right]$$

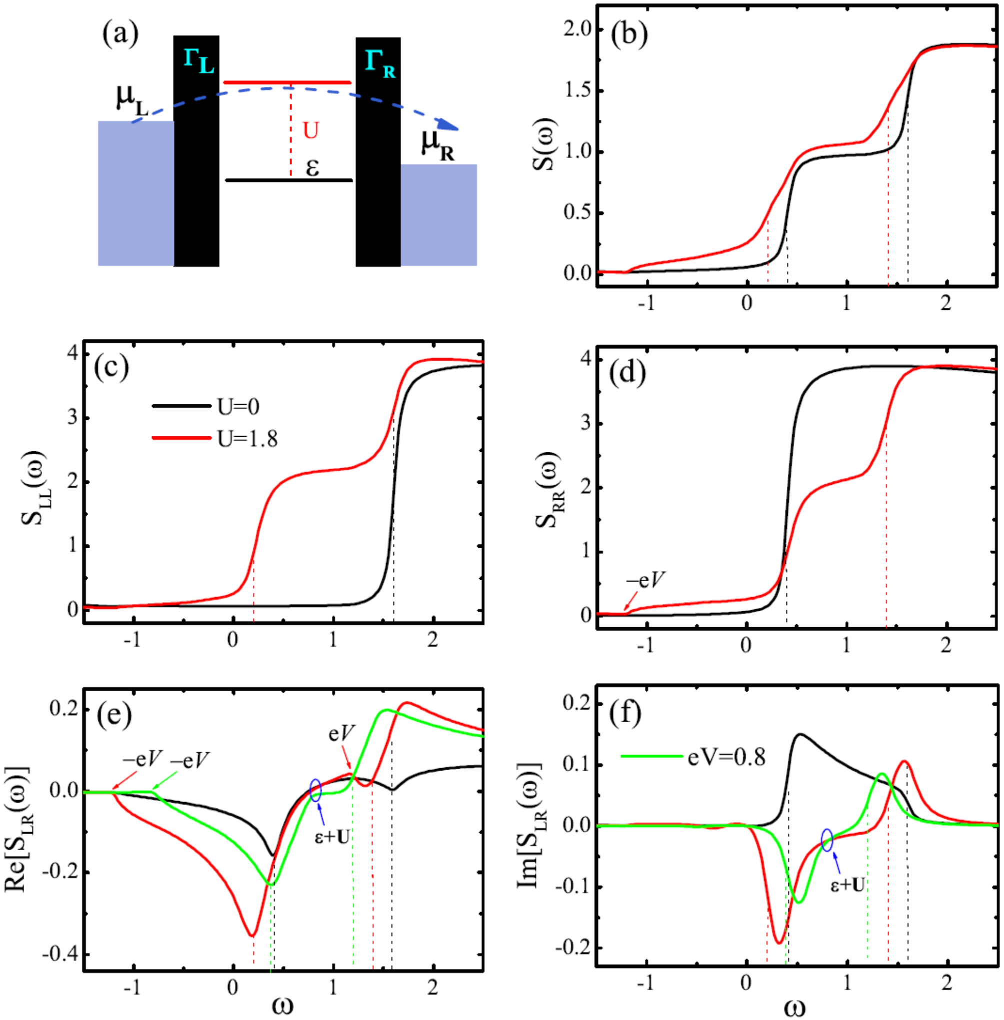
$$\langle\hat{f}_{\alpha\kappa u}^{\sigma}\hat{f}_{\alpha'\kappa' v}^{\sigma'}\rangle_{\mathrm{B}}^{>} = -\delta_{\alpha\kappa,\alpha'\kappa'}^{\sigma,\bar{\sigma}'}\eta_{\alpha\kappa uv}^{\sigma}, \qquad \langle\hat{f}_{\alpha'\kappa' v}^{\sigma'}\hat{f}_{\alpha\kappa u}^{\sigma}\rangle_{\mathrm{B}}^{<} = -\delta_{\alpha\kappa,\alpha'\kappa'}^{\sigma,\bar{\sigma}'}\eta_{\alpha\kappa uv}^{\bar{\sigma}*}$$

$$\mathrm{tr}_{\mathrm{B}}\left[\left(\hat{f}_{j_n}\cdots\hat{f}_{j_1}\right)^{\circ}\hat{a}_{\bar{j}}\hat{f}_{j}\rho_{\mathrm{T}}(t)\right] = (-)^{n}\hat{a}_{\bar{j}}\mathrm{tr}_{\mathrm{B}}\left[\left(\hat{f}_{j_n}\cdots\hat{f}_{j_1}\right)^{\circ}\hat{f}_{j}\rho_{\mathrm{T}}(t)\right]$$

A. Current Noise Spectrum

J.S. Jin, S. K. Wang, Xiao Zheng, YJY, *J. Chem. Phys.* **142**, 234108 (2015)

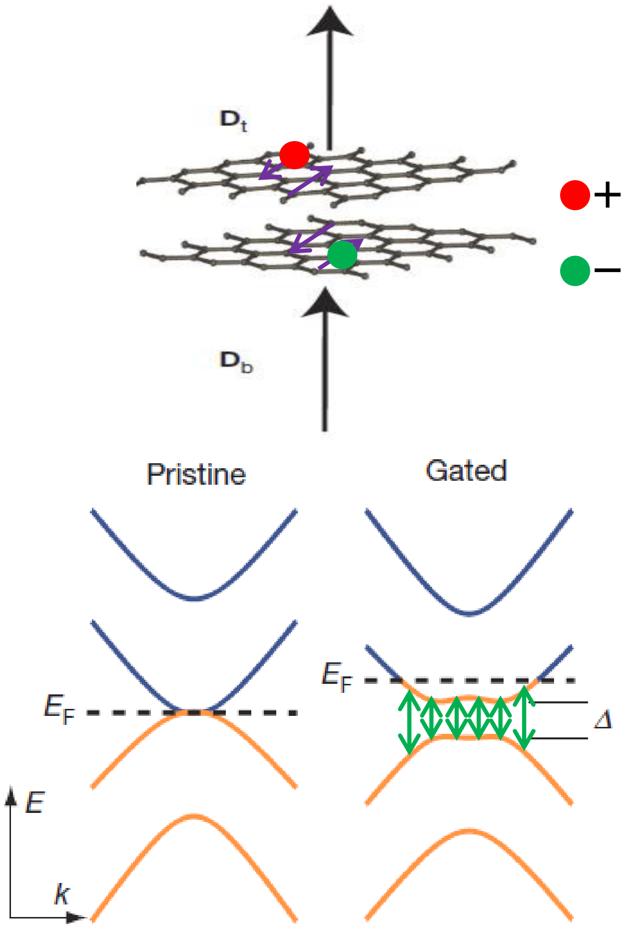
Cotunneling:
No level within bias window

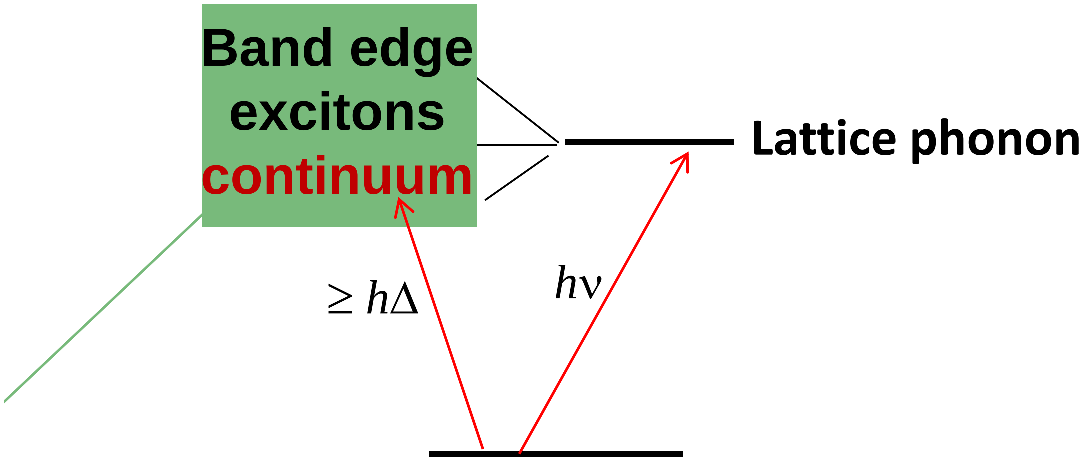


Anti-Stokes processes

Destructive interference occurs when U = 0

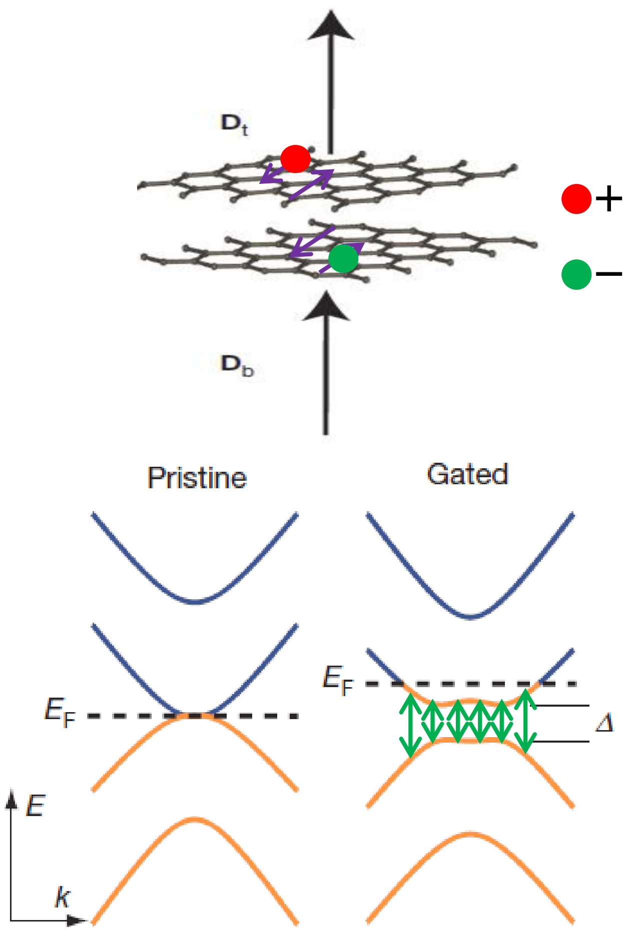
B. Fano Interference



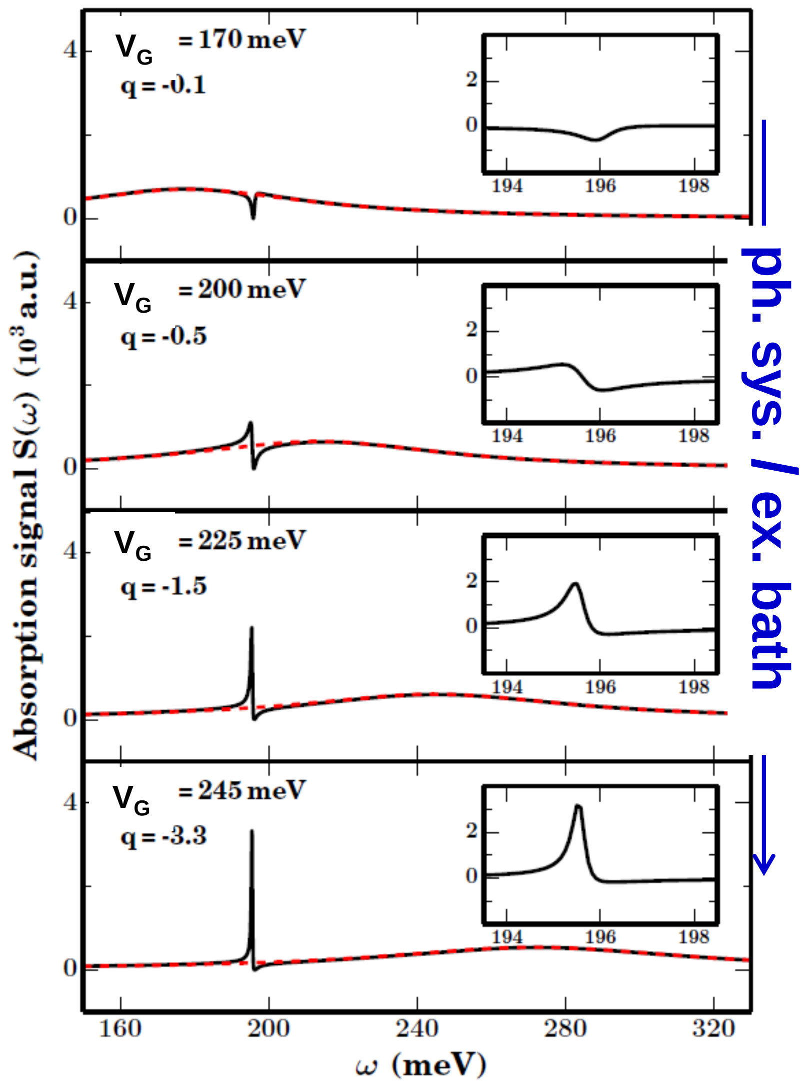


YB Zhang, et al, Nature (2009)

B. Fano Interference



YB Zhang, et al, Nature (2009)



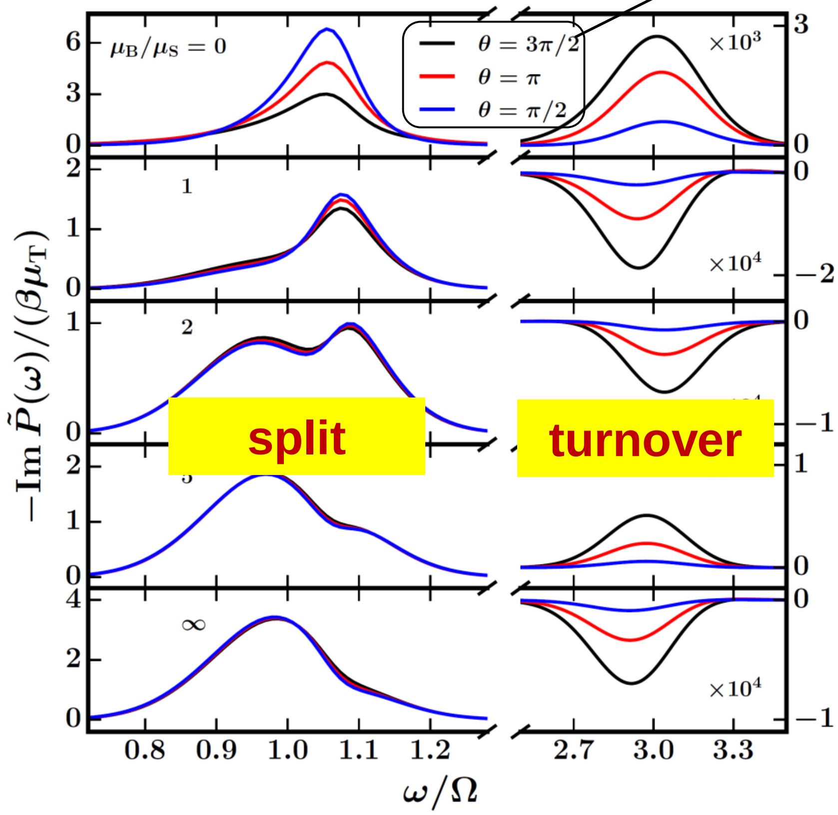
Fano turnover

B. Fano Interference

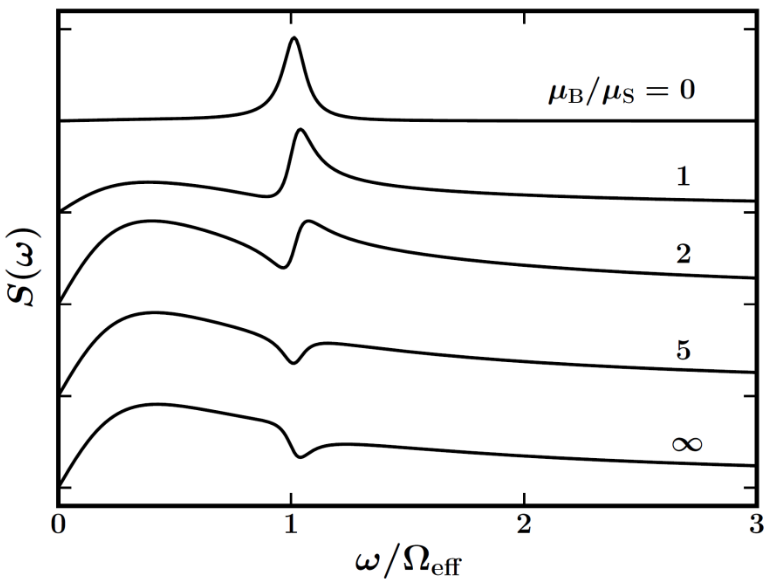
HD Zhang, RX Xu, X Zheng, YJ Yan, *J. Chem. Phys.* **142**, 024112 (2015)

Pulse intensity

Strong field

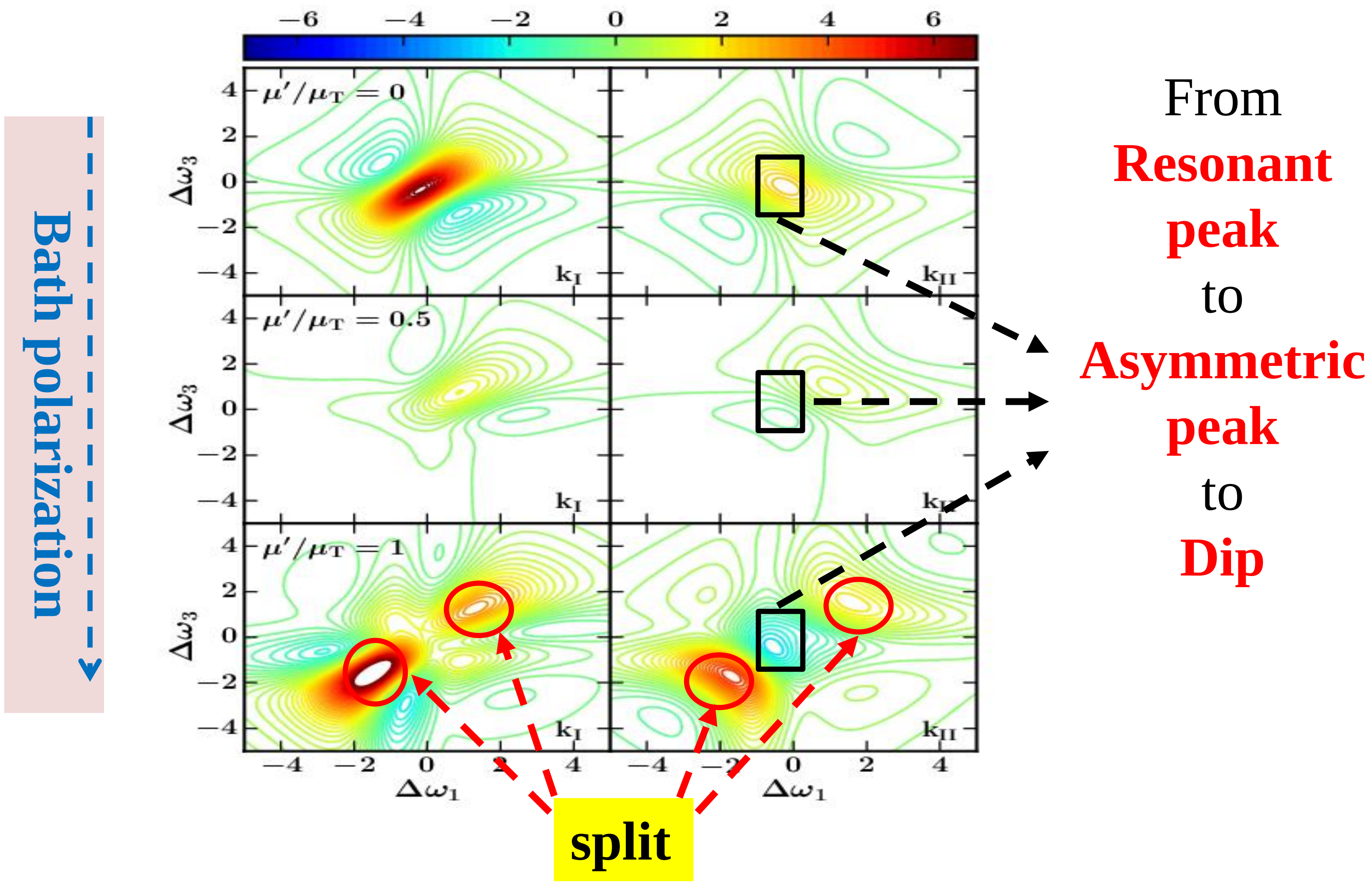


Weak field



B. Fano Interference

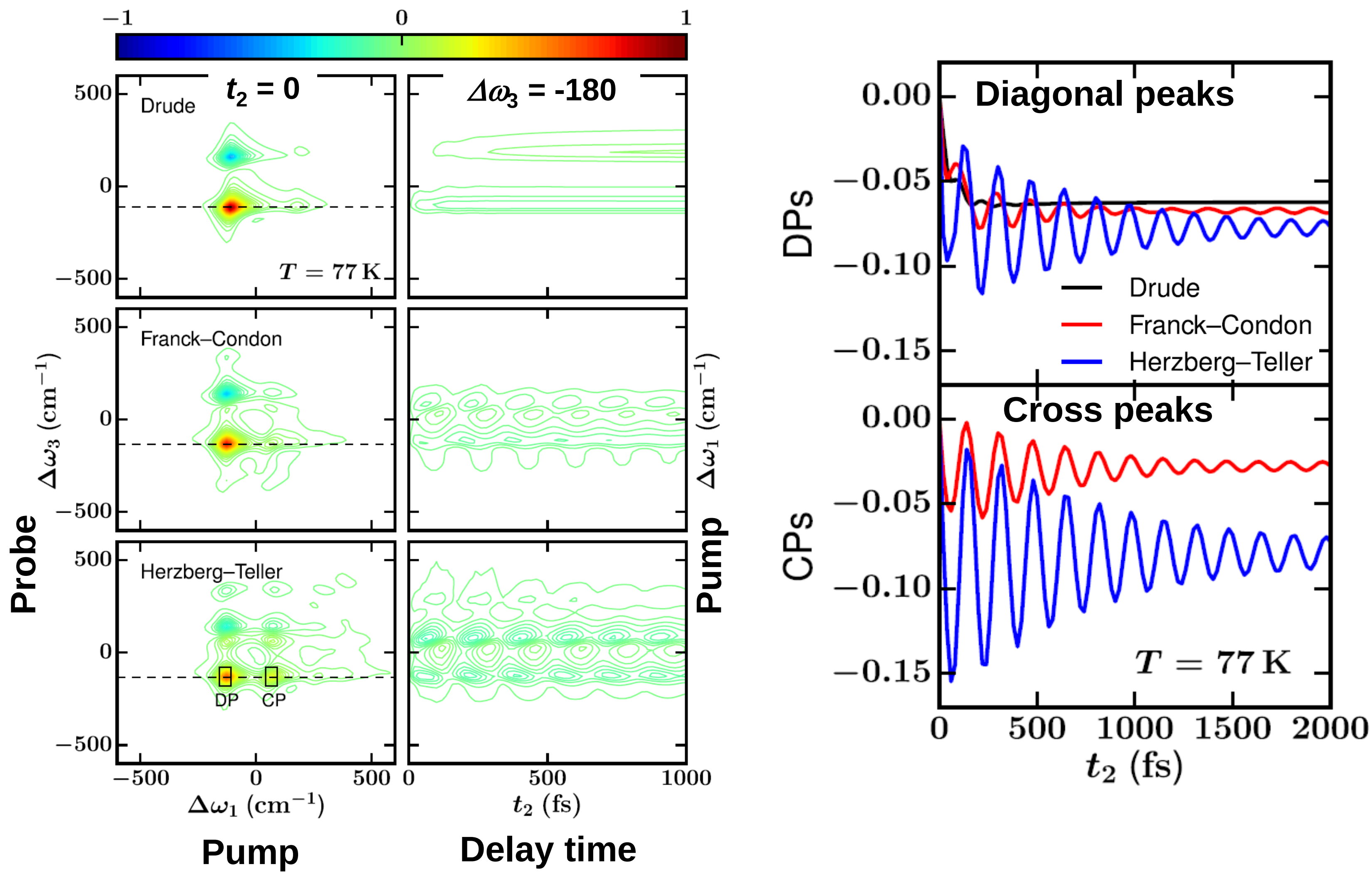
HD Zhang, Q. Qiao, RX Xu & YJY, *Chem. Phys.* **481**, 237 (2016)



C. Herzberg-Teller Vibronic Coupling

HD Zhang, Q. Qiao, RX Xu & YJY, *J. Chem. Phys.* **145**, 204109 (2016)

$$\hat{\mu}_{\text{total}} = (\mu_0 + \mu_1 \mathbf{x})\hat{\mu}_{\text{ele}}$$

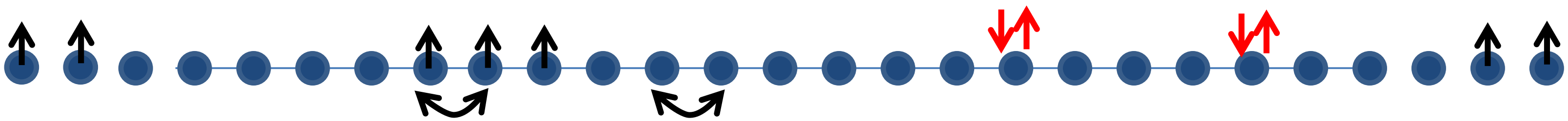


Prospects and Summary

- HEOM method offers an accurate, efficient, and universal tool for characterization of open systems
  - ✓ Equilibrium and nonequilibrium properties
  - ✓ Static and dynamical properties
  - ✓ Real-time electronic dynamics
  - ✓ Strong electron correlation effects
  - ✓ Complex non-Markovian memory effects
  - more to discover …
- HEOM-QUICK package for first-principles simulation on realistic systems and processes

Strongly Correlated Bulk Systems

Hubbard Model (1963)



tight-binding (t) + **Coulomb** (U)

Dynamical Mean-Field Theory **(1992)**

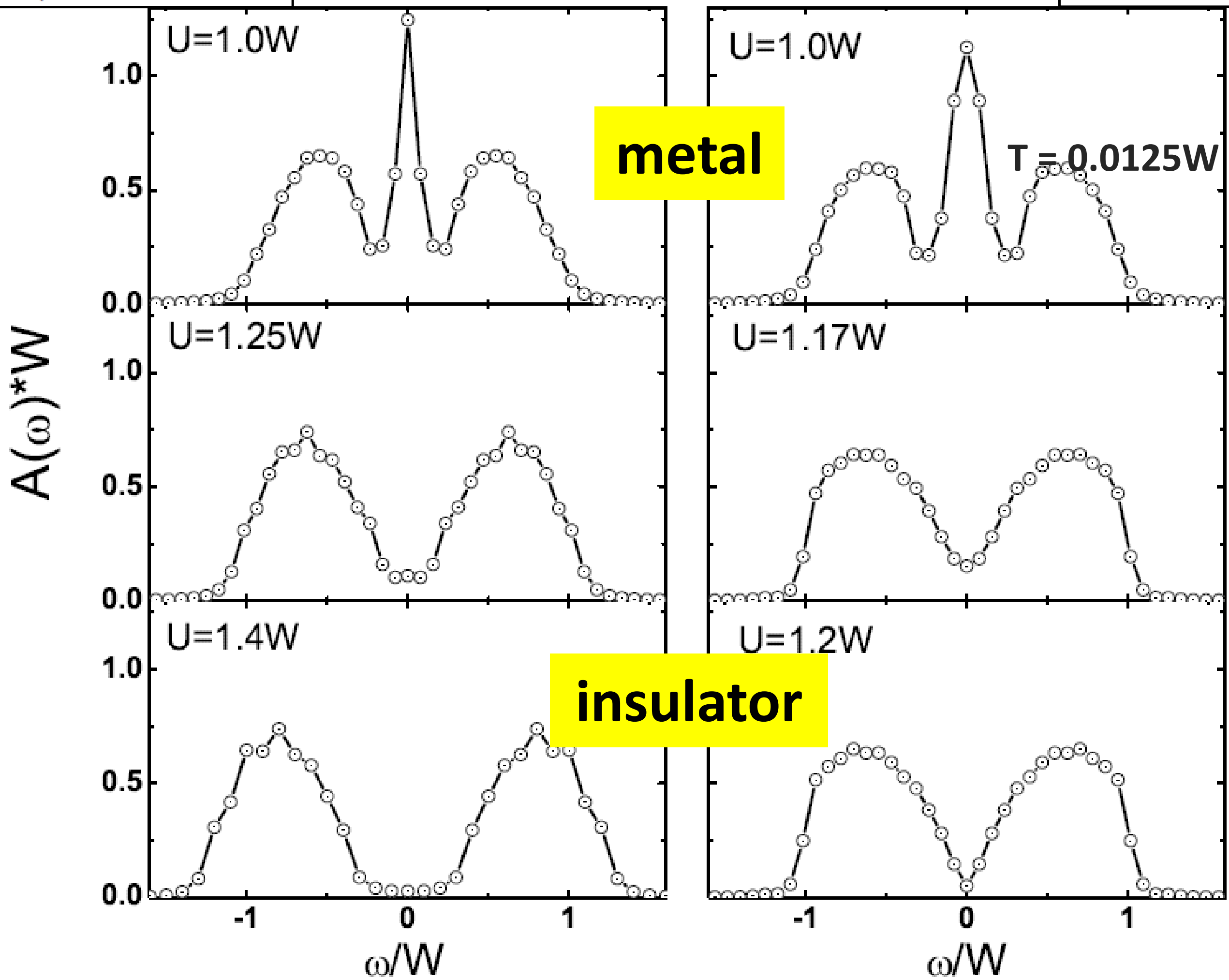
Impurity Anderson Model (1961)

HEOM: Impurity solver for DMFT: D Hou, RL Wang, X Zheng, NH Tong, JH Wei & YJY, *Phys. Rev.* B **90**, 045141 (2014)

Mott Transition: HEOM+DMFT

$$A_0^{\mathrm{h}}(\epsilon) = \frac{1}{\tilde{t}\sqrt{2\pi}} \exp(-\frac{\epsilon^2}{2\tilde{t}^2})$$ hypercubic

Bethe $$A_0^{\mathrm{B}}(\epsilon) = \frac{1}{2\pi\tilde{t}^2}\sqrt{4\tilde{t}^2 - \epsilon^2}$$



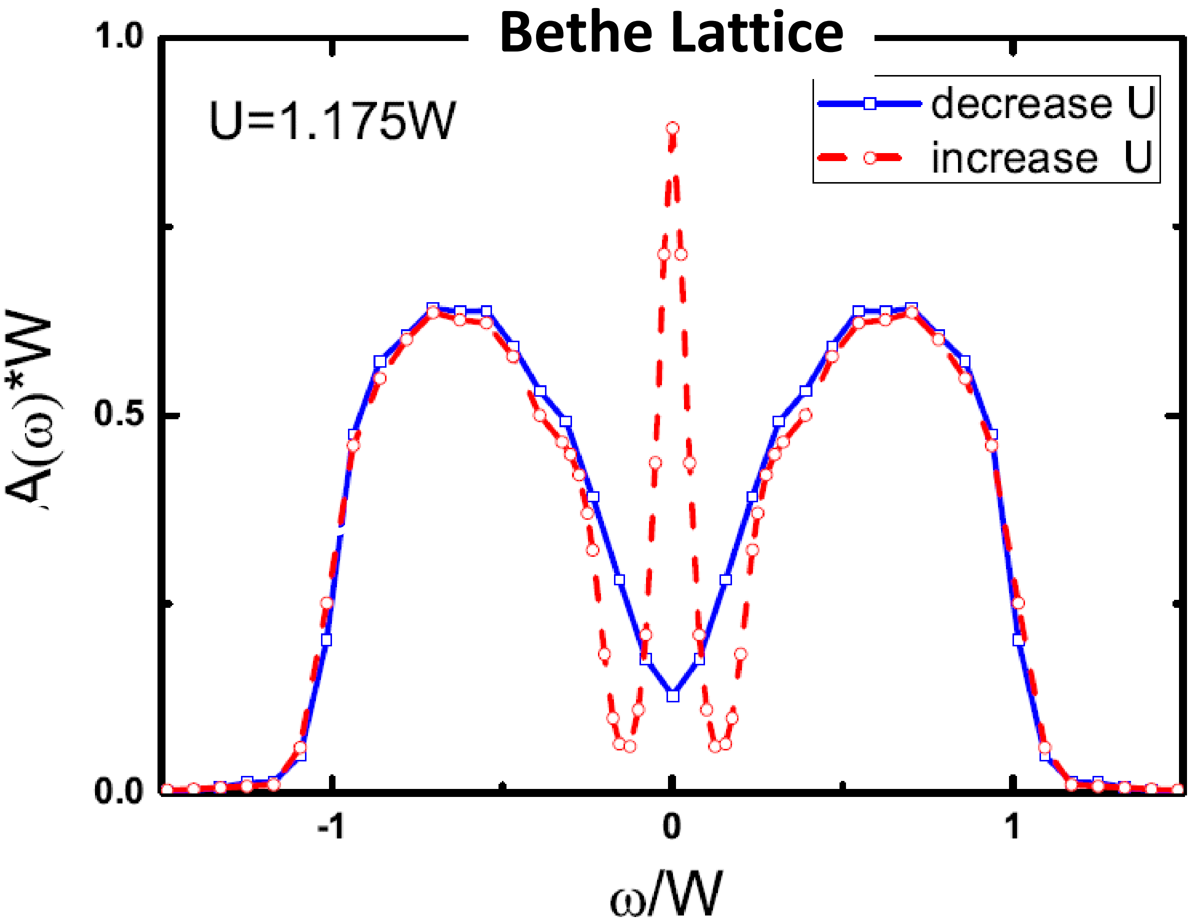
T_C = 0.02W

Bank width:
W=4*t*
(half-fill)

Phys. Rev. B **90**, 045141 (2014)

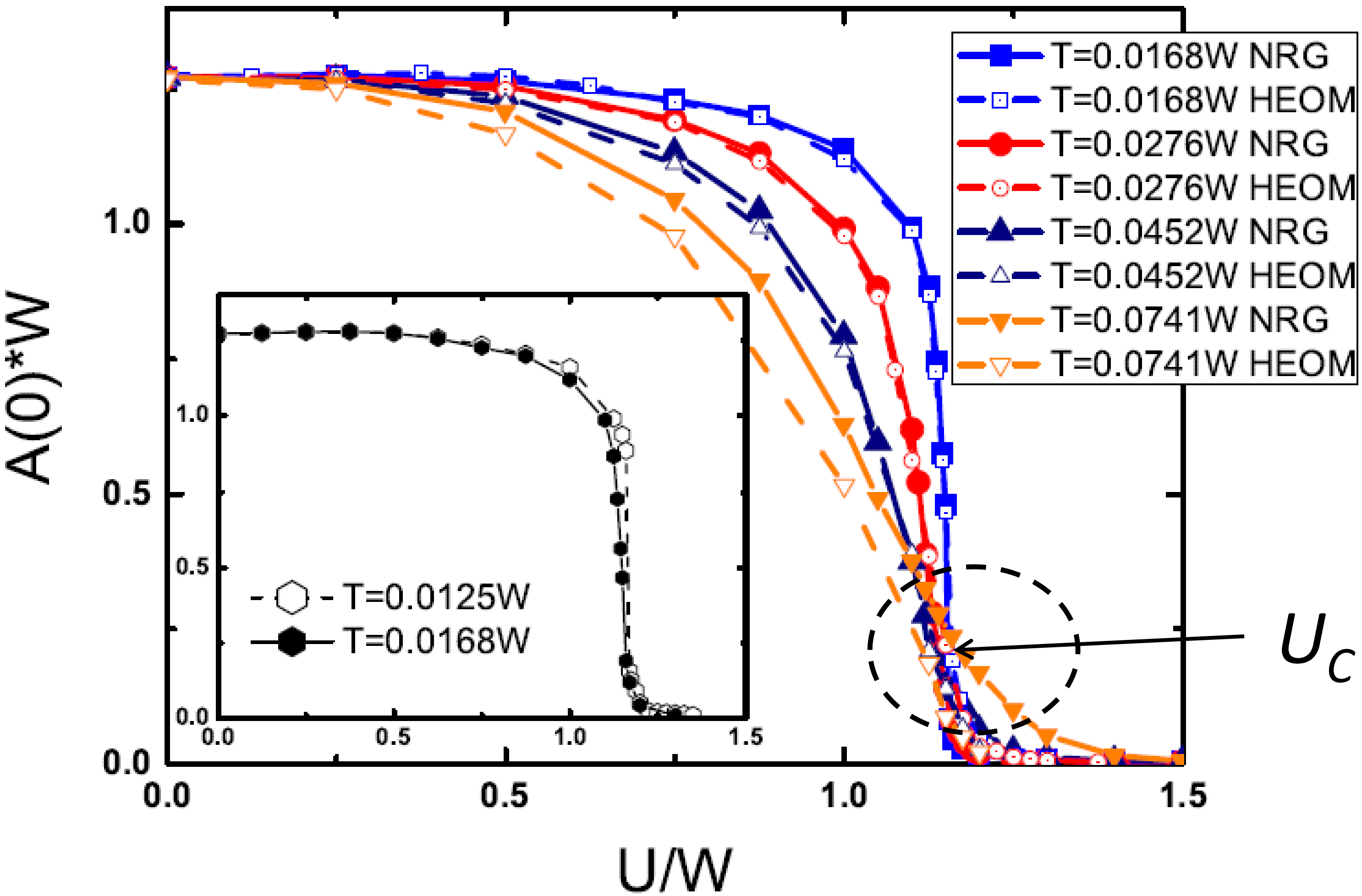
Mott Transition: HEOM+DMFT

Bi-stability at certain $T<T_c$



Phys. Rev. B **90**, 045141 (2014)

Mott Transition: HEOM+DMFT (*vs*. NRG)



Phys. Rev. B **90**, 045141 (2014)

Prospects and Summary

- **Dissipaton algebra + HEOM = DEOM**
  - ✓ **Correlated system-bath entanglement properties: Both steady-state and transient ones**
  - ✓ **Noise spectrum and full counting statistics analysis**
  - ✓ **Quantum thermodynamics of impurity complex**

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Dr. Zhenhua Li (Lanzhou U)

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Mr. Lei Cui -- FSD
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N S F C

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Ministry of Science and Technology of the People´s Republic of China

中国科学技术大学 1958 University of Science and Technology of China

Thank You!

創寰宇學府
育天下英才
嚴濟慈題
一九八八年五月