Memory Kernel Coupling Theory to Spin-Phonon Relaxation in Molecular Qubits

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VISTA, Sep. 3, 2025

Outline

- Background
  - Molecular qubits
  - Phenomenological results and microscopic model
- Nonlinear couplings
  - Exact dynamics: memory kernel coupling theory
  - Linear and quadratic couplings
- Spin-polaron model
  - Experimental results for ZnHOTP
  - New mechanism for spin-lattice relaxation

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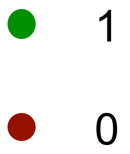
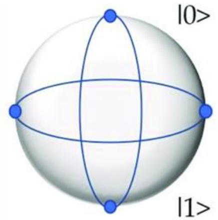
Materials Challenges for QT 2.0

Quantum bit (qubit), the fundamental unit of QT 2.0*



Classical bit

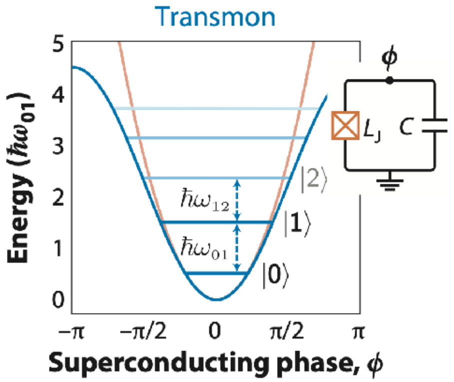


Qubit

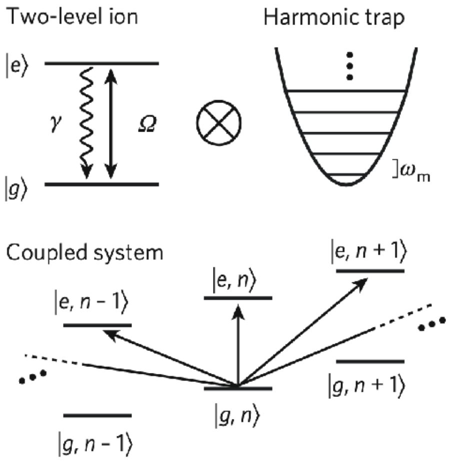
$$|\boldsymbol{\Psi}\rangle = \alpha_1\,|\mathbf{1}\rangle + \alpha_2\,|\mathbf{2}\rangle$$

$$|\boldsymbol{\Psi}_{\text{entangled}}\rangle = \frac{1}{\sqrt{2}}\left(|\text{red}\rangle \otimes |\text{blue}\rangle + |\text{blue}\rangle \otimes |\text{red}\rangle\right)$$

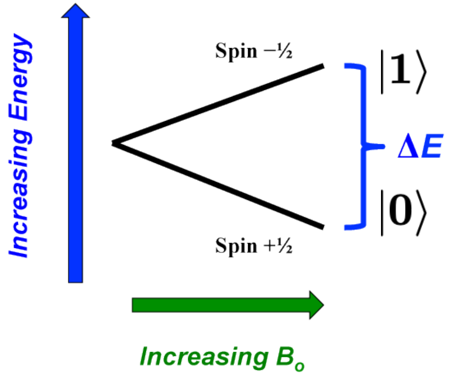
Hypothetically, any (quasi) **two-level system** can be a qubit. *Why challenging?*



Josephson junction



Trapped ion



e/n spin

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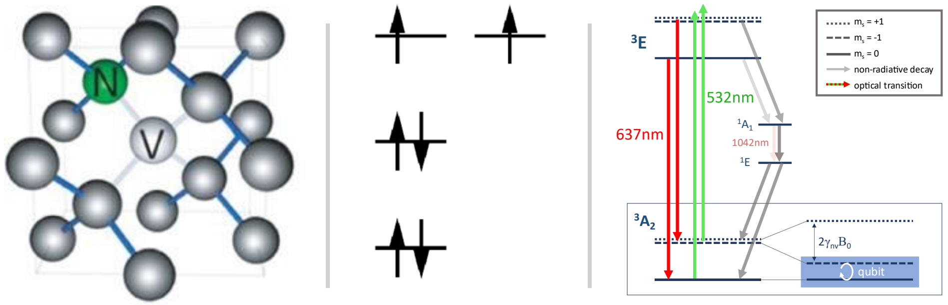
* it is also possible, and practical, to use multi-state quantum bits, commonly known as qudits

Electron spin qubits

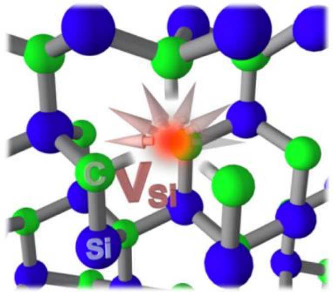
- **Defect spin qubit**

Advantages: room-temperature coherence

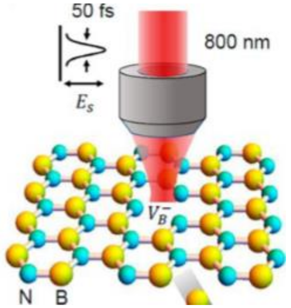
Disadvantages: lack designability and tunability



Nature **455,** 648–651 (2008)



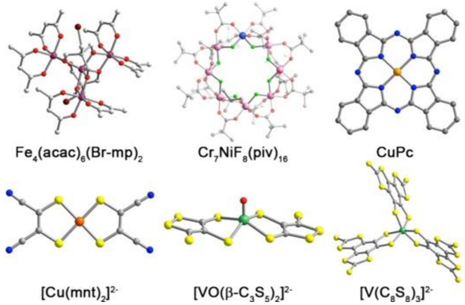
ACS Photonics **7,** 2147–2152 (2020)



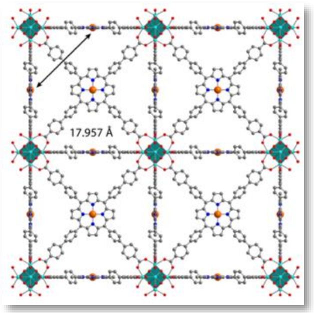
Phys. Rev. B **95**, 161201(2017)

- **Molecular qubit**

Spin center : Metal ions

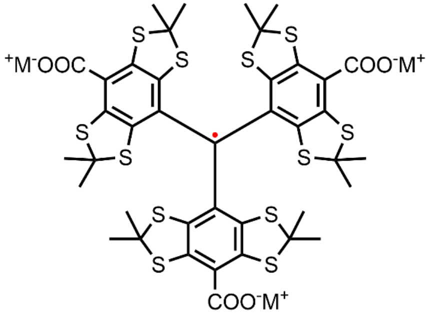


Chem. Mater. **29,** 1885-1897 (2017)

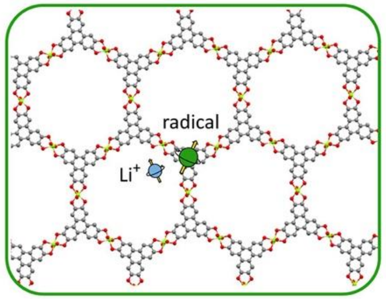


J. Am. Chem. Soc. **144**, 19008-19016 (2022)

Spin center : organic radical



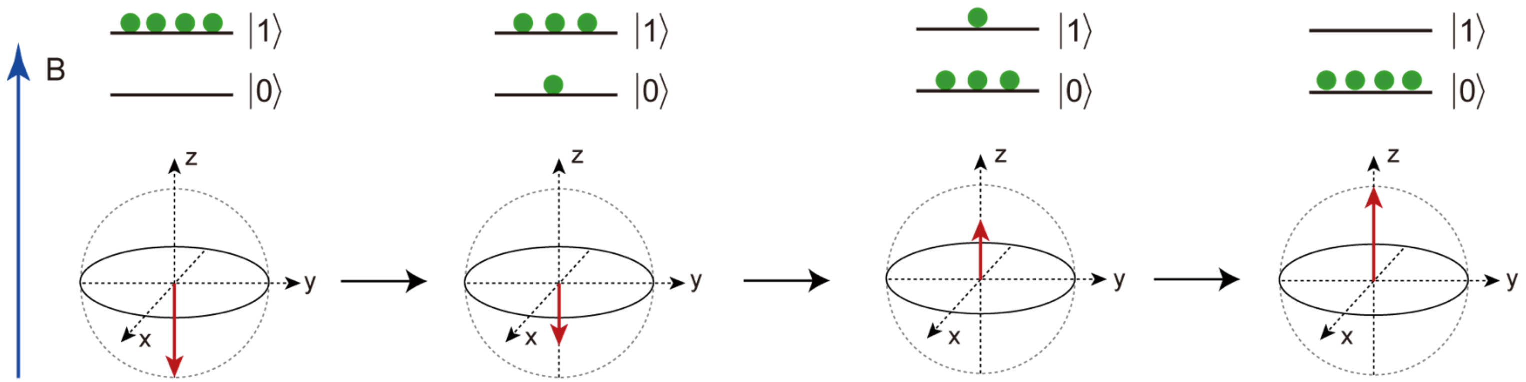
Trityl-CH_3



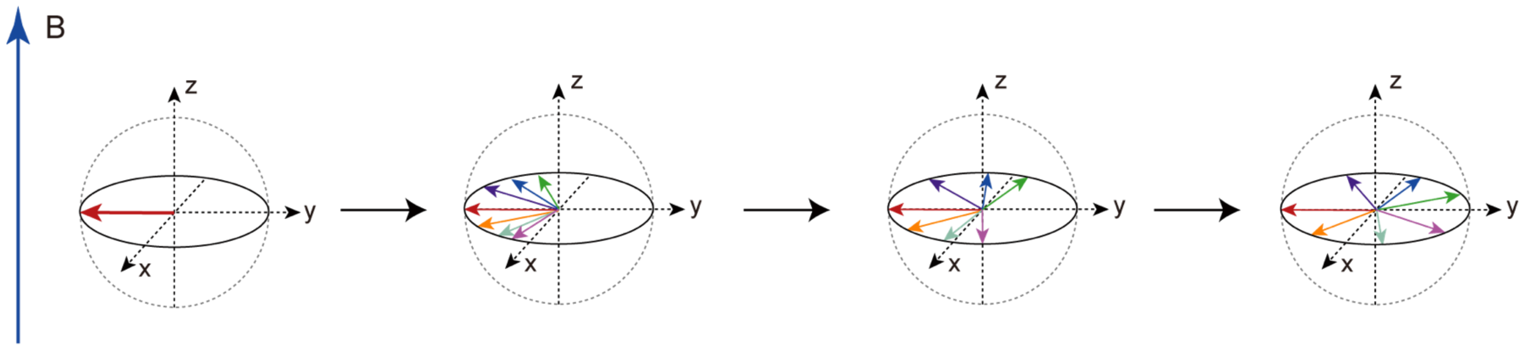
J. Am. Chem. Soc. **144**, 19008-19016 (2022)

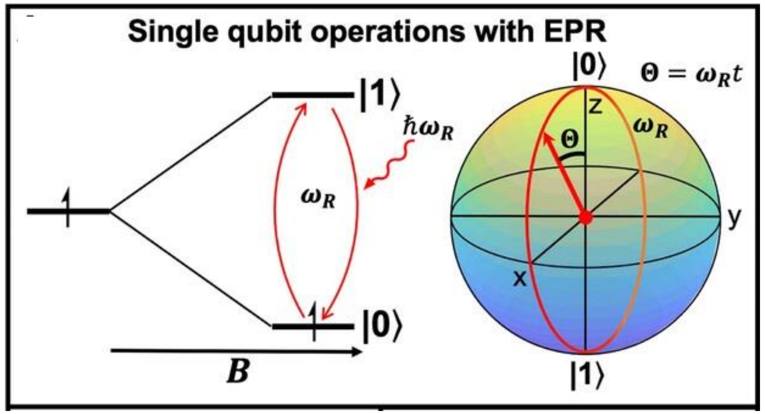
Relaxation time

Spin–lattice relaxation time (T_1)



Decoherence time (T_2)





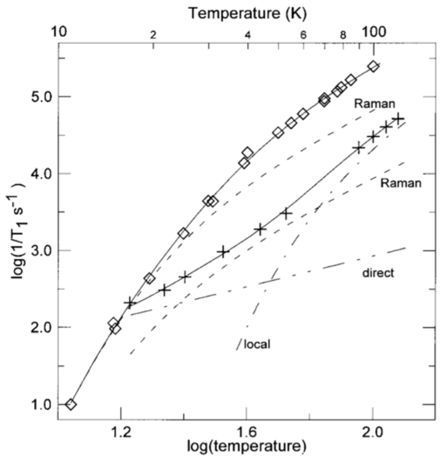
Chem. Eur. J. **27,** 9482-9494 (2021)

Spin-phonon relaxation

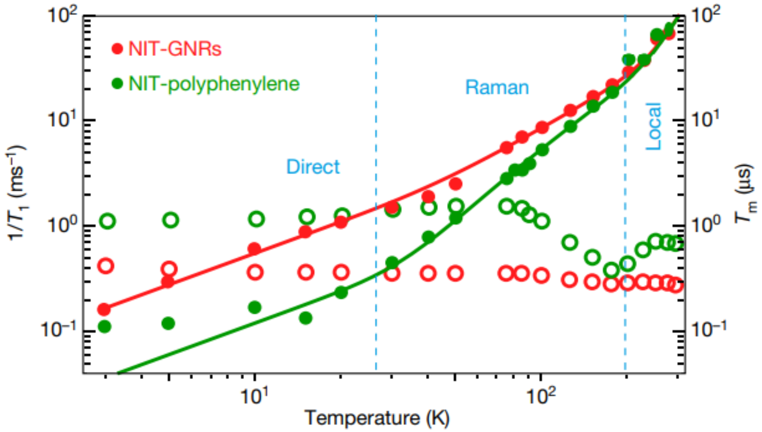
Phonon modes

Spin relaxation mechanism

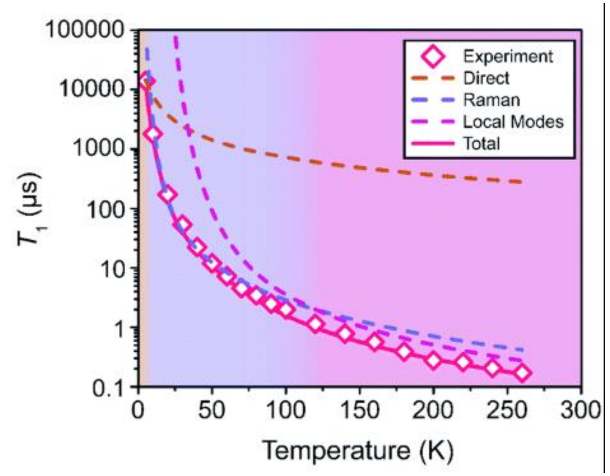
$$\frac{1}{T_1} = A_{dir}T + A_{Ram}\left(\frac{T}{\theta_D}\right)J_8\left(\frac{\theta_D}{T}\right) + A_{loc}\left[\frac{e^{\Delta_{loc}/T}}{(e^{-1})^2}\right] + A_{Orb}\left[\frac{\Delta_{Orb}^3}{e^{\frac{\Delta_{Orb}}{T}}-1}\right] + A_{therm}\left[\frac{2\tau_c}{1+\omega^2\tau_c^2}\right]$$



J. Magn. Reson. **139,** 165–174 (1999)



Nature **557**, 691-695 (2018)

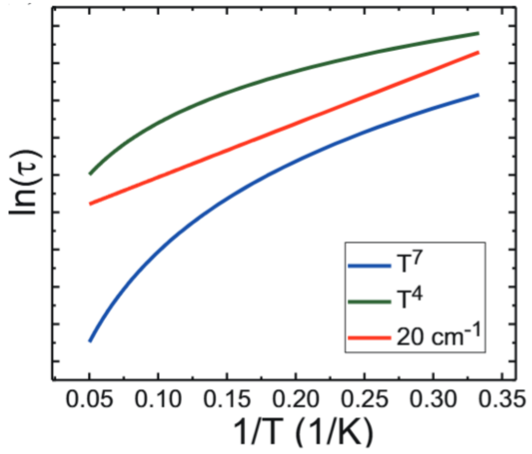


Chem. Sci. **13**, 7034-7045 (2022)

Problems

- The applicable conditions of the formula
- Too many parameters cause overfitting
- Often it's simulation rather than fit

  Simulation will fix some parameters but fit not
- Phonons include acoustic phonons and optical phonons



$$\frac{1}{T_1} = A_{dir}T + A_{Ramn}T^m$$

Phys. Rev. B **103**, 014401 (2021)

Spin-phonon relaxation

Spin relaxation mechanism

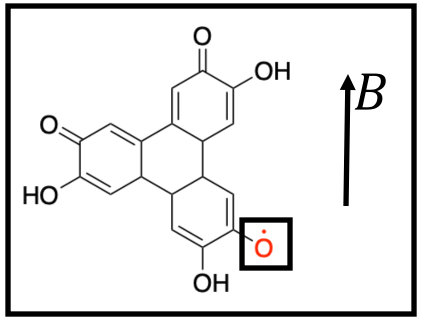
The equation of typical spin relaxation mechanisms

Mechanism	Equation
Direct	$A_{Dir}B^4\frac{e^{\hbar\omega/k_BT}}{e^{\hbar\omega/k_BT}-1}$ Field
Raman	Acoustic $A_{Ram}\left(\frac{T}{\Theta_D}\right)^9\int_0^{\frac{\Theta_D}{T}}x^8\frac{e^x}{(e^x-1)^2}dx$ (sometimes $A_{Ram}T^m$ with $m=2-9$) Optical
Orbach	$A_{Orb}\frac{\Delta^3}{e^{\Delta/k_BT}-1}$ Electronic state
Local mode	$A_{loc}\frac{e^{\hbar\omega_{phonon}/k_BT}}{\left(e^{\hbar\omega_{phonon}/k_BT}-1\right)^2}$ Optical
Thermally activated	$A_{therm}\frac{2\tau_c^0e^{E_a/k_BT}}{1+\omega^2{\tau_c^0}^2e^{2E_a/k_BT}}$ Activation energy
Tumbling-dependent	$\frac{\sum_{i=x,y,z}(g_i-g_e)^2}{9\tau_R}+\frac{2}{5}\left(\frac{\mu_B\omega}{g\beta}\right)^2\left\{\frac{(\Delta g)^2}{3}+(\delta g)^2\right\}J(\omega)+\frac{2}{9}I(I+1)\sum_i(A_i-a_{iso})^2J(\omega)+C_{solvent}\frac{\tau_{solvent}}{1+(\omega\tau_{solvent})^2}$ Anisotropy
Cross relaxation	constant (temperature-independent) Concentration

T: temperature; B: magnetic field strength; ω: Larmor frequency; Θ_D: Debye temperature; Δ: energy of low -lying excited state; ω_{phonon}: energy of local phonon mode. τ_c^0: pre-exponential factor; E_a: activation energy; g_i: principle g value along the i axis; g_e: g value of free electron; τ_R: tumbling correlation time; μ_B: Bohr magneton; $\Delta g = g_{zz} - 0.5(g_{xx}+g_{yy})$; $\delta g = 0.5(g_{xx}-g_{yy})$; $J(\omega)=\frac{\tau_R}{1+(\omega\tau_R)^2}$; I: nuclear spin; A_i: principle component of the nuclear hyperfine constant along the i axis in angular frequency units; a_{iso}: the isotropic nuclear hyperfine constant; $\tau_{solvent}$: correlation time for motion of the solvent relative to the radical; $C_{solvent}$: a function of the dipolar interaction with solvent nuclei. A_{Dir}, A_{Ram}, A_{Orb}, A_{loc}, A_{therm} are pre-factors.

The spin-lattice interaction: collective phonon

Hamiltonian for an unperturbed spin in magnetic field



$$H_s = g\mu_B B\sigma_z$$

Diagonal g-factor g_{zz}

Each ion j has equilibrium $r_j^{(0)}$ and a small displacement Q_j

$$H_{s\text{-}ph} = \mu_B B g_{xz}(r)\sigma_x \quad r_j = r_j^{(0)} + Q_j \quad g_{xz}(r) = g_{xz}^0 + \sum_j Q_j \frac{\partial g_{xz}(r)}{\partial Q_j} + \sum_{jl} Q_j Q_l \frac{\partial^2 g_{xz}(r)}{\partial Q_j \partial Q_l} + \ldots$$

Suppose collective vibration at each ionic site are

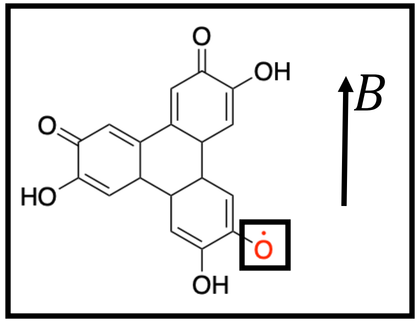
$$Q_j = \hat{x}_B = \sum_k \frac{c_k}{\sqrt{2}}(\hat{b}_k^\dagger + \hat{b}_k)$$

$$H_{ph} = \sum_k \hbar\omega_k(\hat{b}_k^\dagger \hat{b}_k + \frac{1}{2}) = \sum_k \frac{1}{2}\hbar\omega(\hat{q}_k^2 + \hat{p}_k^2)$$

Collective phonon mode: the spectral density function

$$H_{\mathrm{ph}} = \sum_k \frac{1}{2}\hbar\omega(\hat{q}_k^2 + \hat{p}_k^2)$$

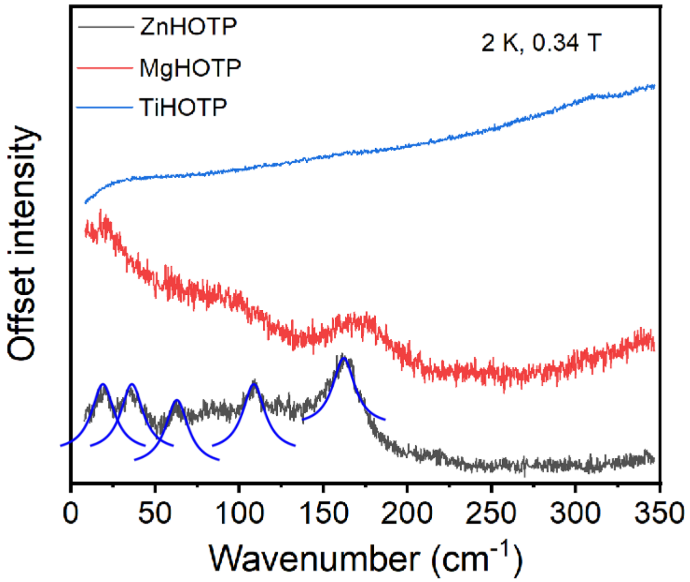
The lattice phonons



$$H_{\mathrm{s}} = g\mu_{\mathrm{B}}B\sigma_z$$

Diagonal g-factor g_{zz}

The collective vibration is characterized by the spectral density



$$\hat{x}_{\mathrm{B}} = \sum_k \frac{c_k}{\sqrt{2}}(\hat{b}_k^\dagger + \hat{b}_k)$$

k-th mode's weight

$$J(\omega \geq 0) = \frac{\pi}{2}\sum_k c_k^2\delta(\omega - \omega_k) = -J(-\omega).$$

The spectral density

Data adapted from Prof. Lei Sun's unpublished work

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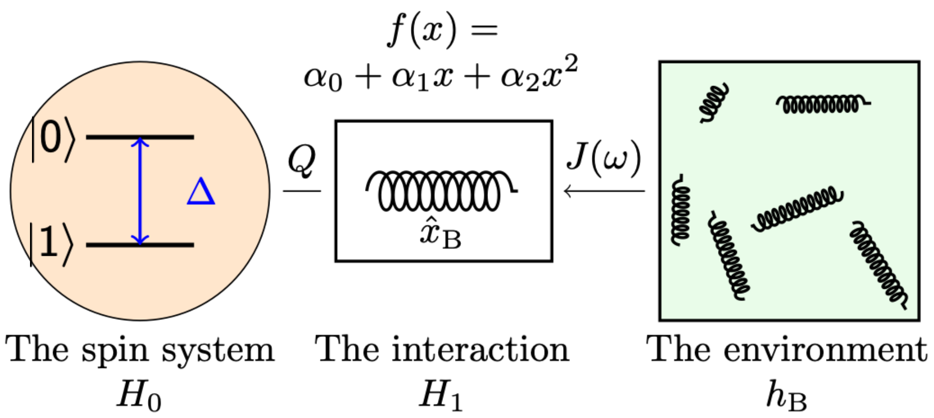
Memory kernel coupling theory

Open quantum systems



Definition of TCFs

$$C_{\mu\mu}(t) \equiv \langle \hat{\mu}(t)\hat{\mu}(0)\rangle = \mathrm{Tr}[\hat{\mu}(0)e^{-i\mathcal{L}t}(\hat{\mu}(0)\rho_{eq})]$$

Define: $\mathcal{P}\hat{O}(t) = \frac{\langle \hat{O}(t), \hat{\mu}(0)\rangle}{\langle \hat{\mu}(0), \hat{\mu}(0)\rangle}\hat{\mu}(0);\ \mathcal{Q} = I - \mathcal{P}$

Mori projection

$$\dot{C}_{\mu\mu}(t) = \Omega C_{\mu\mu}(t) + \int_0^t \mathrm{d}\tau K(\tau) C_{\mu\mu}(t-\tau)$$

(random force)

$$\hat{f}(t) = e^{it(1-\mathcal{P})\mathcal{L}}(1-\mathcal{P})i\mathcal{L}\hat{\mu}(0)$$

(memory kernel)

$$K(t) = \langle i\mathcal{L}\hat{f}(t), \hat{\mu}(0)\rangle\langle \hat{\mu}(0), \hat{\mu}(0)\rangle^{-1}$$

(moment)

$$\Omega = \langle i\mathcal{L}\hat{\mu}(0), \hat{\mu}(0)\rangle\langle \hat{\mu}(0), \hat{\mu}(0)\rangle^{-1}$$

Memory kernel coupling theory

$$\dot{C}_{\mu\mu}(t) = \Omega C_{\mu\mu}(t) + \int_0^t d\tau K(\tau) C_{\mu\mu}(t-\tau)$$

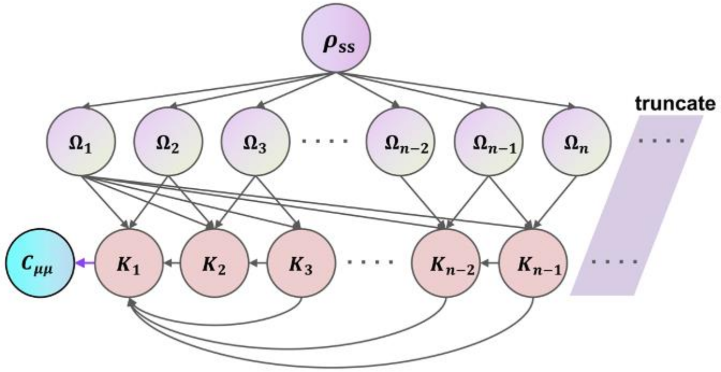
Define: $\Omega_n = \langle (i\mathcal{L})^n \hat{\mu}, \hat{\mu} \rangle \langle \hat{\mu}, \hat{\mu} \rangle^{-1}$

$$K_n(t) = \left\langle (i\mathcal{L})^n \hat{\mu} \hat{f}(t), \hat{\mu} \right\rangle \langle \hat{\mu}, \hat{\mu} \rangle^{-1}$$

$$K_n(0) = \Omega_{n+1} - \Omega_n \Omega_1 \quad \& \quad \dot{K}_n(t) = K_{n+1}(t) - \Omega_n K_1(t)$$

$$\mathcal{L}_K = \begin{pmatrix} -\Omega_1 & 1 & 0 & \cdots & 0 \\ -\Omega_2 & 0 & 1 & \cdots & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ -\Omega_{n-1} & 0 & 0 & \cdots & 1 \\ -\Omega_n & 0 & 0 & \cdots & 0 \end{pmatrix} \quad \& \quad K_n(0) = \begin{pmatrix} K_1(0) \\ K_2(0) \\ \vdots \\ K_n(0) \\ K_{n+1}(0) \end{pmatrix} = \begin{pmatrix} \Omega_2 - \Omega_1\Omega_1 \\ \Omega_3 - \Omega_2\Omega_1 \\ \vdots \\ \Omega_{n+1} - \Omega_n\Omega_1 \\ 0 \end{pmatrix}$$

$$K_n(t) = e^{\mathcal{L}_K t} K_n(0)$$



W. Liu, Y. Su, Y. Wang, W. Dou, Phys. Rev. Lett. (accepted) arXiv:2407.01923

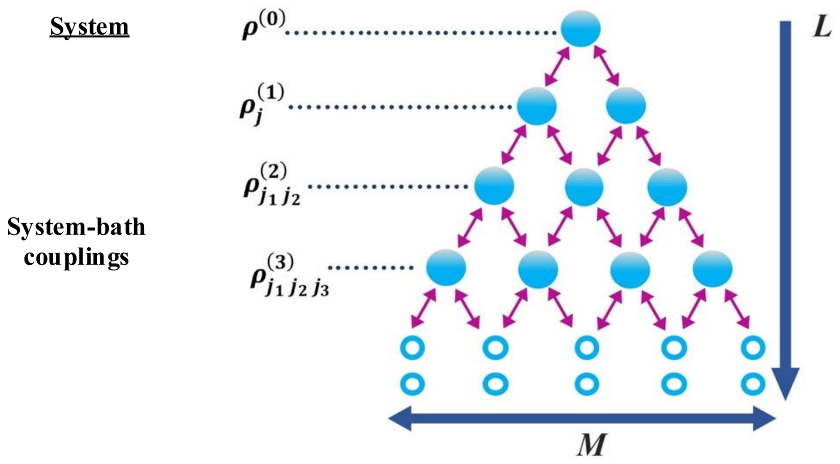
HEOM/DEOM vs MKCT

Nakajima-Zwanzig formalism

$$\dot{\rho}(t) = -\mathrm{i}[H_S, \rho(t)] + \int_0^t d\tau \mathcal{K}(t-\tau)\rho(t)$$

System-bath seperation

HEOM/DEOM

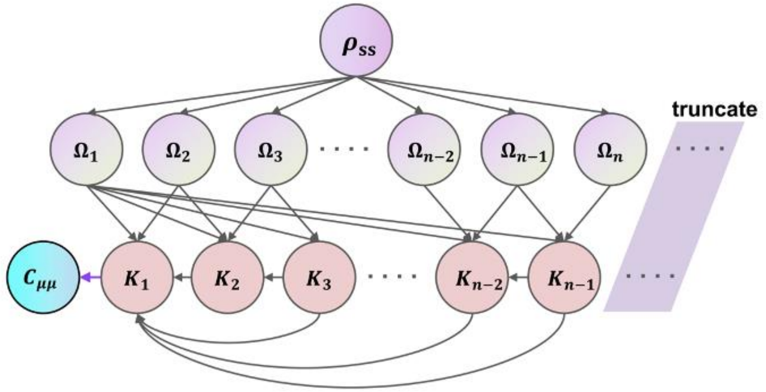


Mori formalism

$$\dot{C}_{\mu\mu}(t) = \Omega_1 C_{\mu\mu}(t) + \int_0^t d\tau K_1(\tau) C_{\mu\mu}(t-\tau)$$

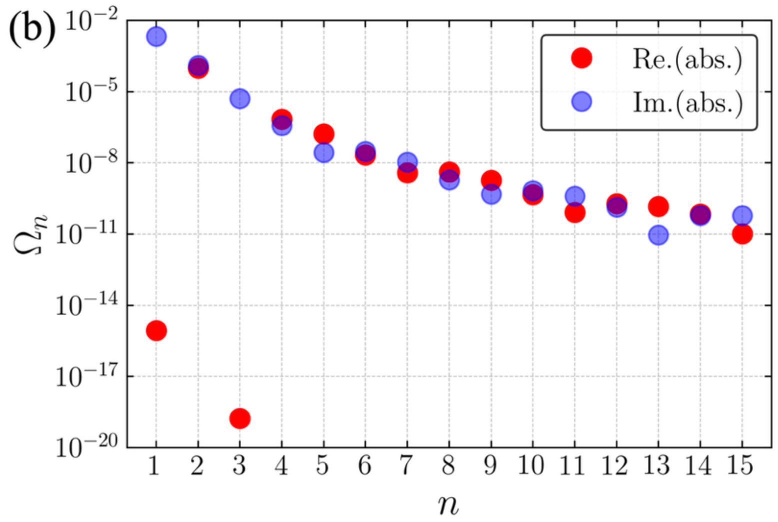
kernel is a number

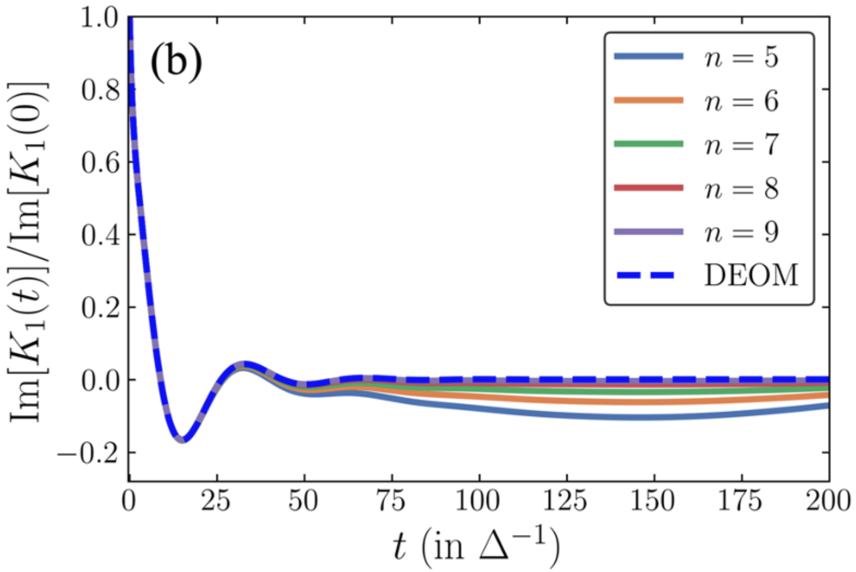
Memory kernel coupling theory



Y Tanimura, JCP 153.2 (2020).
J Shao et al, Chemical Physics Letters 395, 216 (2004)
YJ Yan et al, Frontiers of Physics 11 (2016): 1-27.

MKCT: Spin-boson model





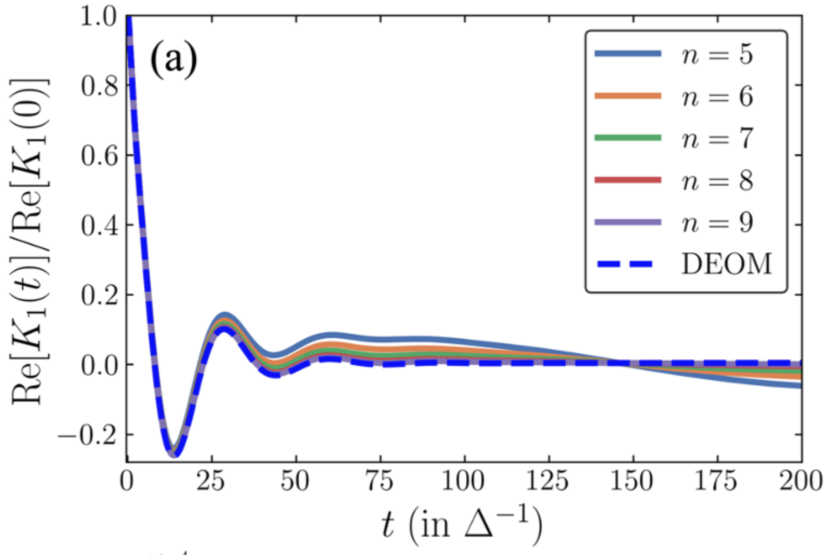
auxiliary kernels

$$\dot{K}_n(t) = K_{n+1}(t) - \Omega_n K_1(t)$$

$$K_n(t) \equiv ((i\mathcal{L})^n \hat{f}(t), \hat{\mu})/(\hat{\mu}, \hat{\mu})$$

Moments

$$\Omega_n \equiv ((i\mathcal{L})^n \hat{\mu}, \hat{\mu})/(\hat{\mu}, \hat{\mu})$$

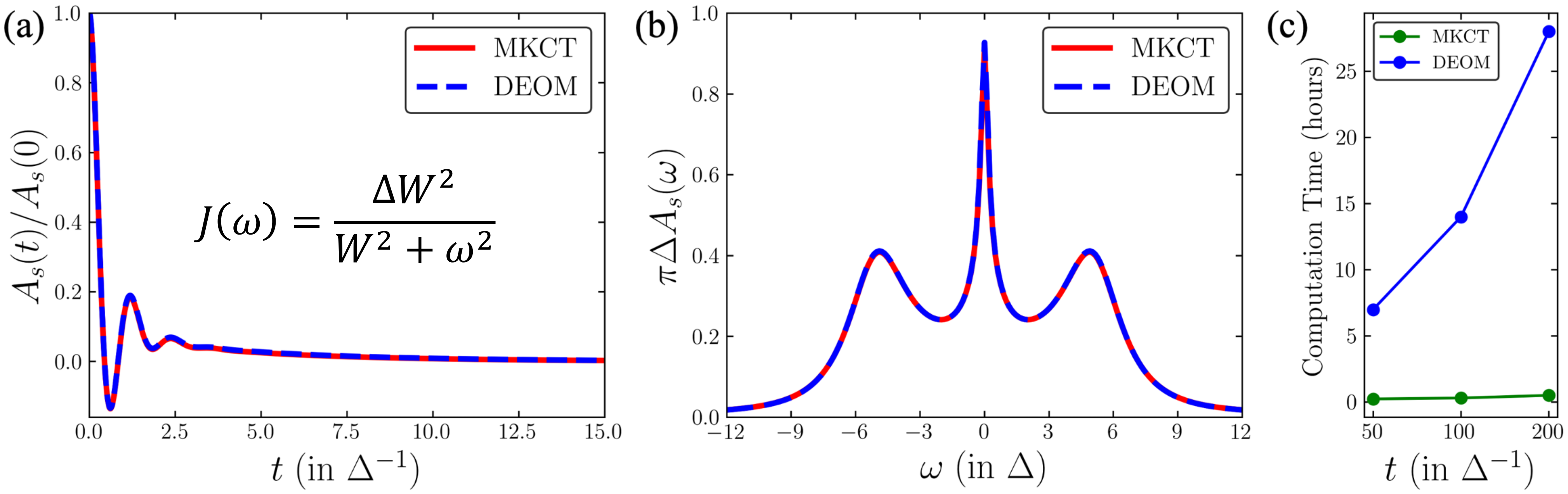


W. Liu, Y. Su, Y. Wang, W. Dou, Phys. Rev. Lett. (accepted) arXiv:2407.01923

MKCT: Anderson impurity model

$$\hat{H} = \xi(\hat{n}_\uparrow + \hat{n}_\downarrow) + U\hat{n}_\uparrow\hat{n}_\downarrow + \sum_{s=\uparrow,\downarrow}\sum_k \epsilon_{ks}\, c^\dagger_{ks}\hat{c}_{ks} + \sum_{s=\uparrow,\downarrow}\sum_k (t_{ks}\, \hat{c}^\dagger_{ks}\hat{d}_s + \mathrm{h.c.})$$

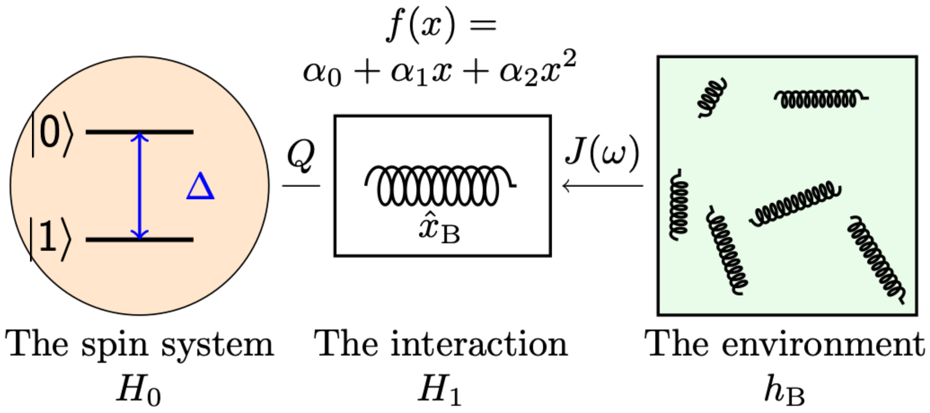
$$A_s(t) = \langle\{\hat{d}_s(t), \hat{d}^\dagger_s(0)\}\rangle, \qquad A_s(\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} \mathrm{d}t\, e^{\mathrm{i}\omega t} A_s(t)$$

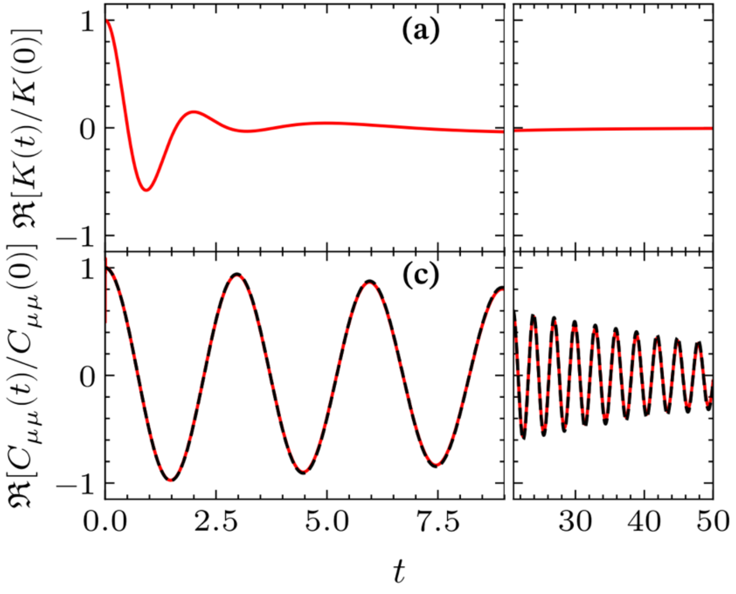


$\xi = -U/2,\ U = 8\Delta,\ k_{\mathrm{B}}T = 0.01\Delta,\ W = 10\Delta$

W. Liu, Y. Su, Y. Wang, W. Dou, Phys. Rev. Lett. (accepted) arXiv:2407.01923

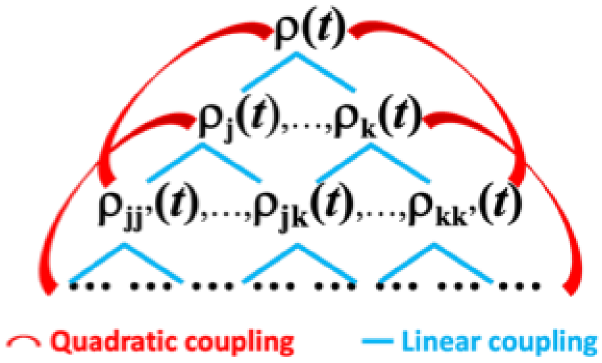
Nonlinear couplings





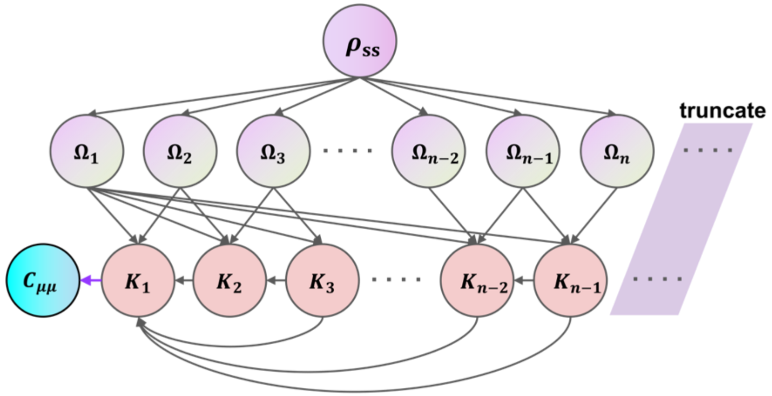
R. Bi, W. Liu, W. Dou, J. Chem. Phys. 162, 224106 (2025)

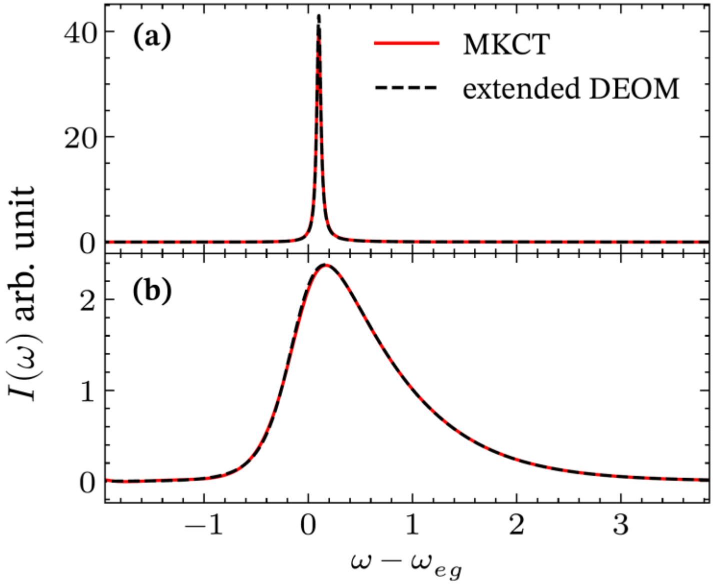
(extended) Dissipaton Equations of Motion (DEOM)



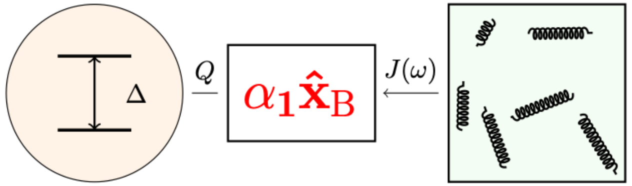
Yan, Y. *Front. Phys.* **2016** 11 (4)
Yan, Y. *JCP* **2018** 148 (11)

Memory Kernel Coupling Theory (MKCT)

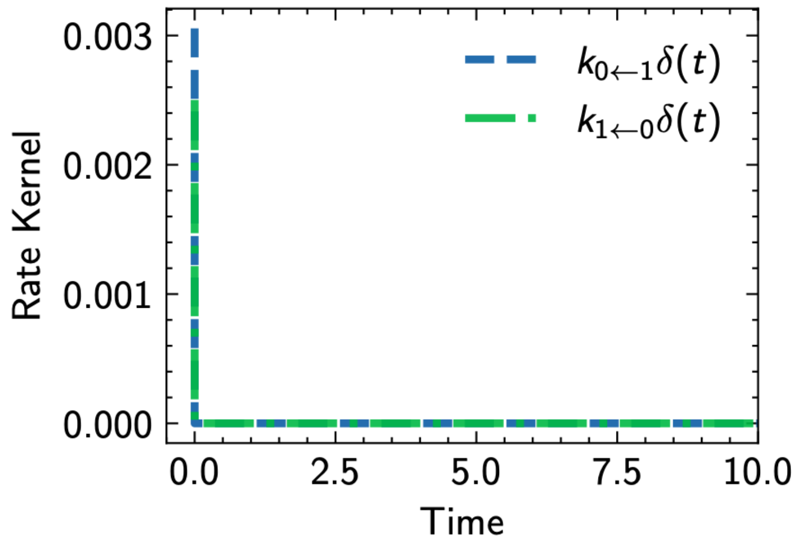




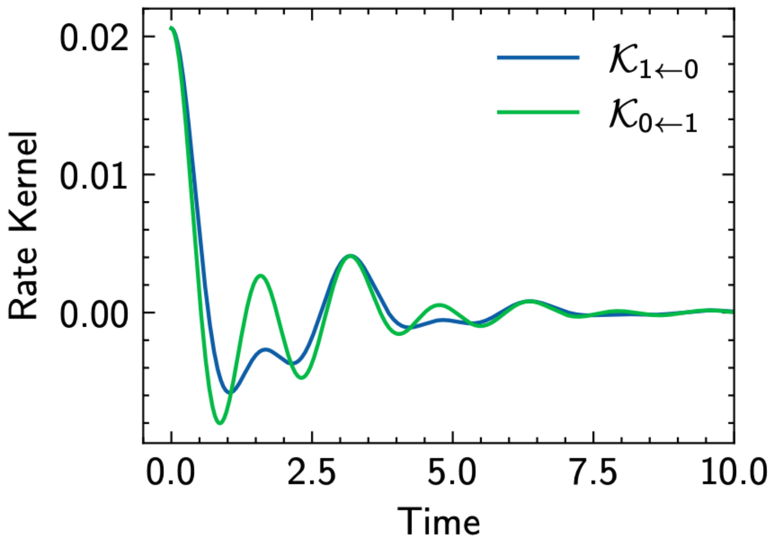
Spin-lattice relaxation results: linear contribution



Raw data: rate kernels v.s. rate constants



Rate constants from FGR



Rate kernels from DEOM

Rate constants are the Markovian approximation to rate kernels

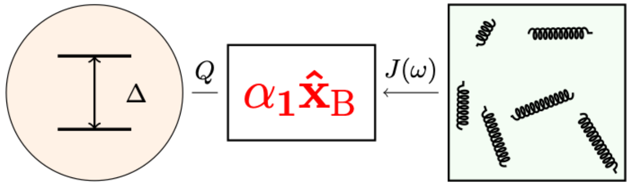
$$\dot{\boldsymbol{p}}(t) = \int_0^t d\tau \tilde{\boldsymbol{K}}(t-\tau;t)\boldsymbol{p}(\tau)$$

$$\mathcal{K}(t) \approx k\delta(t)$$

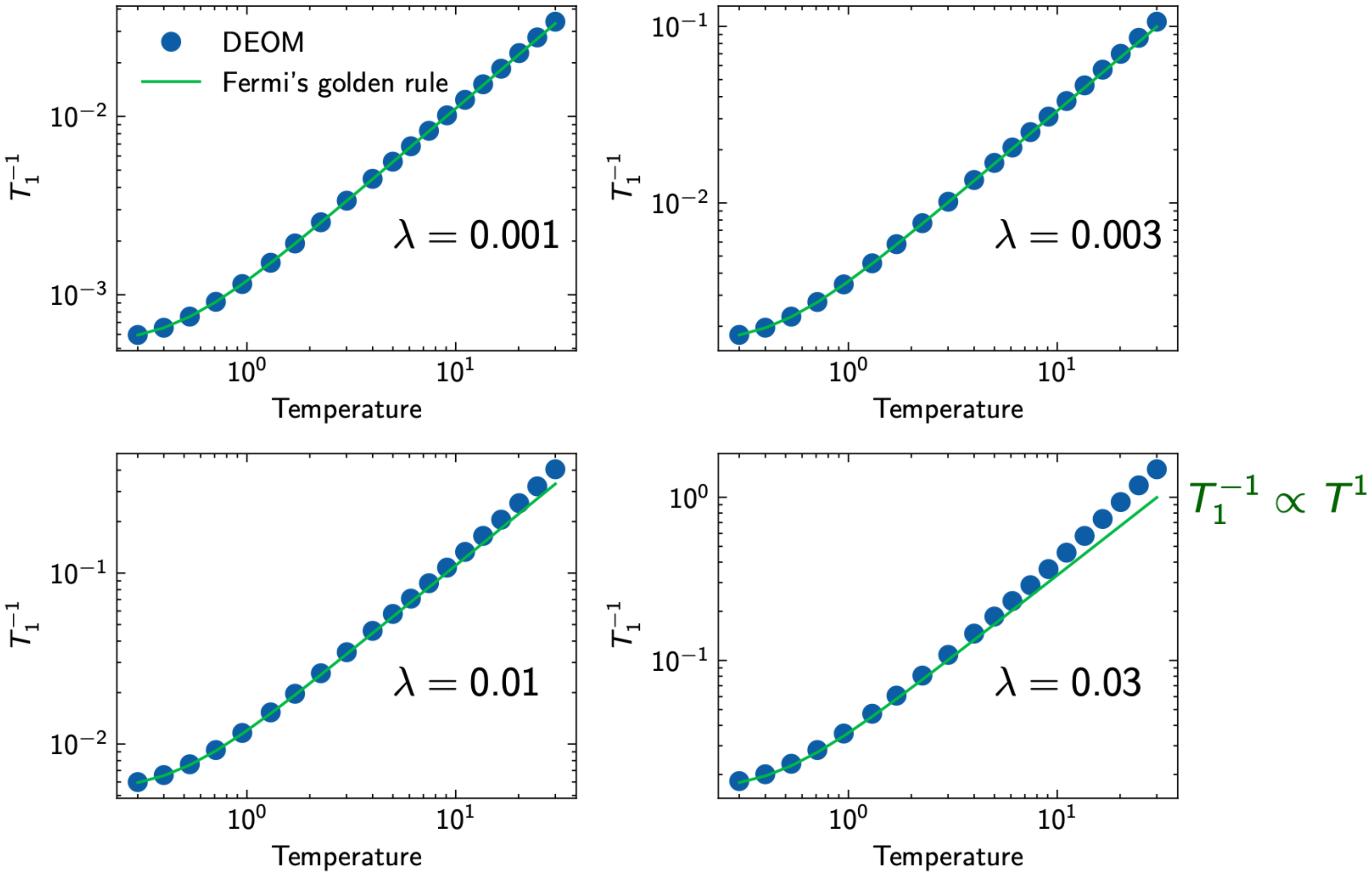
$$k = \int_0^\infty \mathrm{d}t\, \mathcal{K}(t)$$

R. Bi, Y. Su, Y. Wang, L. Sun, W. Dou, J. Chem. Phys. 161, 024105 (2024)

Spin-lattice relaxation results: linear contribution



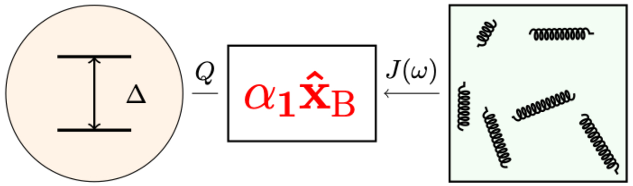
Temperature dependency of T_1



As expected, the golden rule works well for weak interactions;

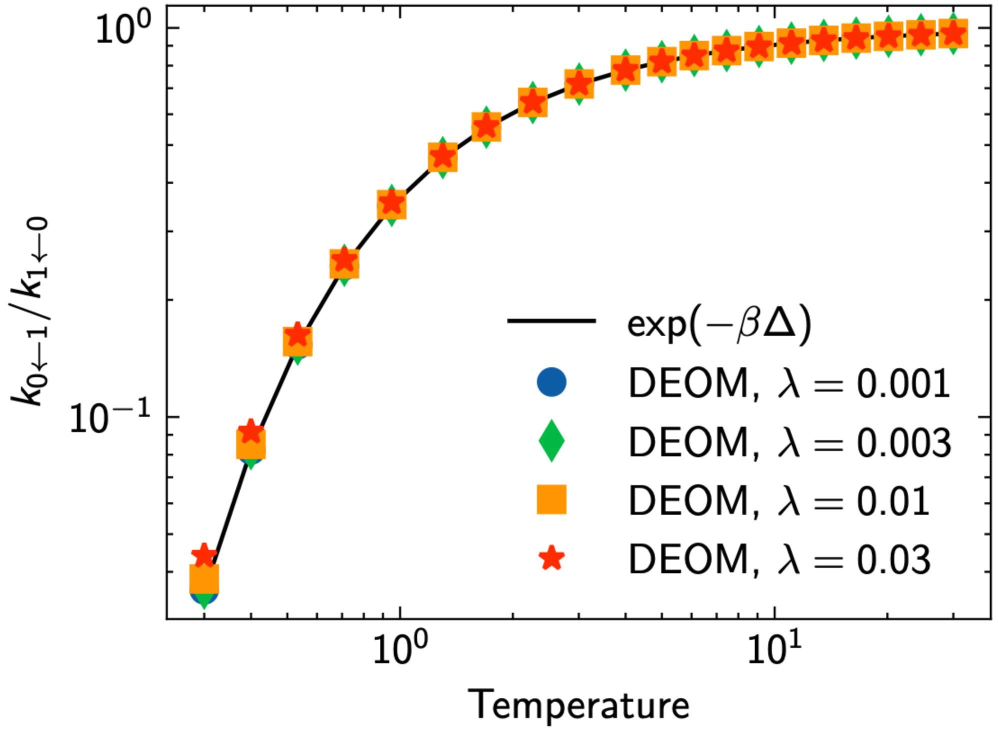
However, underestimate the rates when: high temperature and strong coupling.

Spin-lattice relaxation results: linear contribution



Numerical simulation satisfies the detailed balance

The detailed balance: $k_{0\leftarrow 1} = \exp(-\beta\Delta) k_{1\leftarrow 0}$



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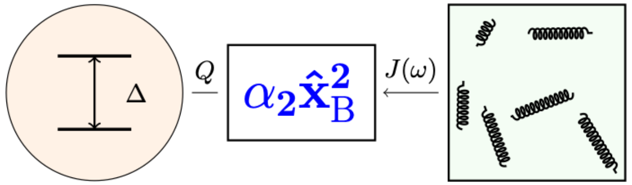
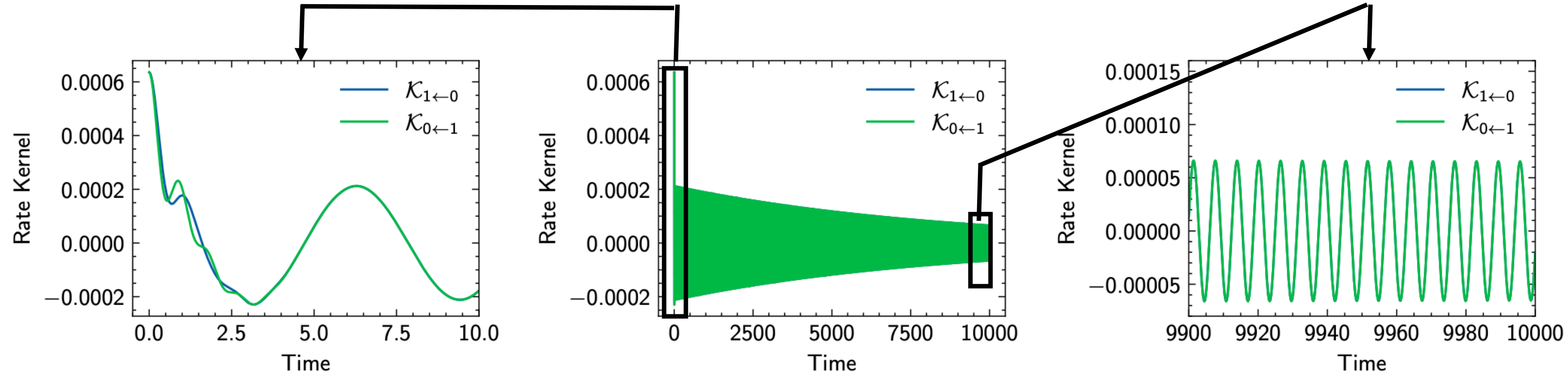
Spin-lattice relaxation results: quadratic contribution

Stationary rate and oscillating rate





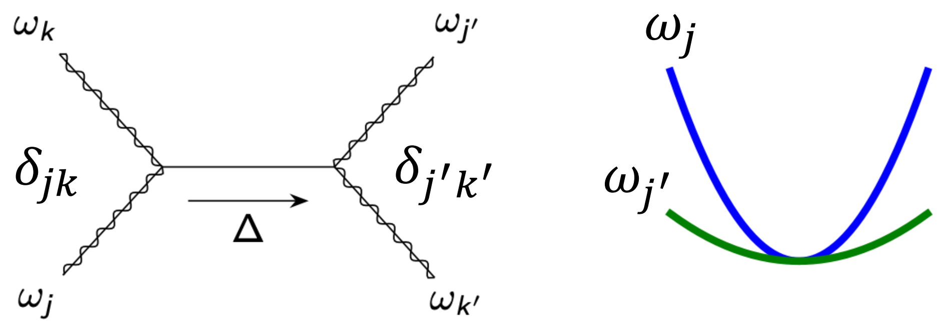
Short memory

Damping

Long memory

$J(\omega)\uparrow$, faster damping

The source of rate kernel oscillation:

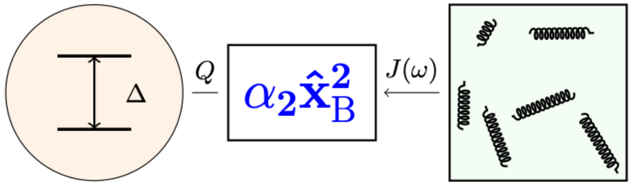


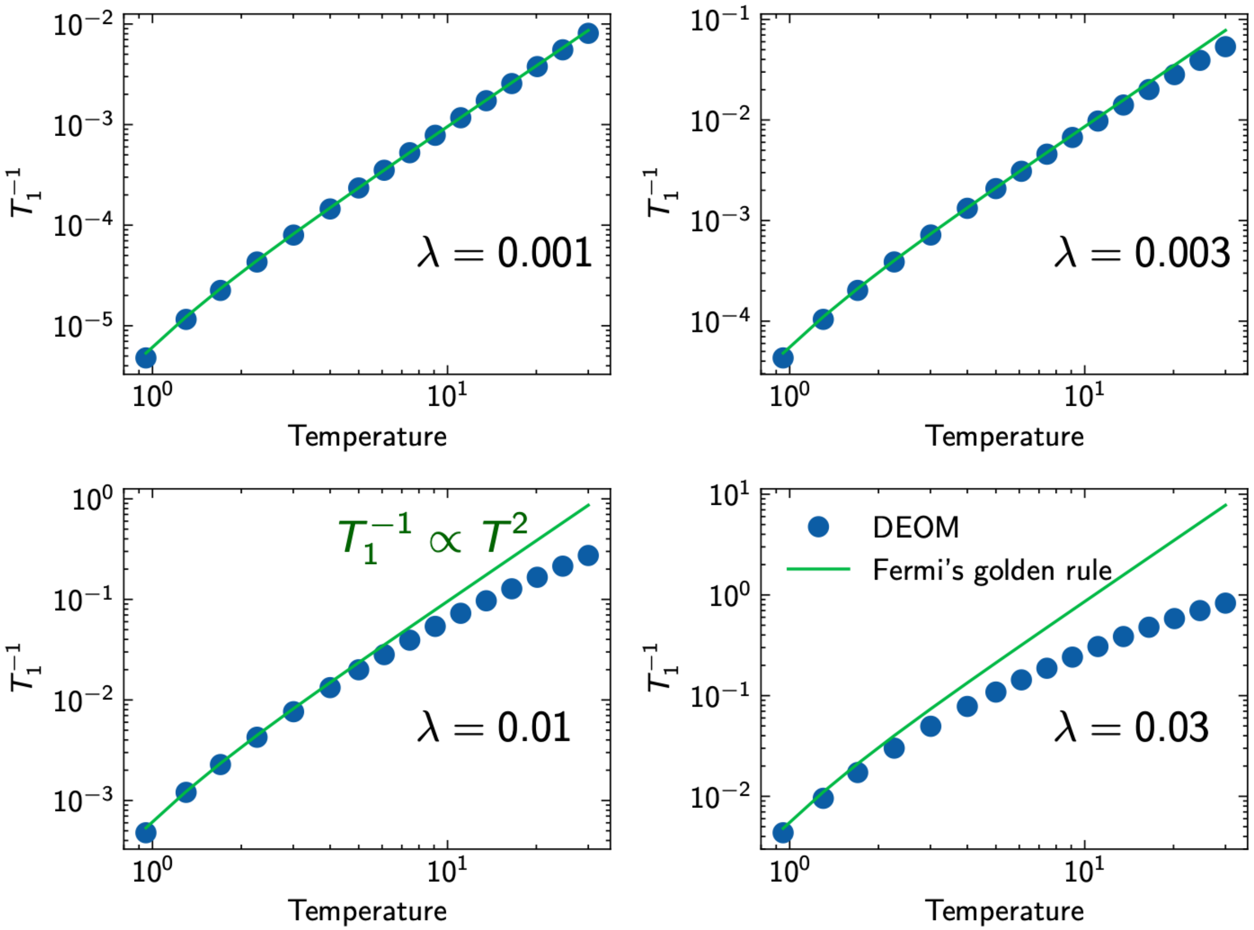
Despite FGR predict

$$k_{\text{oscillatory}} \propto \int_{-\infty}^{\infty} \mathrm{d}t \exp\{\mathrm{i}\Delta/\hbar t\}$$

Rate kernels calculated with DEOM ***always*** damps to 0 (at $t \to \infty$)

Spin-lattice relaxation results: quadratic contribution



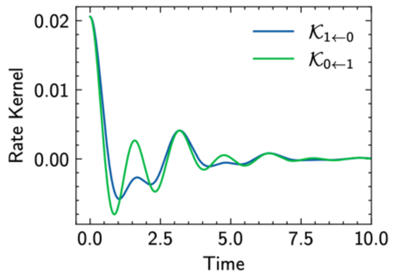


T dependency:

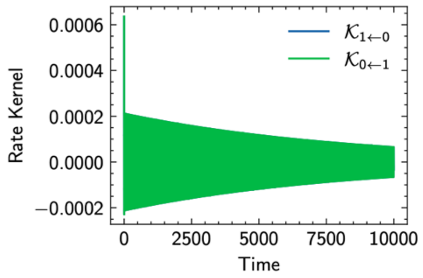
- FGR **overestimates** the rates, different than linear.
- The deviation is more dramatic than linear.
- In strong coupling, T_1 is less temperature dependent than FGR

Quick summary: spin-lattice relaxation

1. The transient behavior of the relaxation are quite different



Linear process:
short memory



Quadratic process:
very long memory, slow decaying

2. The FGR deviates from DEOM when interaction is strong

3. Detailed balance is conserved in both FGR & DEOM simulations.

$$k_{0\leftarrow 1} = \exp(-\beta\Delta)k_{1\leftarrow 0}$$

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Outline

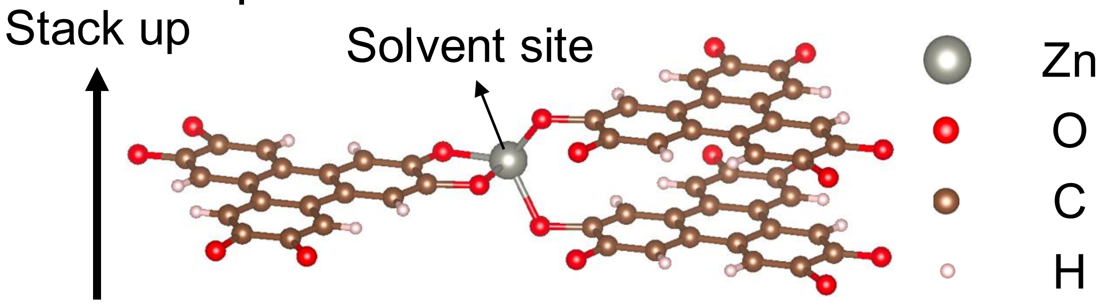
- Background
  - Molecular qubits
  - Phenomenological results and microscopic model

- Nonlinear couplings
  - Exact dynamics: memory kernel coupling theory
  - Linear and quadratic couplings

- Spin-polaron model
  - Experimental results for ZnHOTP
  - New mechanism for spin-lattice relaxation

Temperature insensitive T_1 in ZnHOTP

- MOF qubit material ZnHOTP



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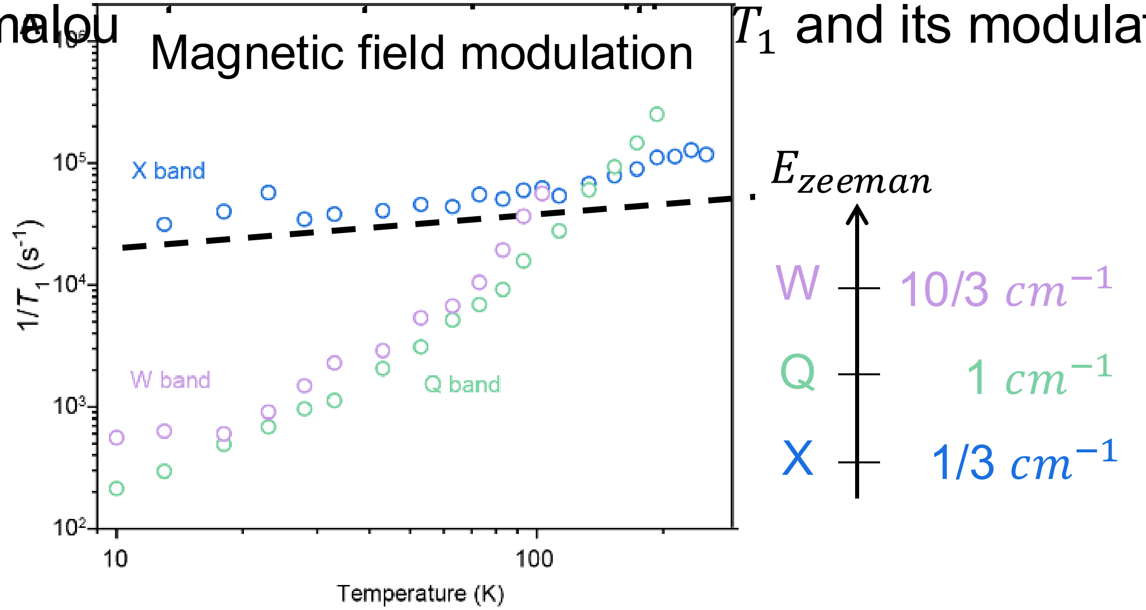
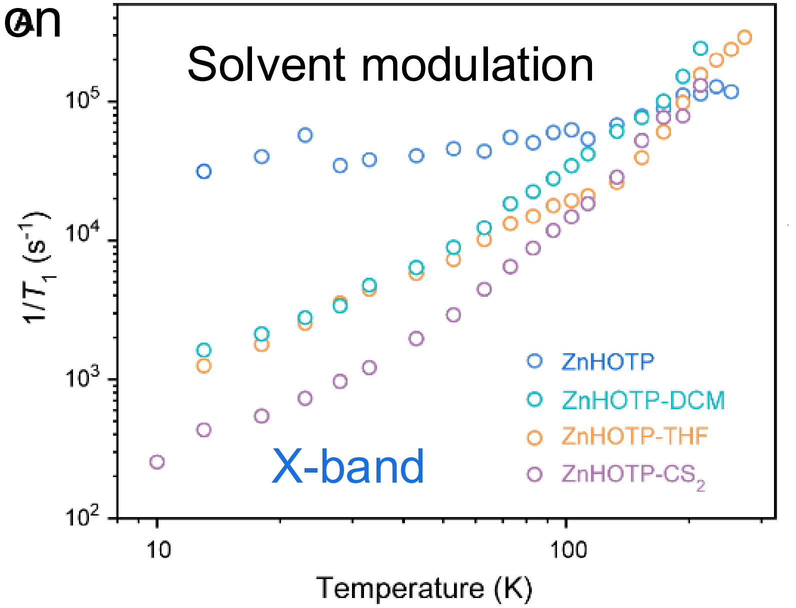
- Anomalou … T_1 and its modulation

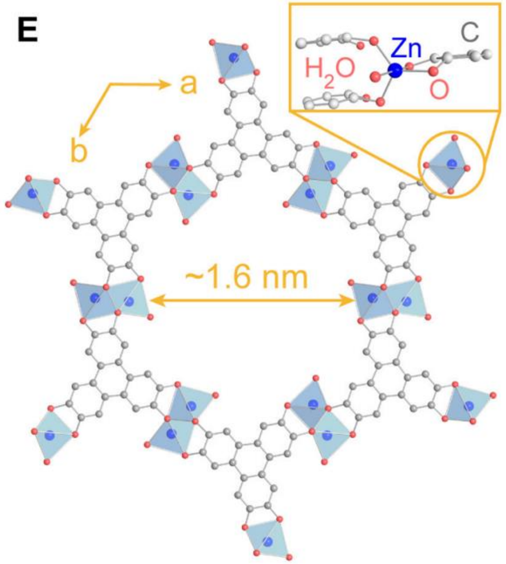


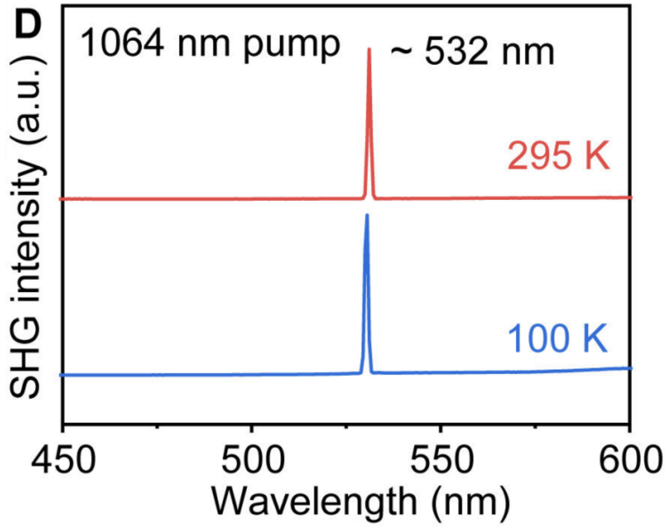


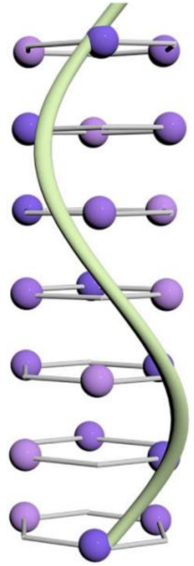
A. Zhou, R. Bi, …, W. Dou*, L. Sun*, arXiv:2506.04885 (2025)

Chirality and the microscopical spin-polaron model

- Chirality of ZnHOTP confirmed via XRD & second harmonic generation (SHG)







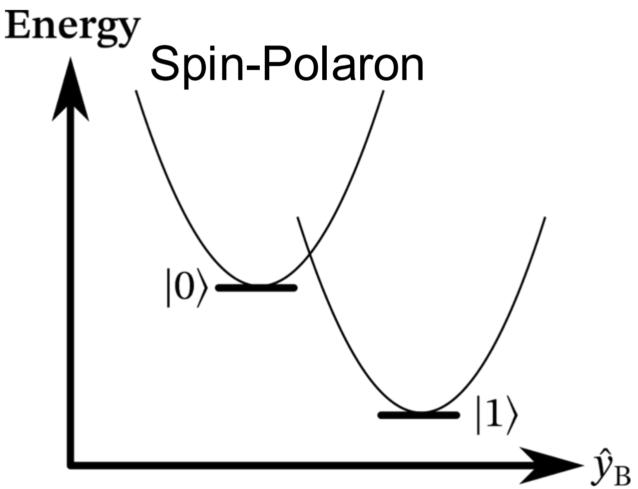
XRD + SHG supports
Space group $P6_3$
Chiral structure

- Microscopic Model

$$\hat{H} = \frac{1}{2}\Delta\hat{\sigma}_z + H_B + \hat{\sigma}_x(\alpha_1\hat{x}_B + \alpha_2\hat{x}_B^2) + \hat{\sigma}_z\hat{y}_B$$

$\hat{x}_B$
Collective lattice mode for relaxation

$\hat{y}_B$
Collective mode for spin-polaron (decoherence)



Chirality

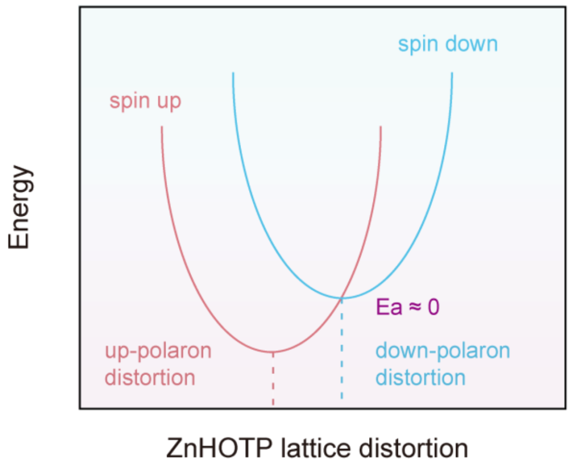
$\hat{y}_B$
Different coupling for $|0\rangle$ and $|1\rangle$

Hypothesis: the spin polaron relaxation mechanism

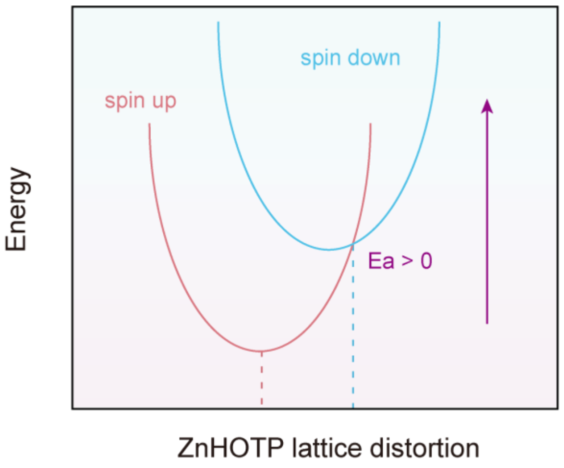
Thermally activated relaxation of spin polarons in ZnHOTP

- Spin and a phonon couple to form a spin polaron
- ZnHOTP powder at X band: activation energy Ea≈0, coincidence!
- Higher magnetic field breaks this coincidence.
- Pore filling with solvent may break or reinforce this coincidence

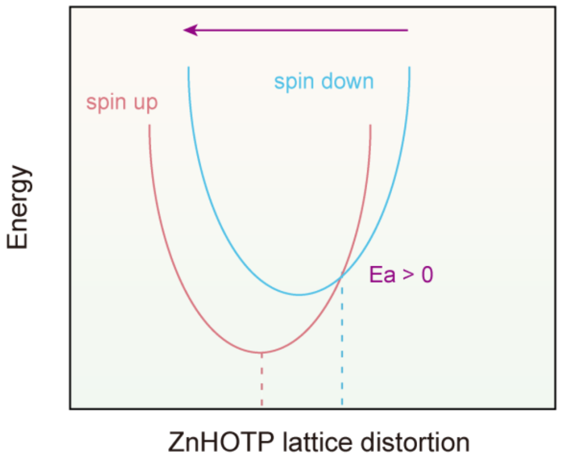
Dry powder at X band



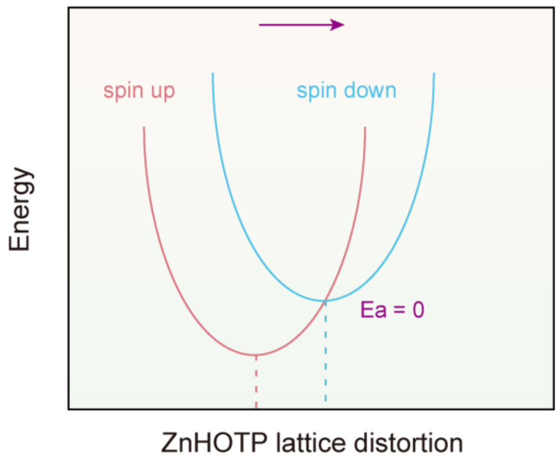
Dry powder at W band



Powder soaked in THF



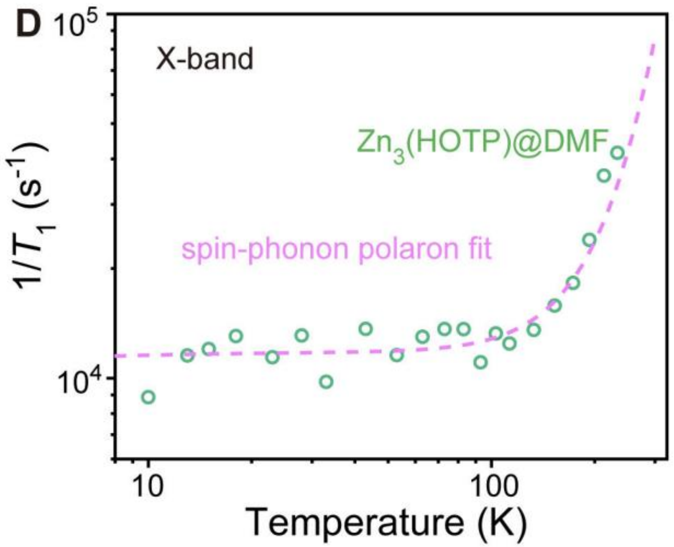
Powder soaked in DMF



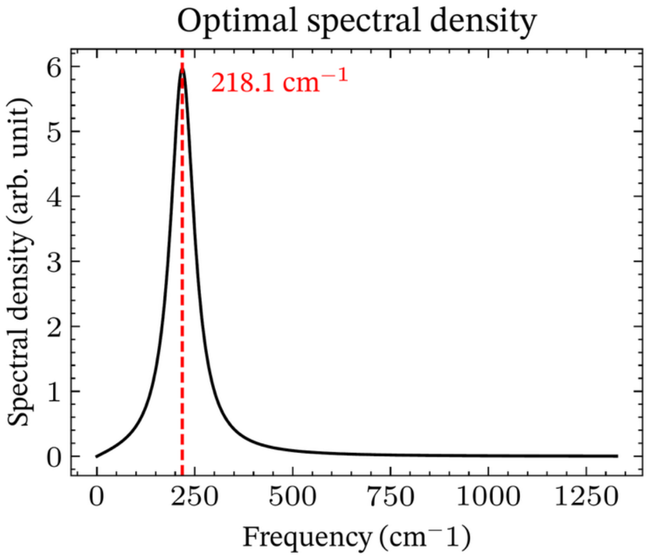
Insights from fitting the experimental data

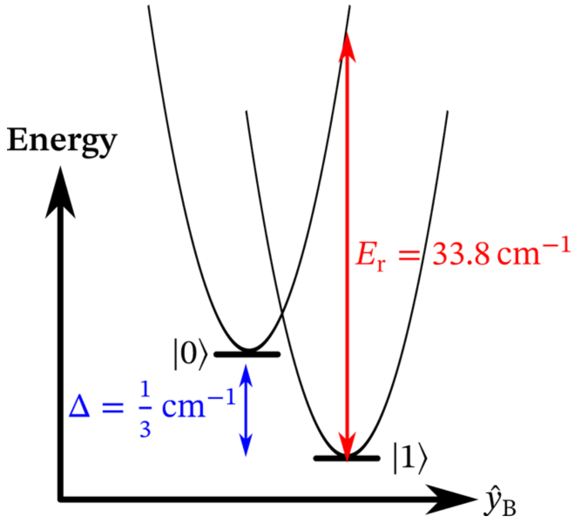
$$k_{0\leftarrow 1}^{\mathrm{quad}} = 2\sqrt{\frac{\pi}{A}}\int_{-\infty}^{\infty}\frac{d\omega}{\pi}\frac{J(\omega)}{1-e^{\beta\omega}}\int_{-\infty}^{\infty}\frac{d\omega'}{\pi}\frac{J(\omega')}{e^{\beta\omega'}-1}\exp\left[-\frac{(\Delta-\omega+\omega'-E_r)^2}{4A}\right]+$$

$$\sqrt{\frac{\pi}{A}}\left[\int_0^{\infty}\frac{d\omega}{\pi}J(\omega)\coth\left(\frac{\beta\omega}{2}\right)\right]^2\exp\left[-\frac{(\Delta-E_r)^2}{4A}\right]$$



$$J(\omega) = \frac{2\lambda\zeta\omega_B^2\omega}{(\omega^2-\omega_B^2)^2+\zeta^2\omega^2}$$





ω_B (cm^{-1})	ζ (cm^{-1})	ω_{max} (cm^{-1})	E_r (cm^{-1})
221.2	74.7	218.1	33.8

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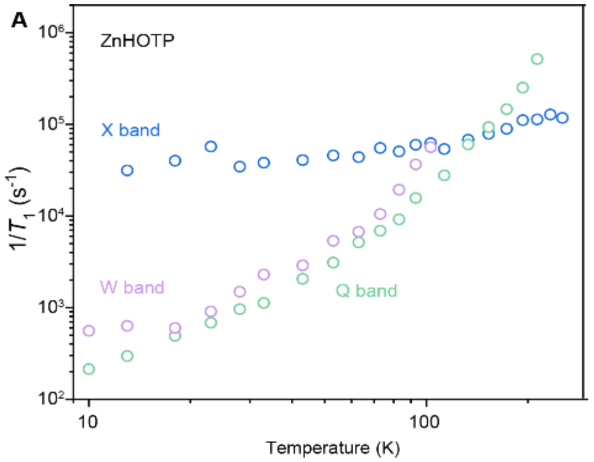
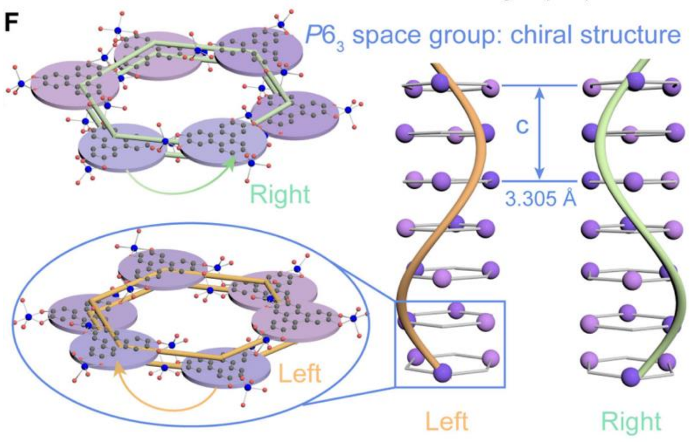
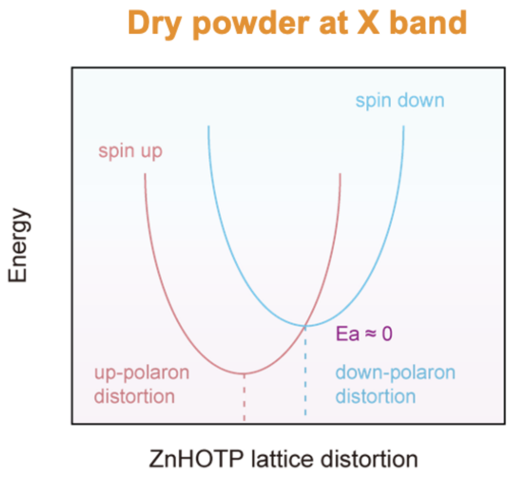
Quick summary: spin-polaron model

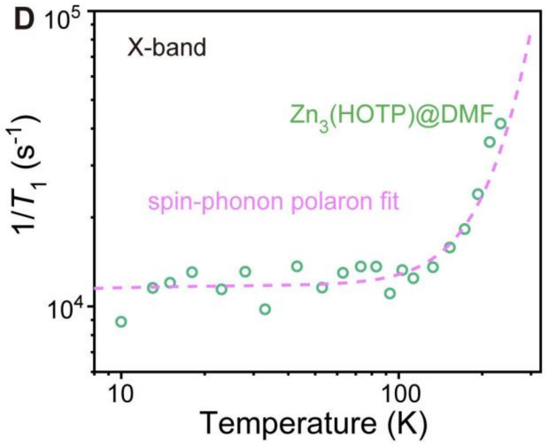
1. Spin relaxation rate ZnHOTP: No temperature dependence.





2. ZnHOTP is chiral, forming spin-polaron. With different magnetic field and solvent environment, such behaviors are gone

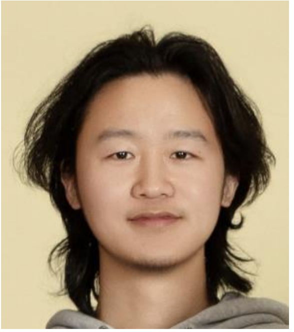




Thank you!

Students:

Wei Liu (MKCT)



Ruihao Bi (spin-polaron)

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Yao Wang @ USTC

Group Members :

Acknowledge:

WESTLAKE UNIVERSITY

NSFC
National Natural Science Foundation of China