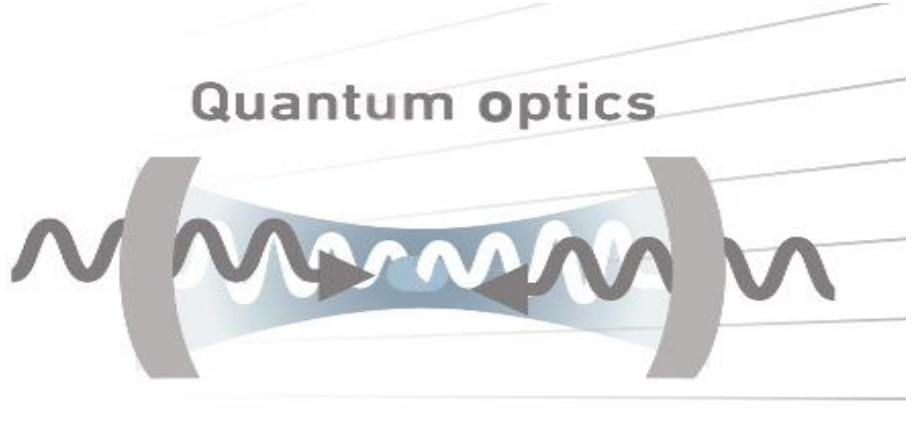
Floquet nonadiabatic dynamics: electron and energy transfer driven by light-matter interactions

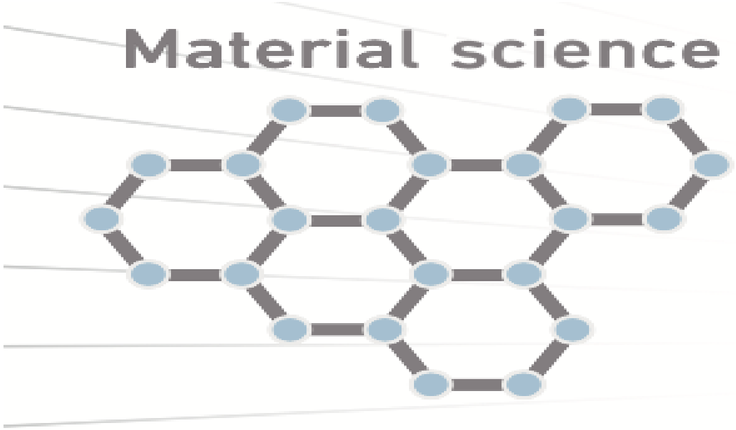
Presenter: Jingqi Chen (Westlake University, China)
Supervisor: Prof. Wenjie Dou

E-mail:chenjingqi@westlake.edu.cn

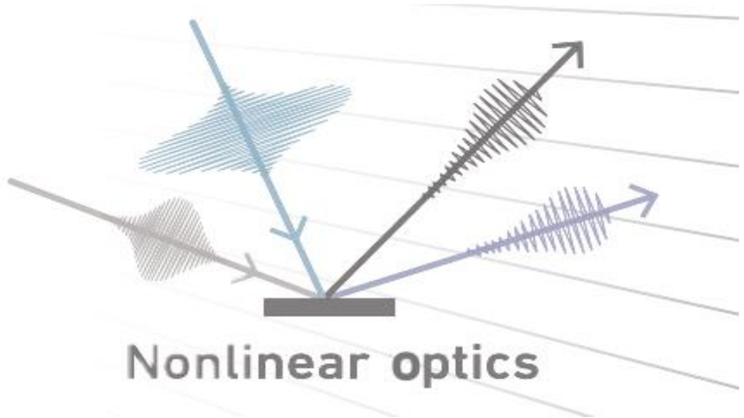
Strong light-matter interactions



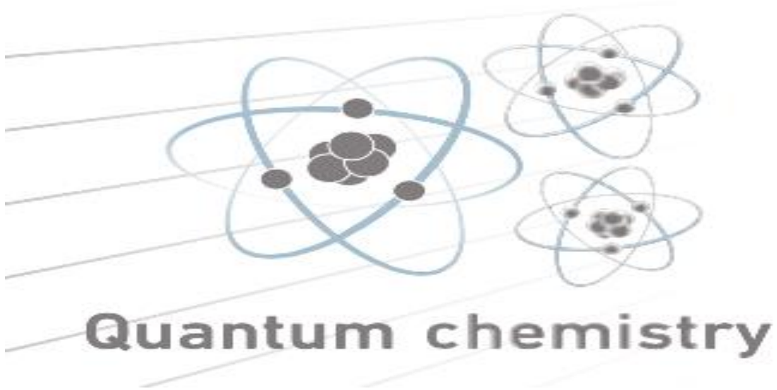
[1] Liu R, Zhou Z K, Yu Y C, et al. Physical review letters, 2017, 118(23): 237401.



[2] Koppens F H L, Chang D E, García de Abajo F J. Nano letters, 2011, 11(8).



[3] Stern L, Desiatov B, Goykhman I, et al. Nature communications, 2013, 4(1): 1-7.



[4] Hertzog M, Wang M, Mony J, et al. Chemical Society Reviews, 2019, 48(3): 937-961.

Strong light-matter interactions

Some applications:

1. Photo-electrical catalysis
2. Plasmonic polariton

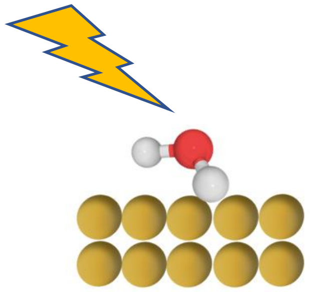
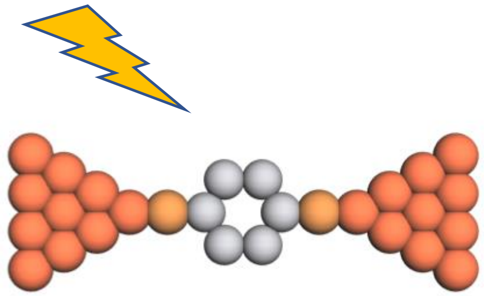


Photo-electrical catalysis



Plasmonic polariton

Theoretical Challenges:

1. Time-dependent driving from light
2. Strong light-matter interactions
3. Nonadiabatic electron transfer at metal surface

$$H = H_s + A\cos(\Omega t)$$

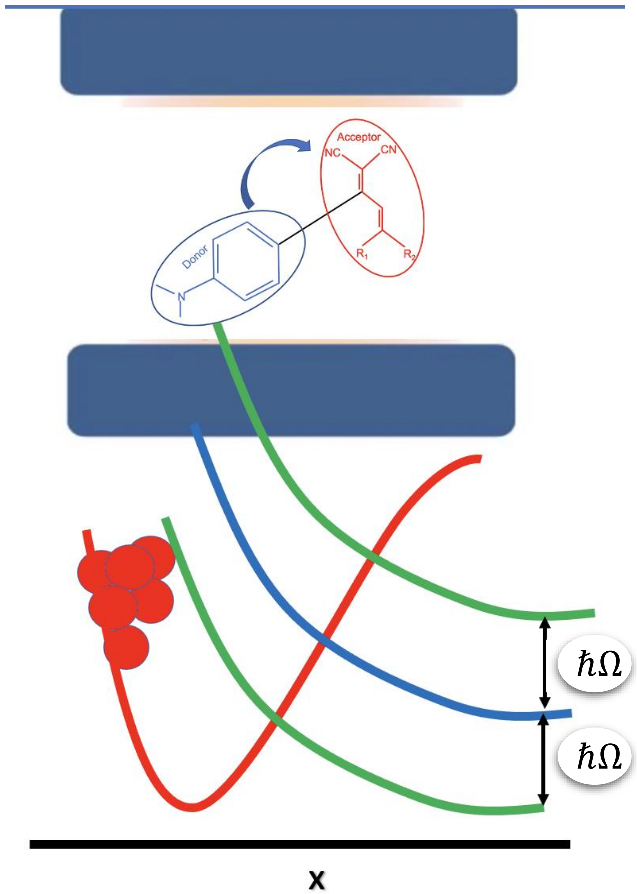
Floquet Hamiltonian model

Time-dependent to time-independent (time average)

$$[\sum_{n=-N}^{N}\frac{1}{T}\int_0^T dt[e^{-im\Omega t}[h_s]e^{in\Omega t}]-n\hbar\Omega\delta_{mn}]c_n(r)=\varepsilon c_m(r)$$

$$\underbrace{\left[\sum_{n=N}[h_s]_{mn}-n\hbar\Omega\delta_{mn}\right]}_{h_F}c_n(r)=\varepsilon c_m(r)$$

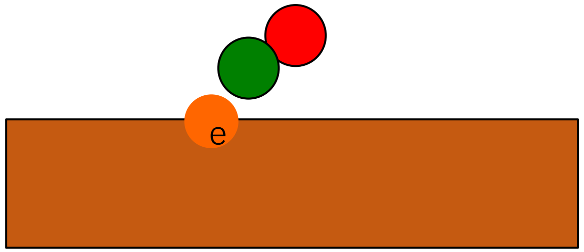
$$h_F=\begin{pmatrix}\ddots & \vdots & \vdots & \vdots & \cdots \\ \cdots & h_{n-1,n-1}+(n-1)\hbar\Omega & h_{n-1,n} & h_{n-1,n+1} & \cdots \\ \cdots & h_{n,n-1} & h_{n,n}+n\hbar\Omega & h_{n,n+1} & \cdots \\ \cdots & h_{n-1,n-1} & h_{n+1,n} & h_{n+1,n+1}+(n+1)\hbar\Omega & \cdots \\ \cdots & \vdots & \vdots & \vdots & \ddots\end{pmatrix}$$



The non-zero off-diagonal parts are responsible for the emission and absorption of photons

Electronic friction in nonadiabatic dynamics

Electronic friction model[1]:



$$-m_\alpha \ddot{R}_\alpha = -F_\alpha + \sum_\nu \gamma_{\alpha\nu} \dot{R}_\nu - \delta\hat{F}_\alpha$$

F_α, $\gamma_{\alpha\nu}$, $\bar{D}_{\alpha\nu}$ (the correlation function of $\delta\hat{F}_\alpha$) are the coefficient of the Fokker-Planck equation[2], A is the pure nuclear density:

$$\partial_t \mathcal{A} = -\sum_\alpha \frac{P_\alpha}{m_\alpha}\partial_\alpha \mathcal{A} - \sum_\alpha F_\alpha \frac{\partial \mathcal{A}}{\partial P_\alpha} + \sum_{\alpha\nu} \gamma_{\alpha\nu} \frac{\partial}{\partial P_\alpha}\left(\frac{P_\nu}{m_\nu}\mathcal{A}\right) + \sum_{\alpha\nu} \bar{D}^S_{\alpha\nu} \frac{\partial^2 \mathcal{A}}{\partial P_\alpha \partial P_\nu}$$

where

$$F_\alpha = -tr_e\left(\partial_\alpha \hat{H} \hat{\rho}_{ss}\right) \qquad \gamma_{\alpha\nu} = -\int_0^\infty dt\, tr_e\left(\partial_\alpha \hat{H} e^{-i\hat{H}t/\hbar} \partial_\nu \hat{\rho}_{ss} e^{i\hat{H}t/\hbar}\right)$$

$$\bar{D}^S_{\alpha\nu} = \frac{1}{2}\int_0^\infty dt\, tr_e\left(e^{i\hat{H}t/\hbar} \delta\hat{F}_\alpha e^{-i\hat{H}t/\hbar} (\delta\hat{F}_\nu \hat{\rho}_{ss} + \hat{\rho}_{ss}\delta\hat{F}_\nu)\right) \qquad \delta\hat{F}_\alpha \equiv -\partial_\alpha \hat{H} + tr_e\left(\partial_\alpha \hat{H} \hat{\rho}_{ss}\right)$$

[1] Dou, Wenjie, and Joseph E. Subotnik. *The Journal of Chemical Physics* 148.23 (2018): 230901.
[2] Dou, Wenjie, Gaohan Miao, and Joseph E. Subotnik. *Physical Review Letters* 119.4 (2017): 046001.

Floquet electronic friction model in terms of nonequilibrium Green's function

Expression of $\gamma_{\alpha\nu}$ in terms of Green's functions

recall: $\gamma_{\alpha\nu} = -\int_0^{\infty} dt\, tr_e\left(\partial_\alpha \hat{H} e^{-i\hat{H}t/\hbar} \partial_\nu \hat{\rho}_{ss} e^{i\hat{H}t/\hbar}\right)$

Define:

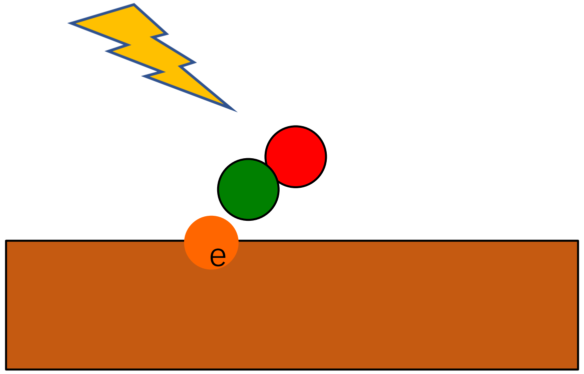
$$\mathcal{G}^{\mathrm{R/A}} = (\epsilon - \mathcal{H} \pm i\eta)^{-1}$$

$$\sigma_{qp}^{\mathrm{ss}} \equiv \mathrm{Tr}\left\{\hat{\rho}_{\mathrm{ss}} \hat{d}_p^\dagger \hat{d}_q\right\} = \int_{-\infty}^{\infty} \frac{d\epsilon}{2\pi i} \mathcal{G}_{qp}^<(\epsilon)$$

$$\mathcal{G}^<(\epsilon) = \mathcal{G}^{\mathrm{R}}(\epsilon) \Pi^< \mathcal{G}^{\mathrm{A}}(\epsilon)$$

So we get:

$$\gamma_{\alpha\nu} = -\frac{\hbar}{2\pi} \int_{-\infty}^{+\infty} d\epsilon Tr\{\partial_\alpha h_s G^R \partial_\nu h_s G^<\} + H.c.$$



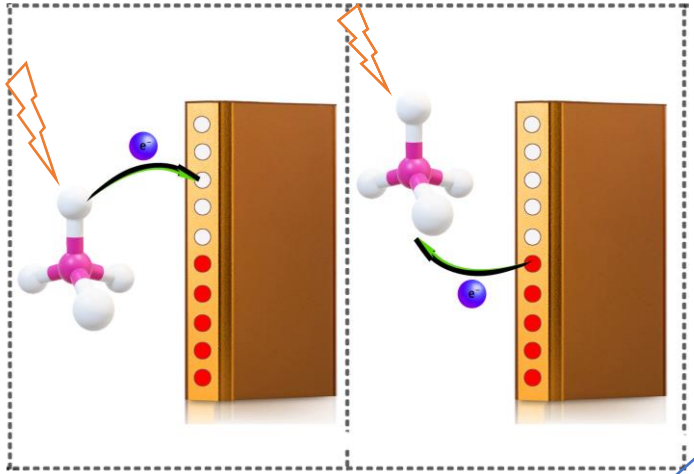
Then we need to transfer all the terms into **Floqeut notation**:

$$[\gamma_{\alpha\nu}]_F = -\frac{\hbar}{2\pi(2N+1)} \int_{-\infty}^{+\infty} d\epsilon Tr\{\partial [h_s]_F G_F^R \partial [h_s]_F G_F^<\} + H.c.$$

[1] Mosallanejad, Vahid, Jingqi Chen, and Wenjie Dou. *arXiv preprint arXiv:2206.07894* (2022).

Application I: one-level Hamiltonian model

Anderson-Holstein (AH) model: System, bath, and coupling.



$$H_{tot} = H_s + H_b + H_c,$$

$$H_s = [E(x) + A\cos(\Omega t)]d^+d + \frac{1}{2}\hbar\omega(x^2 + p^2),$$

$$H_b = \Sigma_k \epsilon_k c_k^+ c_k,$$

$$H_c = \Sigma_k V_k (c_k^+ d + d^+ c_k).$$

$$E(x) = \sqrt{2}gx + E_d$$

g is the electron-phonon coupling strength, we define the renormalized energy as $\bar{E}_d \equiv E_d - E_r$, where $E_r = g^2/\hbar\omega$ is the reorganization energy.

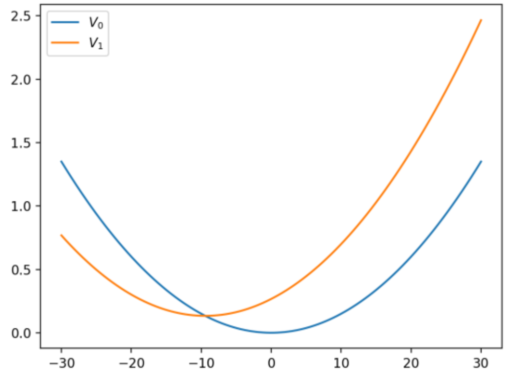
Detail for system Hamiltonian H_s

$$H_\alpha = V_\alpha + A\cos(\Omega t) + \frac{1}{2}\hbar\omega p^2, \alpha = 0, 1$$

$$V_0 = \frac{1}{2}\hbar\omega x^2$$

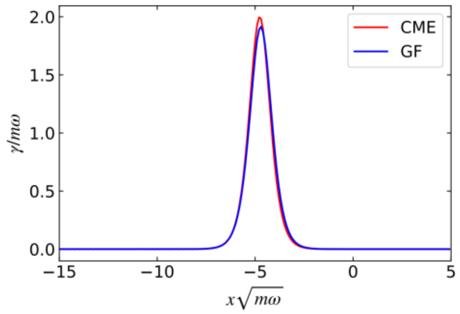
$$V_1 = \frac{1}{2}\hbar\omega x^2 + E(x)$$

In the diabatic states, there are two potential surfaces 1 means impurity occupied and 0 means unoccupied.



Application I: one-level Anderson-Holstein model

A = 0

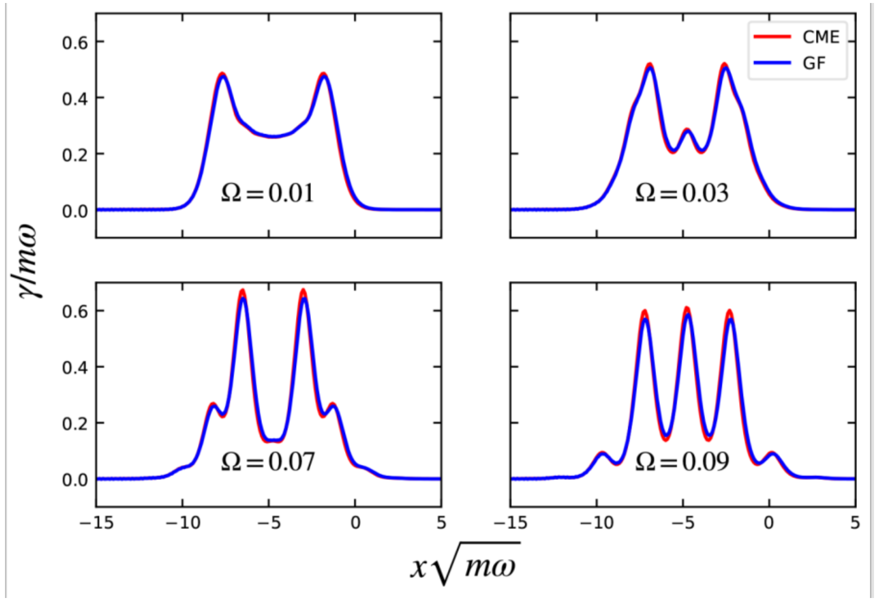


Recall: $-m_\alpha \ddot{R}_\alpha = -F_\alpha + \sum_\nu \gamma_{\alpha\nu} \dot{R}_\nu - \delta \hat{F}_\alpha$

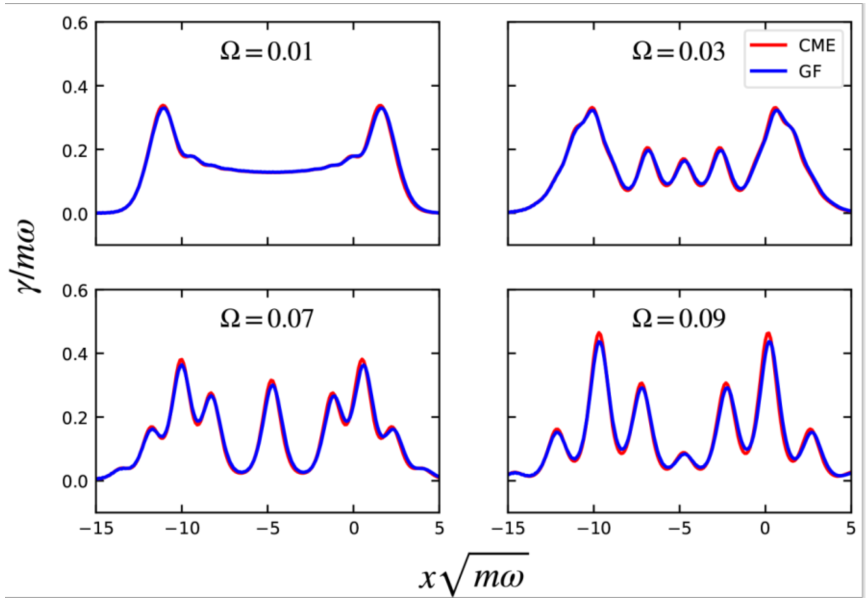
Floquet friction as a function of position for the AH model (change the frequency and the strength of the light).

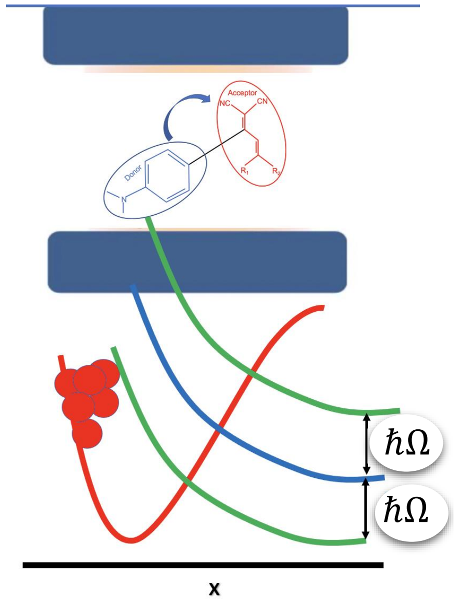
By numerically doing the integration, we know light only changes the distribution of the friction.

A = 0.1



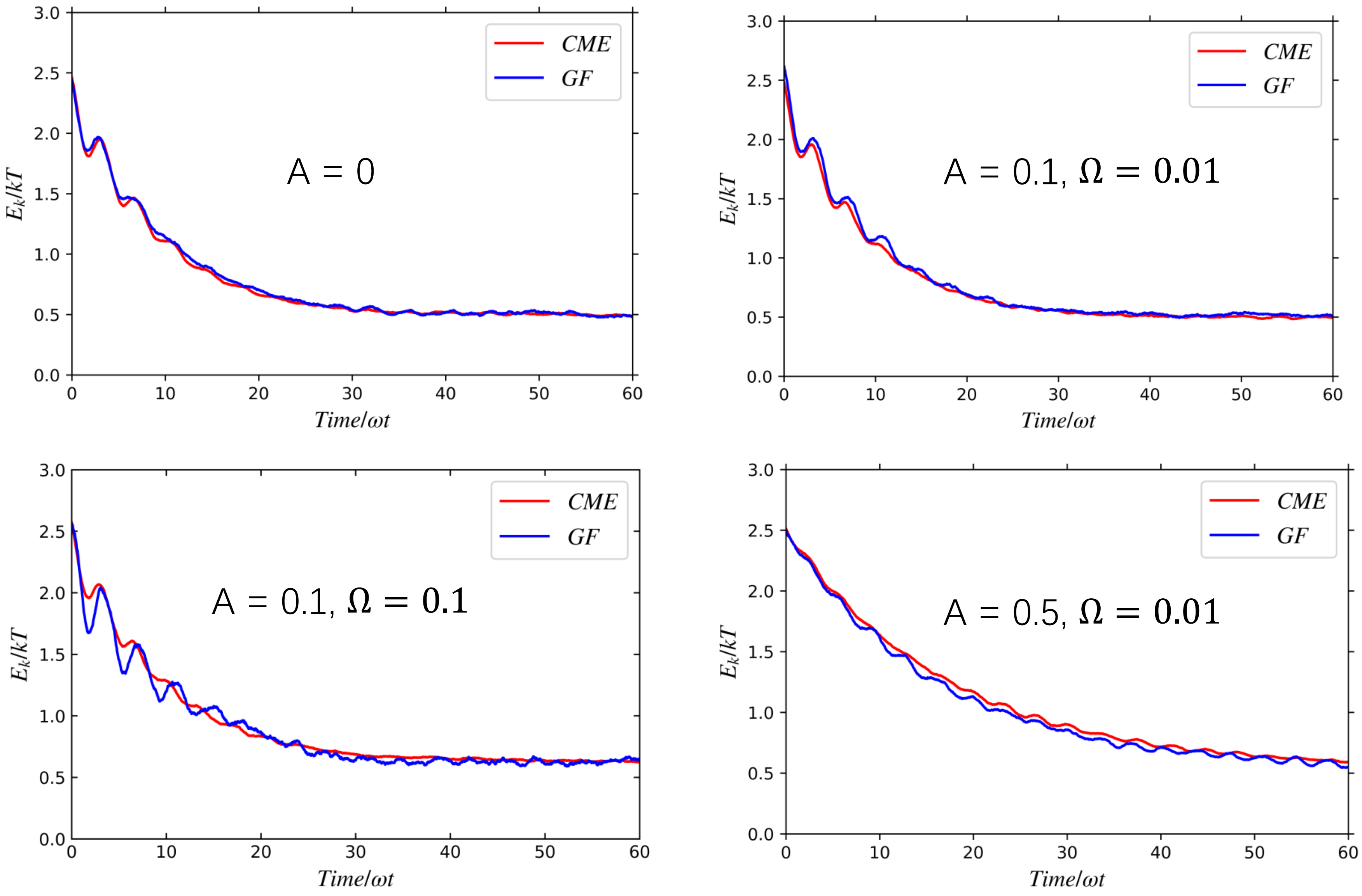
A = 0.2



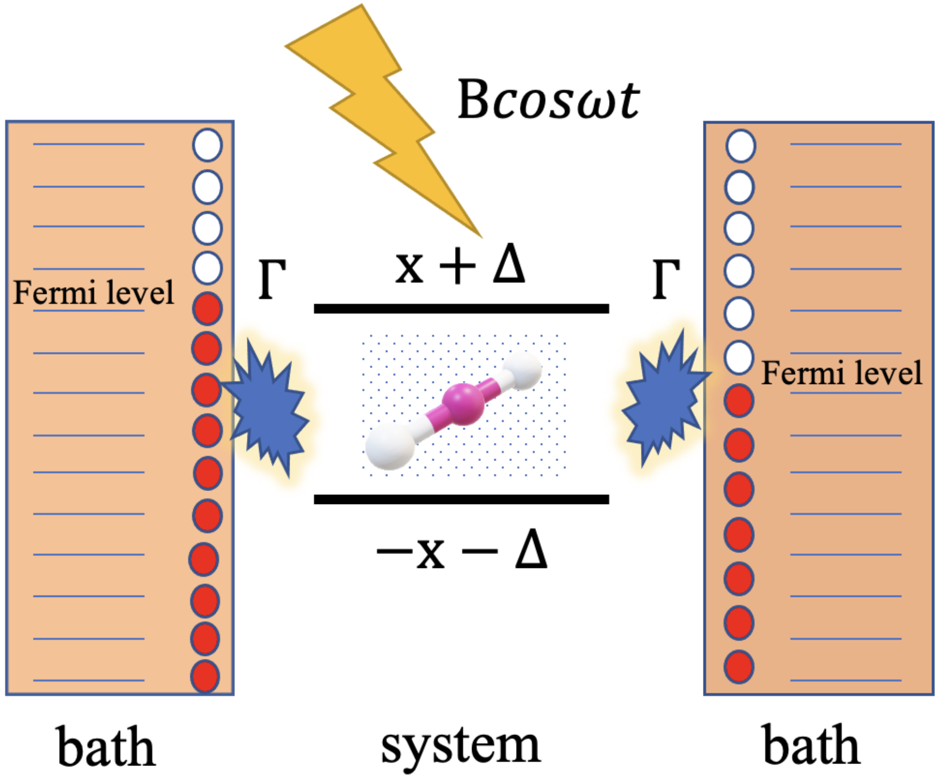


Application I: one-level Anderson-Holstein model

Recall: $-m_\alpha \ddot{R}_\alpha = -F_\alpha + \sum_\nu \gamma_{\alpha\nu} \dot{R}_\nu - \delta \hat{F}_\alpha$



Application II : two-level Hamiltonian model



Our system Hamiltonian:

$$[h^s](x,y,t) = \begin{pmatrix} x+\Delta & Ay + B\cos(\omega t) \\ Ay + B\cos(\omega t) & -x-\Delta \end{pmatrix}$$

We calculated the $\gamma_{xx}, \gamma_{yy}, \gamma_{xy}^{A}$, and γ_{xy}^{s}. Where

$$\gamma_{xy}^{A} = \frac{\gamma_{xy} - \gamma_{yx}}{2}$$

Lorenz-like force

$$\gamma_{xy}^{s} = \frac{\gamma_{xy} + \gamma_{yx}}{2}$$

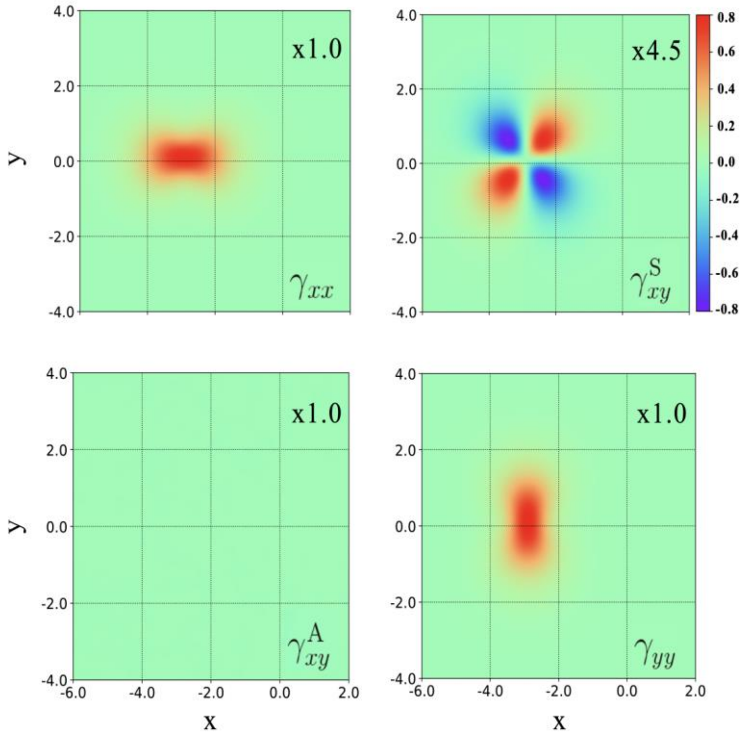
Dissipative process

[1] Mosallanejad, Vahid, Jingqi Chen, and Wenjie Dou. *arXiv preprint arXiv:2206.07894* (2022).

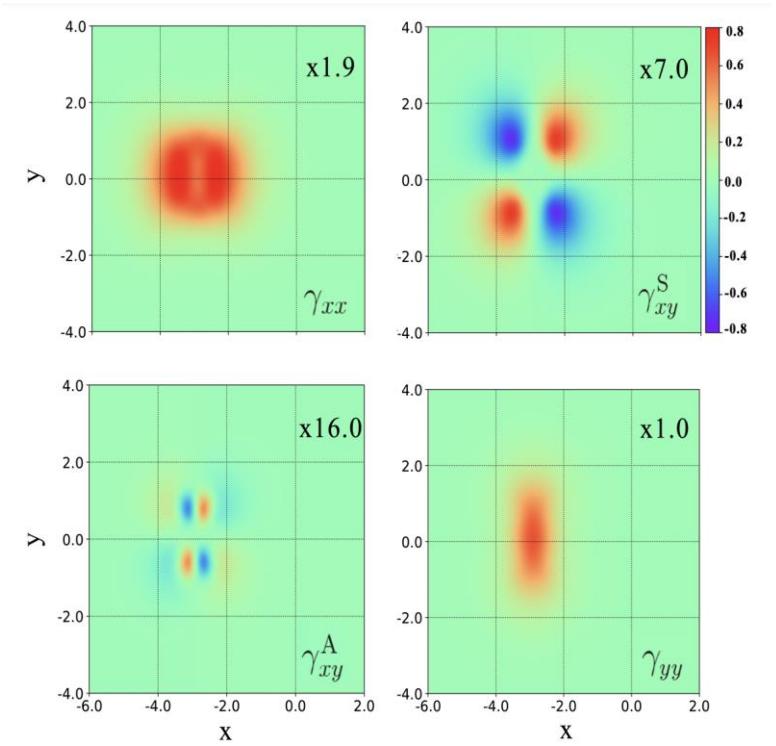
Application II : two-level Hamiltonian model (at equilibrium)

(light/photon can introduce a Lorenz-like force)

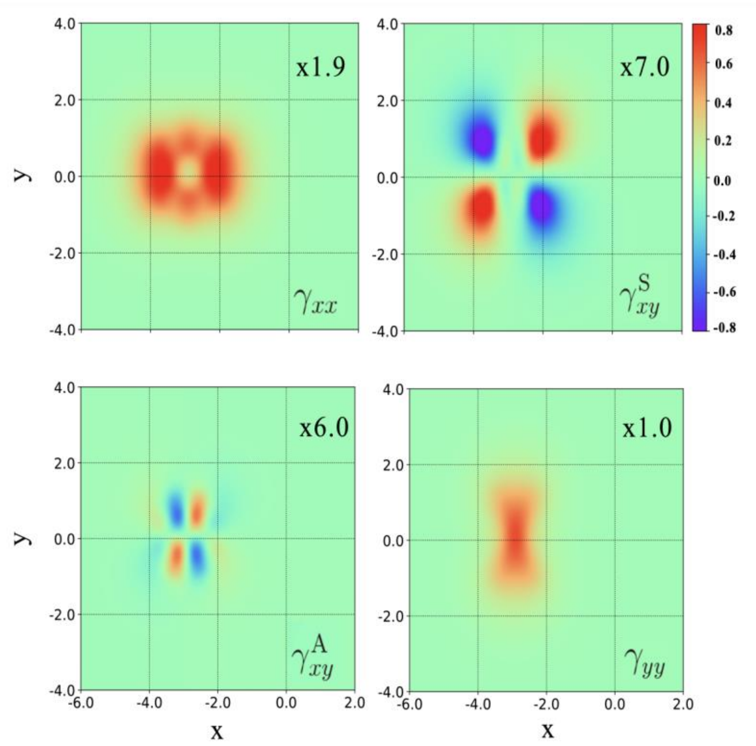
a: without light



b: light with lower frequency



c: light with higher frequency



[1] Mosallanejad, Vahid, Jingqi Chen, and Wenjie Dou. *arXiv preprint arXiv:2206.07894* (2022).

Conclusion

1. Light-matter interaction affects the distribution of friction.
2. Light-matter interaction affects the dynamics process.
3. Light-matter interaction introduces a Lorenz-like force.

Outlook (in process)

1. How bias affects the Lorenz-like force (the non-equilibrium case).
2. How this Lorenz-like force affects the dynamics (we need to reduce the calculation cost, like machine-learning).

Coauthors: Dr. Vahid Mosallanejad & Prof. Wenjie Dou

Our website: https://dougroup.westlake.edu.cn/

Thanks for listening!