Diagrammatic Quantum Monte Carlo toward The Calculation of Transport Properties in Disordered Semiconductors

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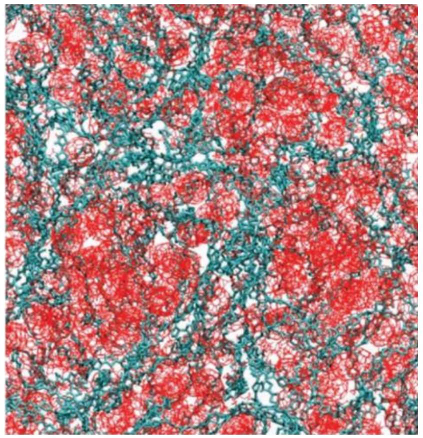
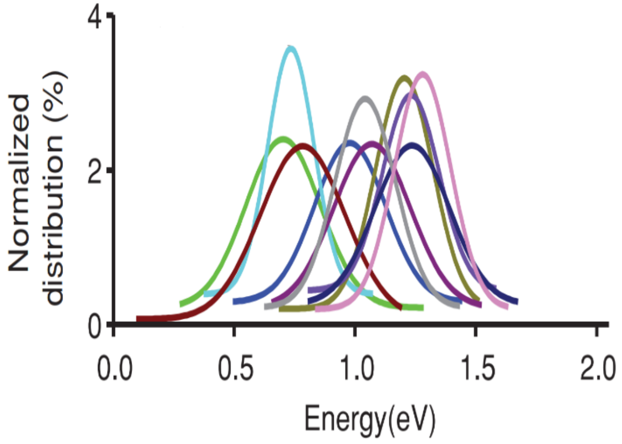
4/13/2022

Microscopic disorders in materials

Structural disorders induce certain variations in the electronic properties of materials

Static disorder



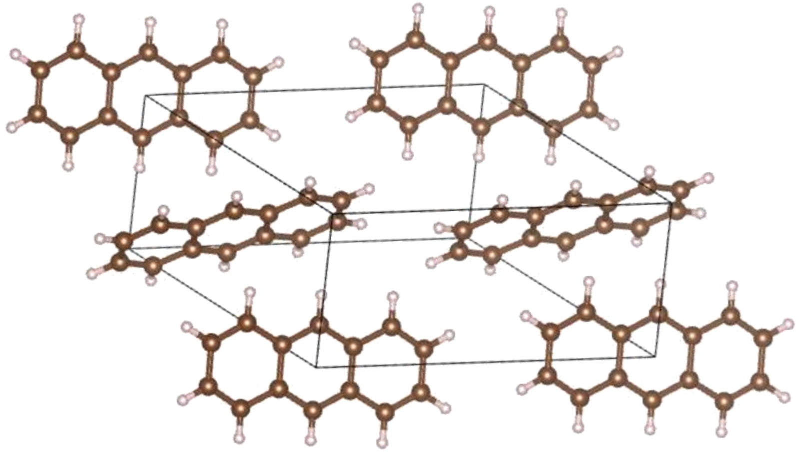


Zheng et al. Adv. Energy Mater. 2019, 9, 1803926.

- **From structural imperfections like impurities, vacancies, …**
- **Do not obviously vary over a long time scale**
- **Random in nature**

Dynamic disorder

(Electron-phonon interaction)

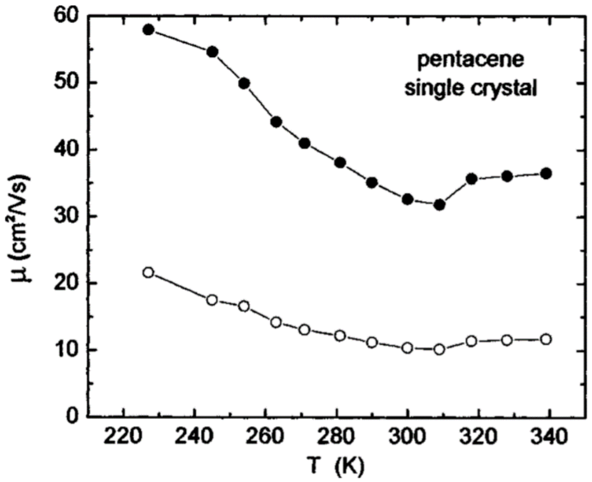


- **From the continuous motion of nuclei**
- **Dynamically vary at a short time scale** (fs to ps)

Local and nonlocal disorders refer to the variations in the electronic-state energies and electronic couplings, respectively

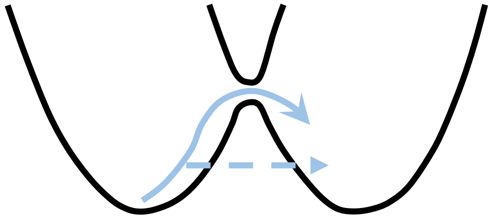
The influences of disorders on charge carrier transport

Band-like mobility in organic single crystal



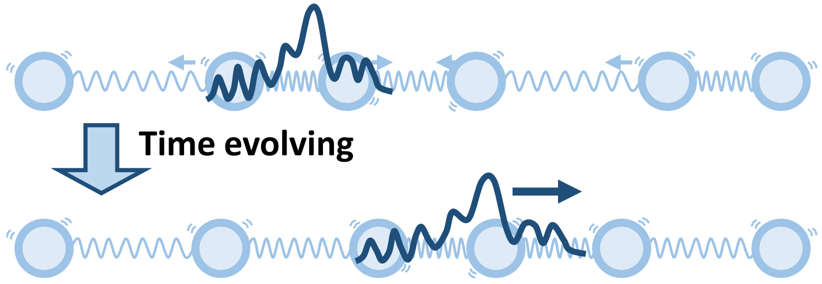
Jurchescu et al. Appl. Phys. Lett. 2004, 84, 3061.

Nuclear tunneling



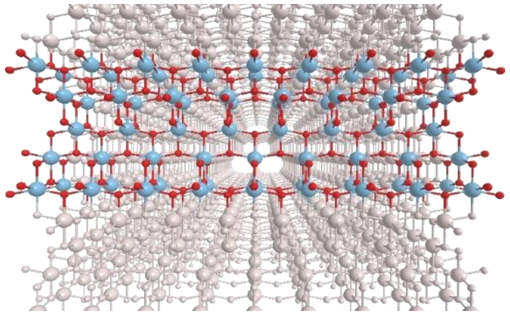
Nan et al. Phys. Rev. B 2009, 79, 115203.
Asadi et al. Nat. Commun. 2013, 4, 1710.

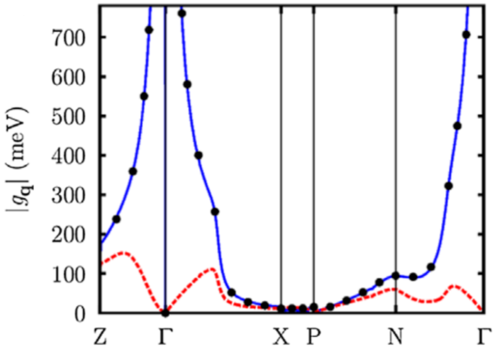
Transient localization



Troisi et al. Phys. Rev. Lett. 2006, 96, 086601.
Ciuchi et al. Phys. Rev. B 2011, 83, 081202.

Electron-phonon interaction in anatase TiO_2



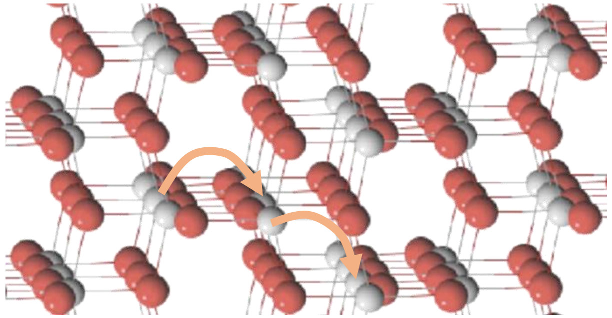


Verdi and Giustino, Phys. Rev. Lett. 2015, 115, 176401.

Boltzmann transport equation

$$\frac{\partial f_{n\boldsymbol{k}}(\boldsymbol{r},t)}{\partial t} = -\left[\nabla_{\boldsymbol{r}} f_{n\boldsymbol{k}}(\boldsymbol{r},t)\cdot \boldsymbol{v}_{n\boldsymbol{k}} + \hbar^{-1}\nabla_{\boldsymbol{k}} f_{n\boldsymbol{k}}(\boldsymbol{r},t)\cdot \boldsymbol{F}\right] + \mathcal{I}\left[f_{n\boldsymbol{k}}\right]$$

Hopping model for TiO_2



Deskin et al. Phys. Rev. B 2007, 75, 195212.
Spreafico et al. Phys. Chem. Chem. Phys. 2014, 16, 26144.

Quantum dynamics beyond perturbation approximation

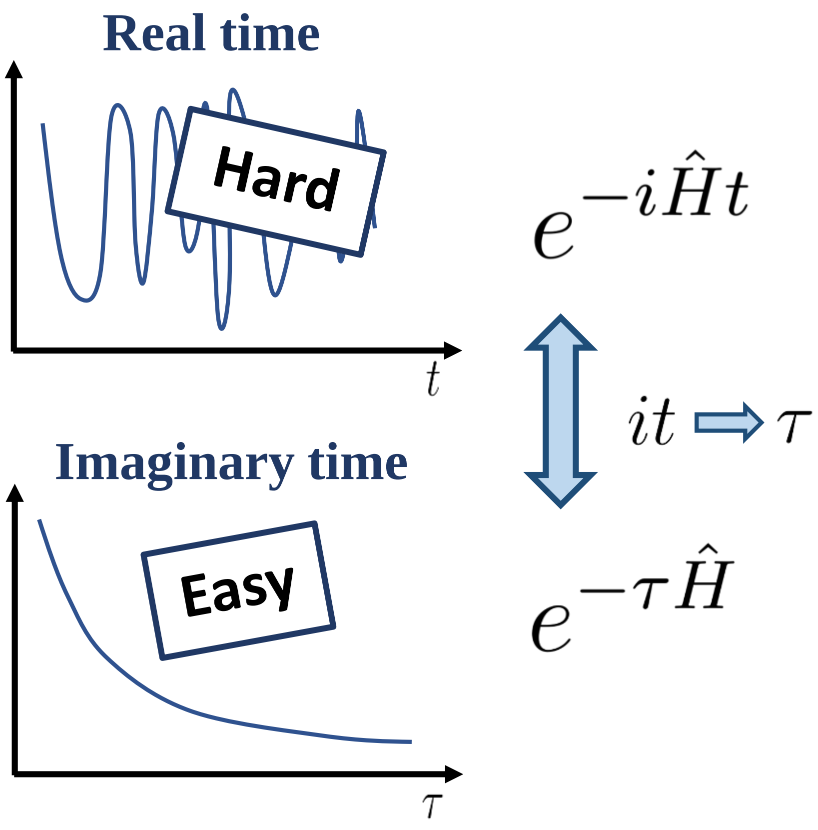
Currently available methods

Numerically exact:

ML-MCTDH, TD-DMRG, HEOM, QUAPI, hierarchy of SSE, …

Approximate:

Mixed quantum-classical approach, quantum master equation, perturbative SSE, …



Requirements for simulations in semiconductors

- ☐ **Treating various types of disorders nonperturbatively**
- ☐ **Free of finite-size effects and applicable to 3D systems**
- ☐ **Flexible to be combined with first-principles calculations**
- ☐ **Full quantum dynamics**

These requirements can be achieved much easier in imaginary time

Matsubara formalism and Diagrammatic QMC

Imaginary-time data

⇩ **Analytic continuation**

Real-time data

Current autocorrelation function

$$G_{\alpha\beta}(\tau) = \frac{1}{Z}\mathrm{Tr}\left\{e^{\tau\hat{H}}\hat{J}_\alpha e^{-\tau\hat{H}}\hat{J}_\beta e^{-\beta\hat{H}}\right\}$$

$$G_{\alpha\alpha}(\tau) = \frac{1}{\pi}\int_{-\infty}^{+\infty} \mathrm{d}\omega \frac{\omega e^{-\tau\omega}}{1-e^{-\beta\omega}}\underline{\sigma_\alpha(\omega)}$$

Optical conductivity

One-particle Green's function

$$C_{n\mathbf{k}}(\tau) = \frac{1}{Z}\langle \mathrm{vac}|\mathrm{Tr}_{ph}\{e^{\tau\hat{H}}\hat{c}_{n\mathbf{k}}e^{-\tau\hat{H}}\hat{c}^\dagger_{n\mathbf{k}}e^{-\beta\hat{H}}\}|\mathrm{vac}\rangle$$

$$\sum_n C_{n\mathbf{k}}(\tau) = \int_{-\infty}^{\infty} \mathrm{d}\omega \frac{e^{-\tau\omega}}{e^{-\beta\omega}+1}\underline{A(\mathbf{k},\omega)}$$

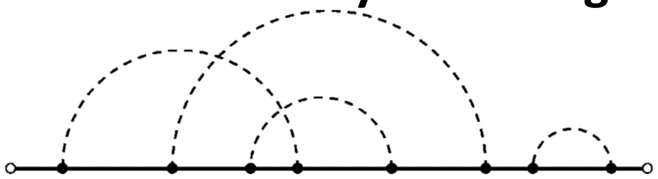
Spectral function

G. D. Mahan, Many-particle physics (Springer Science & Business Media, 2013)

Basic idea of DQMC

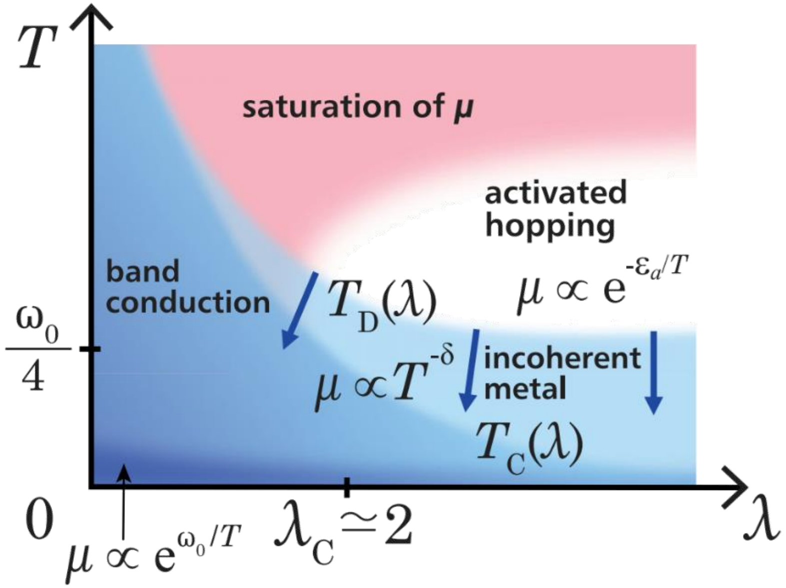
Summation of Feynman diagrams

$$e^{-\beta\hat{H}} =$$



Beard et al. Phys. Rev. Lett. 1996, 77, 5130.; Prokof'ev et al. JETP Lett. 1996, 64, 911; Prokof'ev et al. Sov. Phys. JETP, 1998, 87, 310; Mishchenko et al. Phys. Rev. B 2000, 62, 6317.

DQMC study on Holstein model



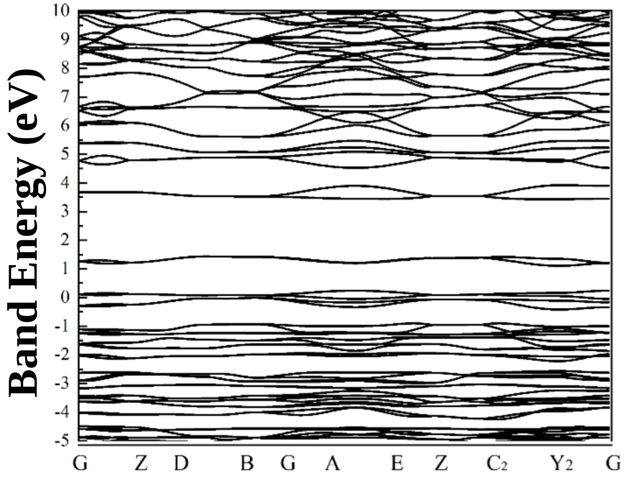
Mishchenko et al. Phys. Rev. Lett. 2015, 114, 146401.

Methodology of DQMC (dynamic disorder)

$$\hat{H} = \hat{H}_{el} + \hat{H}_{ph} + \hat{H}_{el-ph}$$

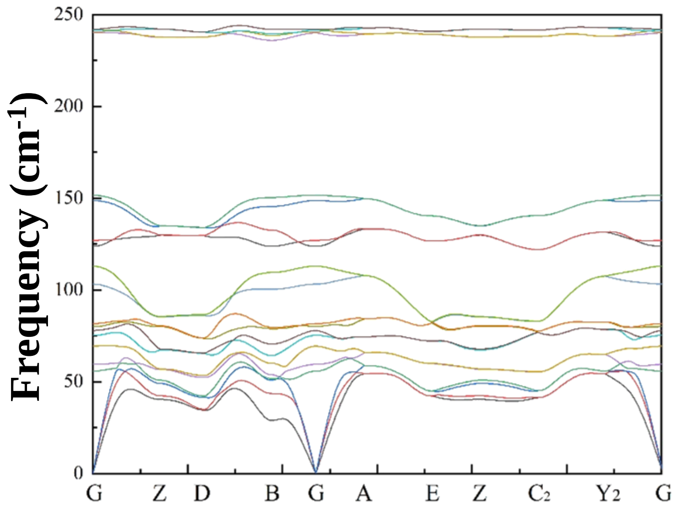
Electron

$$\hat{H}_{el} = \sum_{n\mathbf{k}} \underline{\epsilon_{n\mathbf{k}}} \hat{c}^{\dagger}_{n\mathbf{k}} \hat{c}_{n\mathbf{k}}$$



Phonon

$$\hat{H}_{ph} = \sum_{\nu\mathbf{q}} \underline{\omega_{\nu\mathbf{q}}} \left(\hat{b}^{\dagger}_{\nu\mathbf{q}} \hat{b}_{\nu\mathbf{q}} + \frac{1}{2} \right)$$

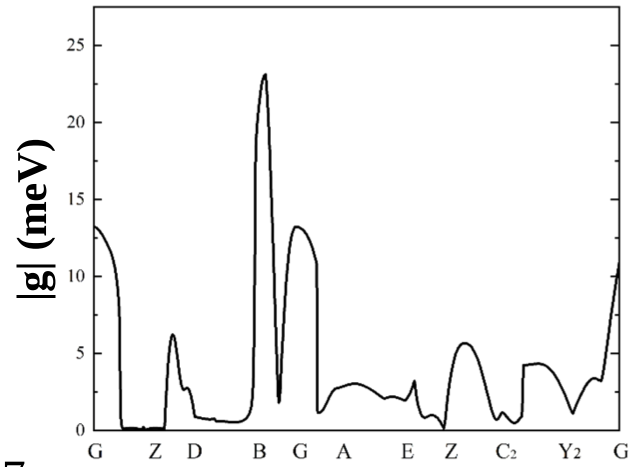


Electron-phonon interaction

$$\hat{H}_{el-ph} = \sum_{\nu\mathbf{q}} \hat{A}^{\dagger}_{\nu\mathbf{q}} \otimes \hat{B}_{\nu\mathbf{q}}$$

$$\hat{A}^{\dagger}_{\nu\mathbf{q}} = N^{-\frac{3}{2}} \sum_{nm\mathbf{k}} \underline{g_{nm\mathbf{k}\mathbf{q}\nu}} \hat{c}^{\dagger}_{n,\mathbf{k}+\mathbf{q}} \hat{c}_{m\mathbf{k}}$$

$$\hat{B}_{\nu\mathbf{q}} = \hat{b}_{\nu\mathbf{q}} + \hat{b}^{\dagger}_{\nu,-\mathbf{q}}$$



Parameters can be directly obtained from DFT and DFPT

Baroni et al., Rev. Mod. Phys., 73, 515, 2001; Giustino, Rev. Mod. Phys., 89, 015003, 2017.

Methodology of DQMC (dynamic disorder)

Electron

Phonon

Zero-order term: $\hat{H}_0 = \hat{H}_{el} + \hat{H}_{ph}$ **Interaction term:** $\hat{V} = \hat{H}_{el-ph} = \sum_{\nu\mathbf{q}} \hat{A}^{\dagger}_{\nu\mathbf{q}} \otimes \hat{B}_{\nu\mathbf{q}}$

Expanding Partition function into infinite series

$$Z = \mathrm{Tr}\{e^{-\beta\hat{H}}\} = \sum_{\kappa=0}^{\infty} \int_0^{\beta} \mathrm{d}\tau_{2\kappa} \int_0^{\tau_{2\kappa}} \mathrm{d}\tau_{2\kappa-1} \cdots \int_0^{\tau_2} \mathrm{d}\tau_1 \mathrm{Tr}\left\{e^{-\beta\hat{H}_0} \mathcal{T}_+ \hat{V}(\tau_{2\kappa}) \cdots \hat{V}(\tau_1)\right\}$$

$$\boxed{|n\mathbf{k}\rangle \equiv \hat{c}^{\dagger}_{n\mathbf{k}}|\mathrm{vac}\rangle}$$

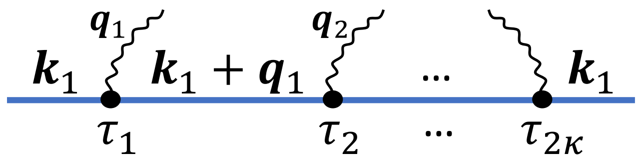
$$= \sum_{\kappa=0}^{\infty} \sum_{\nu_1\mathbf{q}_1} \cdots \sum_{\nu_{2\kappa}\mathbf{q}_{2\kappa}} \int_0^{\beta} \mathrm{d}\tau_{2\kappa} \cdots \int_0^{\tau_2} \mathrm{d}\tau_1 \mathrm{Tr}\left\{e^{-\beta\hat{H}_{el}} \mathcal{T}_+ \hat{A}^{\dagger}_{\nu_{2\kappa}\mathbf{q}_{2\kappa}}(\tau_{2\kappa}) \cdots \hat{A}^{\dagger}_{\nu_1\mathbf{q}_1}(\tau_1)\right\}$$

$$\times \mathrm{Tr}\left\{e^{-\beta\hat{H}_{ph}} \mathcal{T}_+ \hat{B}_{\nu_{2\kappa}\mathbf{q}_{2\kappa}}(\tau_{2\kappa}) \cdots \hat{B}_{\nu_1\mathbf{q}_1}(\tau_1)\right\}$$

$$\boxed{\hat{A}^{\dagger}_{\nu\mathbf{q}} = N^{-\frac{3}{2}} \sum_{nm\mathbf{k}} g_{nm\mathbf{k}\mathbf{q}\nu} \hat{c}^{\dagger}_{n,\mathbf{k}+\mathbf{q}} \hat{c}_{m\mathbf{k}}}$$

$$Z = \sum_{\kappa=0}^{\infty} \sum_{\mathbf{k}_1} \sum_{m_1\cdots m_{2\kappa}} \sum_{\nu_1\mathbf{q}_1} \cdots \sum_{\nu_{2\kappa}\mathbf{q}_{2\kappa}} \int_0^{\beta} \mathrm{d}\tau_{2\kappa} \cdots \int_0^{\tau_2} \mathrm{d}\tau_1 \underline{\delta_{\mathbf{q}_1+\cdots+\mathbf{q}_{2\kappa},\mathbf{0}}} N^{-3\kappa} \left[\prod_{l=1}^{2\kappa} g_{m_{l+1}m_l\mathbf{k}_l\mathbf{q}_l\nu_l}\right]$$

$$\times \exp\left\{-\sum_{l=1}^{2\kappa} (\tau_l - \tau_{l-1})\epsilon_{m_l\mathbf{k}_l}\right\} \underline{Z_{ph}\langle \mathcal{T}_+ \hat{B}_{\nu_{2\kappa}\mathbf{q}_{2\kappa}}(\tau_{2\kappa}) \cdots \hat{B}_{\nu_1\mathbf{q}_1}(\tau_1)\rangle_{ph}}$$



Methodology of DQMC (dynamic disorder)

Wick's theorem: **Thermal average over multiple products of phonon coordinates = All possible pairwise combinations of binary thermal averages**

$$\langle \mathcal{T}_+ \hat{B}_{\nu_1 \mathbf{q}_1}(\tau_1) \cdots \hat{B}_{\nu_{2\kappa} \mathbf{q}_{2\kappa}}(\tau_{2\kappa}) \rangle_{ph}$$
$$= \sum_{\substack{\text{all possible} \\ \text{pairings}}} \langle \mathcal{T}_+ \hat{B}_{\nu_{i_1} \mathbf{q}_{i_1}}(\tau_{i_1}) \hat{B}_{\nu_{i_2} \mathbf{q}_{i_2}}(\tau_{i_2}) \rangle_{ph} \times \cdots$$
$$\times \langle \mathcal{T}_+ \hat{B}_{\nu_{i_{2\kappa-1}} \mathbf{q}_{i_{2\kappa-1}}}(\tau_{i_{2\kappa-1}}) \hat{B}_{\nu_{i_{2\kappa}} \mathbf{q}_{i_{2\kappa}}}(\tau_{i_{2\kappa}}) \rangle_{ph}$$

Binary thermal average:

$$\langle \mathcal{T}_+ \hat{B}_{\nu \mathbf{q}}(\tau) \hat{B}_{\nu' \mathbf{q}'}(\tau') \rangle_{ph} = \delta_{\nu\nu'} \delta_{\mathbf{q},-\mathbf{q}'} \alpha_{\nu \mathbf{q}}(|\tau - \tau'|)$$

Free phonon propagator:

$$\alpha_{\nu \mathbf{q}}(\tau) = n_{\nu \mathbf{q}} e^{\tau \omega_{\nu \mathbf{q}}} + (n_{\nu \mathbf{q}} + 1) e^{-\tau \omega_{\nu \mathbf{q}}}$$

$$Z = \sum_{\kappa=0}^{\infty} \sum_{\mathbf{k}_1} \sum_{m_1 \cdots m_{2\kappa}} \sum_{\nu_1 \mathbf{q}_1} \cdots \sum_{\nu_{2\kappa} \mathbf{q}_{2\kappa}} \int_0^{\beta} \mathrm{d}\tau_{2\kappa} \cdots \int_0^{\tau_2} \mathrm{d}\tau_1 N^{-3\kappa} Z_{ph} \left[\prod_{l=1}^{2\kappa} g_{m_{l+1} m_l \mathbf{k}_l \mathbf{q}_l \nu_l} \right] \exp\left\{ -\sum_{l=1}^{2\kappa} (\tau_l - \tau_{l-1}) \epsilon_{m_l \mathbf{k}_l} \right\}$$
$$\times \sum_{\substack{\text{all possible} \\ \text{pairings}}} \delta_{\nu_{i_1} \nu_{i_2}} \delta_{\mathbf{q}_{i_1}, -\mathbf{q}_{i_2}} \cdots \delta_{\nu_{i_{2\kappa-1}} \nu_{i_{2\kappa}}} \delta_{\mathbf{q}_{i_{2\kappa-1}}, -\mathbf{q}_{i_{2\kappa}}} \alpha_{\nu_{i_1} \mathbf{q}_{i_1}}(\tau_{i_1} - \tau_{i_2}) \cdots \alpha_{\nu_{i_{2\kappa-1}} \mathbf{q}_{i_{2\kappa-1}}}(\tau_{i_{2\kappa-1}} - \tau_{i_{2\kappa}})$$

Wang and Zhao, arXiv:2203.12480, 2022.

Methodology of DQMC (dynamic disorder)

$$Z=\sum_{\kappa=0}^{\infty}\sum_{\mathbf{k}_1}\sum_{m_1\cdots m_{2\kappa}}\sum_{\nu_1\mathbf{q}_1}\cdots\sum_{\nu_{2\kappa}\mathbf{q}_{2\kappa}}\int_0^{\beta}\mathrm{d}\tau_{2\kappa}\cdots\int_0^{\tau_2}\mathrm{d}\tau_1 N^{-3\kappa}Z_{ph}\left[\prod_{l=1}^{2\kappa}g_{m_{l+1}m_l\mathbf{k}_l\mathbf{q}_l\nu_l}\right]\exp\left\{-\sum_{l=1}^{2\kappa}(\tau_l-\tau_{l-1})\epsilon_{m_l\mathbf{k}_l}\right\}$$
$$\times\sum_{\substack{\text{all possible}\\ \text{pairings}}}\delta_{\nu_{i_1}\nu_{i_2}}\delta_{\mathbf{q}_{i_1},-\mathbf{q}_{i_2}}\cdots\delta_{\nu_{i_{2\kappa-1}}\nu_{i_{2\kappa}}}\delta_{\mathbf{q}_{i_{2\kappa-1}},-\mathbf{q}_{i_{2\kappa}}}\alpha_{\nu_{i_1}\mathbf{q}_{i_1}}(\tau_{i_1}-\tau_{i_2})\cdots\alpha_{\nu_{i_{2\kappa-1}}\mathbf{q}_{i_{2\kappa-1}}}(\tau_{i_{2\kappa-1}}-\tau_{i_{2\kappa}})$$

Recast into a form suitable for the Monte Carlo implementation: $Z=\sum_{\kappa=0}^{\infty}\sum_{\mathbf{x}_\kappa}\mathcal{Z}(\mathbf{x}_\kappa)$

Monte Carlo configuration space

$$\mathbf{x}_\kappa\equiv(\mathbf{k}_1;m_1,\cdots,m_{2\kappa};\nu_{i_1},\mathbf{q}_{i_1},\tau_{i_1},\tau_{i_2};\nu_{i_3},\mathbf{q}_{i_3},\tau_{i_3},\tau_{i_4};\cdots;\nu_{i_{2\kappa-1}},\mathbf{q}_{i_{2\kappa-1}},\tau_{i_{2\kappa-1}},\tau_{i_{2\kappa}})$$

Summation over MC "grids"

$$\sum_{\mathbf{x}_\kappa}\equiv\sum_{\mathbf{k}_1}\sum_{m_1\cdots m_{2\kappa}}\int_0^{\beta}\int_0^{\tau_{2\kappa}}\cdots\int_0^{\tau_2}\sum_{\substack{\text{all possible}\\ \text{pairings}}}\sum_{\nu_{i_1}\mathbf{q}_{i_1}}\sum_{\nu_{i_3}\mathbf{q}_{i_3}}\cdots\sum_{\nu_{i_{2\kappa-1}}\mathbf{q}_{i_{2\kappa-1}}}$$

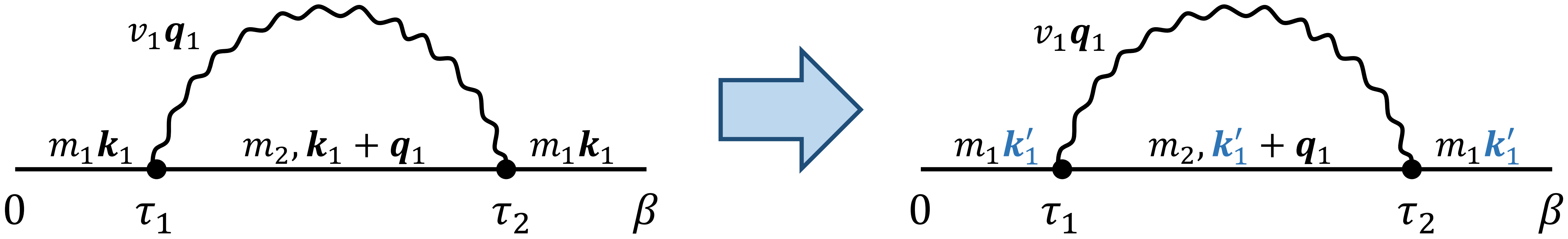
Concrete expression at each MC "grid"

$$\mathcal{Z}(\mathbf{x}_\kappa)=\underline{N^{-3\kappa}Z_{ph}\mathrm{d}\tau_1\cdots\mathrm{d}\tau_{2\kappa}}\left[\prod_{l=1}^{2\kappa}g_{m_{l+1}m_l\mathbf{k}_l\mathbf{q}_l\nu_l}\right]\exp\left\{-\sum_{l=1}^{2\kappa}(\tau_l-\tau_{l-1})\epsilon_{m_l\mathbf{k}_l}\right\}$$
$$\times\alpha_{\nu_{i_1}\mathbf{q}_{i_1}}(\tau_{i_1}-\tau_{i_2})\cdots\alpha_{\nu_{i_{2\kappa-1}}\mathbf{q}_{i_{2\kappa-1}}}(\tau_{i_{2\kappa-1}}-\tau_{i_{2\kappa}})$$

<u>Wang</u> and Zhao, arXiv:2203.12480, 2022.

Methodology of DQMC (dynamic disorder)

Basic updates for MC configurations: Change the end electronic crystal momentum



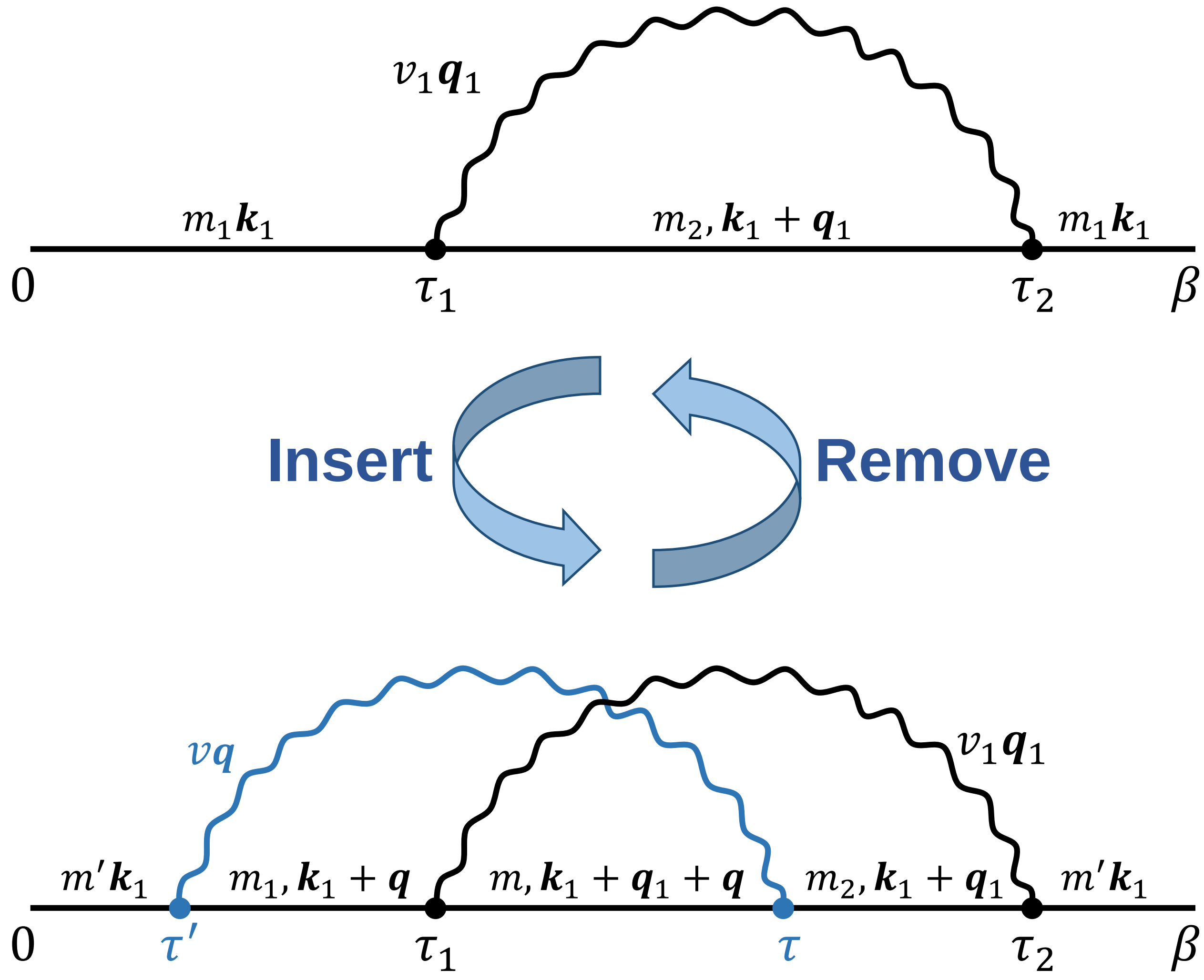
Acceptance ratio for changing $\boldsymbol{k}_1$:

$$R = e^{-(\beta-\tau_2+\tau_1)(\epsilon_{m_1\mathbf{k}_1'}-\epsilon_{m_1\mathbf{k}_1})-(\tau_2-\tau_1)(\epsilon_{m_2,\mathbf{k}_1'+\mathbf{q}_1}-\epsilon_{m_2,\mathbf{k}_1+\mathbf{q}_1})} \times \left| \frac{g_{m_2 m_1 \mathbf{k}_1' \mathbf{q}_1 \nu_1} g_{m_1 m_2, \mathbf{k}_1'+\mathbf{q}_1, -\mathbf{q}_1, \nu_1}}{g_{m_2 m_1 \mathbf{k}_1 \mathbf{q}_1 \nu_1} g_{m_1 m_2, \mathbf{k}_1+\mathbf{q}_1, -\mathbf{q}_1, \nu_1}} \right|$$

The calculation of the acceptance ratio is very simple and fast

Methodology of DQMC (dynamic disorder)

Basic updates for MC configurations: Insert or remove an interaction vertex pair



Acceptance ratio for inserting:

$$R = \frac{\beta^2 N_b^2 N_{ph}^2}{6} \frac{|g_1' g_2' g_3' g_4'|}{|g_1 g_2|} \times e^{-\Delta(\beta\epsilon)} \alpha_{\nu\mathbf{q}}(\tau - \tau')$$

N_b is the number of electronic bands

N_{ph} is the number of phonon branches

The computational cost is independent of the total number of unit cells N.

Methodology of DQMC (static disorder)

How to express the static disorder in reciprocal space?

One-dimensional toy model

Static disorder in real space

$$\hat{H}_{sd} = \sum_n \gamma_n \hat{c}_n^\dagger \hat{c}_n$$

Gaussian random variables

$$\langle \gamma_1^2 \rangle = \langle \gamma_2^2 \rangle = \cdots = \langle \gamma_N^2 \rangle = \Delta^2$$

Translational invariant

Transform to reciprocal space

$$\hat{H}_{sd} = N^{-\frac{1}{2}} \sum_{kq} \left(N^{-\frac{1}{2}} \sum_n \gamma_n e^{-iqr_n} \right) \hat{c}_{k+q}^\dagger \hat{c}_k$$

$$\boxed{\begin{cases} \hat{c}_{k+q}^\dagger = N^{-\frac{1}{2}} \sum_n e^{i(k+q)r_n} \hat{c}_n^\dagger \\ \hat{c}_k = N^{-\frac{1}{2}} \sum_n e^{-ikr_n} \hat{c}_n \end{cases}}$$

Define: $D_q = \frac{1}{\Delta} N^{-\frac{1}{2}} \sum_n \gamma_n e^{-iqr_n}$

$$\begin{cases} D_q^* = D_{-q} \\ \langle D_q D_{q'} \rangle = \delta_{q,-q'} \end{cases}$$

Decoupled

$\{D_q\}$ **constitute a complete basis set and is equivalent to** $\{\gamma_n\}$

Reciprocal-space expression:

$$\hat{H}_{sd} = N^{-\frac{1}{2}} \Delta \sum_{kq} D_q \hat{c}_{k+q}^\dagger \hat{c}_k$$

Methodology of DQMC (static disorder)

General expressions for static disorder

Static disorder in real space

$$\hat{H}_{sd} = \sum_{\bar{\mu}} \sum_{\mathbf{R}} \gamma_{\bar{\mu}\mathbf{R}} \left(\hat{c}^{\dagger}_{\bar{n}\mathbf{R}} \hat{c}_{\bar{m},\mathbf{R}+\bar{\mathbf{R}}_e} + \hat{c}^{\dagger}_{\bar{m},\mathbf{R}+\bar{\mathbf{R}}_e} \hat{c}_{\bar{n}\mathbf{R}} \right)$$

$$\boxed{\bar{\mu} \equiv (\bar{n}, \bar{m}, \bar{\mathbf{R}}_e)}$$

Covariance property: $\langle \gamma_{\bar{\mu}\mathbf{R}} \gamma_{\bar{\mu}',\mathbf{R}+\Delta\mathbf{R}} \rangle = \underline{\Gamma_{\bar{\mu}\bar{\mu}'\Delta\mathbf{R}}}$

Static disorder in reciprocal space

$$\hat{H}_{sd} = \sum_{\mu\mathbf{q}} D_{\mu\mathbf{q}} \hat{C}^{\dagger}_{\mu\mathbf{q}}$$

$$\hat{C}^{\dagger}_{\mu\mathbf{q}} = N^{-\frac{3}{2}} \sum_{nm\mathbf{k}} f_{nm\mathbf{k}\mathbf{q}\mu} \hat{c}^{\dagger}_{n,\mathbf{k}+\mathbf{q}} \hat{c}_{m\mathbf{k}}$$

$$\begin{cases} (D_{\mu\mathbf{q}})^* = D_{\mu,-\mathbf{q}} \\ \langle D_{\mu\mathbf{q}} \rangle = 0 \\ \langle D_{\mu\mathbf{q}} D_{\mu'\mathbf{q}'} \rangle = \delta_{\mu\mu'} \delta_{\mathbf{q},-\mathbf{q}'} \end{cases}$$

$$f_{nm\mathbf{k}\mathbf{q}\mu} = \underline{\sqrt{\lambda_{\mu\mathbf{q}}}} \sum_{\bar{\mu}} \underline{(\hat{\Phi}^{\dagger}_{\mathbf{q}})_{\bar{\mu}\mu}} \left[e^{i\mathbf{k}\cdot\bar{\mathbf{R}}_e} (\hat{U}_{\mathbf{k}+\mathbf{q}})_{n\bar{n}} (\hat{U}^{\dagger}_{\mathbf{k}})_{\bar{m}m} + e^{-i(\mathbf{k}+\mathbf{q})\cdot\bar{\mathbf{R}}_e} (\hat{U}_{\mathbf{k}+\mathbf{q}})_{n\bar{m}} (\hat{U}^{\dagger}_{\mathbf{k}})_{\bar{n}m} \right]$$

$$\hat{H}_{el-ph} = \sum_{\nu\mathbf{q}} \hat{A}^{\dagger}_{\nu\mathbf{q}} \otimes \hat{B}_{\nu\mathbf{q}}$$

$$\hat{A}^{\dagger}_{\nu\mathbf{q}} = N^{-\frac{3}{2}} \sum_{nm\mathbf{k}} g_{nm\mathbf{k}\mathbf{q}\nu} \hat{c}^{\dagger}_{n,\mathbf{k}+\mathbf{q}} \hat{c}_{m\mathbf{k}}$$

$\hat{H}_{sd}$ in reciprocal space resembles $\hat{H}_{el-ph}$ very much

Wang and Zhao, arXiv:2203.12480, 2022.

Methodology of DQMC (static disorder)

$$\hat{H} = \hat{H}_{el} + \hat{H}_{sd}$$

Zero-order term: $\hat{H}_0 = \hat{H}_{el}$

Interaction term: $\hat{V} = \hat{H}_{sd} = \sum_{\mu\mathbf{q}} D_{\mu\mathbf{q}} \hat{C}^{\dagger}_{\mu\mathbf{q}}$

Expanding Partition function into infinite series

$$Z = \sum_{\kappa=0}^{\infty} \sum_{\mathbf{k}_1} \sum_{m_1 \cdots m_{2\kappa}} \sum_{\mu_1 \mathbf{q}_1} \cdots \sum_{\mu_{2\kappa} \mathbf{q}_{2\kappa}} \int_0^{\beta} \mathrm{d}\tau_{2\kappa} \cdots \int_0^{\tau_2} \mathrm{d}\tau_1 \underline{\delta_{\mathbf{q}_1 + \cdots + \mathbf{q}_{2\kappa}, \mathbf{0}}} N^{-3\kappa} \left[\prod_{l=1}^{2\kappa} f_{m_{l+1} m_l \mathbf{k}_l \mathbf{q}_l \mu_l} \right]$$

$$\times \exp\left\{ -\sum_{l=1}^{2\kappa} (\tau_l - \tau_{l-1}) \epsilon_{m_l \mathbf{k}_l} \right\} \underline{D_{\mu_{2\kappa} \mathbf{q}_{2\kappa}} \cdots D_{\mu_1 \mathbf{q}_1}}$$

$g_{m_{l+1} m_l \mathbf{k}_l \mathbf{q}_l \nu_l}$

$\langle \mathcal{T}_+ \hat{B}_{\nu_1 \mathbf{q}_1}(\tau_1) \cdots \hat{B}_{\nu_{2\kappa} \mathbf{q}_{2\kappa}}(\tau_{2\kappa}) \rangle_{ph}$

This expression is analytic and **may be suitable** for the Monte Carlo implementation …

But most of the terms cancel out with each other to give a zero average due to the random nature of $D_{\mu q}$.

Must find a way to pick out the terms that really contribute to Z …

Wang and Zhao, arXiv:2203.12480, 2022.

Methodology of DQMC (static disorder)

Generalized Wick's theorem for static disorder

(Proven by the central limit theorem)

$$\mathcal{Q}_{2\kappa,\mathbf{k}_0} = N^{-3\kappa}\sum_{\mu_1\mathbf{q}_1}\cdots\sum_{\mu_{2\kappa}\mathbf{q}_{2\kappa}}\delta_{\mathbf{q}_1+\cdots+\mathbf{q}_{2\kappa},\mathbf{k}_0}D_{\mu_1\mathbf{q}_1}\cdots D_{\mu_{2\kappa}\mathbf{q}_{2\kappa}}Y_{2\kappa}(\mu_1,\mathbf{q}_1;\cdots;\mu_{2\kappa},\mathbf{q}_{2\kappa})$$

$$=\delta_{\mathbf{k}_0,\mathbf{0}}N^{-3\kappa}\sum_{\mu_1\mathbf{q}_1}\cdots\sum_{\mu_\kappa\mathbf{q}_\kappa}|D_{\mu_1\mathbf{q}_1}|^2\cdots|D_{\mu_\kappa\mathbf{q}_\kappa}|^2\sum_{\substack{\text{all possible}\\ \text{pairings}}}Y_{2\kappa}(\text{paired})+\mathcal{O}(N^{-\frac{3}{2}})$$

Terms in which all $D_{\mu\boldsymbol{q}}$ are in pairwise combination with each other contribute to Z.

$$Z=\sum_{\kappa=0}^{\infty}\sum_{\mathbf{k}_1}\sum_{m_1\cdots m_{2\kappa}}\sum_{\mu_1\mathbf{q}_1}\cdots\sum_{\mu_{2\kappa}\mathbf{q}_{2\kappa}}\int_0^{\beta}\mathrm{d}\tau_{2\kappa}\cdots\int_0^{\tau_2}\mathrm{d}\tau_1 N^{-3\kappa}\left[\prod_{l=1}^{2\kappa}f_{m_{l+1}m_l\mathbf{k}_l\mathbf{q}_l\mu_l}\right]\exp\left\{-\sum_{l=1}^{2\kappa}(\tau_l-\tau_{l-1})\epsilon_{m_l\mathbf{k}_l}\right\}$$
$$\times\sum_{\substack{\text{all possible}\\ \text{pairings}}}\delta_{\mu_{i_1}\mu_{i_2}}\delta_{\mathbf{q}_{i_1},-\mathbf{q}_{i_2}}\cdots\delta_{\mu_{i_{2\kappa-1}}\mu_{i_{2\kappa}}}\delta_{\mathbf{q}_{i_{2\kappa-1}},-\mathbf{q}_{i_{2\kappa}}}|D_{\mu_{i_1}\mathbf{q}_{i_1}}|^2\cdots|D_{\mu_{i_{2\kappa-1}}\mathbf{q}_{i_{2\kappa-1}}}|^2+\underline{\mathcal{O}(N^{-\frac{3}{2}})}$$

Wang and Zhao, arXiv:2203.12480, 2022.

One-dimensional molecular chain model

Electron:

Electronic coupling

$$\hat{H}_{el} = \underline{V} \sum_n (\hat{c}^\dagger_{n+1}\hat{c}_n + \mathrm{H.c.})$$

Phonon:

Intramolecular phonon

Intermolecular phonon

$$\hat{H}_{ph} = \underline{\frac{1}{2}\sum_n\sum_j\left[\hat{P}^2_{nj} + \omega_j^2\hat{Q}^2_{nj}\right]} + \underline{\frac{1}{2}\sum_n \hat{p}_n^2}$$
$$\underline{+\frac{1}{2}\omega^2_{\mathrm{off}}\sum_n\left[(1-2b_0)\hat{x}_n^2 + b_0(\hat{x}_n - \hat{x}_{n+1})^2\right]}$$

Electron-phonon interaction:

Local el-ph

Nonlocal el-ph

$$\hat{H}_{el-ph} = \underline{\sum_n\sum_j g_j\hat{Q}_{nj}\hat{c}^\dagger_n\hat{c}_n} + \underline{\frac{g_{\mathrm{off}}}{\sqrt{2}}\sum_n(\hat{x}_n - \hat{x}_{n+1})(\hat{c}^\dagger_{n+1}\hat{c}_n + \mathrm{H.c.})}$$

Static disorder:

Local sd

Nonlocal sd

$$\hat{H}_{sd} = \underline{\sum_n \gamma_n\hat{c}^\dagger_n\hat{c}_n} + \underline{\sum_n\tilde{\gamma}_n(\hat{c}^\dagger_{n+1}\hat{c}_n + \mathrm{H.c.})}$$

Dynamic disorder strength

$$\lambda_{\mathrm{loc}} = \sum_j \frac{g_j^2}{2\omega_j^2}$$

$$\lambda_{\mathrm{non}} = \frac{g^2_{\mathrm{off}}}{2\omega^2_{\mathrm{off}}}$$

Static disorder strength

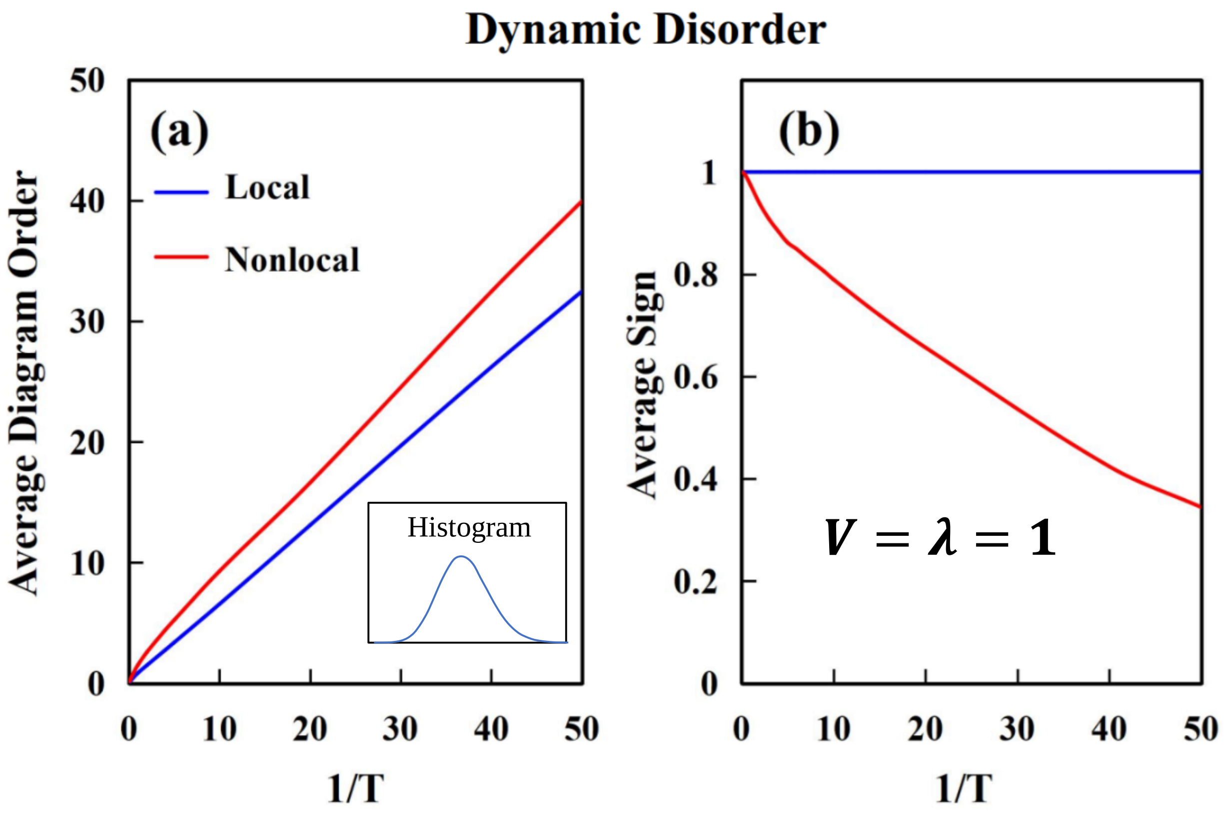
$$\langle\gamma_n^2\rangle = \Delta^2_{\mathrm{loc}}$$

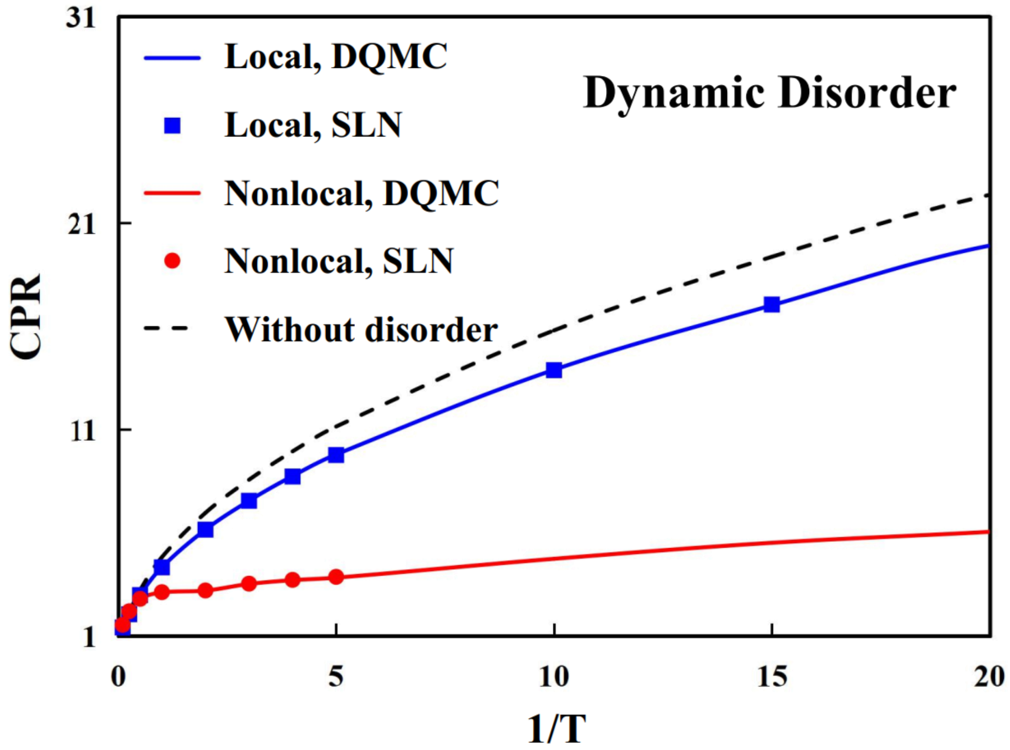
$$\langle\tilde{\gamma}_n^2\rangle = \Delta^2_{\mathrm{non}}$$

Results of DQMC are obtained in the thermodynamic limit $N \to \infty$

Wang and Zhao, arXiv:2203.12480, 2022.

One-dimensional molecular chain model





*SLN: Stochastic Liouville von Nemann equation

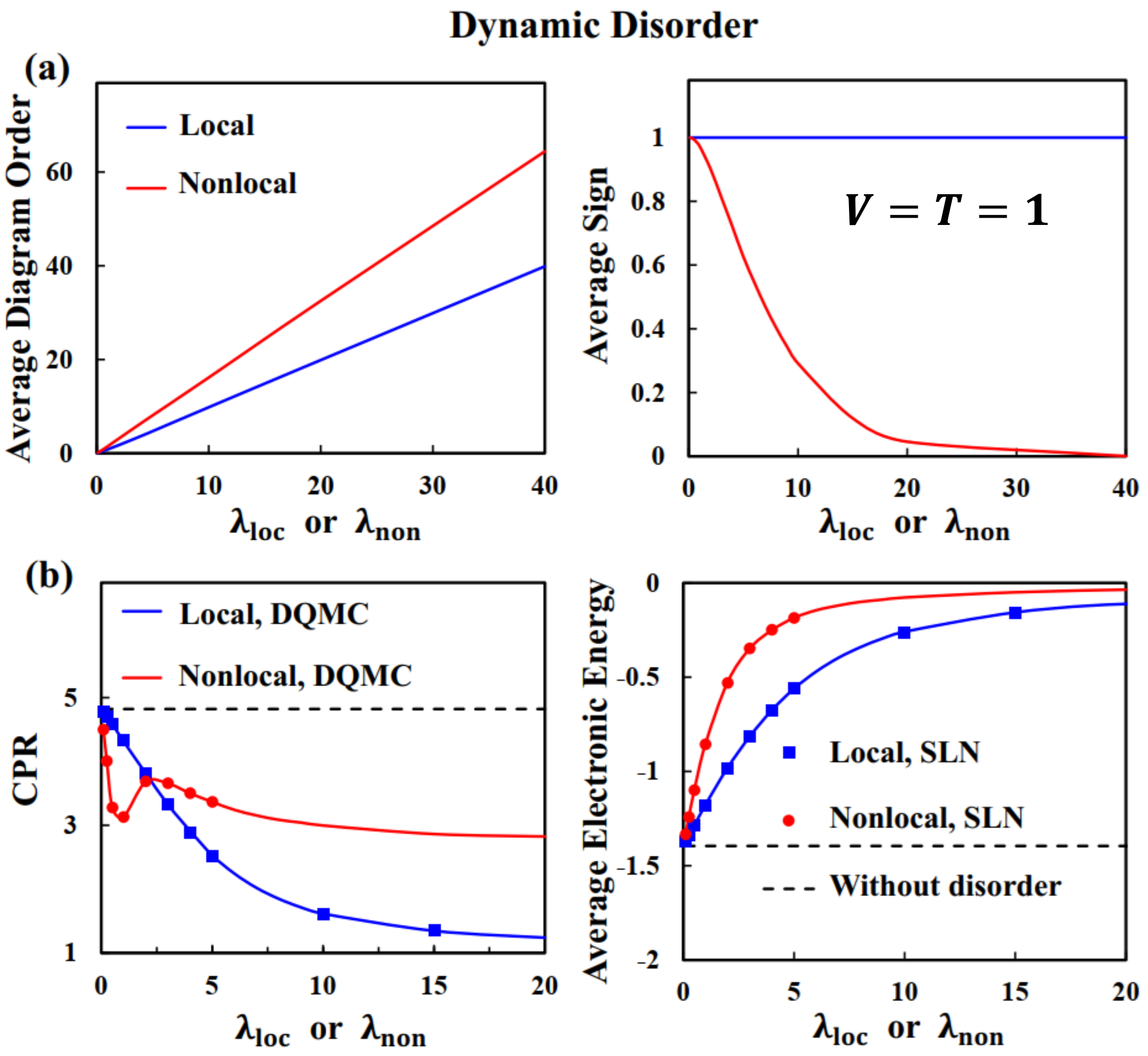
Average diagram order linearly depends on 1/T.

Negligible sign problem for nonlocal dynamic disorder.

Nonlocal dynamic disorder strongly suppresses the real-space coherence of the charge carrier.

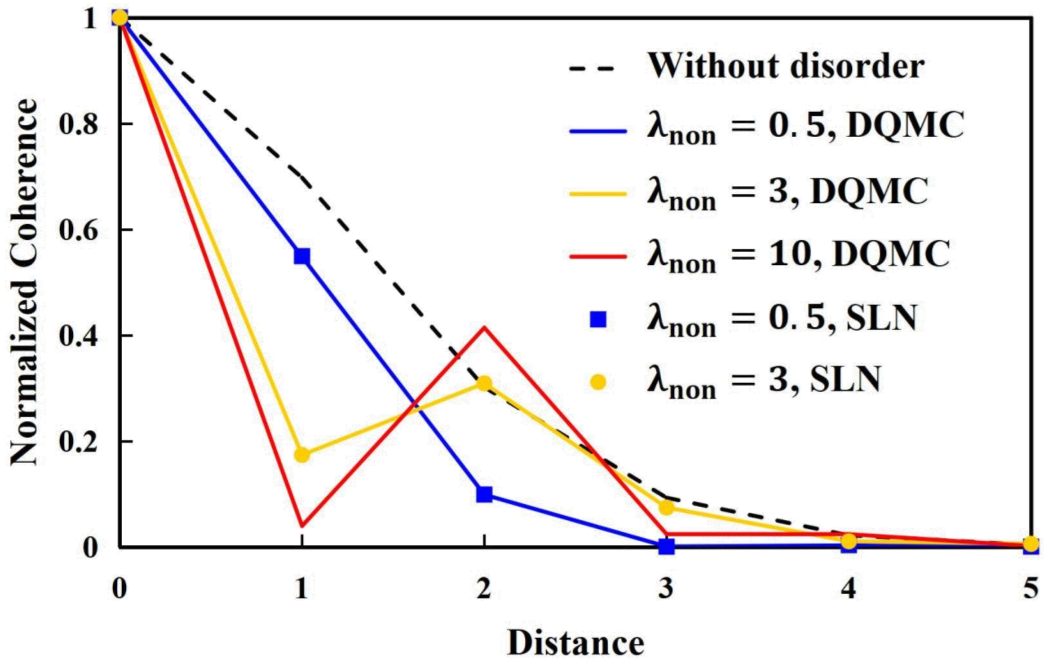
Wang and Zhao, arXiv:2203.12480, 2022.

One-dimensional molecular chain model



Average diagram order **linearly** depends on λ.

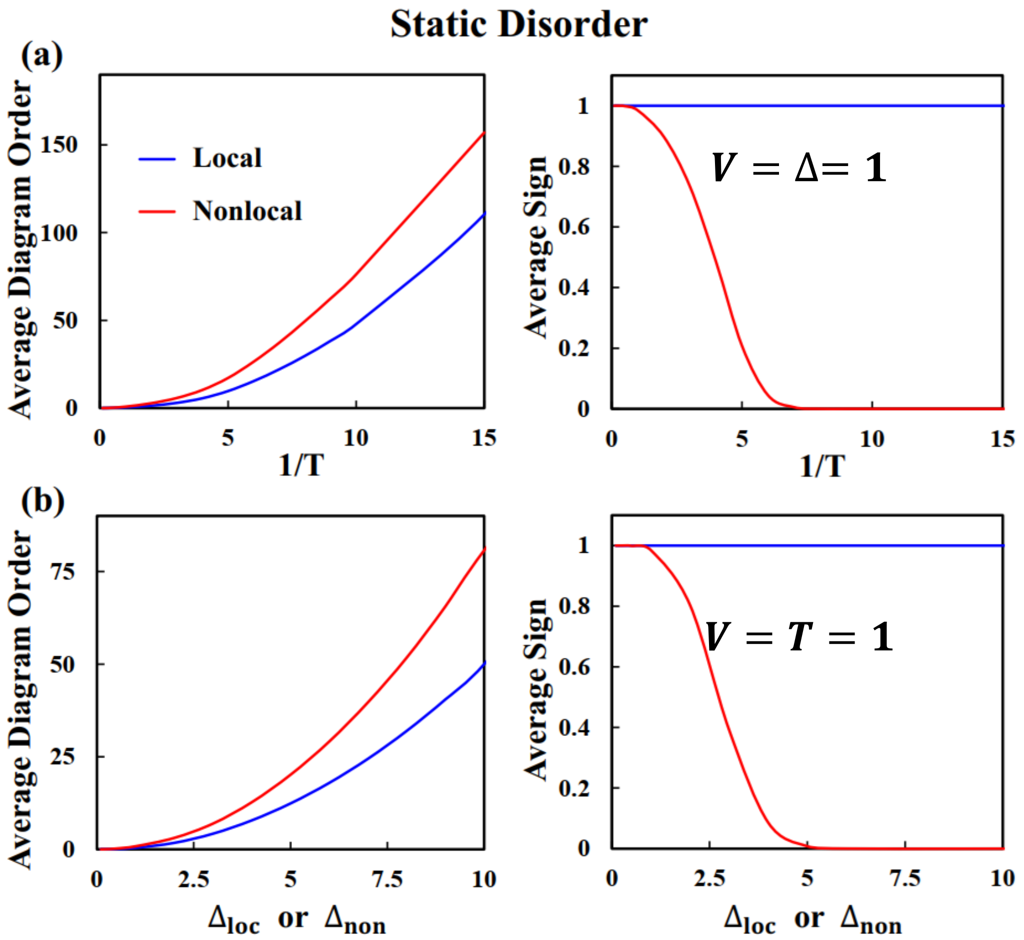
Significant sign problem for **very large** λ_{non} (>20).

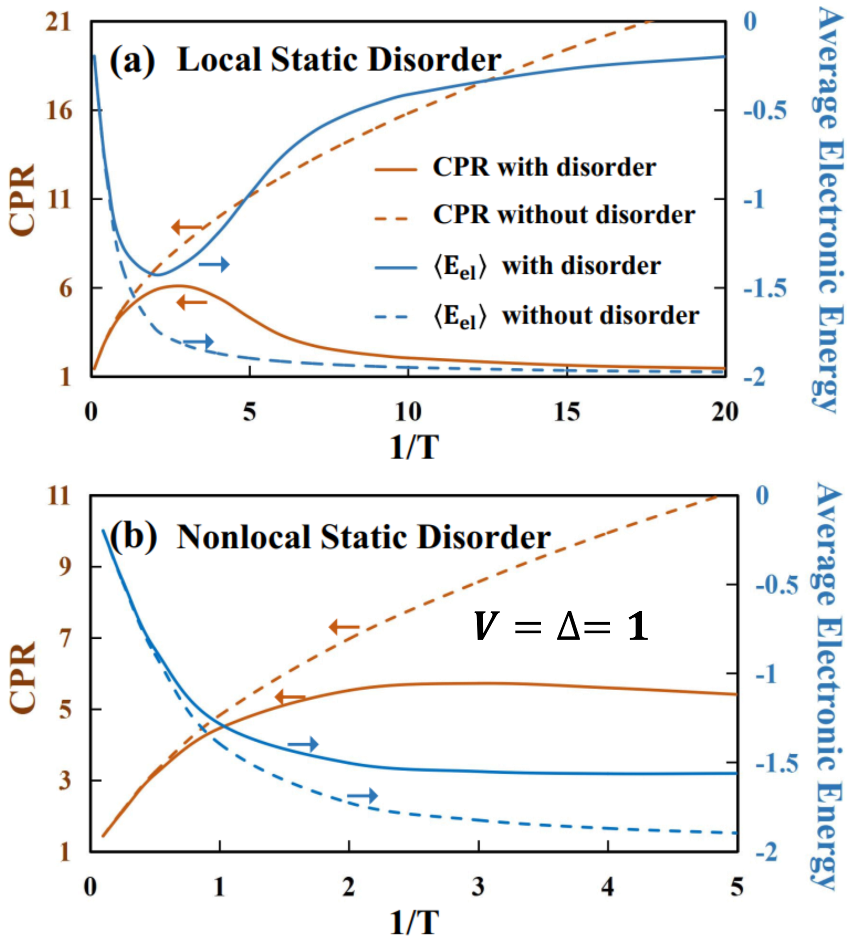


Dual role of nonlocal disorder on coherence

Wang and Zhao, arXiv:2203.12480, 2022.

One-dimensional molecular chain model





Average diagram order **quadratically** depends on 1/T or Δ.

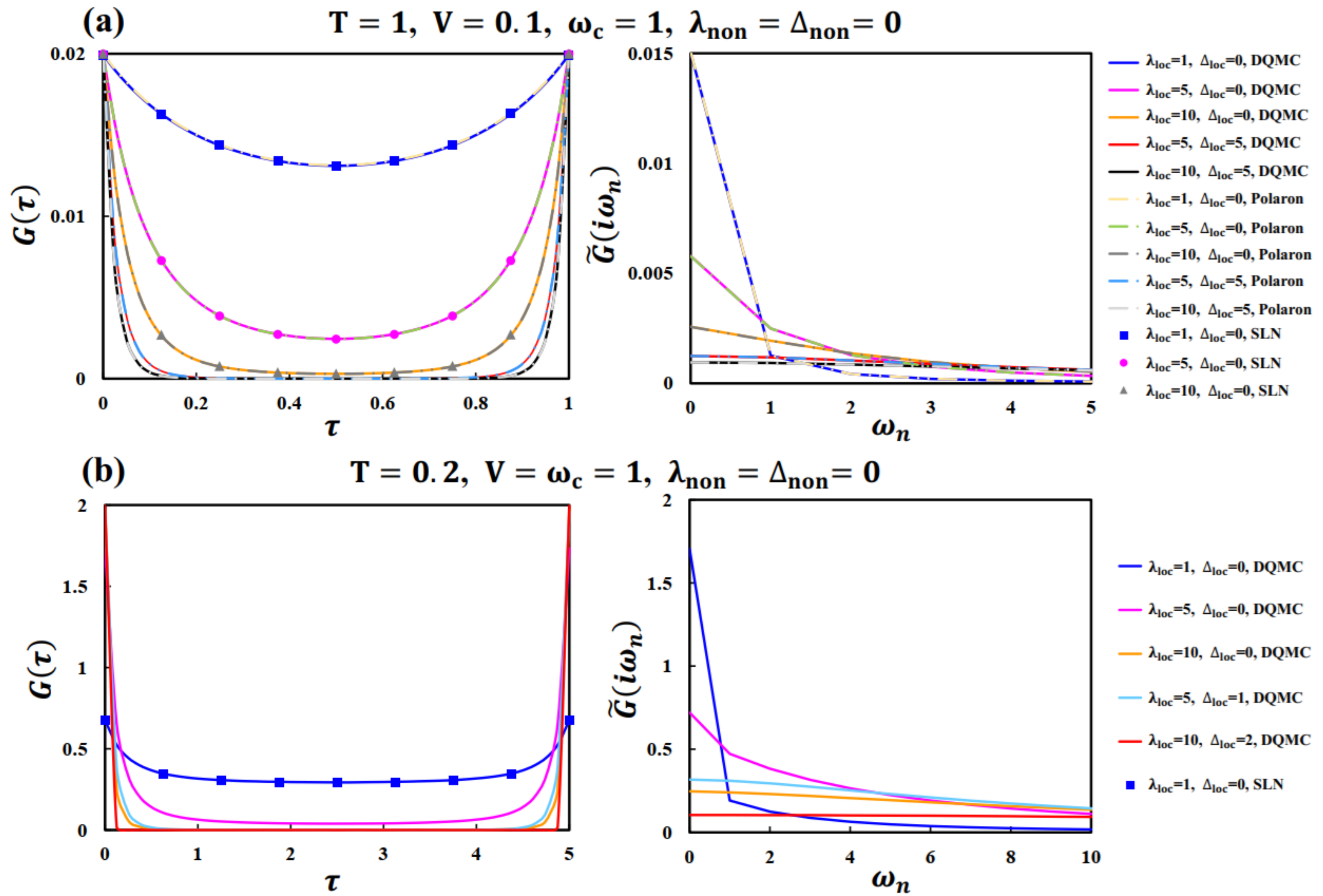
Sign problem is **more significant** for (nonlocal) static disorder

Influence of static disorder emerges at **low temperatures**

Wang and Zhao, arXiv:2203.12480, 2022.

One-dimensional molecular chain model

Imaginary-time (left) and imaginary-frequency (right) current autocorrelation functions



$$G_{\alpha\beta}(\tau) = \frac{1}{Z}\mathrm{Tr}\left\{e^{\tau\hat{H}}\hat{J}_\alpha e^{-\tau\hat{H}}\hat{J}_\beta e^{-\beta\hat{H}}\right\}$$

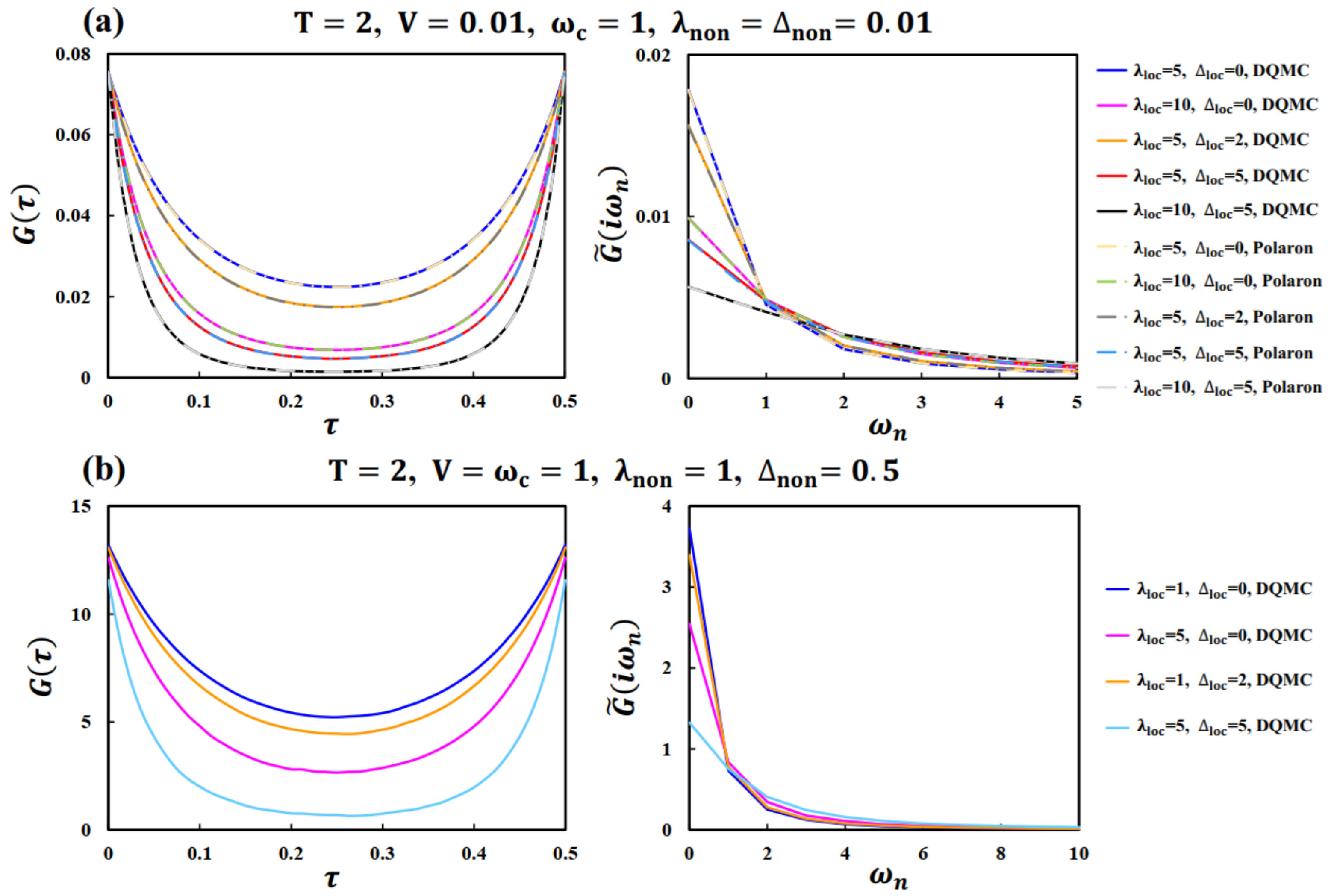
$$\widetilde{G}_{\alpha\beta}(i\omega_n) = \int_0^\beta \mathrm{d}\tau e^{i\omega_n\tau}G_{\alpha\beta}(\tau)$$

Converged DQMC results can be obtained in the regimes from weak to strong disorder strengths for a broad temperature range.

Wang and Zhao, arXiv:2203.12480, 2022.

One-dimensional molecular chain model

Imaginary-time (left) and imaginary-frequency (right) current autocorrelation functions



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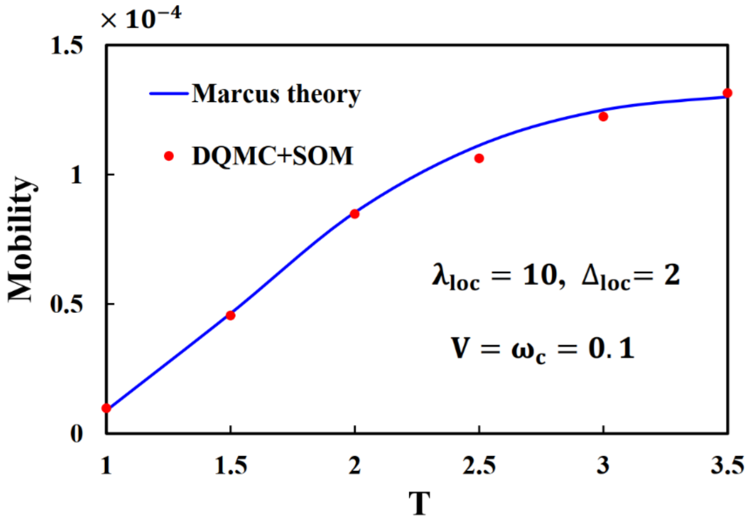
Converged DQMC results can be obtained in the regimes from weak to strong disorder strengths for a broad temperature range.

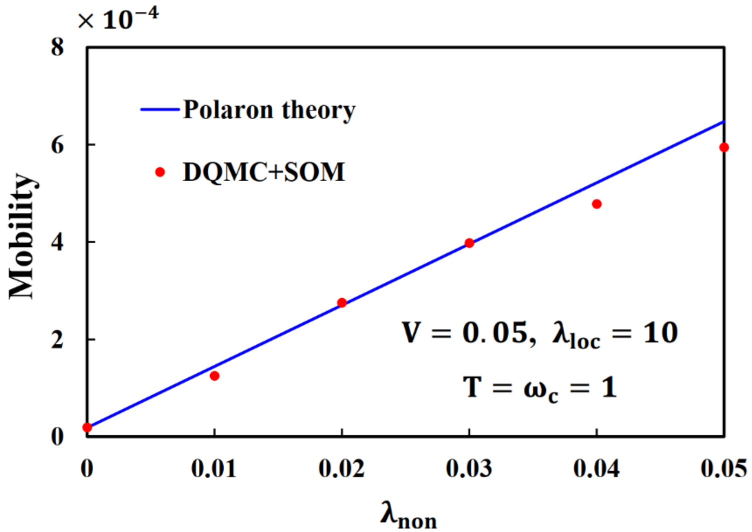
Wang and Zhao, arXiv:2203.12480, 2022.

One-dimensional molecular chain model

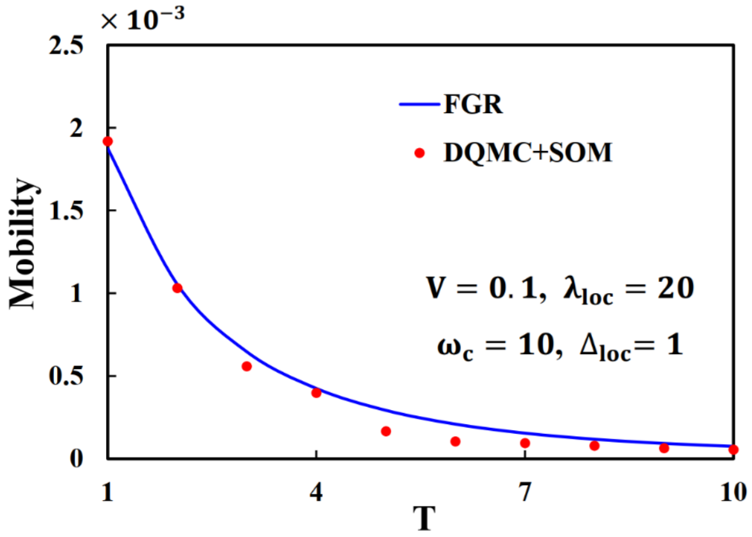
Thermally-activated hopping



Phonon-assisted transport



Nuclear tunneling



*SOM: stochastic optimization method for numerical analytic continuation

DQMC+SOM can give accurate mobilities in strong disorder regimes.

Significant errors may exist at some temperatures for the nuclear tunneling regime

Wang and Zhao, arXiv:2203.12480, 2022.

Summary

DQMC for the accurate and efficient calculations of charge carrier transport properties in disordered semiconductors.

- ✓ Treating various types of disorders nonperturbatively
- ✓ Free of finite-size effects and applicable to 3D systems
- ✓ Full quantum dynamics
- ✓ Flexible to be combined with first-principles calculations

Next step:

- ☐ Interpolation of DFT/DFPT parameters to infinitely large-sized systems
- ☐ Parameterization of the static disorder

Acknowledgements

Supervisors:

Prof. Yi Zhao

Prof. WanZhen Liang

Prof. Binju Wang

Group members:

Thanks for your patient listening!