Non-equilibrium electron dynamics from real-time quantum embedding

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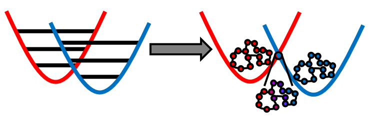
Kretchmer Group: New simulation methods for electron dynamics in complex environments

Method Development

Multi-faceted research group working at the interface of electronic structure and quantum dynamics

Classically Isomorphic Methods

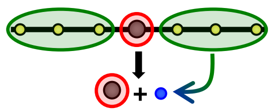
Map a complicated quantum system to a computationally tractable classical system



Real-Time Electronic Structure

Solve the time *dependent* Schrödinger equation – Quantum embedding

Subsystem coupled to *large* environment

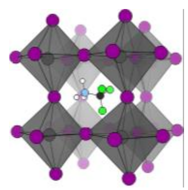


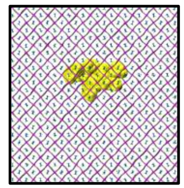
Subsystem coupled to *small* environment

Transport Dynamics in Correlated Materials

Examine electron-nuclear, electron-electron, and spin-spin interactions in governing the non-equilibrium transport of electrons

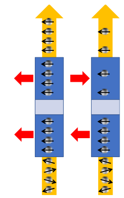
Charge-transport in perovskites





Explicit electron in fully atomistic simulation

Spin-transport across interfaces

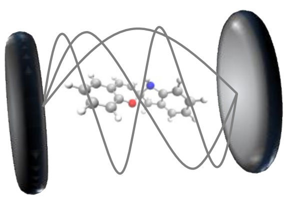


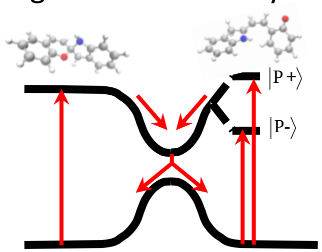
Magnetic tunnel junctions

Chirality-induced spin selectivity

Chemical Dynamics in Optical Cavities

Investigate the influence of *quantum* light on chemical dynamics

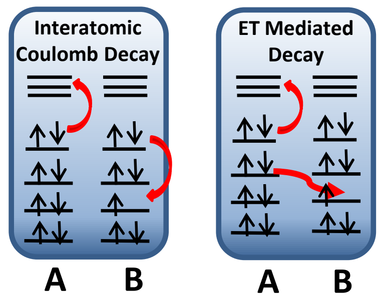


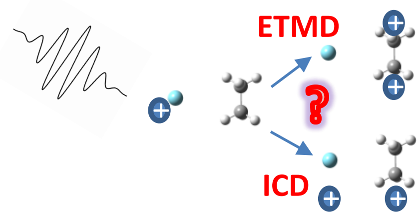


- Strong coupling between a molecular system and quantized modes of light can modify the *energy landscape*
- High-temperature Bose-Einstein condensates as a "quantum solvent" to modify chemistry based on charge-transfer

Electron Dynamics in Weakly Bound Systems

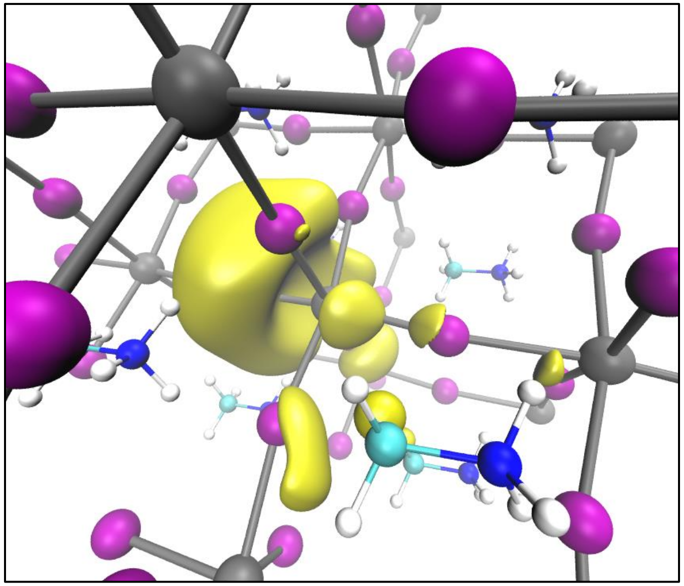
Ionization of a core electron initiates competing ultrafast electronic processes that lead to fragmentation in VdW and H-bonded systems



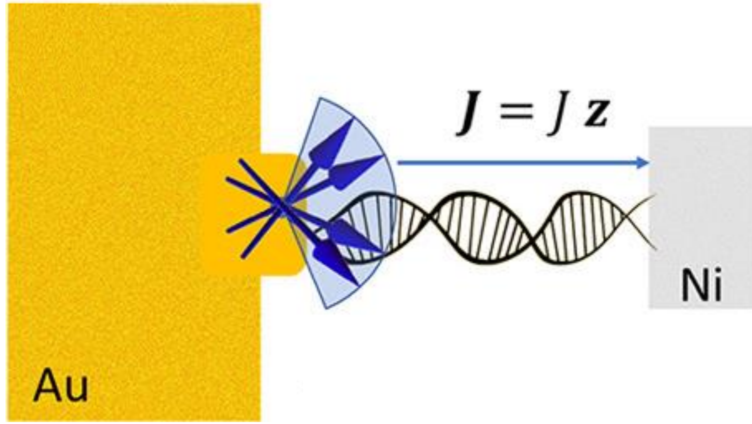


Non-Equilibrium Electron Dynamics

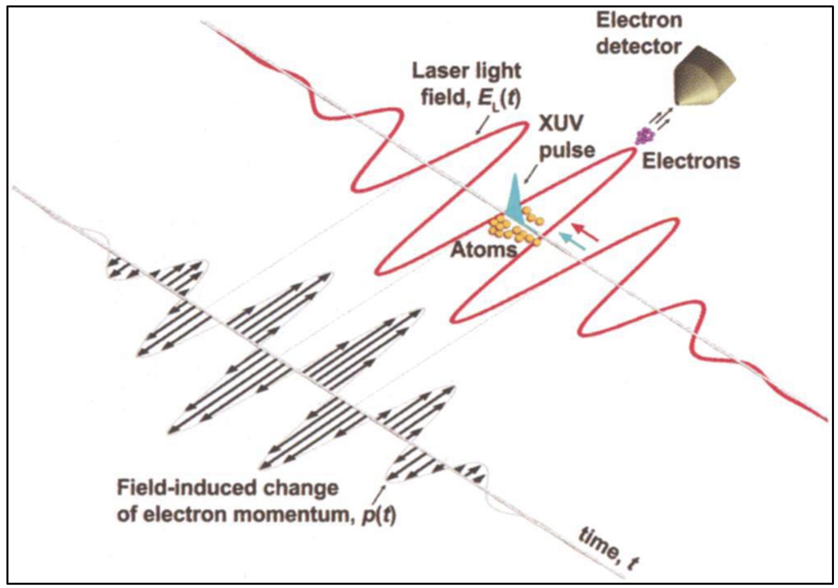
Photoexcited Materials



Spin Dynamics and Selectivity



Laser Driven Electron Dynamics



Electronic motion even in the absence of nuclear motion

Non-Equilibrium Electron Dynamics

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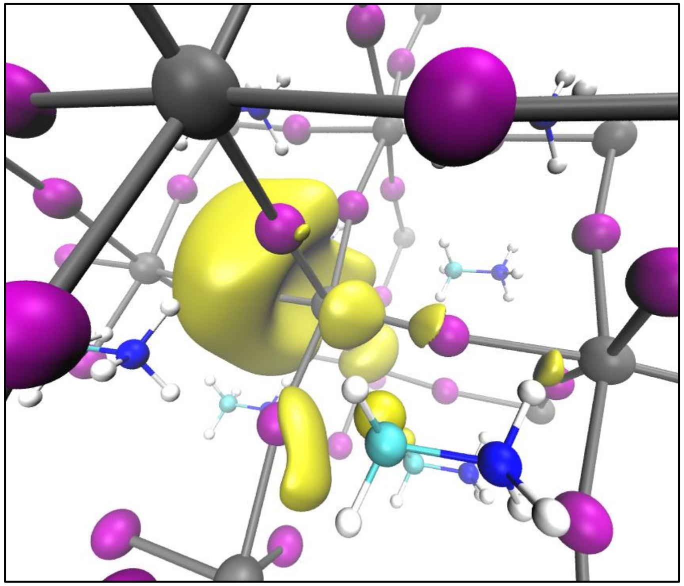

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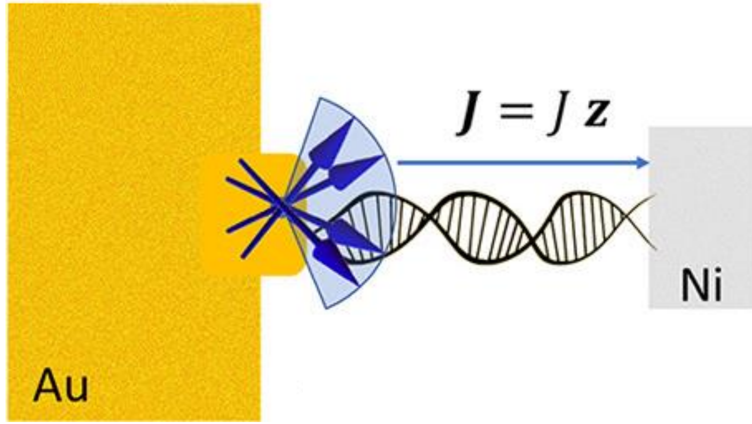

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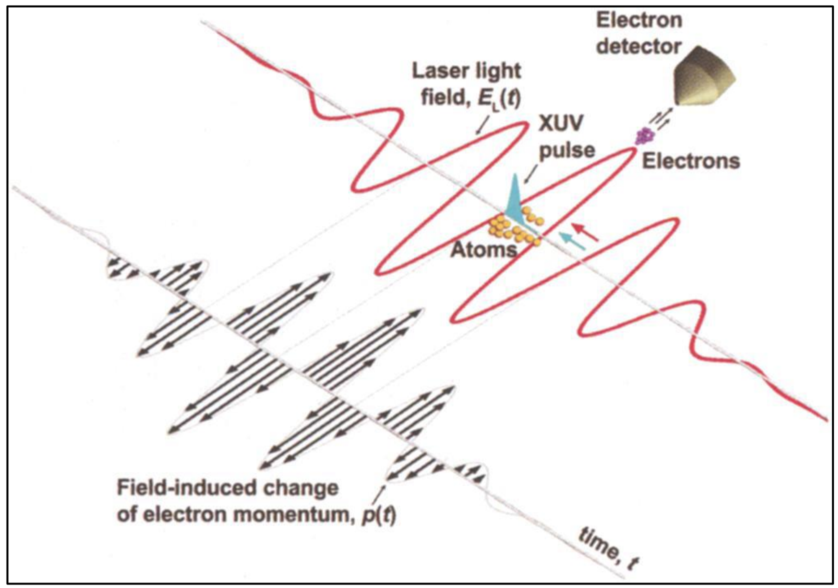
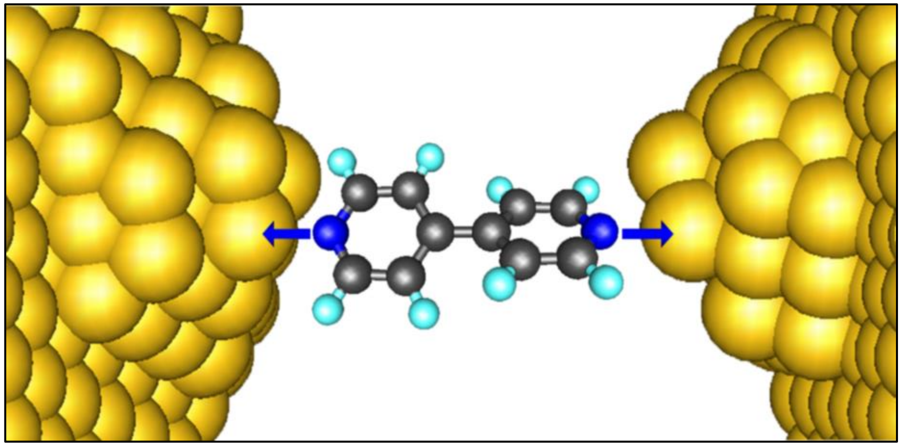
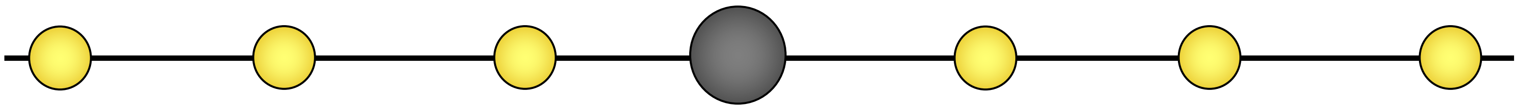


Develop efficient and accurate method for the direct simulation of the ***electronic wavefunction*** in strongly correlated systems

Quantum Embedding

Obtain accurate properties of a small subsystem without performing expensive calculation on the full system





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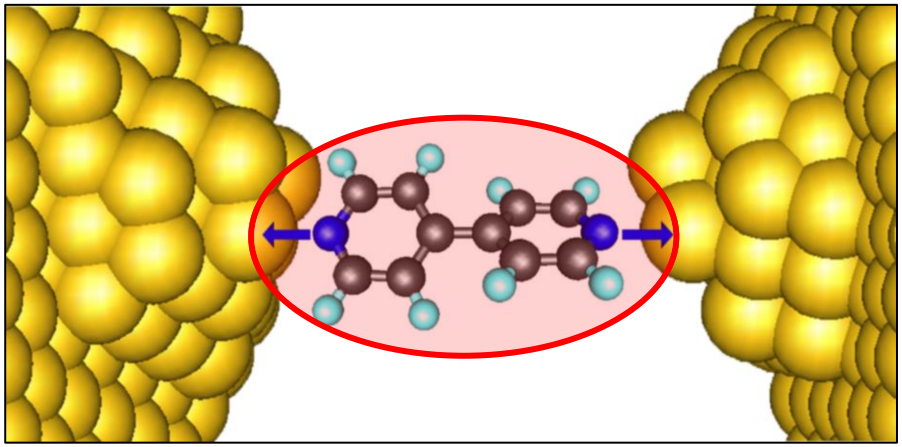

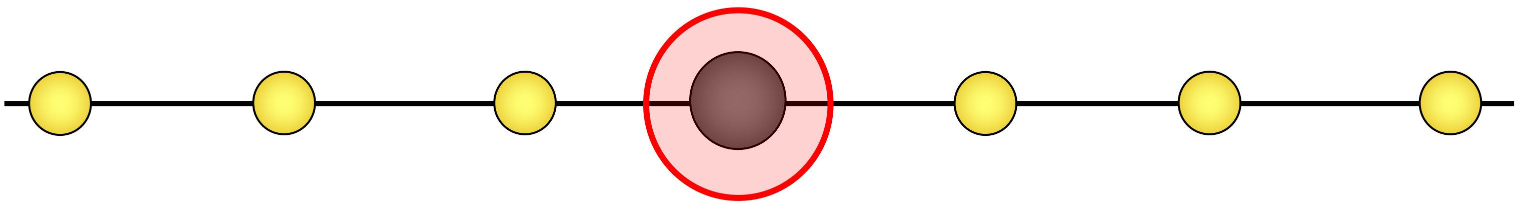

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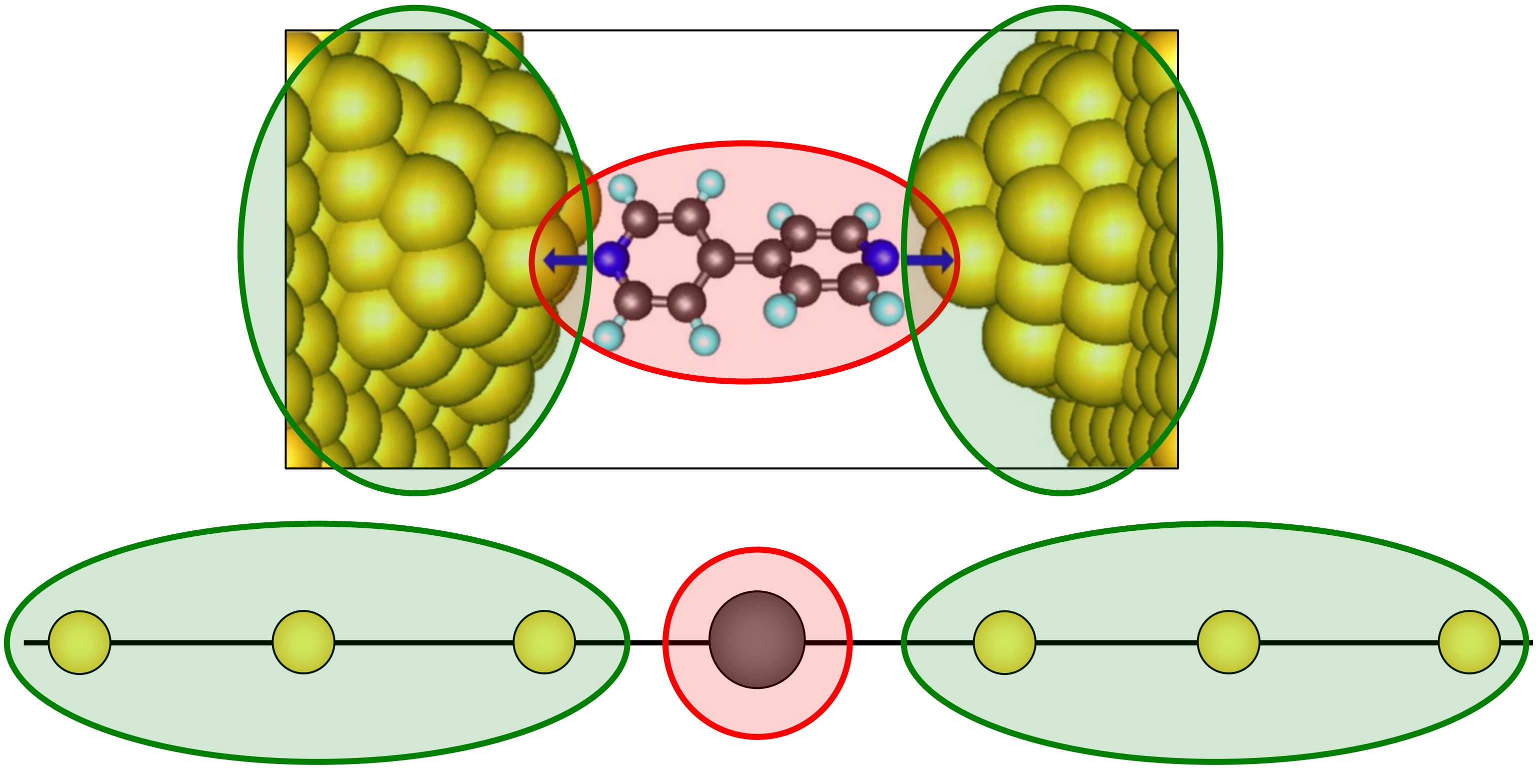
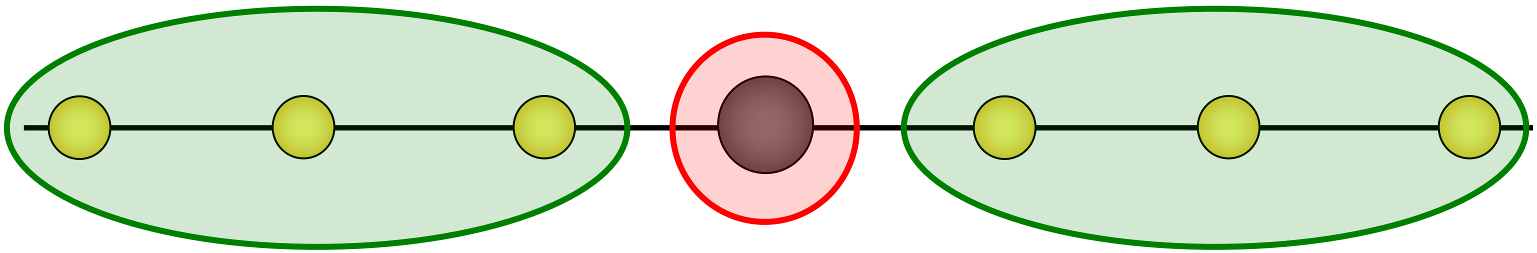


How to account for effects of the surrounding environment?

Density Matrix Embedding Theory

Surrounding environment treated as a quantum bath of the same size as the subsystem – Schmidt Decomposition



Schmidt decomposition:

$$|\Psi\rangle = \sum_{i}^{N_A} \sum_{j}^{N_B} \Psi_{ij} |A_i\rangle |B_j\rangle$$

Start with product of subsystem (A_i) and environment (B_j) states in **LARGE** space of dimension $N_a \times N_b$

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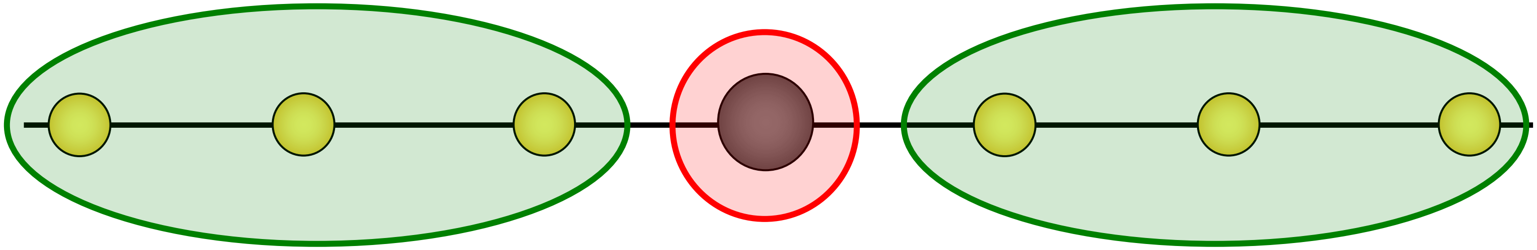

Schmidt decomposition:

$$|\Psi\rangle = \sum_{i}^{N_A} \sum_{j}^{N_B} \Psi_{ij} |A_i\rangle |B_j\rangle = \sum_{i}^{N_A} \sum_{j}^{N_B} \sum_{\alpha}^{\min(N_A,N_B)} U_{i\alpha} \lambda_\alpha V^{\dagger}_{\alpha j} |A_i\rangle |B_j\rangle$$

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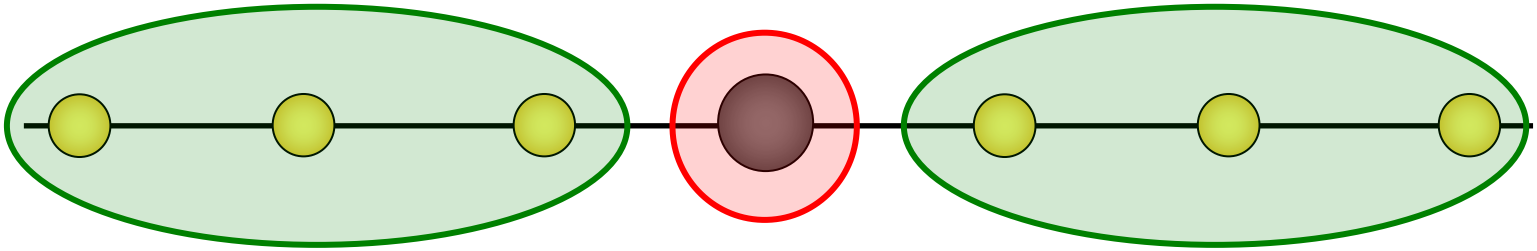

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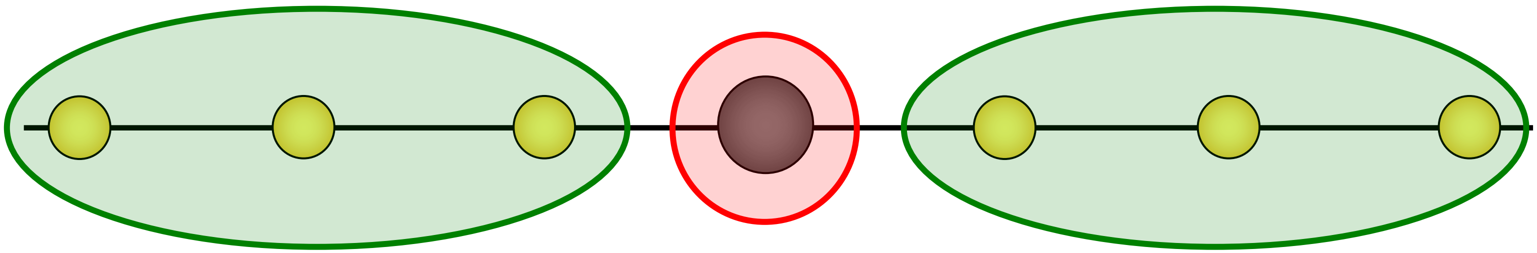
Start with product of subsystem (A_i) and environment (B_j) states in **LARGE** space of dimension N_a x N_b

End with product of subsystem $(\tilde{A}_\alpha)$ and new environment $(\tilde{B}_\alpha)$ states in **SMALL** space of dimension N_a x N_a

Density Matrix Embedding Theory

Surrounding environment treated as a quantum bath of the same size as the subsystem – Schmidt Decomposition



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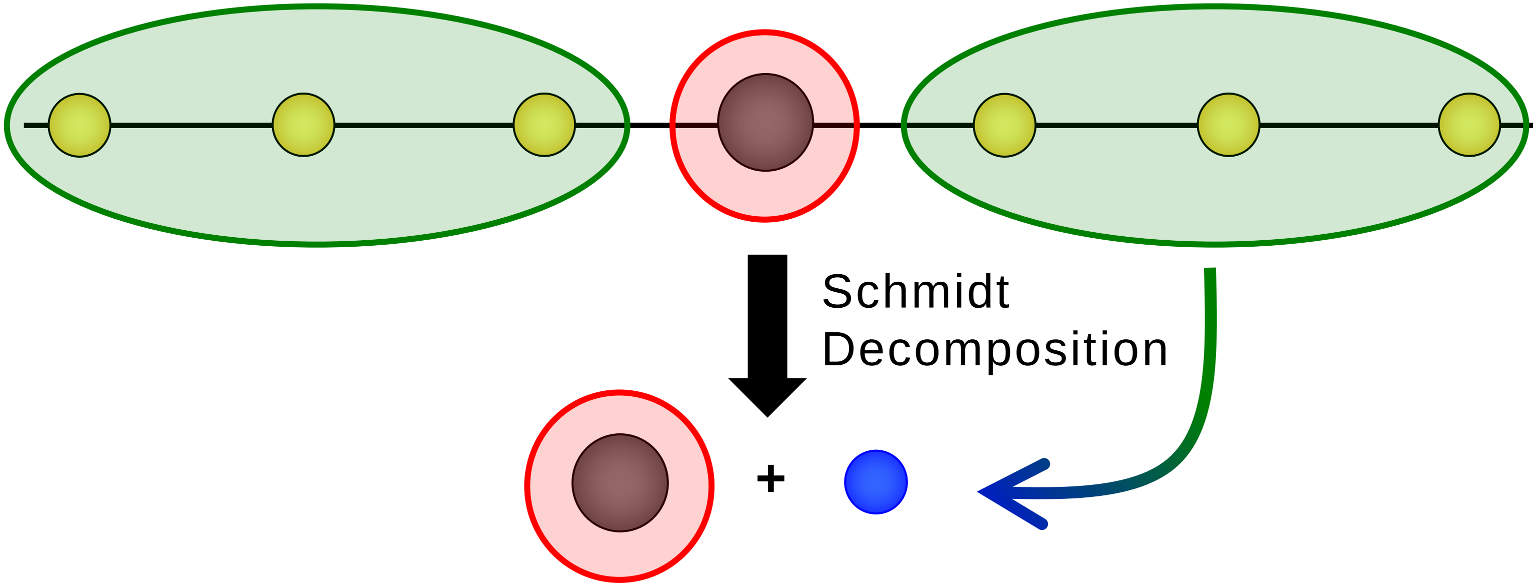
Start with product of subsystem (A_i) and environment (B_j) states in **LARGE** space of dimension N_a x N_b

End with product of subsystem ($\tilde{A}_\alpha$) and multi-electron bath ($\tilde{B}_\alpha$) states in **SMALL** space of dimension N_a x N_a

Density Matrix Embedding Theory

Surrounding environment treated as a quantum bath of the same size as the subsystem – Schmidt Decomposition



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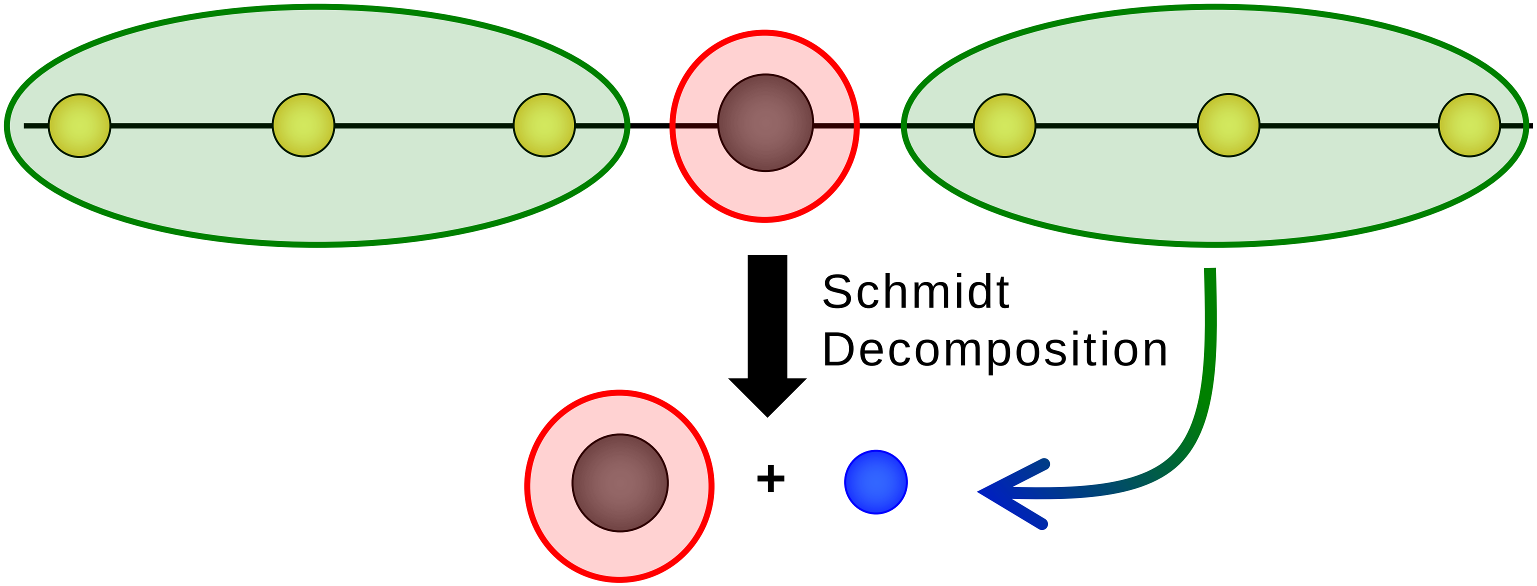

The good: in principle have a method to exactly embed a fragment in a bath of the same size as the fragment itself

Density Matrix Embedding Theory

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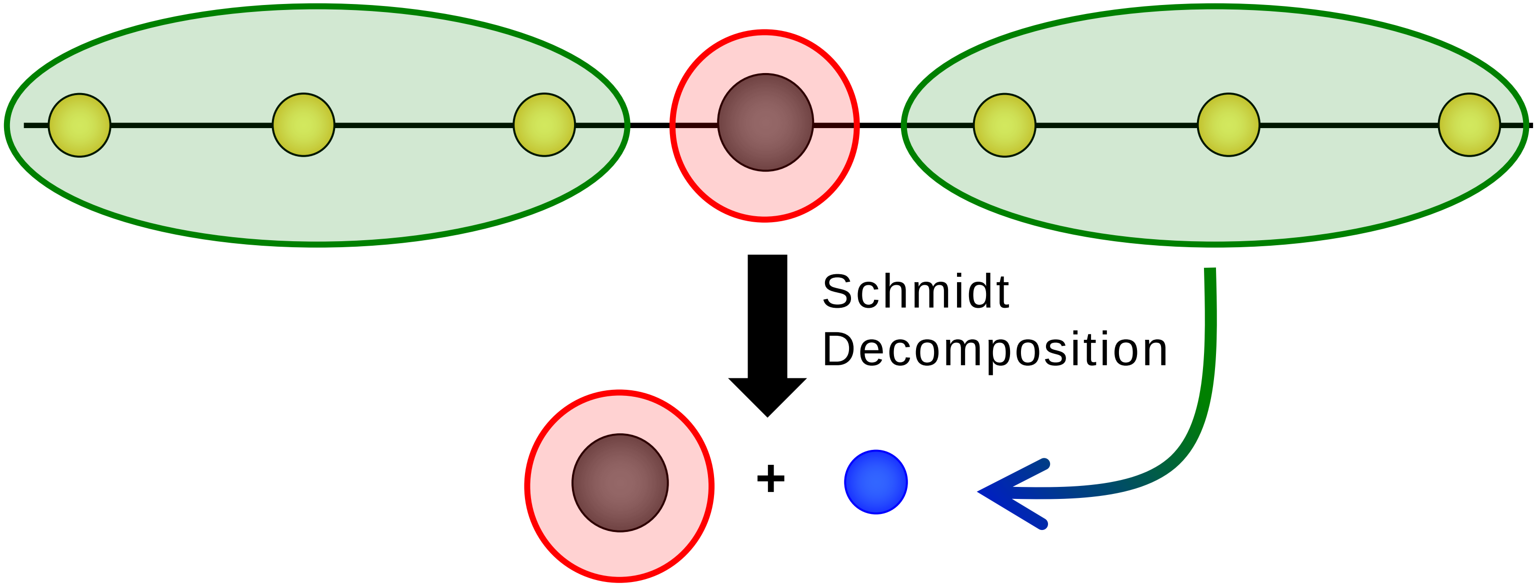

The good: in principle have a method to exactly embed a fragment in a bath of the same size as the fragment itself

The bad: knowledge of the exact wavefunction is needed to construct the bath states

Density Matrix Embedding Theory

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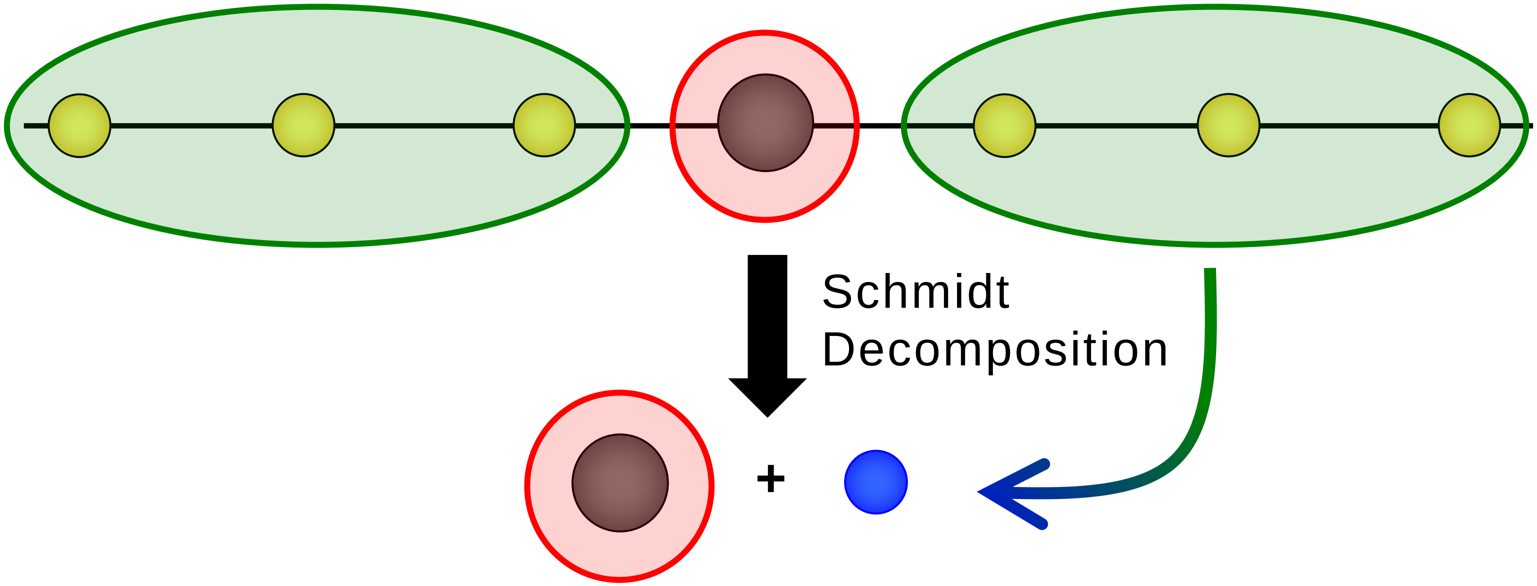
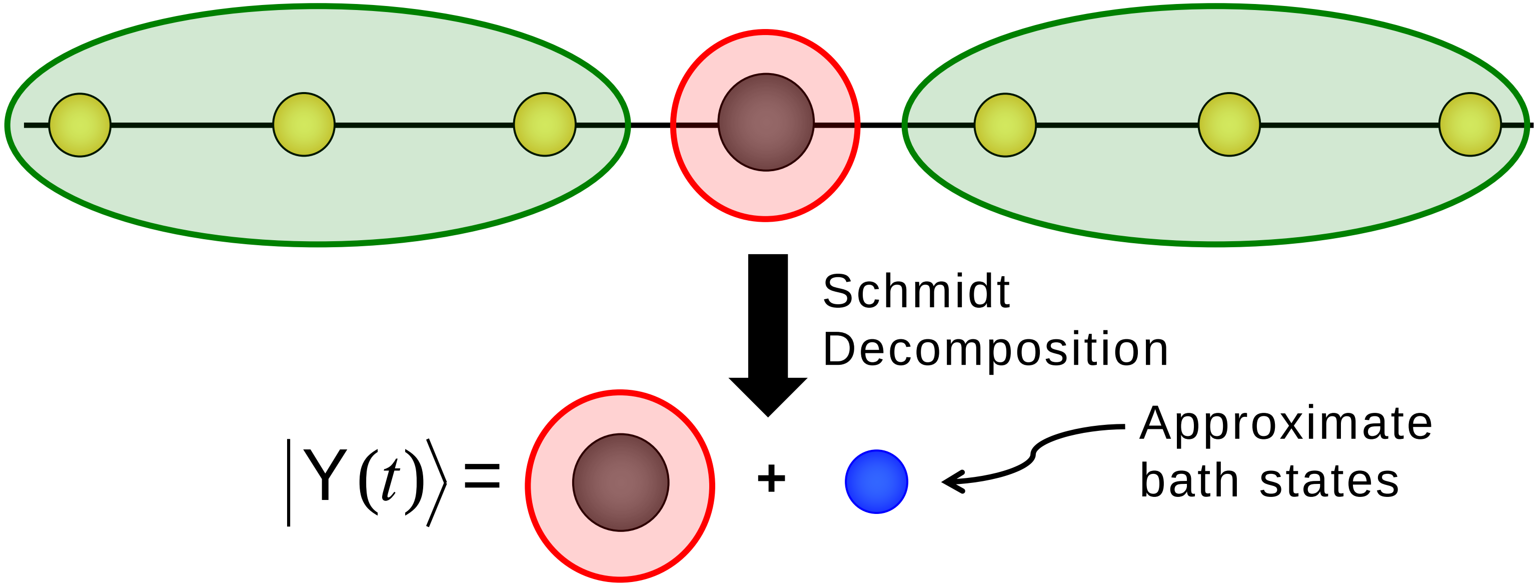


The Fix – Static DMET:

1. Construct the bath states from *mean-field* wavefunction on the total system
2. Perform *correlated* calculation utilizing these bath states
3. Introduce self-consistency between mean-field wavefunction and correlated calculation – one-electron reduced density matrix

Real-Time DMET



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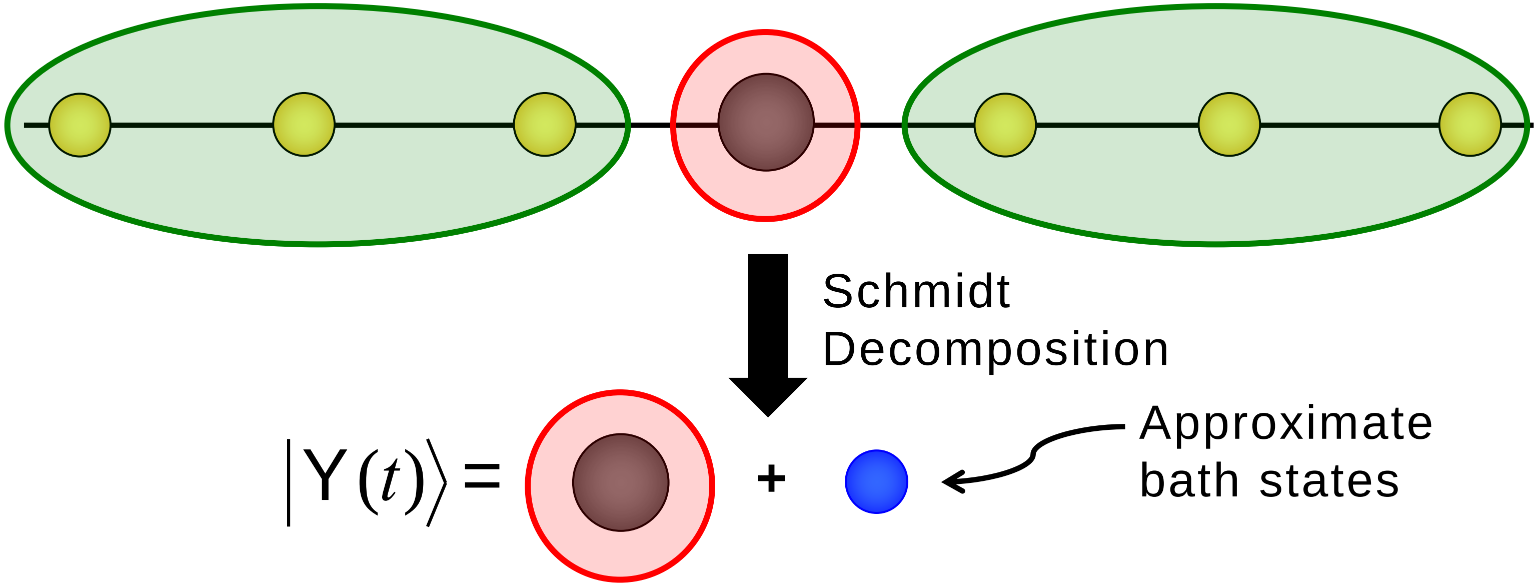
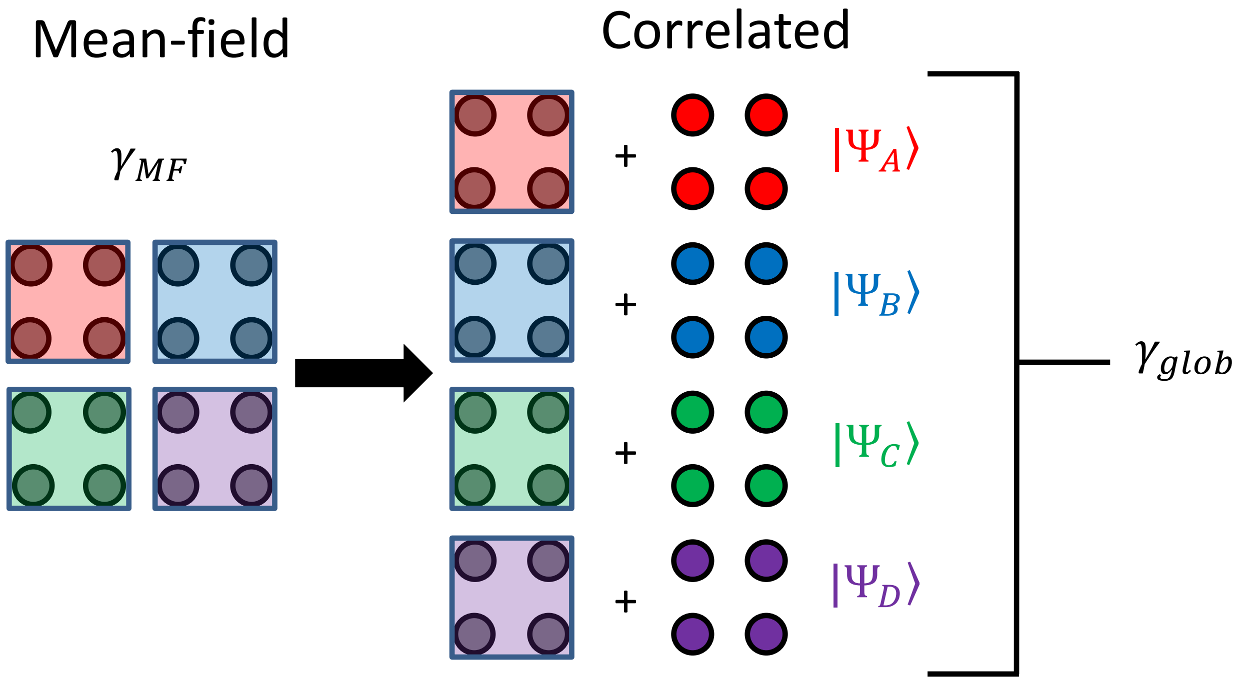


- Initial formulation utilized time-dependent variational principle to derive equations of motion for embedding wavefunction
- Equations of motion bare resemblance to time-dependent CAS

Multi-Fragment Extension

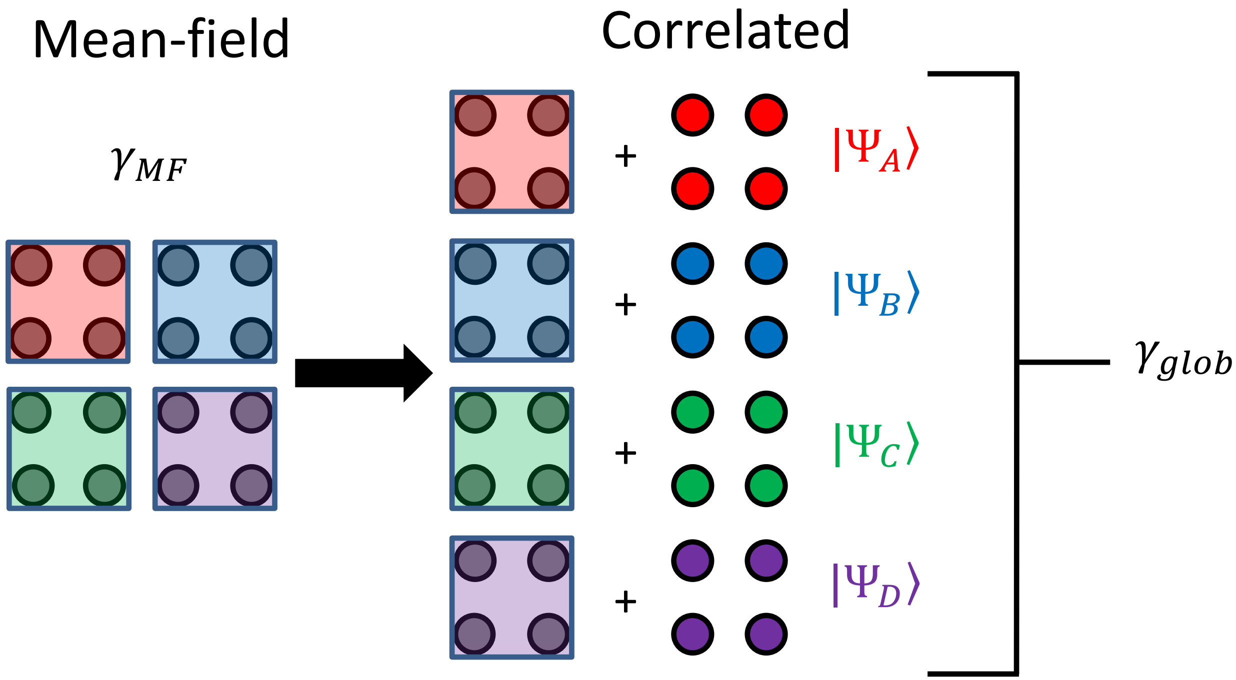


Separate correlated embedding calculations all derived from same total-system mean-field calculation

"Stitch" together embedding calculations through democratic partitioning of operators

$$\left\langle \hat{a}_i^\dagger\ \hat{a}_j + \hat{a}_j^\dagger\ \hat{a}_i \right\rangle = \langle \Psi_{x(i)} | \hat{a}_i^\dagger\ \hat{a}_j | \Psi_{x(i)} \rangle + \left\langle \Psi_{x(j)} | \hat{a}_j^\dagger\ \hat{a}_i | \Psi_{x(j)} \right\rangle$$

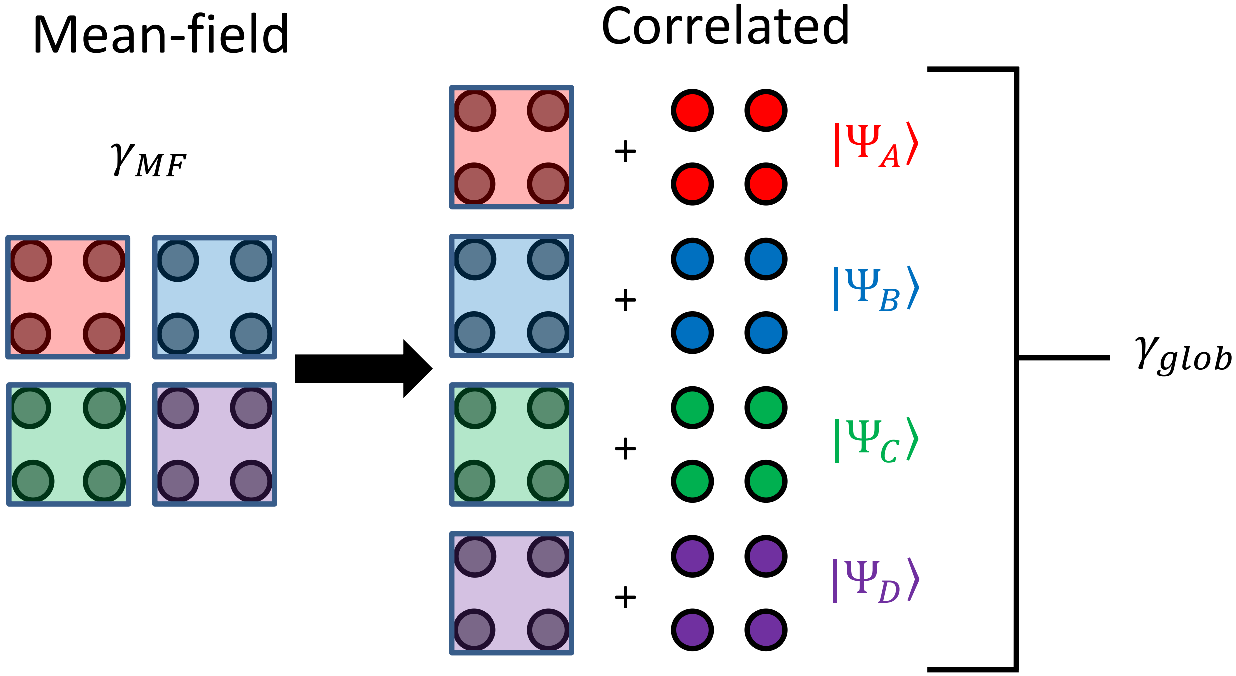
Multi-Fragment Extension



Difficulty for Dynamics:

- Conventional DMET matching condition between mean-field and embedding calculations breaks down
- TDVP does not allow for multiple fragments

Multi-Fragment Extension

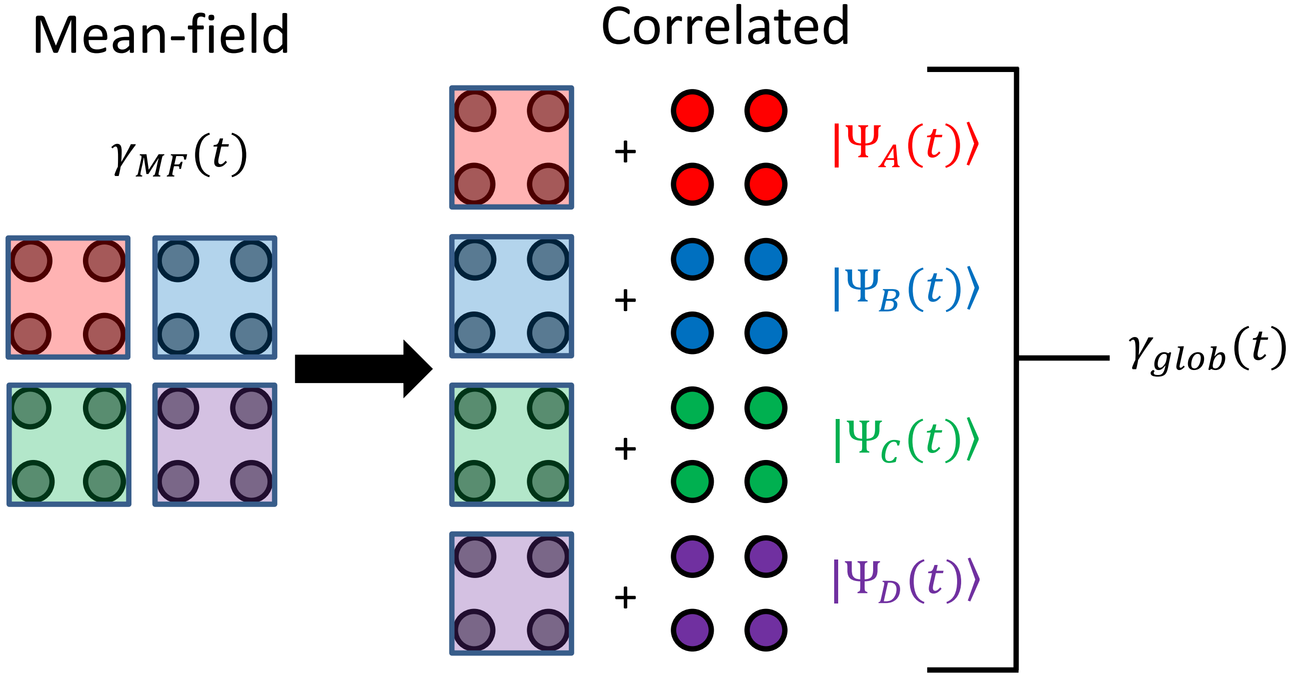


Solution:

- Take advantage of a different form of static DMET – projected DMET
- pDMET has an analytical matching condition between γ_{MF} and γ_{glob}

(Yehorova and Kretchmer, *JCP 2023*)

Real-Time pDMET



General Idea: Simultaneously propagate mean-field wavefunction of full system and correlated wavefunction for each fragment and its bath, such that the pDMET conditions are met at each point in time

(Yehorova and Kretchmer, *JCP 2023*)

Real-Time pDMET

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Real-Time pDMET

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Condition 1: Bath for each fragment obtained from Schmidt decomposition of mean-field 1RDM

$$\gamma_{\mathrm{env}}^{\mathrm{MF}}(t)|a^{\mathrm{A}}(t)\rangle = \lambda_a^{\mathrm{A}}|a^{\mathrm{A}}(t)\rangle$$

(Yehorova and Kretchmer, *JCP 2023*)

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Condition 2: Mean-field 1RDM obtained from natural orbitals of global 1RDM formed from all fragments

$$\gamma^{\mathrm{MF}}(t) = 2C(t)C(t)^{\dagger}$$

$$\gamma^{\mathrm{glob}}(t) = C(t)\Lambda(t)C^{\dagger}(t)$$

(Yehorova and Kretchmer, *JCP 2023*)

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Time-dependence of DMET wavefunction for each fragment:

$$i|\dot{\Psi}^{\mathrm{A}}\rangle = \sum_m i\dot{c}^{\mathrm{A}}_m|m^{\mathrm{A}}\rangle + c^{\mathrm{A}}_m X^{\mathrm{A}}|m^{\mathrm{A}}\rangle$$

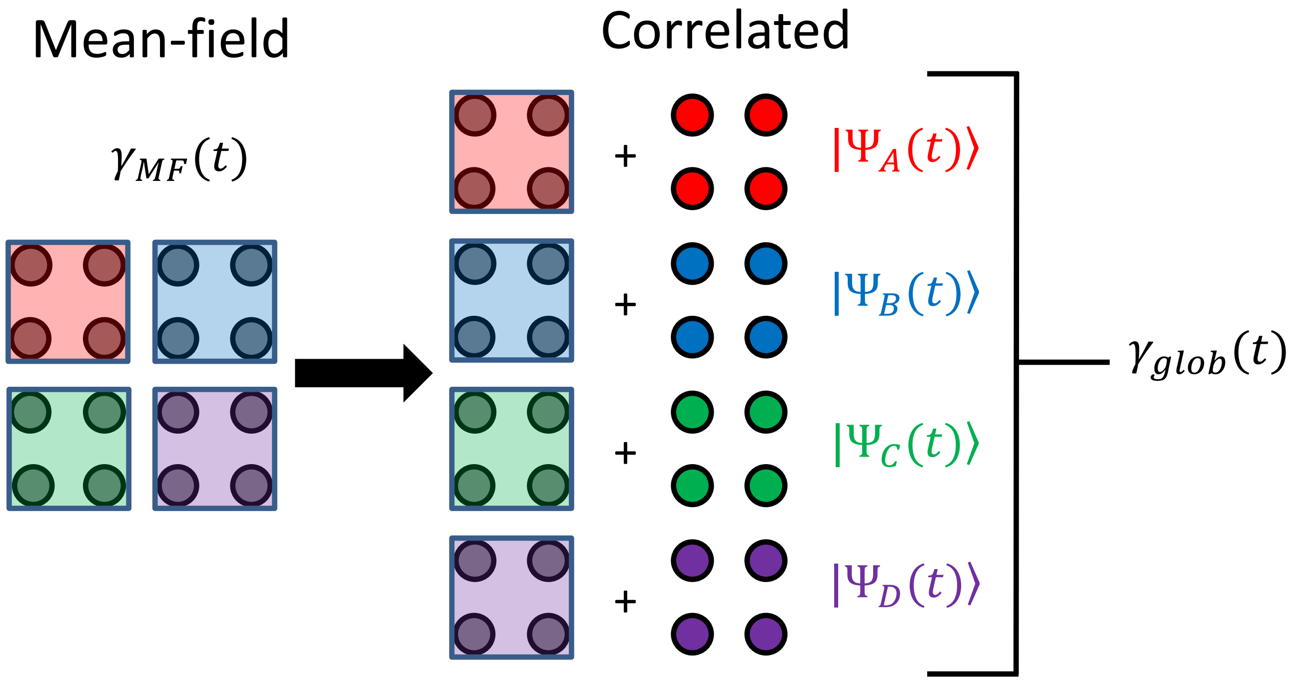
$\Rightarrow$

$\dot{c}^{\mathrm{A}}_m$ obtained from TDSE projected into the embedding space

X^{A} obtained from pDMET conditions at each point in time

(Yehorova and Kretchmer, *JCP 2023*)

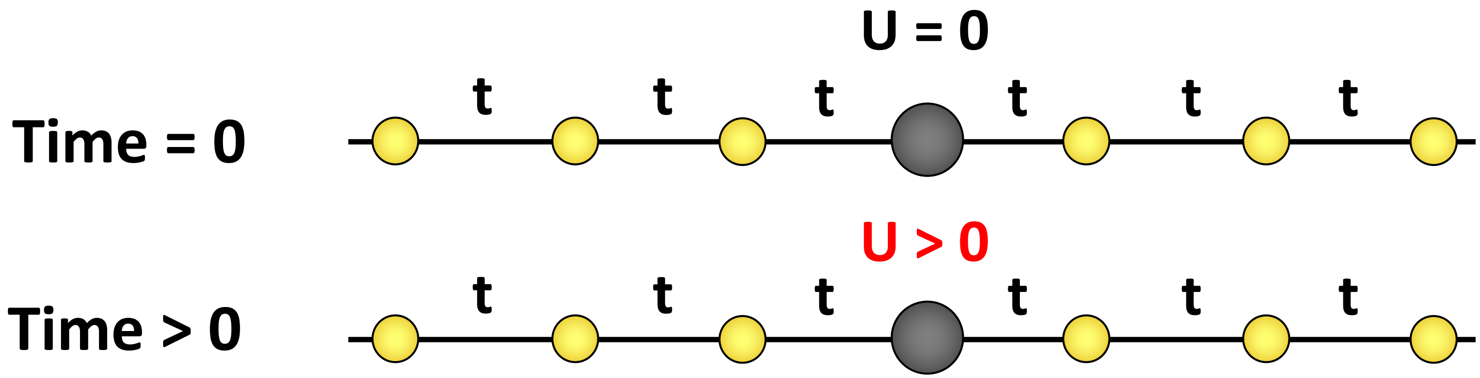
Real-Time pDMET

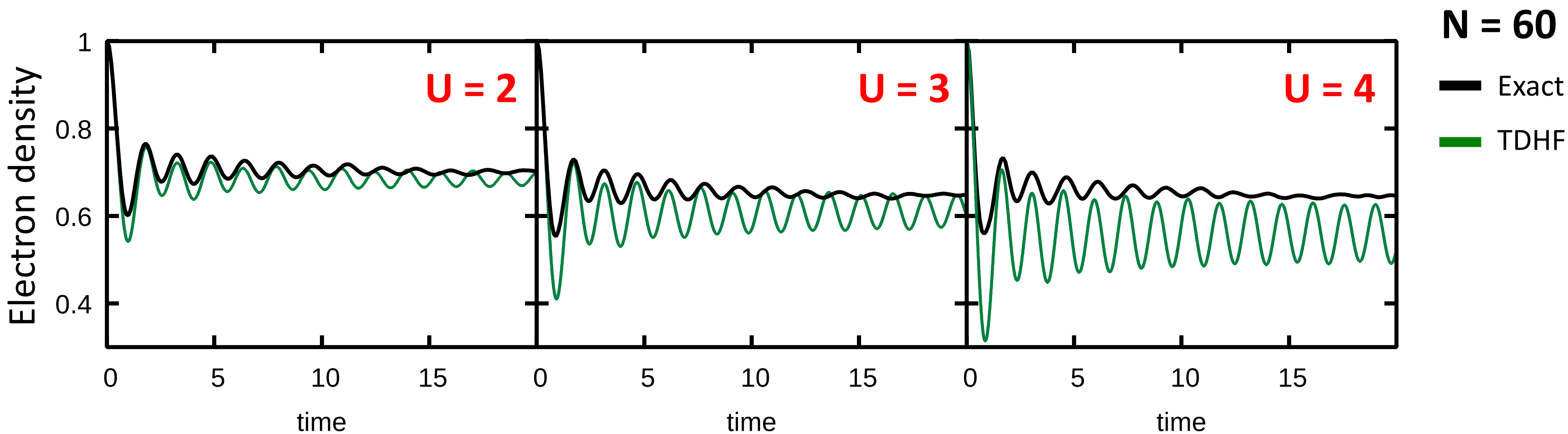


- Exact in non-interacting limit
- Exact in large subsystem limit
- Allows for correlation between subsystem and environment
- Do not need to specify specific area of high accuracy

(Yehorova and Kretchmer, *JCP 2023*)

Single Impurity Anderson Model





(Yehorova and Kretchmer, *JCP 2023*)

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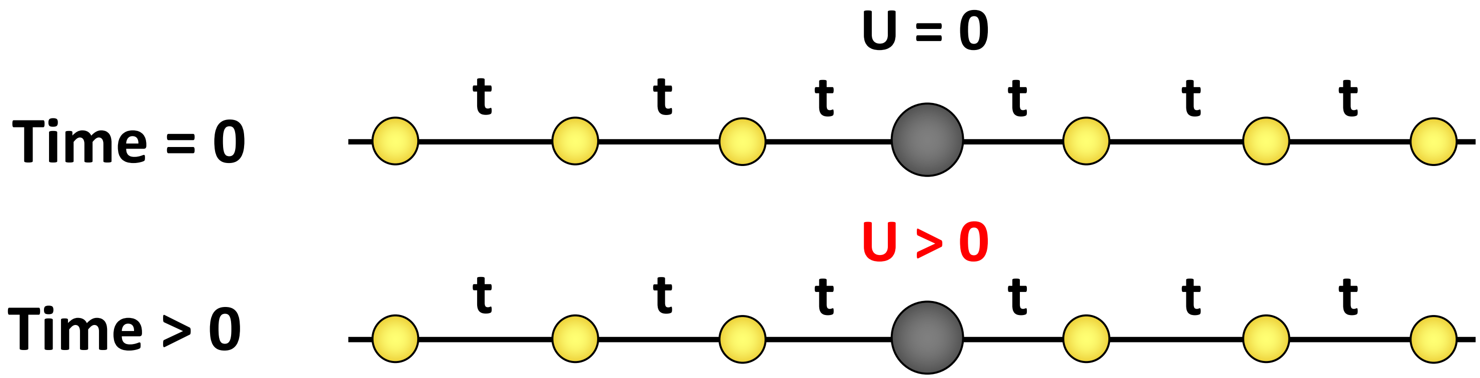

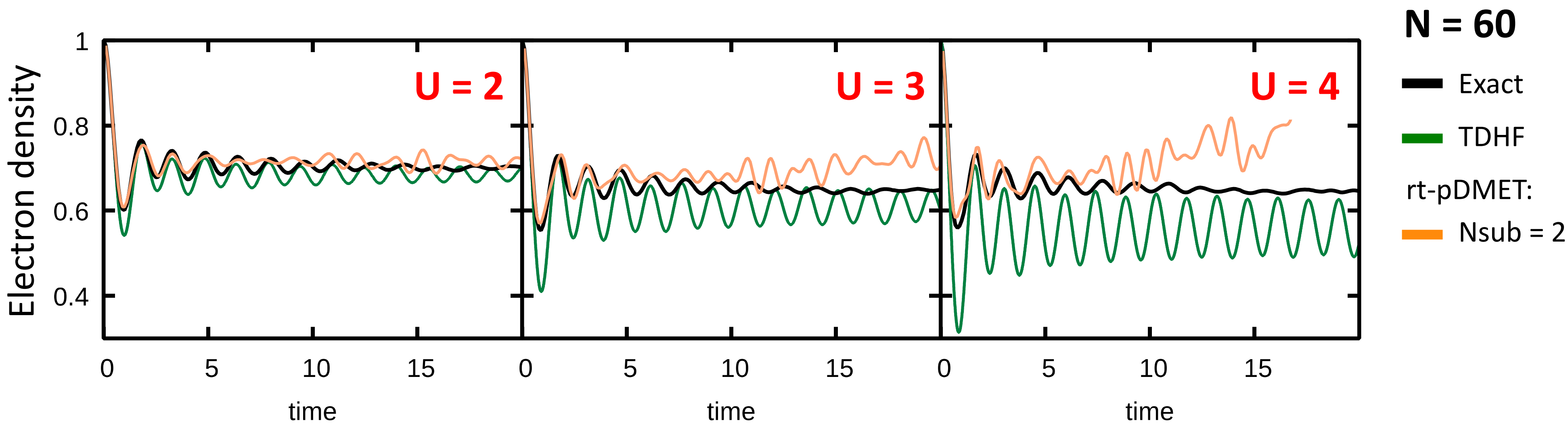

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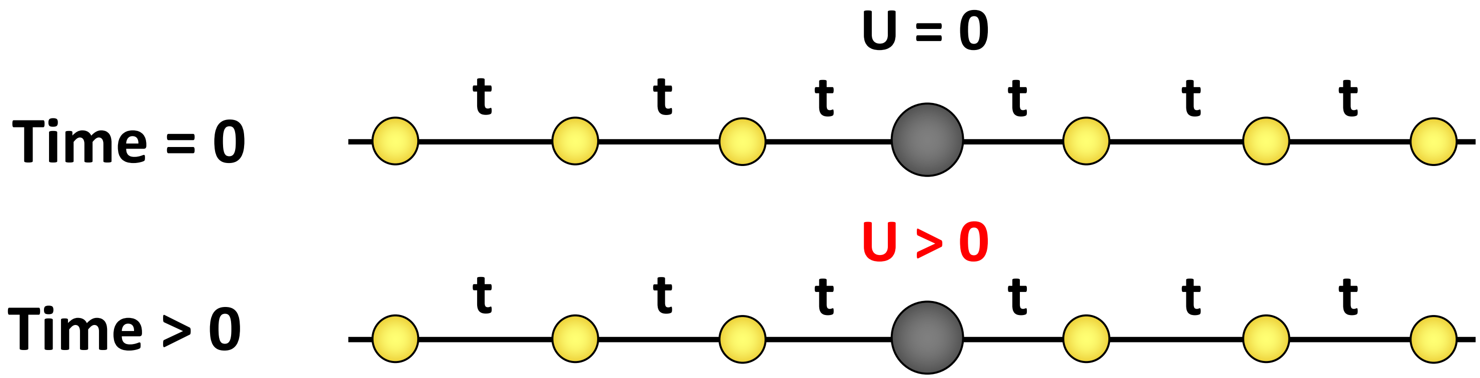

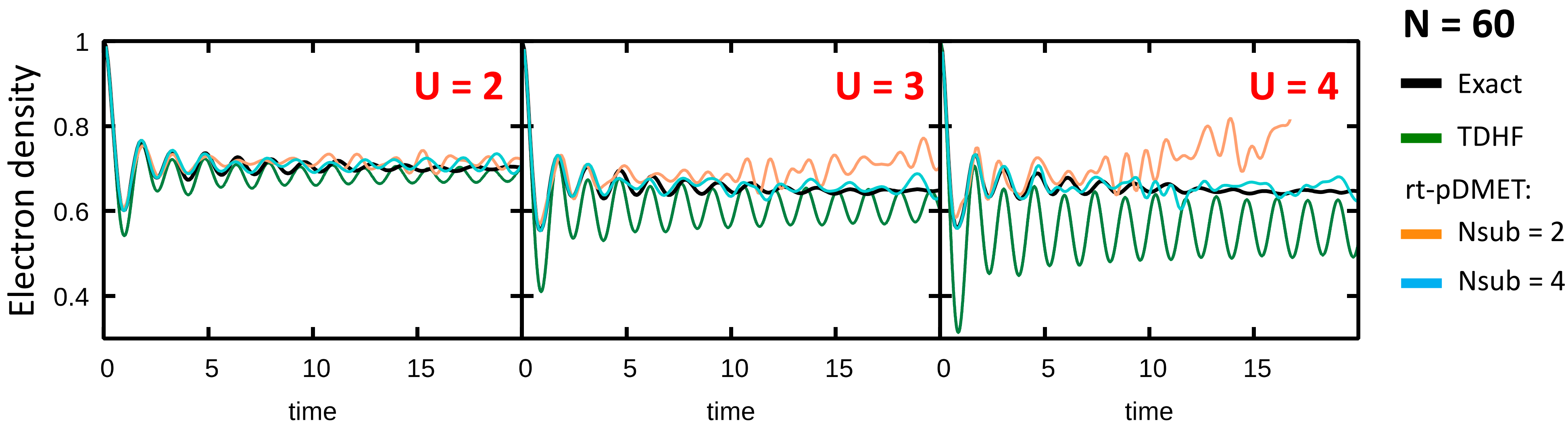

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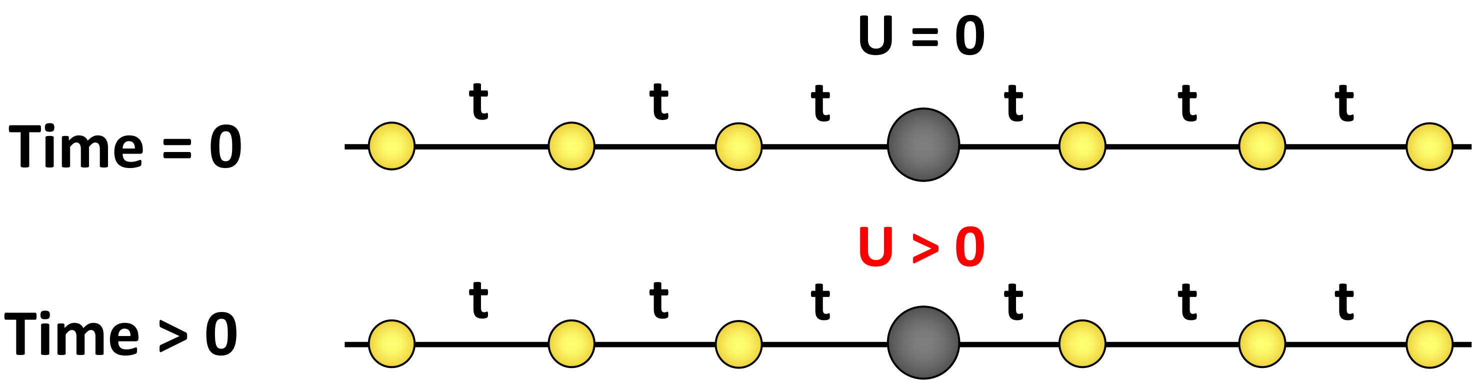
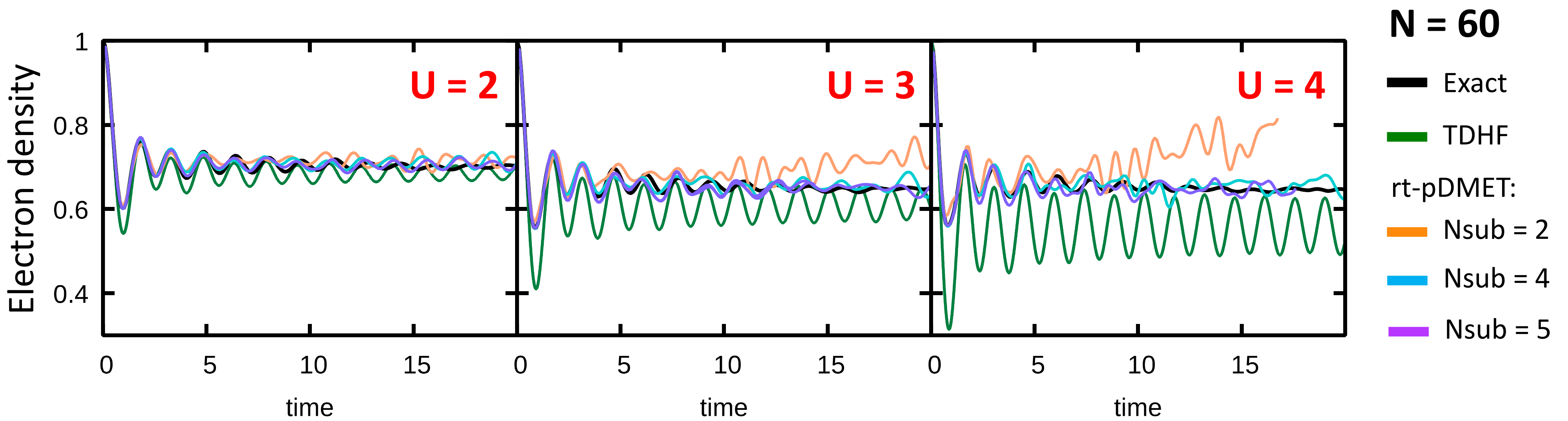
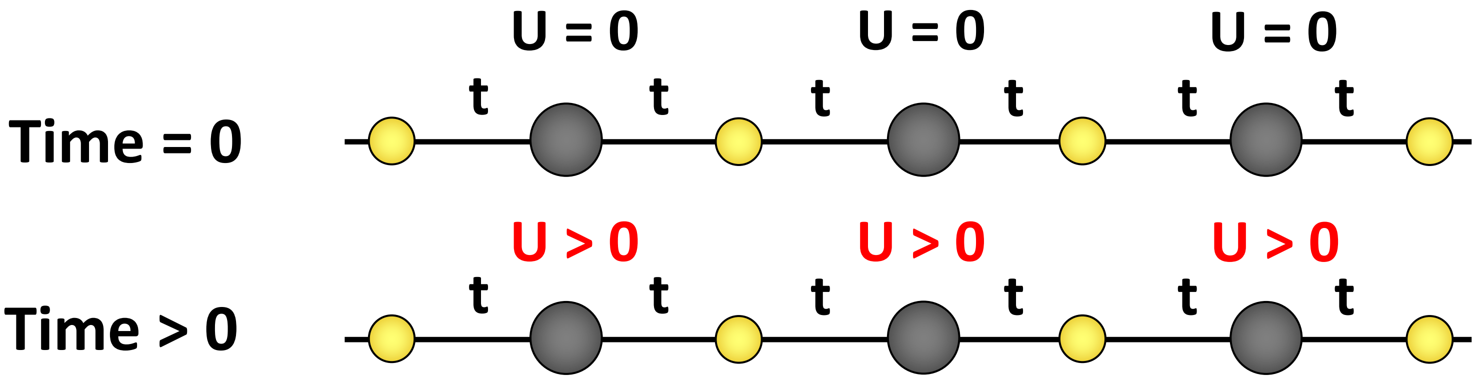


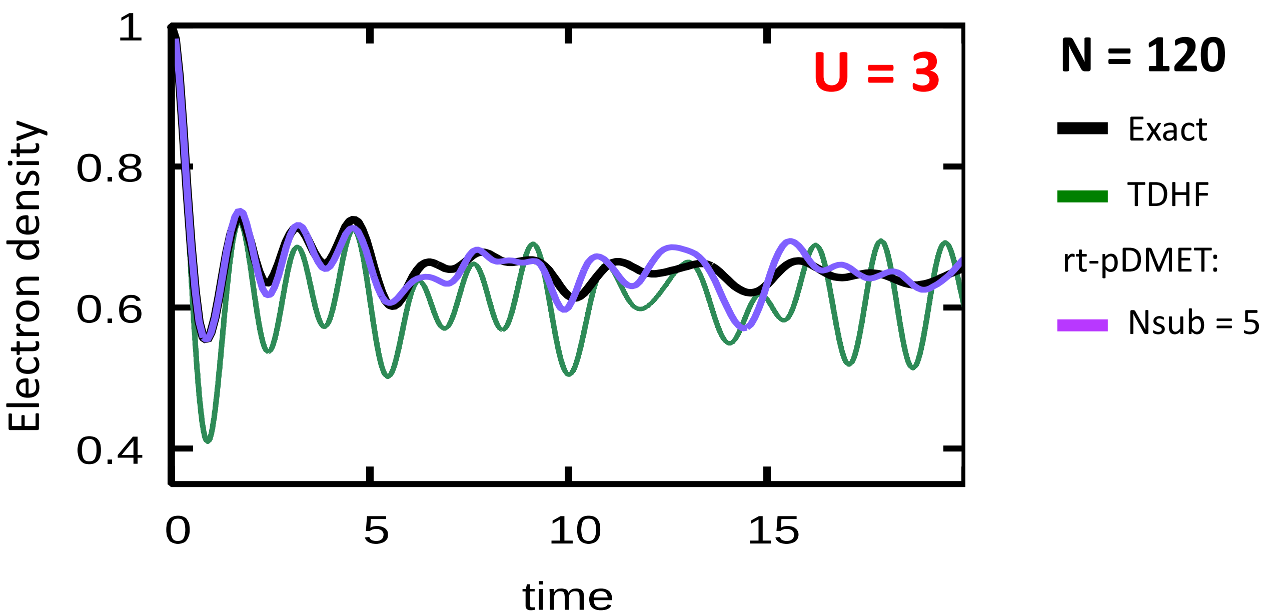


Real-time pDMET converges to the exact answer even in the strongly correlated regime

(Yehorova and Kretchmer, *JCP 2023*)

Multi-Impurity Anderson Model





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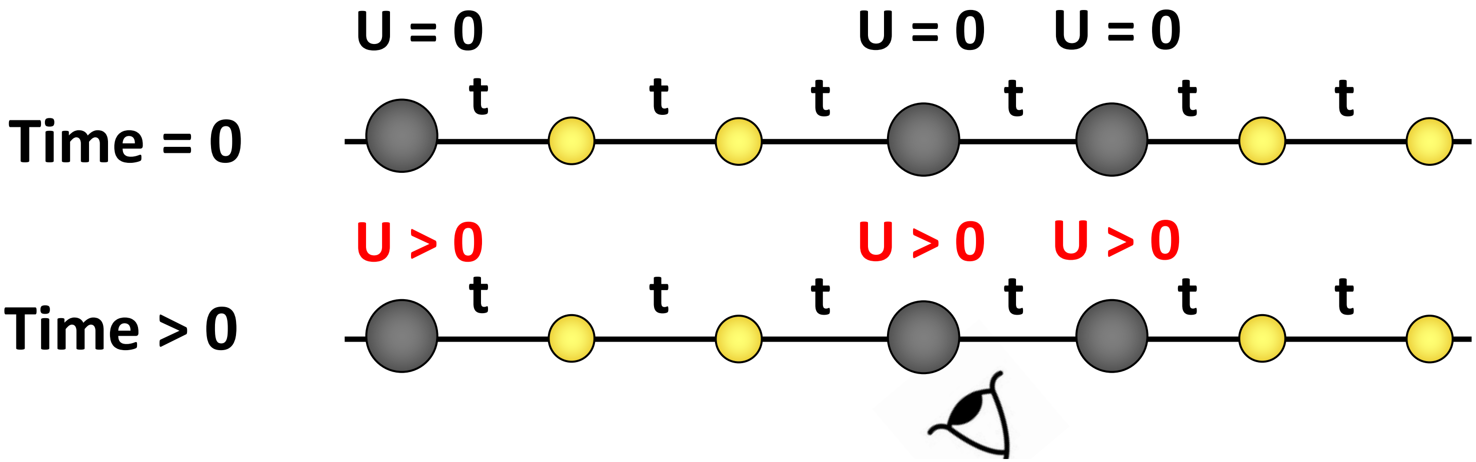
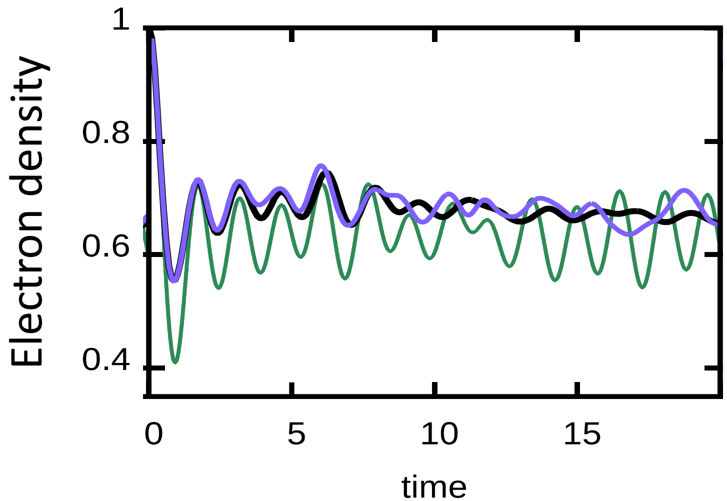




N = 120

Exact

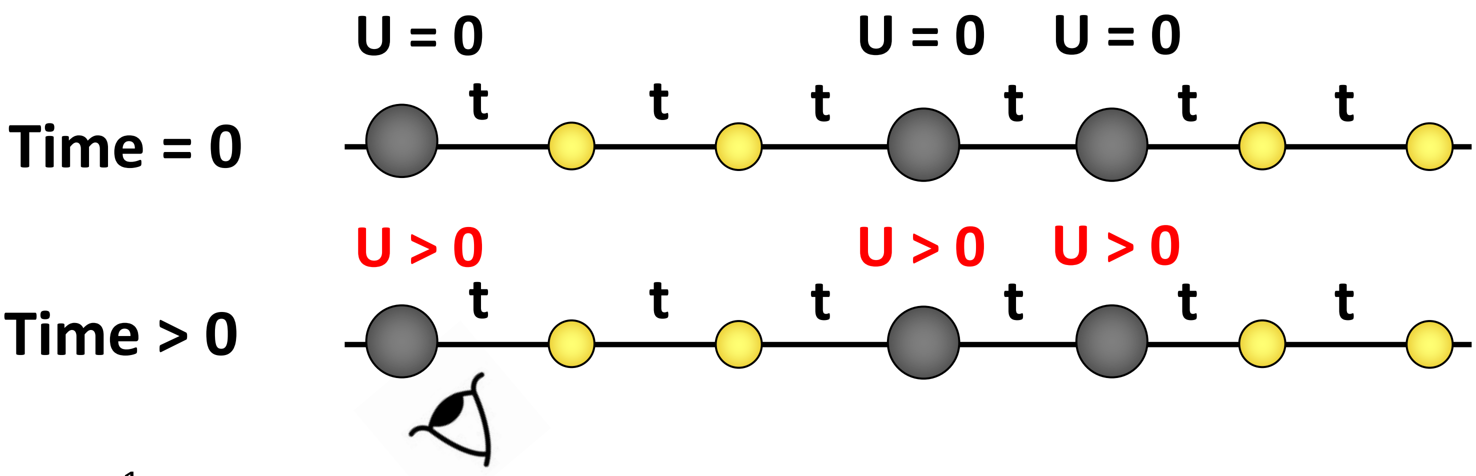
TDHF

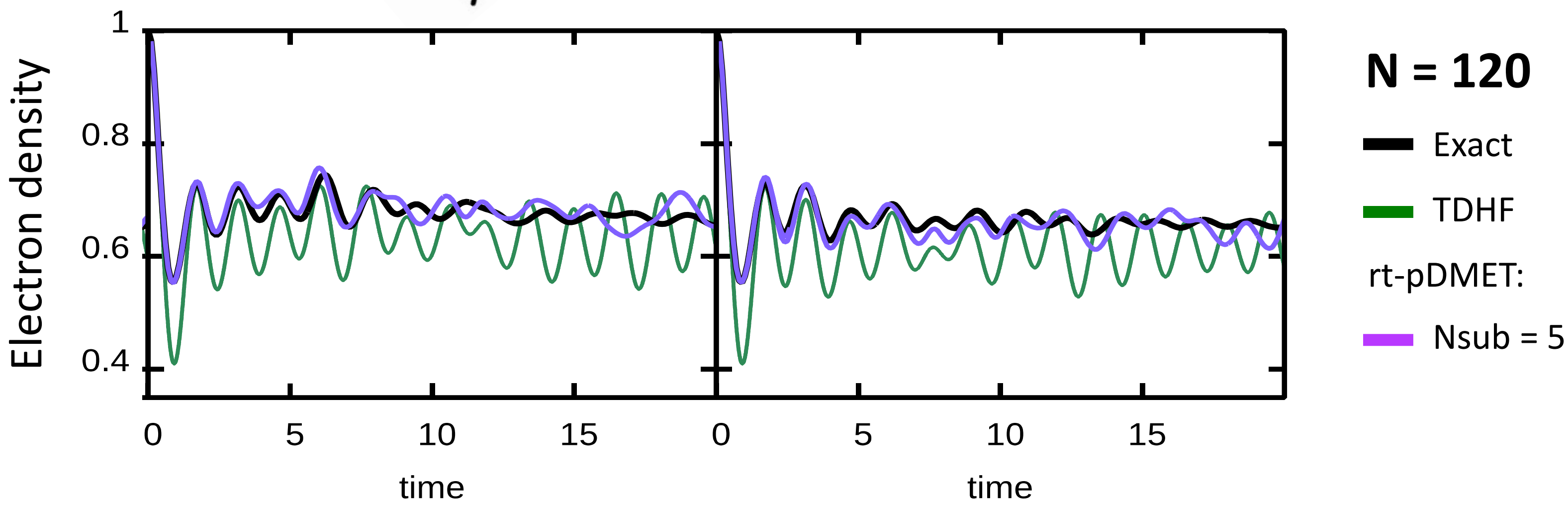
rt-pDMET:

Nsub = 5

(Yehorova and Kretchmer, *JCP 2023*)

Multi-Impurity Anderson Model



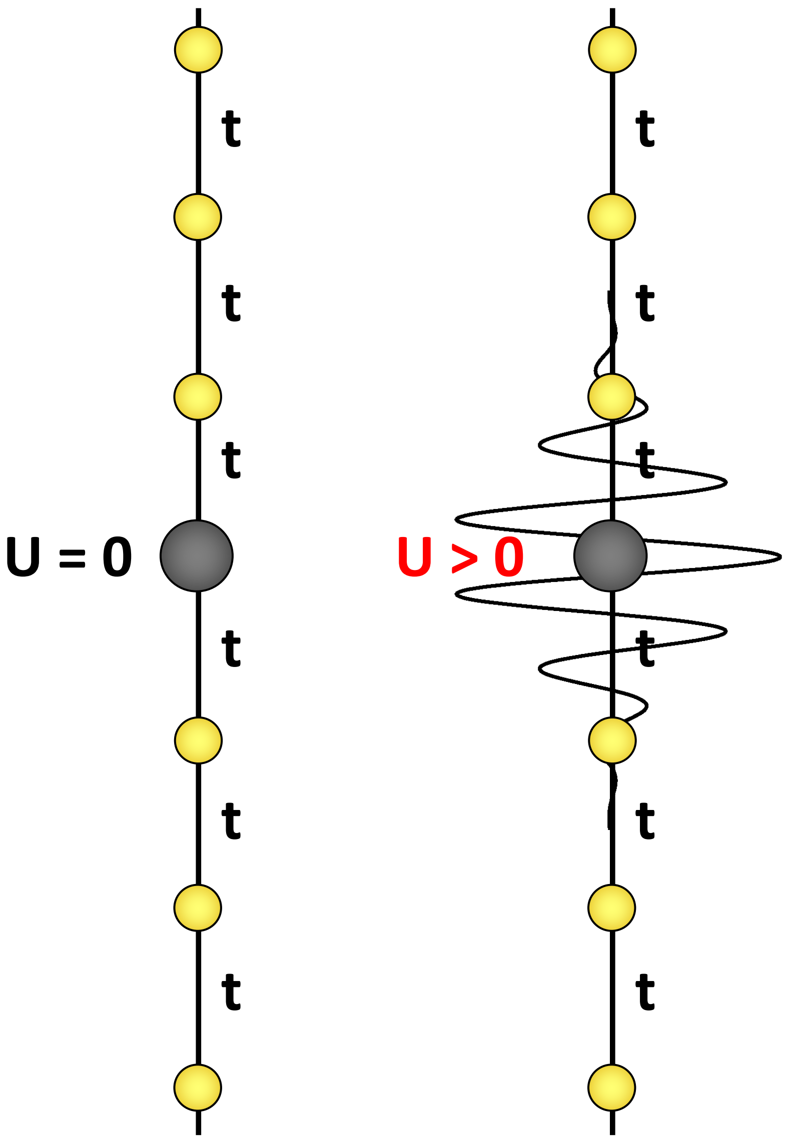


Real-time pDMET accurately treats all regions of space even for a disordered system

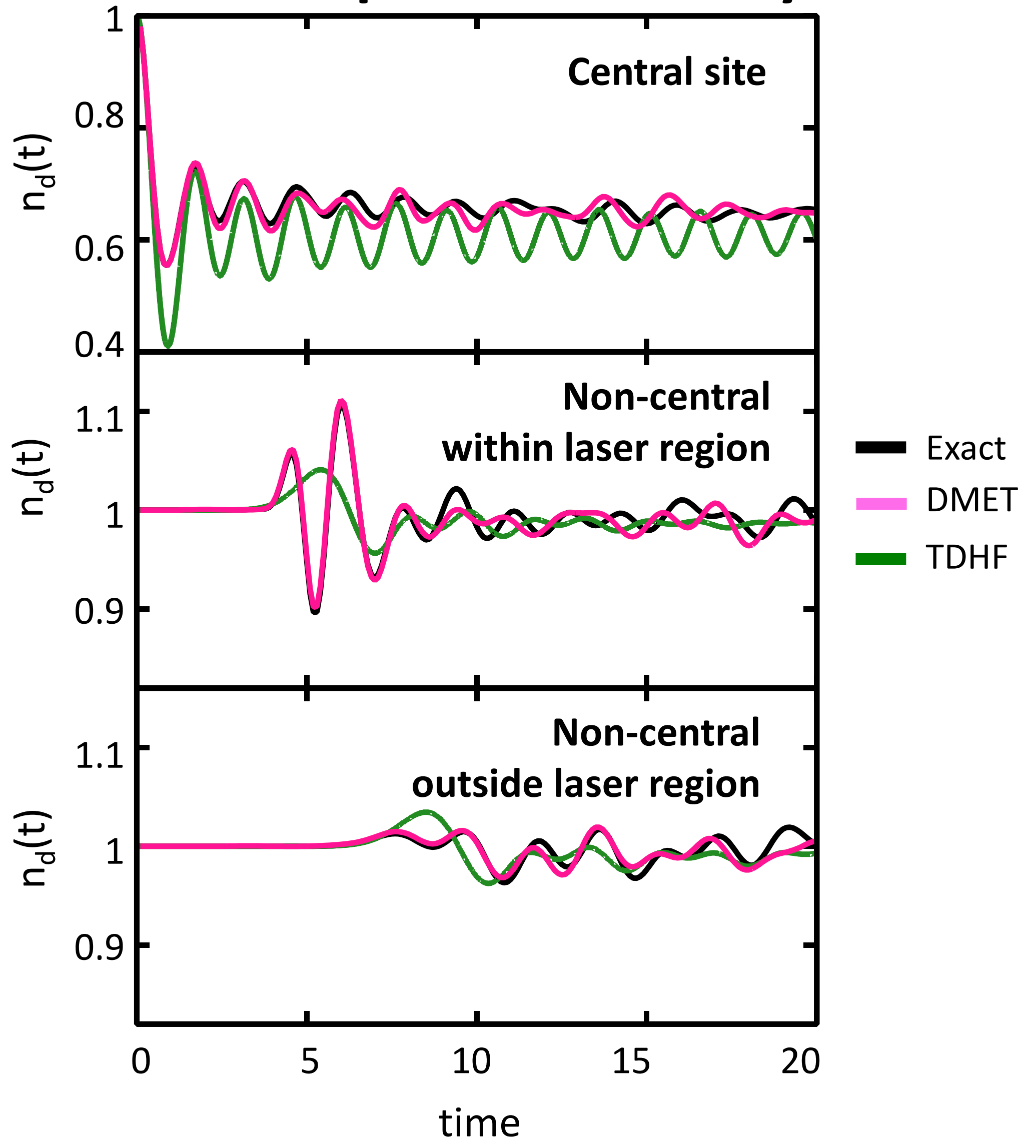
(Yehorova and Kretchmer, *JCP 2023*)

Laser-Driven Electron Dynamics

Time = 0 **Time > 0**

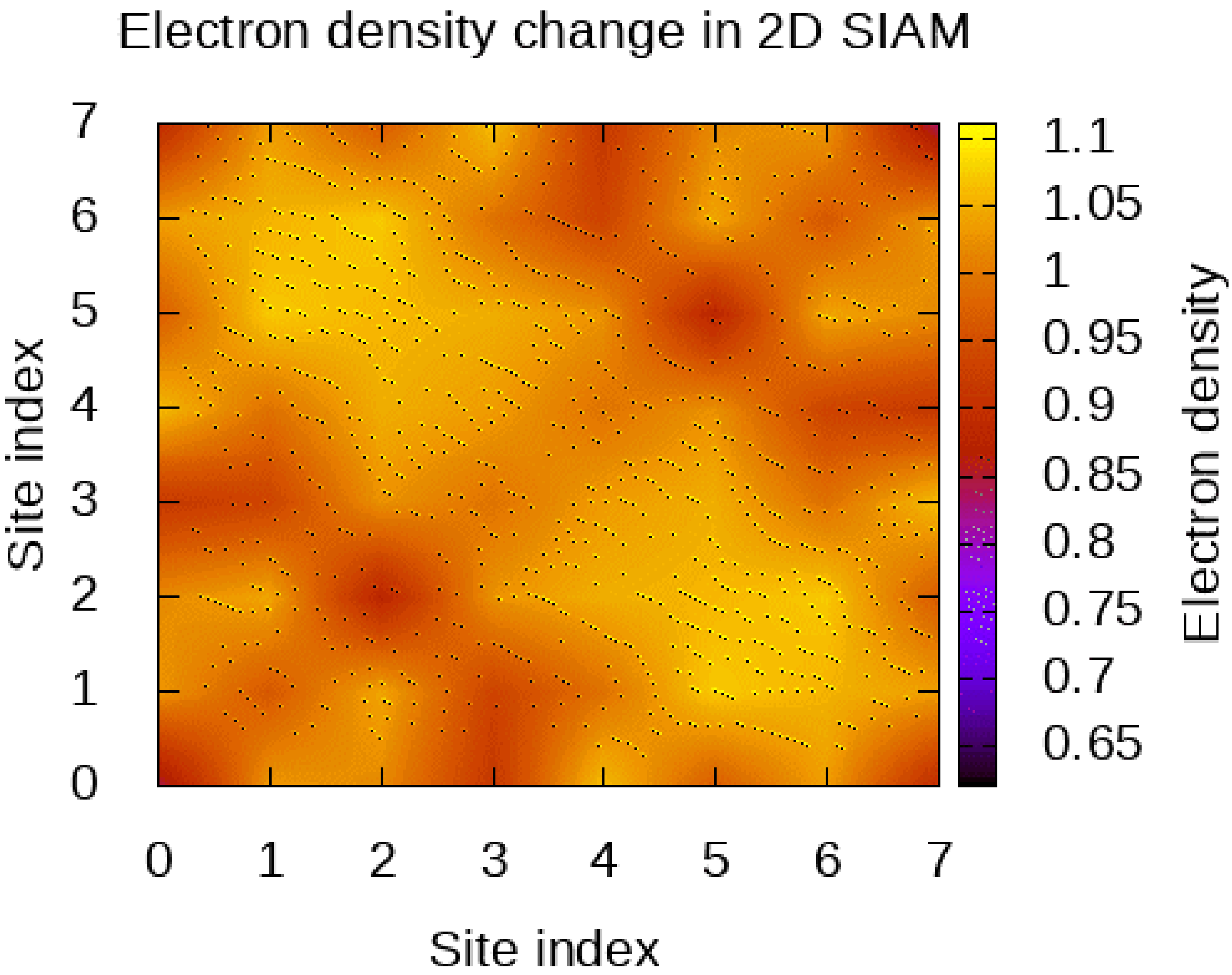


Time-dependent density



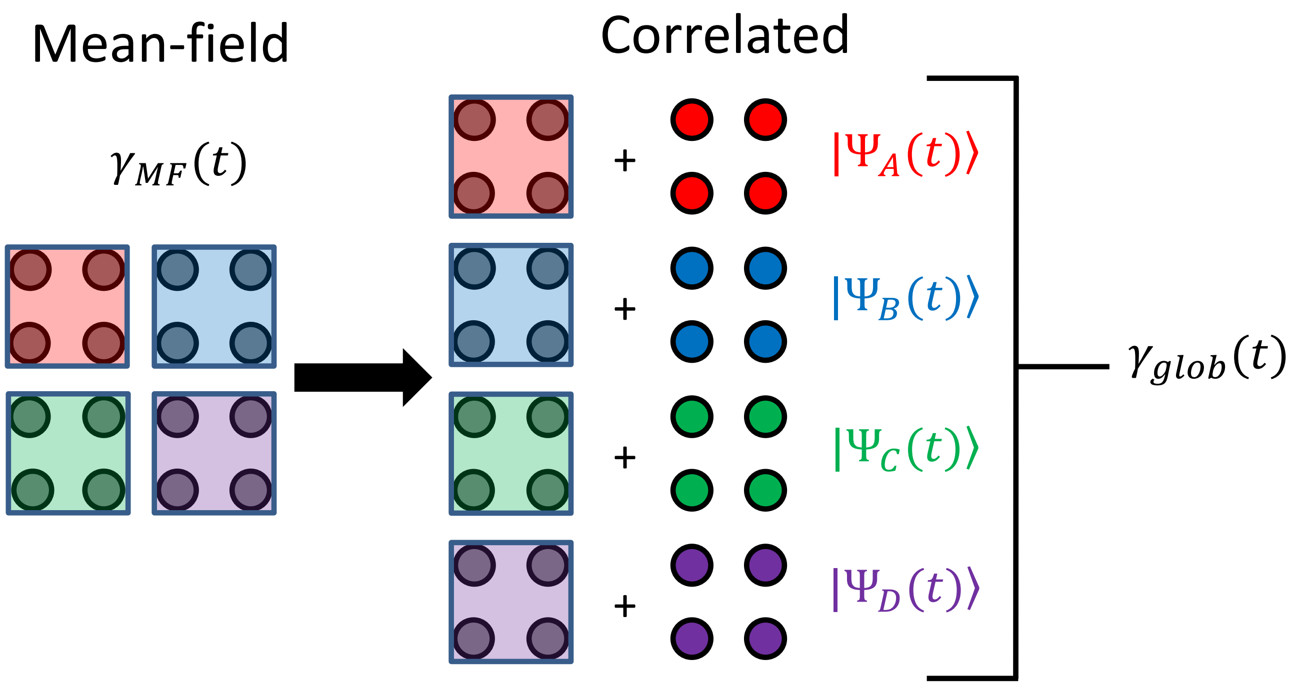
(Yehorova and Kretchmer, *JCP 2023*)

Multi-dimensional Impurity Model



(Yehorova and Kretchmer, *JCP 2023*)

Conclusions

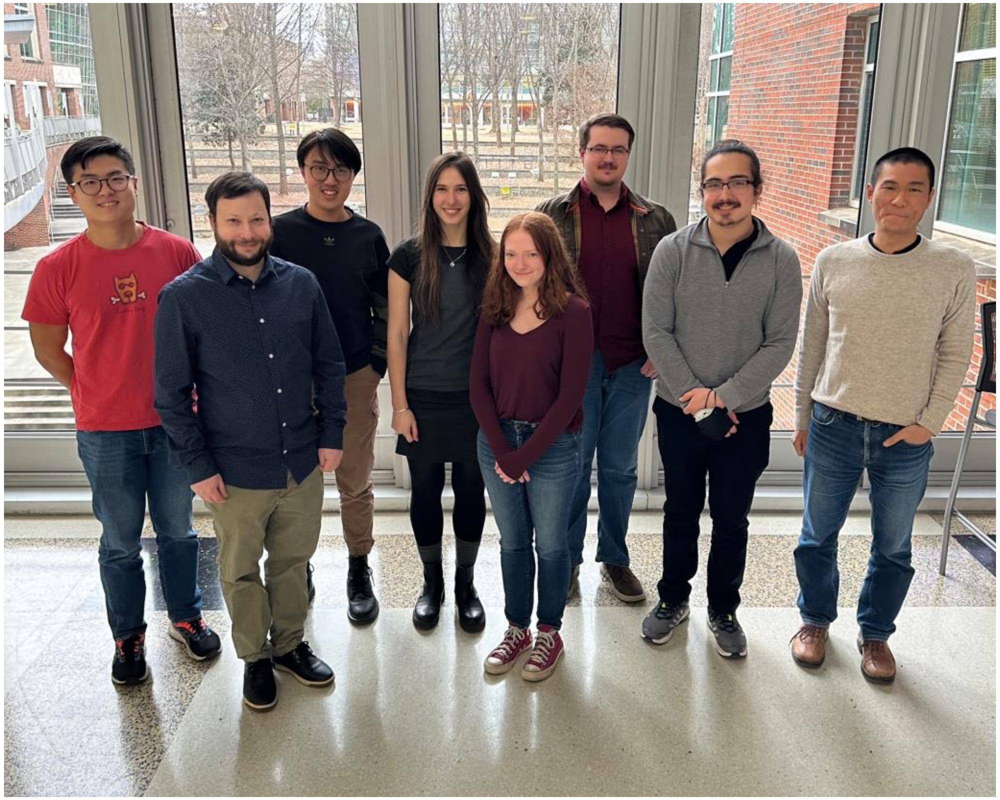


Real-time projected density matrix embedding theory

- Multi-fragment real-time quantum embedding method
- Non-equilibrium electron dynamics in strongly correlated systems
- Accurately treat dynamics across entire system

(Yehorova and Kretchmer, *JCP 2023*)

Acknowledgements



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