Density matrix embedding theory: A one-electron reduced density matrix functional perspective

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Multinodal event: CECAM-FR-RA, CECAM-FR-GSO

Description | Participants | Participate

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- Emmanuel Fromager (University of Strasbourg)
- Pierre-Francois Loos (CNRS)
- Vincent Robert (Institut de Chimie de Strasbourg)
- Pina Romaniello (Université de Toulouse)
- Julien Toulouse (Sorbonne Université)

Pre-register now at **istpc@unistra.fr**

Website: **https://lcqs.unistra.fr/istpc-2024/**

On the quantum embedding of (strongly correlated) electrons

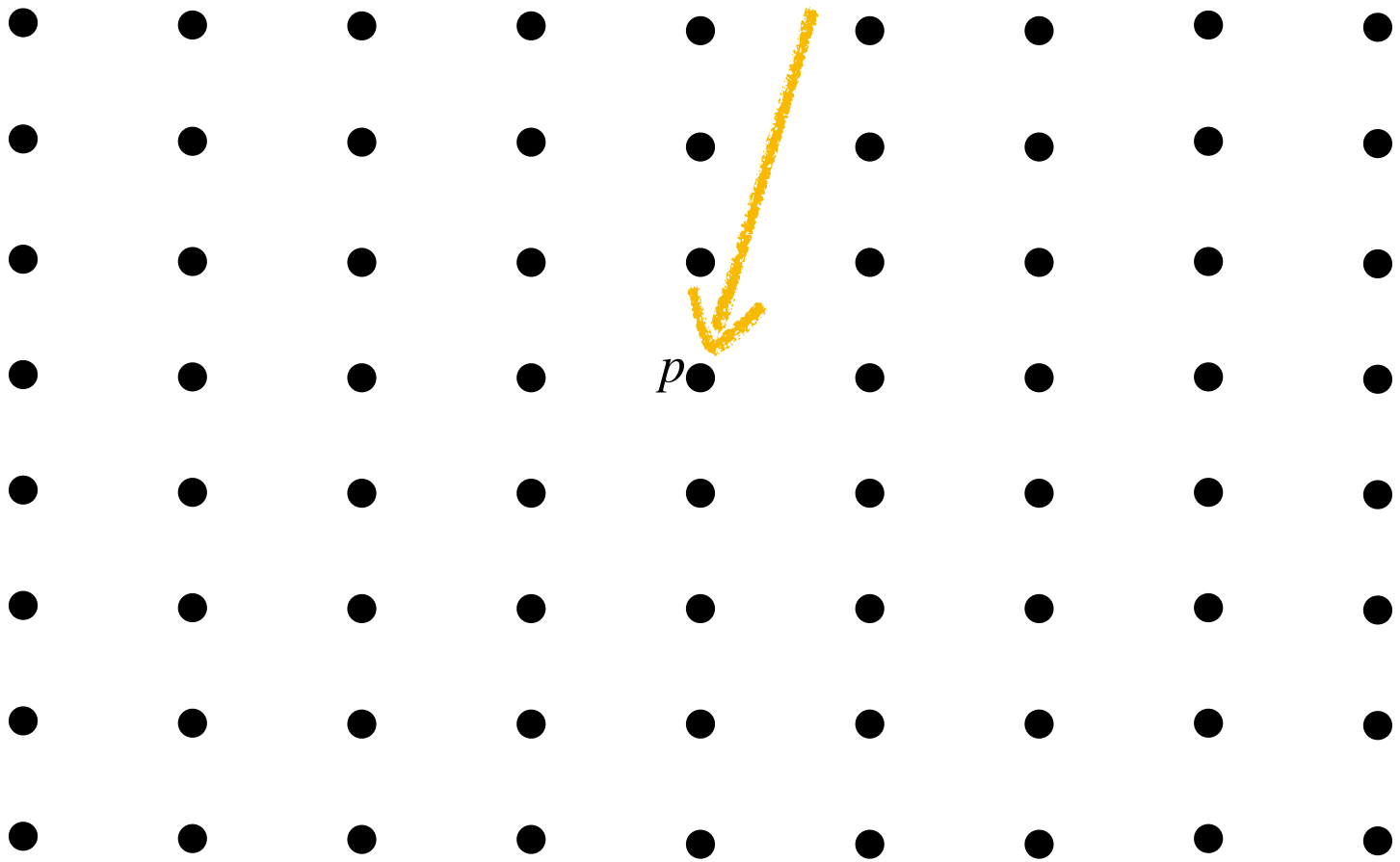
Keywords: *Second quantization, exponential wall, localised orbitals, fragmentation.*

Local evaluation of the energy (in a localised spin-orbital basis)

So-called "lattice representation"

$\chi_p(\mathbf{r})$

Atomic or localized molecular orbital



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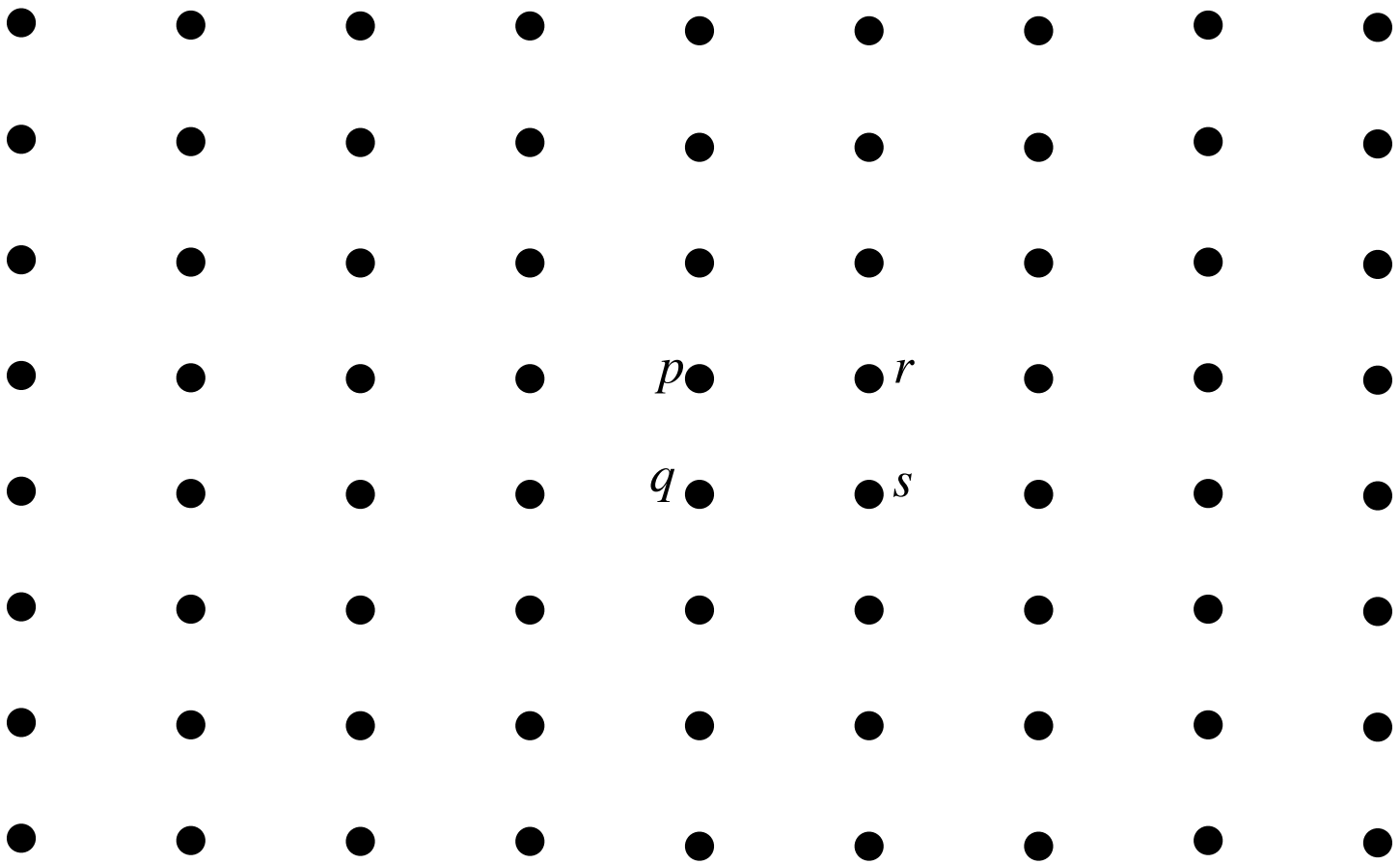
$$\langle \hat{H} \rangle = \sum_{pq} h_{pq} \underbrace{\langle \hat{c}_p^\dagger \hat{c}_q \rangle}_{\text{One-electron density matrix (1RDM)}} + \frac{1}{2} \sum_{pqrs} \langle pq \,|\, rs \rangle \underbrace{\langle \hat{c}_p^\dagger \hat{c}_q^\dagger \hat{c}_s \hat{c}_r \rangle}_{\text{Two-electron density matrix (2RDM)}}$$



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Schrödinger equation in second quantization

$$\hat{H}\,|\Psi_0\rangle = E_0\,|\Psi_0\rangle$$

***Step 1**: Choose a one-electron basis of molecular spin orbitals* $\{\varphi_P\}_{P=1,2,3,\ldots,\mathscr{M}}$

***Step 2**: Implement the Hamiltonian in second quantization in that basis*

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See the video for further explanations*

*https://www.youtube.com/watch?v=FQBrEI57pDA

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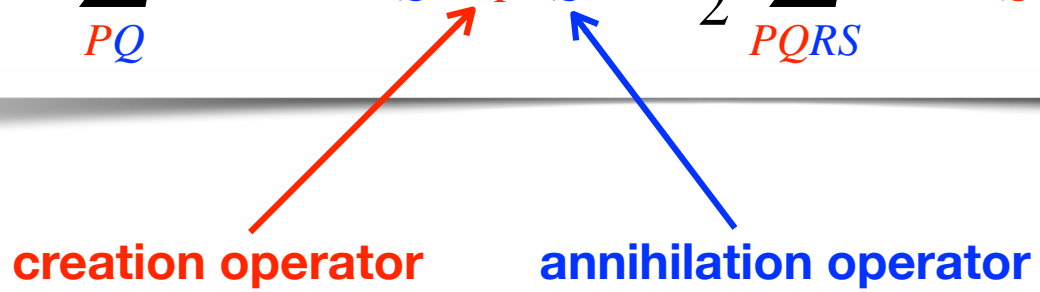

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$$\int d\mathbf{x}\, \varphi_P(\mathbf{x}) \left(-\frac{1}{2}\nabla_{\mathbf{r}}^2 + v_{\text{elec}-\text{nuclei}}(\mathbf{x}) \right) \varphi_Q(\mathbf{x})$$

One-electron integrals

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Two-electron integrals

$$\int d\mathbf{x}_1 \int d\mathbf{x}_2 \; \varphi_P(\mathbf{x}_1)\varphi_Q(\mathbf{x}_2) \frac{1}{|\,\mathbf{r}_1 - \mathbf{r}_2\,|} \varphi_R(\mathbf{x}_1)\varphi_S(\mathbf{x}_2)$$

Evaluation of the energy from the reduced density matrices

$$E_0 = \langle \Psi_0 | \hat{H} | \Psi_0 \rangle \overset{\text{notation}}{=} \langle \hat{H} \rangle_{\Psi_0}$$

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$$= \sum_{PQ} h_{PQ} \langle \hat{c}^\dagger_P \hat{c}_Q \rangle_{\Psi_0} + \frac{1}{2} \sum_{PQRS} g_{PQRS} \langle \hat{c}^\dagger_P \hat{c}^\dagger_Q \hat{c}_S \hat{c}_R \rangle_{\Psi_0}$$

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One-electron reduced density matrix (1RDM)

$$\gamma_{PQ} = \langle \hat{c}_P^\dagger \hat{c}_Q \rangle_{\Psi_0}$$

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One-electron reduced density matrix (1RDM)

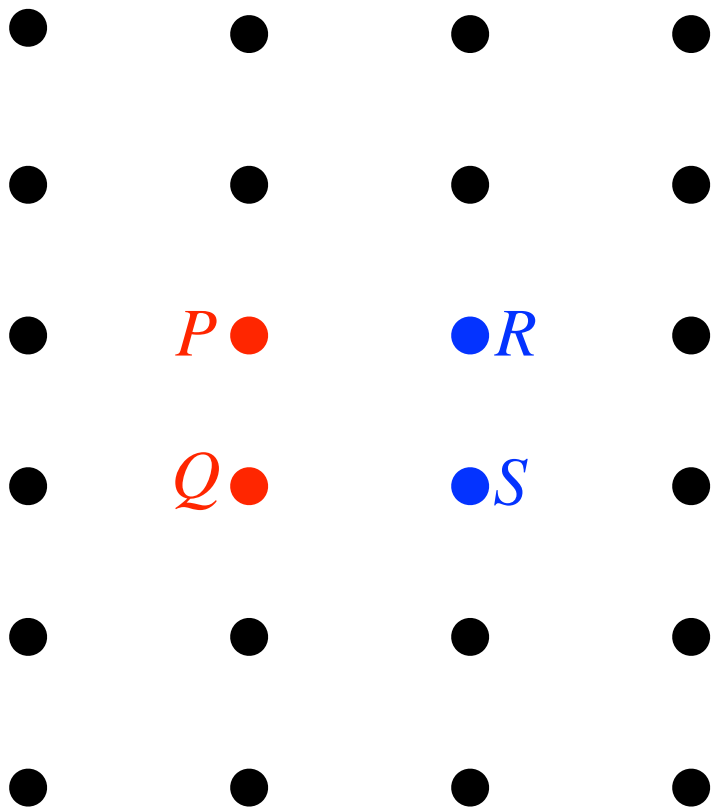
Two-electron reduced density matrix (2RDM)

$$\gamma_{PQ} = \langle \hat{c}_P^\dagger \hat{c}_Q \rangle_{\Psi_0}$$

$$\Gamma_{PQSR} = \langle \hat{c}_P^\dagger \hat{c}_Q^\dagger \hat{c}_S \hat{c}_R \rangle_{\Psi_0}$$

Meaning of the reduced density matrices

Let's consider a 2D lattice of localised spin-orbitals



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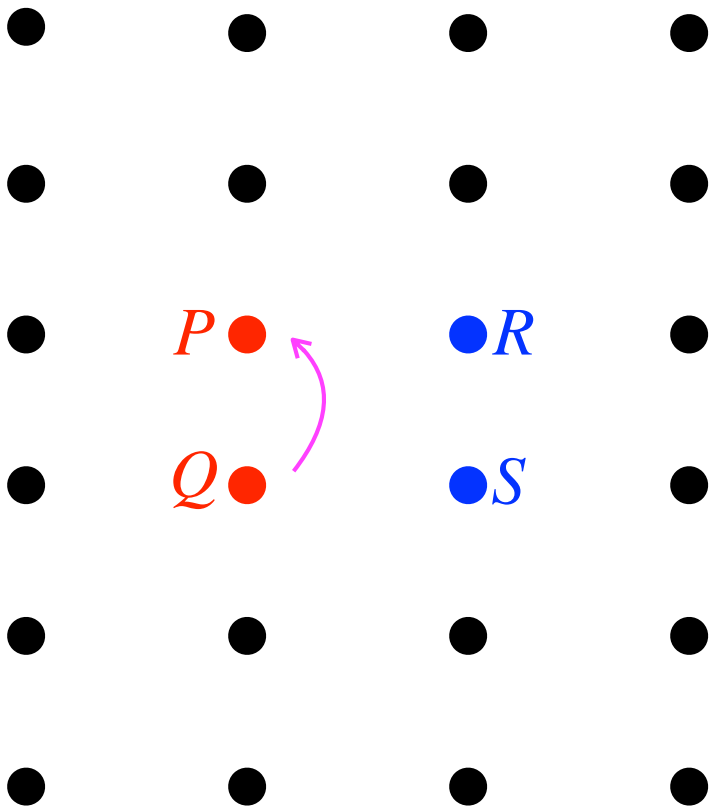

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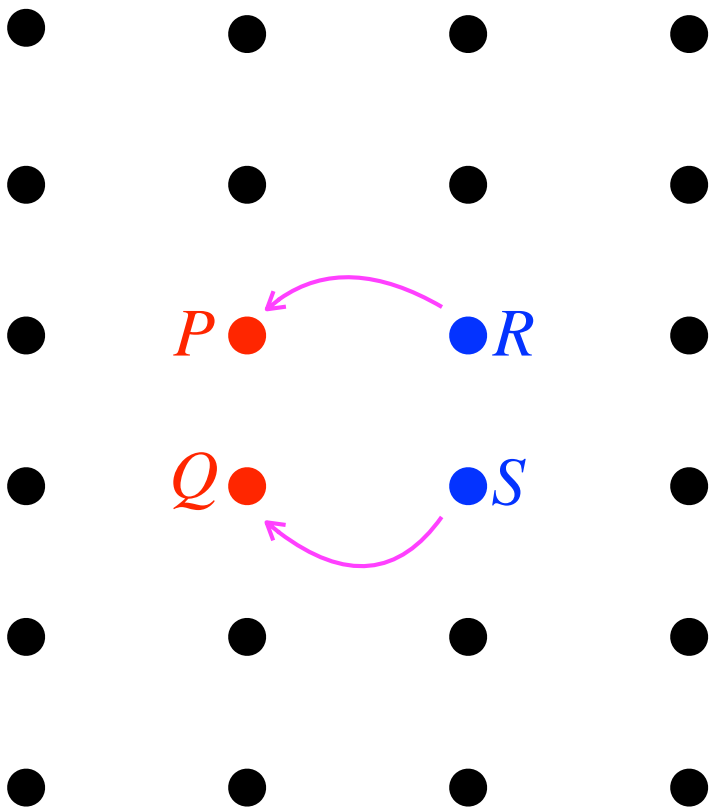

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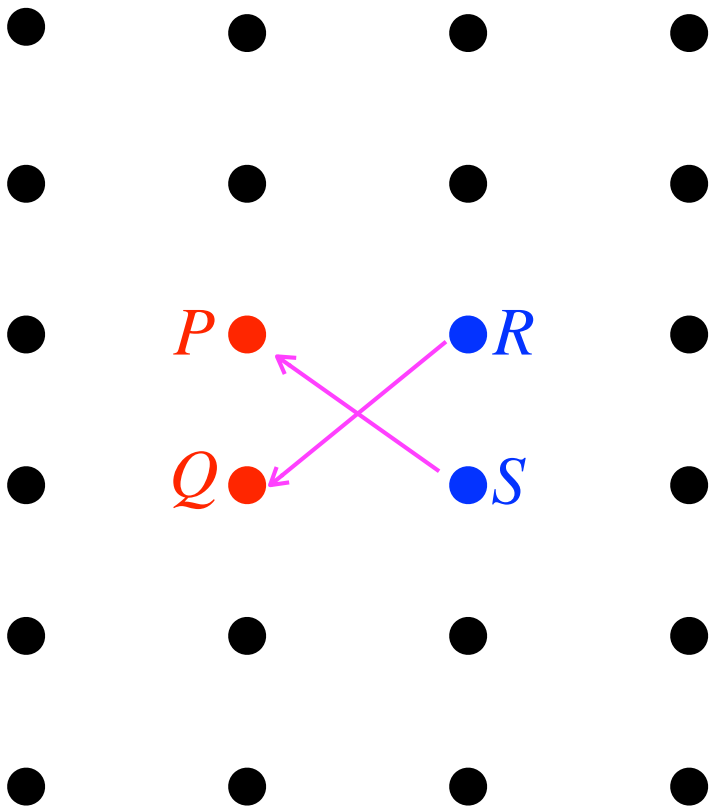

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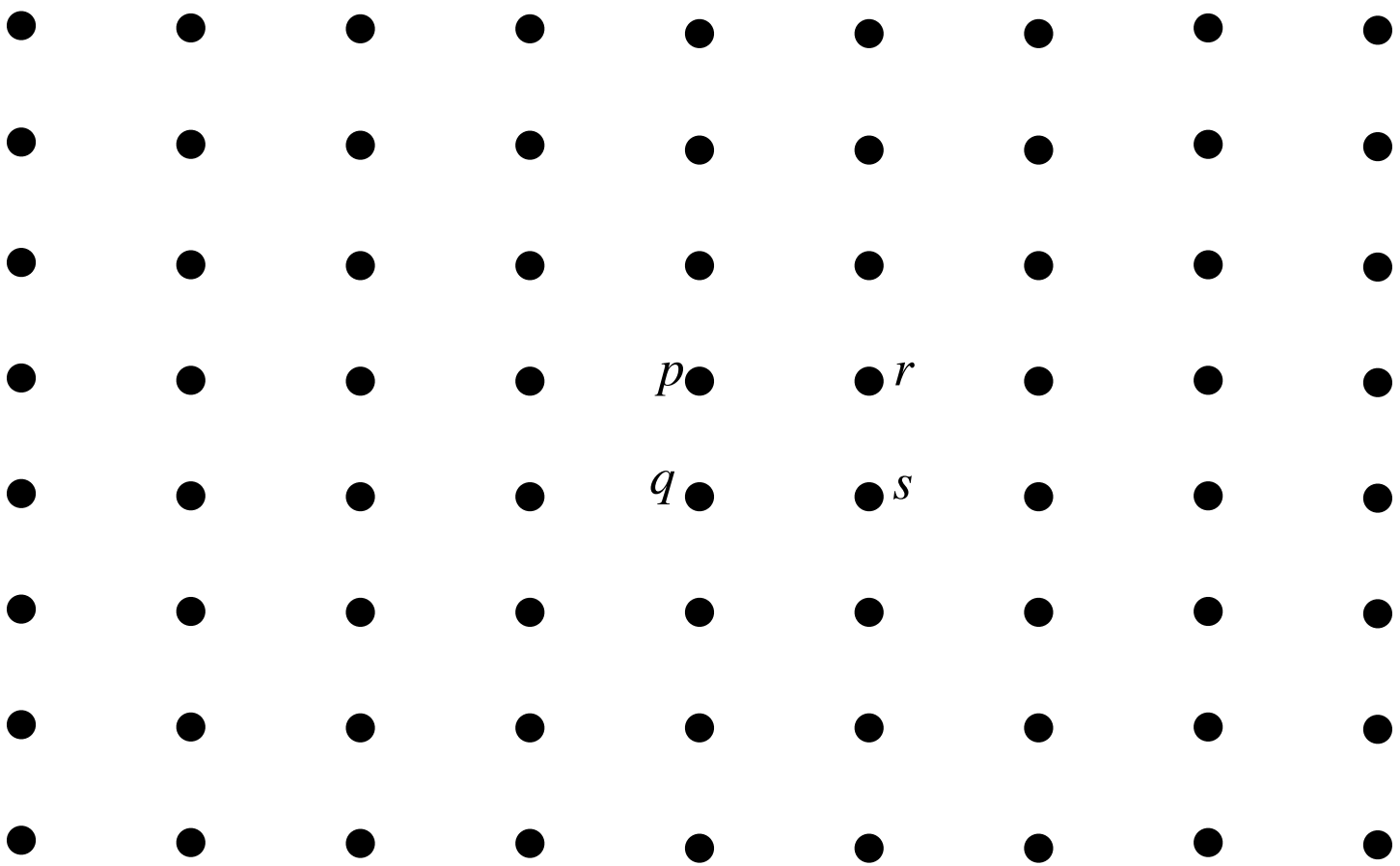

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Fragmentation

for treating strong local electron correlations

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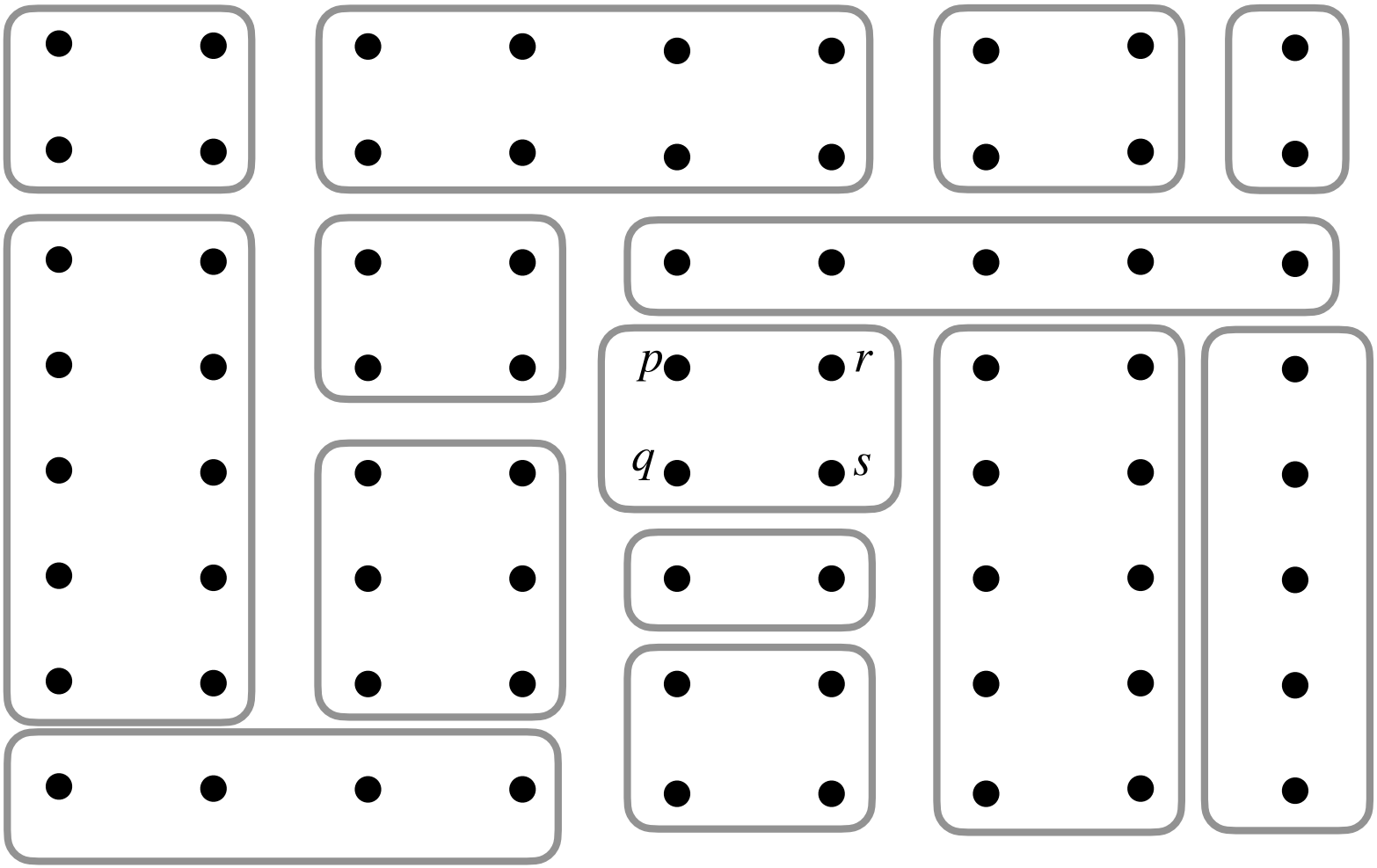

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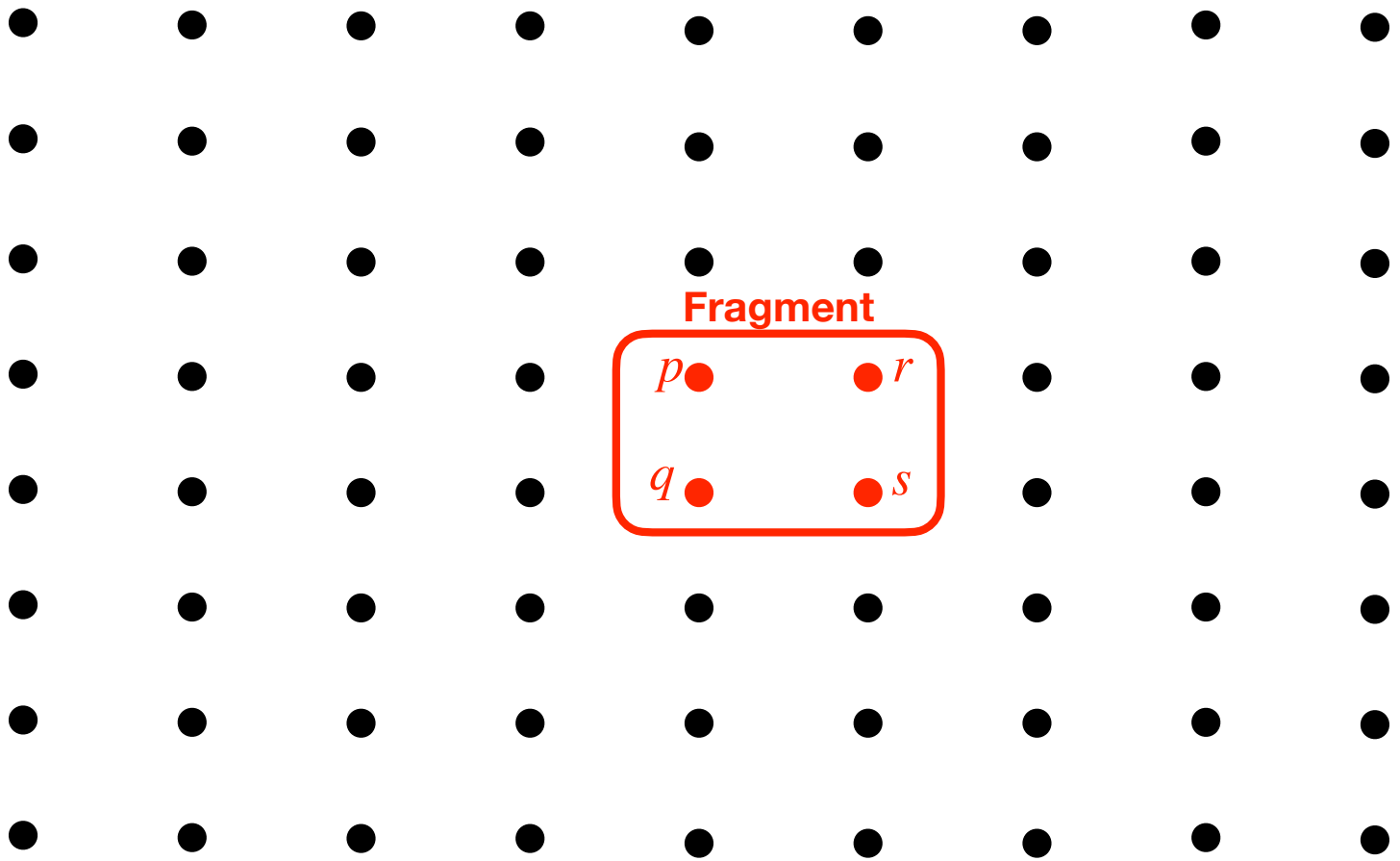

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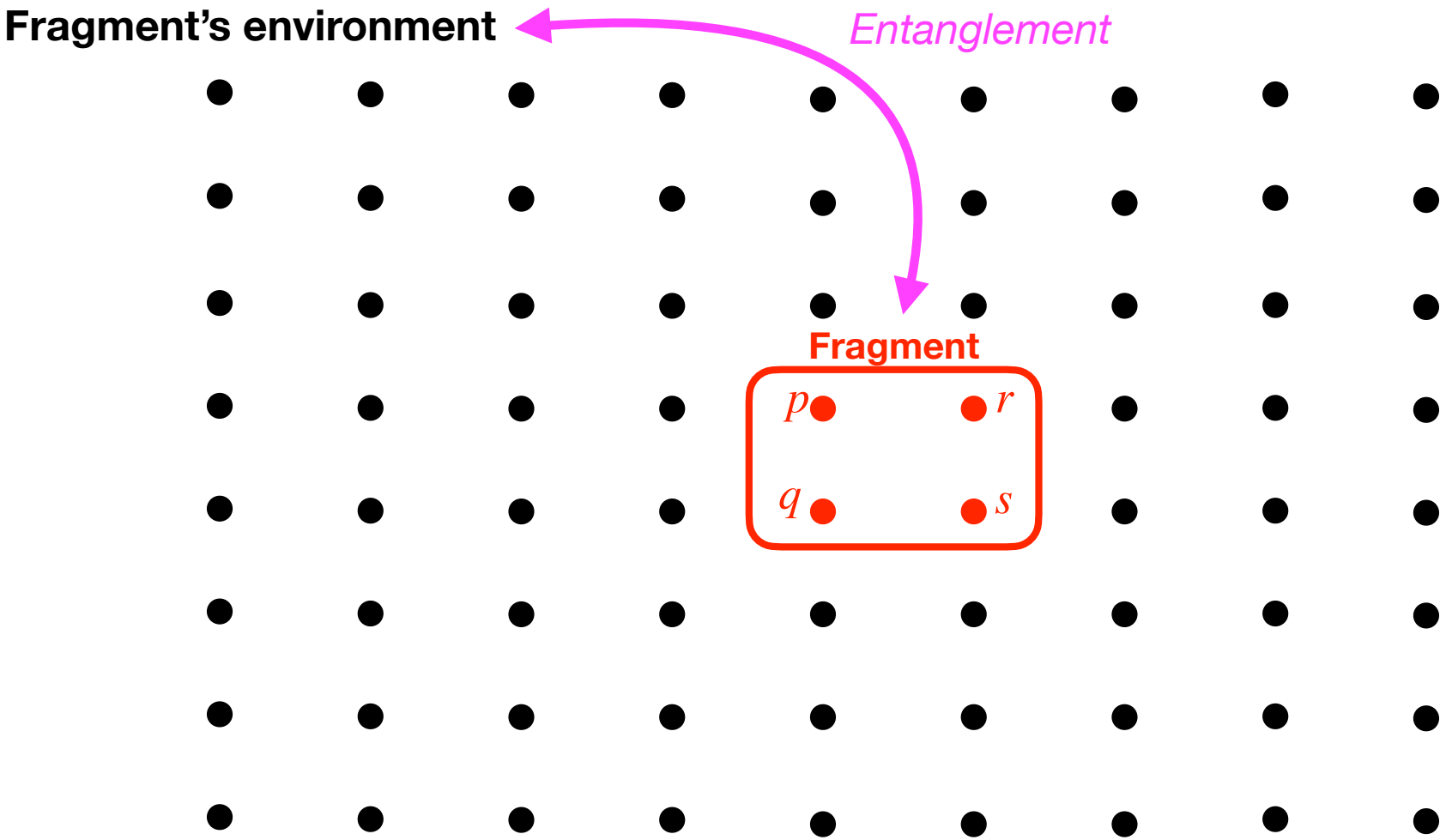

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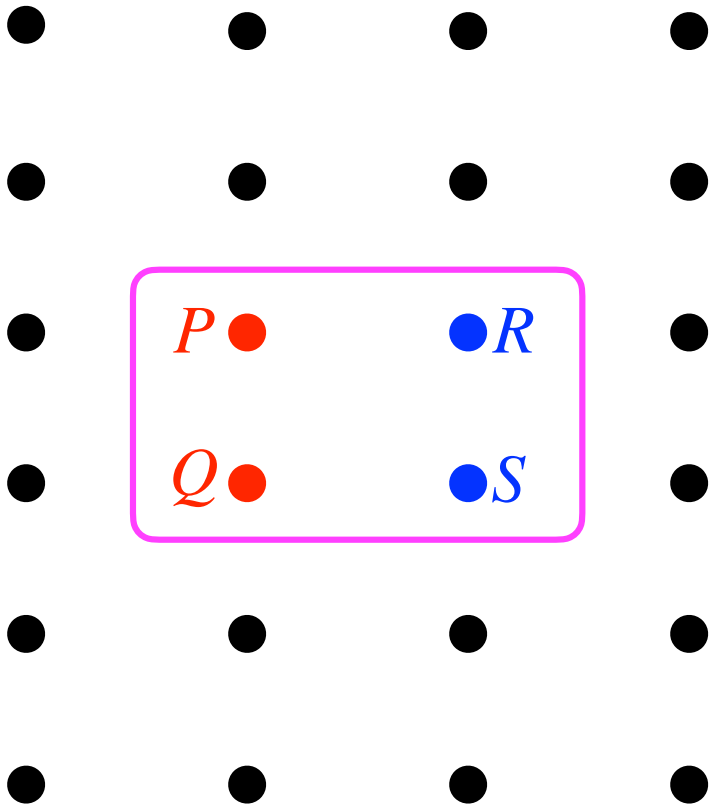
Quantum entanglement of a fragment with its environment

*The $PQRS$ orbital fragment is **NOT disconnected** from the other orbitals*



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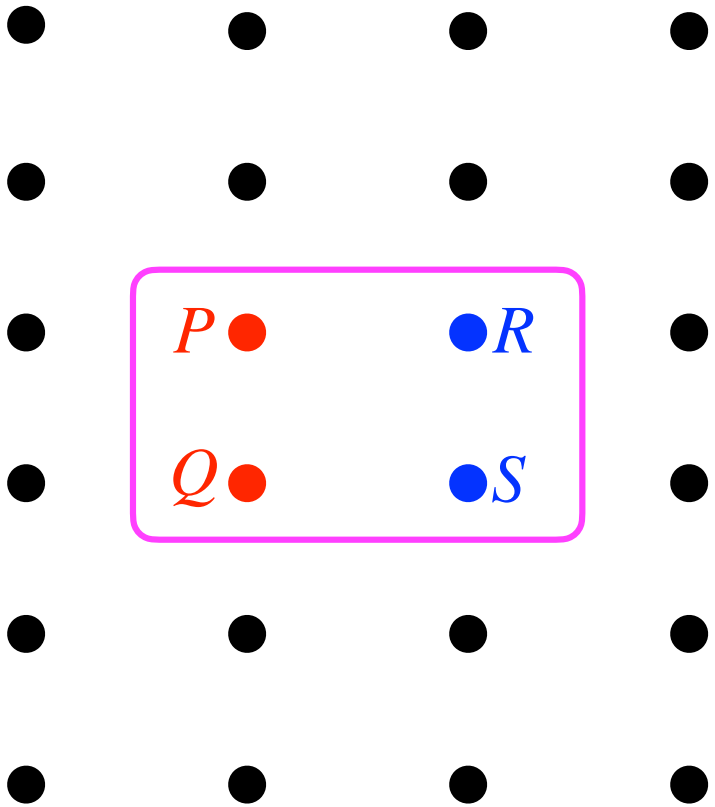

Open quantum subsystem

Quantum entanglement of a fragment with its environment

$$\hat{H} \equiv \sum_{PQ} h_{PQ}\, \hat{c}_P^\dagger \hat{c}_Q + \frac{1}{2} \sum_{PQRS} g_{PQRS}\, \hat{c}_P^\dagger \hat{c}_Q^\dagger \hat{c}_S \hat{c}_R$$

In principle, we need to **solve the Schrödinger equation** in order to evaluate the (ground-state) energy:

$$\hat{H}\,|\Psi_0\rangle = E_0\,|\Psi_0\rangle$$

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In principle, we need to **solve the Schrödinger equation** in order to evaluate the (ground-state) energy:

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A $|\Psi_0\rangle$ consisting of electrons simply distributed among ***disconnected fragments cannot*** match $\hat{H}\,|\Psi_0\rangle$***!***

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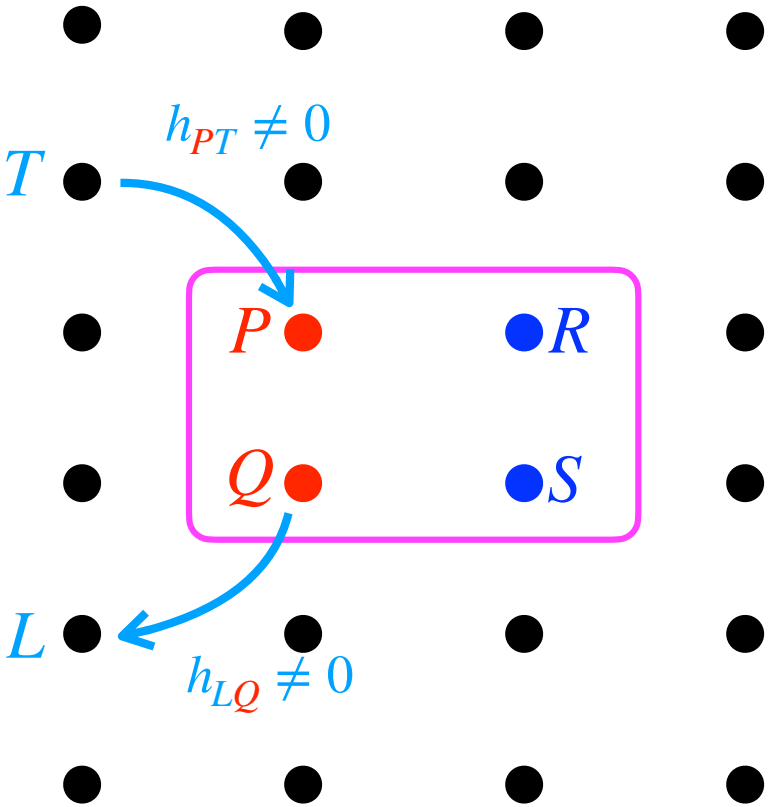
Summation running over the **full lattice!**



Entanglement

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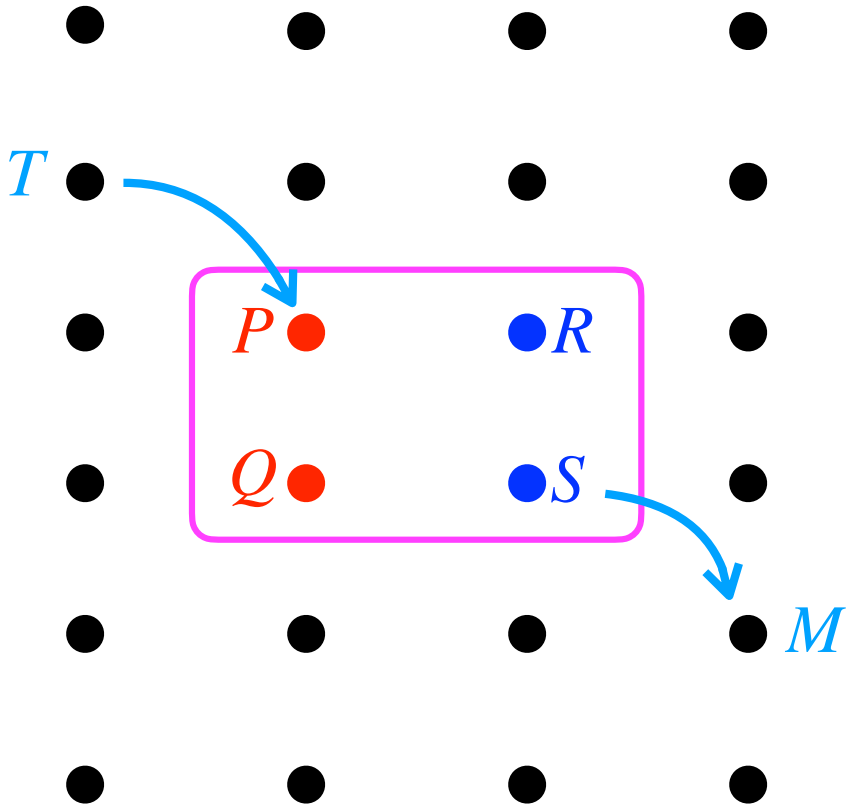


$$g_{PMTS} \neq 0$$

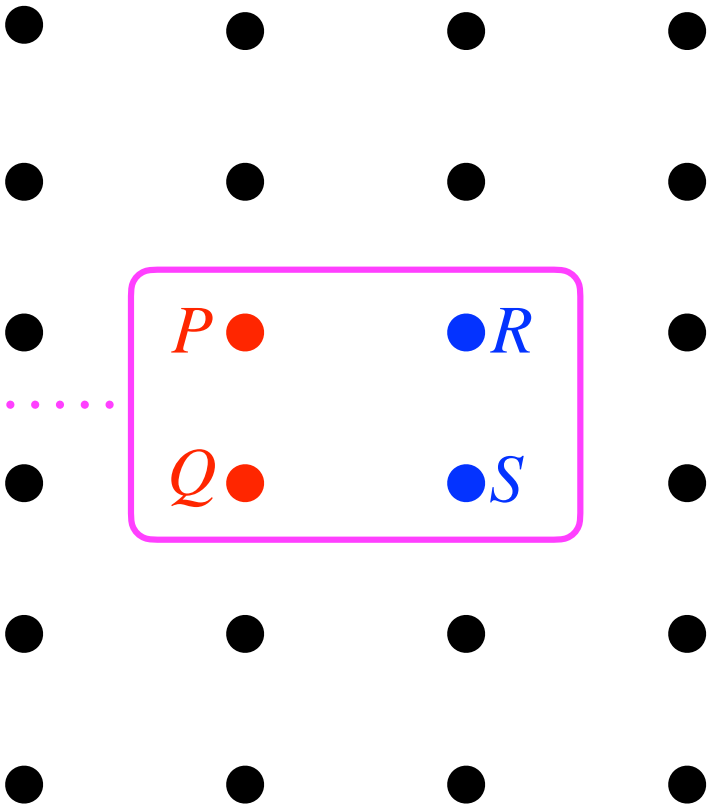
Entanglement

Quantum entanglement of a fragment with its environment

The evaluation of the RDMs requires, in principle, the ***wave function*** Ψ_0 ***of the entire system***

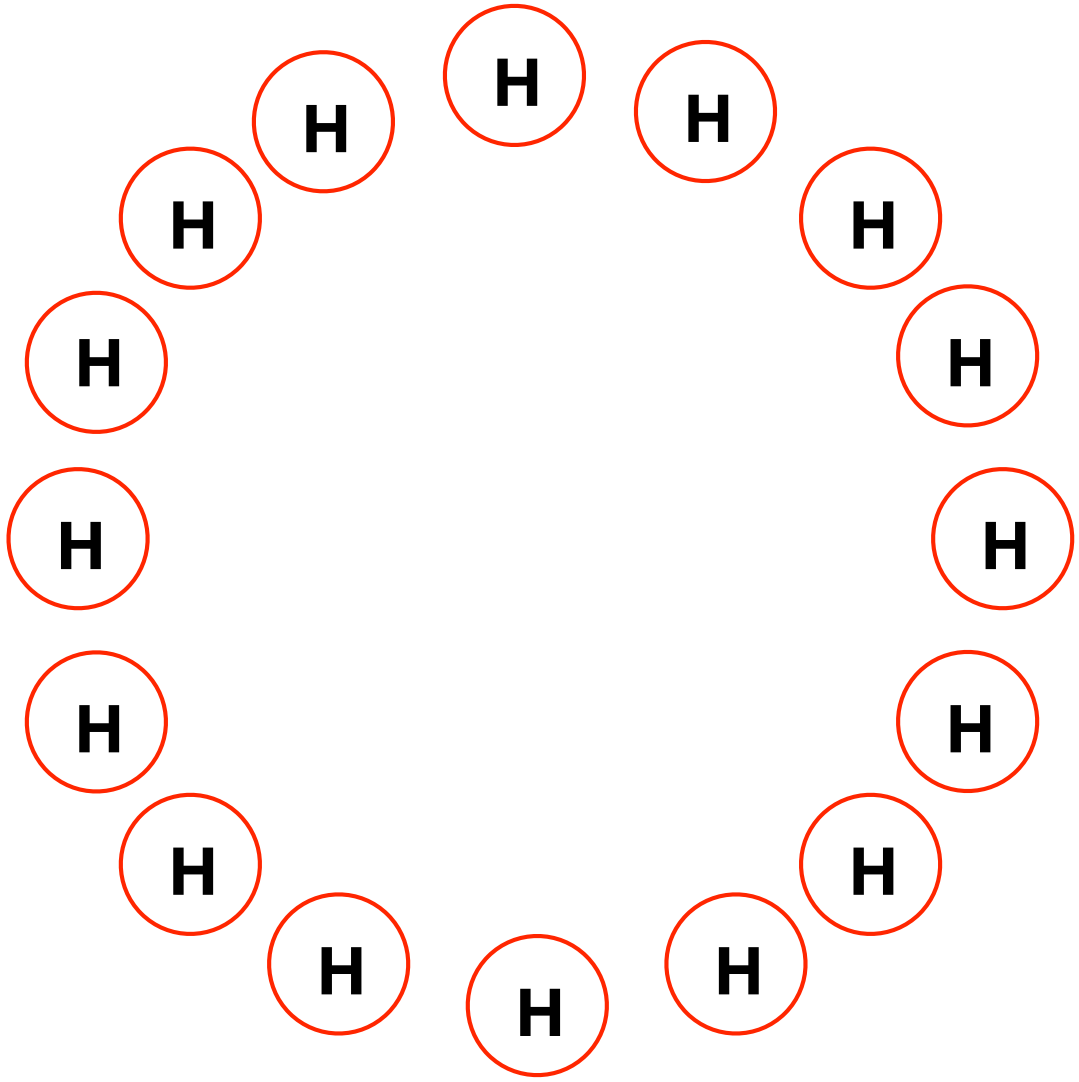
$$\gamma_{PQ} = \langle \hat{c}_P^\dagger \hat{c}_Q \rangle_{\Psi_0}$$

$$\Gamma_{PQSR} = \langle \hat{c}_P^\dagger \hat{c}_Q^\dagger \hat{c}_S \hat{c}_R \rangle_{\Psi_0}$$



How many localized configurations in total?

(in a minimal basis of $1s$ orbitals)



$$\mathscr{M} = 2 \times N$$

Spin

Number of atoms = number of electrons

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$$\mathscr{M} = 2 \times N$$

$$N_{\text{conf.}} = \frac{\mathscr{M}!}{N!(\mathscr{M}-N)!} = \frac{(2N)!}{(N!)^2}$$

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$$N! \approx \sqrt{2\pi N}\left(\frac{N}{e}\right)^N$$

Stirling formula for large N values

$$\approx \frac{2^{2N}}{\sqrt{\pi N}} = \frac{e^{2N \ln 2}}{\sqrt{\pi N}}$$

How many localized configurations in total?

(in a minimal basis of $1s$ orbitals)

$$N_{\text{conf.}} \approx \frac{e^{2N \ln 2}}{\sqrt{\pi N}}$$

*The **to-be-diagonalized** Hamiltonian is a $N_{\text{conf.}} \times N_{\text{conf.}}$ matrix!*

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"Exponential wall"

*The **to-be-diagonalized** Hamiltonian is a $N_{\text{conf.}} \times N_{\text{conf.}}$ matrix!*

How many localized configurations in total?

(in a minimal basis of $1s$ orbitals)

$$N_{\text{conf.}} \approx \frac{e^{2N \ln 2}}{\sqrt{\pi N}} \overset{N=50}{\approx} 10^{29}$$

How many localized configurations in total?

(in a minimal basis of $1s$ orbitals)

$$N_{\text{conf.}} \approx \frac{e^{2N \ln 2}}{\sqrt{\pi N}} \overset{N=400}{\approx} 1.88 \times 10^{239}$$

*Philosophy of **density matrix embedding theory** (DMET)*

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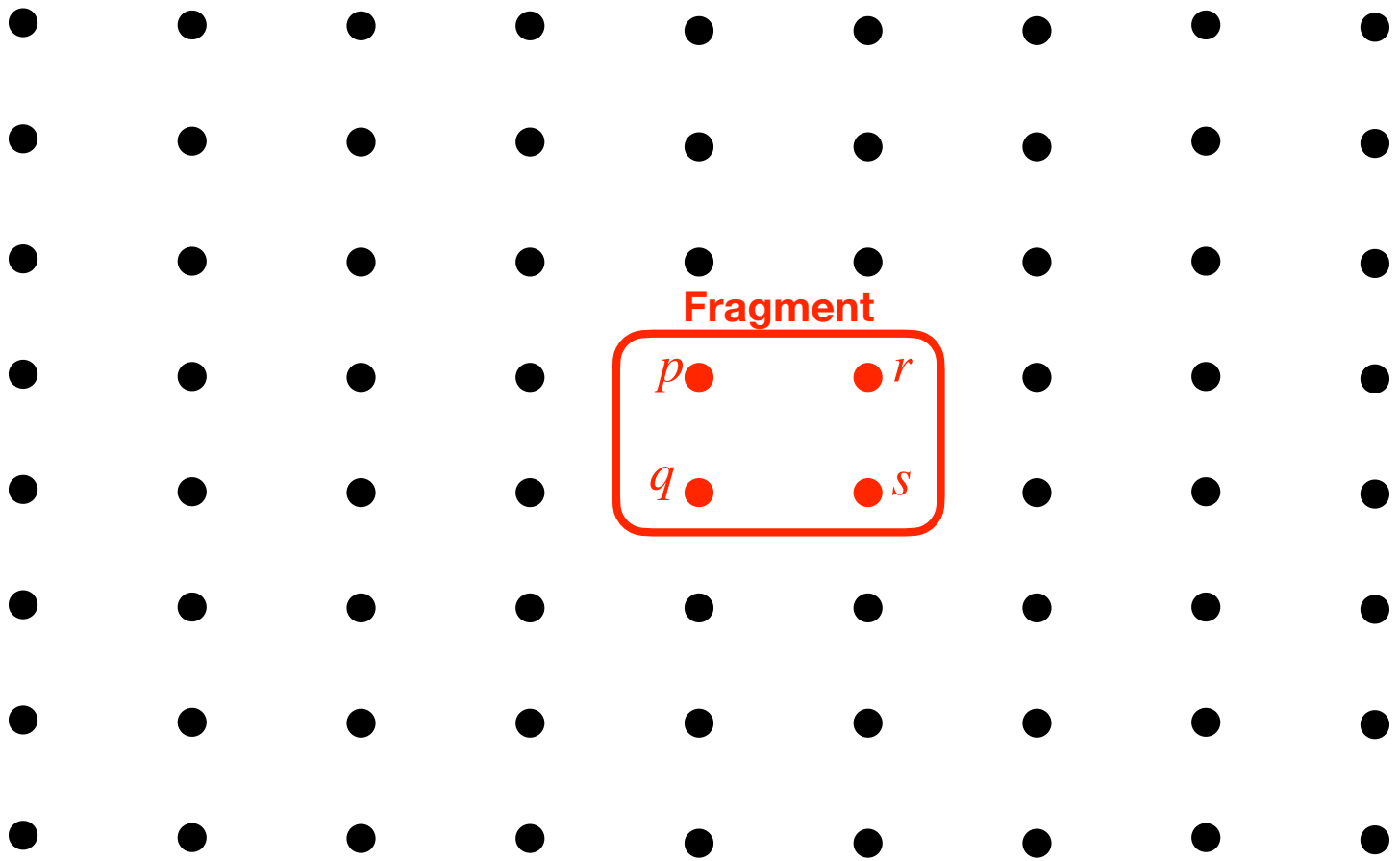

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What are we aiming at?

Reduction in size of the problem to be solved:

$$\langle \hat{c}_p^\dagger \hat{c}_q \rangle_{full\ system} \approx \langle \hat{c}_p^\dagger \hat{c}_q \rangle_{\Psi^{\mathscr{C}}}$$

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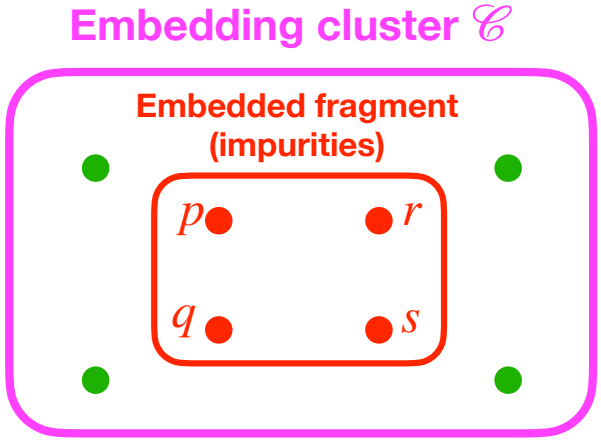
Quantum bath
≡ electronic reservoir



$\Psi^{\mathscr{C}}$ **Few-electron**
correlated wave function

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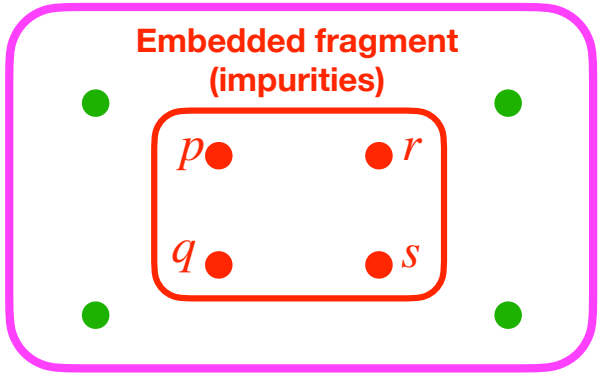
$$\langle \hat{c}_p^\dagger \hat{c}_q \rangle_{full\ system} \approx \langle \hat{c}_p^\dagger \hat{c}_q \rangle_{\Psi^{\mathscr{C}}}$$

$$\langle \hat{c}_p^\dagger \hat{c}_q^\dagger \hat{c}_s \hat{c}_r \rangle_{full\ system} \approx \langle \hat{c}_p^\dagger \hat{c}_q^\dagger \hat{c}_s \hat{c}_r \rangle_{\Psi^{\mathscr{C}}}$$

4 orbitals here: Why and how?

Quantum bath
≡ electronic reservoir

Embedding cluster $\mathscr{C}$



$\Psi^{\mathscr{C}}$ **Few-electron** correlated wave function

G. Knizia and G. K.-L. Chan, Phys. Rev. Lett. ***109****, 186404 (2012).*
S. Wouters, C. A. Jiménez-Hoyos, Q. Sun, and G. K.-L. Chan, J. Chem. Theory Comput. 12, 2706 (2016).
S. Sekaran, M. Tsuchiizu, M. Saubanère, and E. Fromager, Phys. Rev. B **104**, 035121 (2021).
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↓

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≡ electronic reservoir

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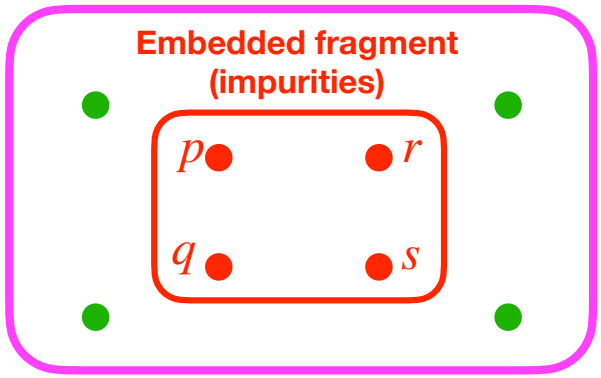

$\Psi^{\mathscr{C}}$

How many?

↓

Few-electron
correlated wave function

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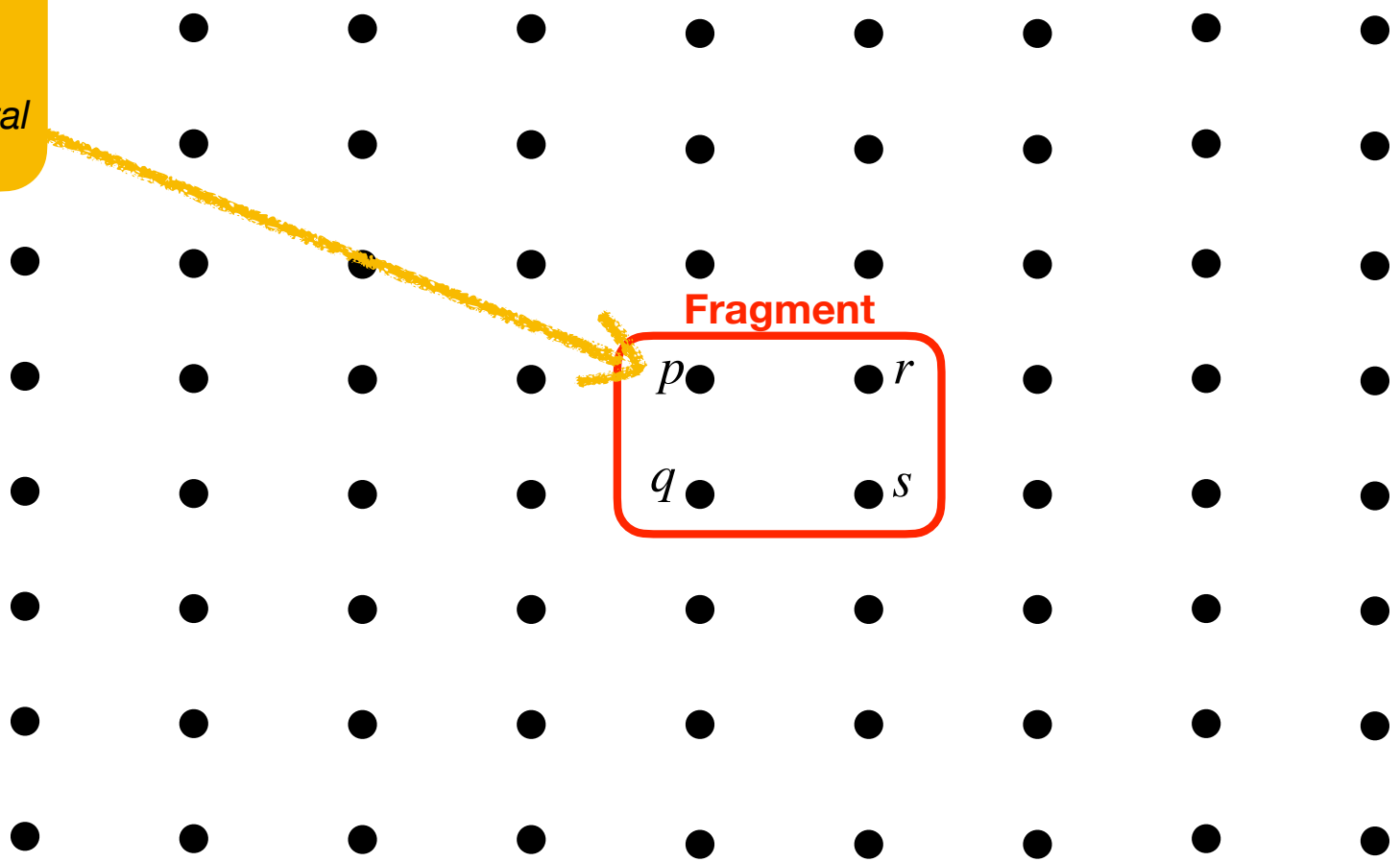
S. Sekaran, O. Bindech, and E. Fromager, J. Chem. Phys. **159**, 034107 (2023).

Clusterization through a unitary one-electron transformation

So-called "lattice representation"

$\chi_p(\mathbf{r})$

Atomic or localized molecular orbital



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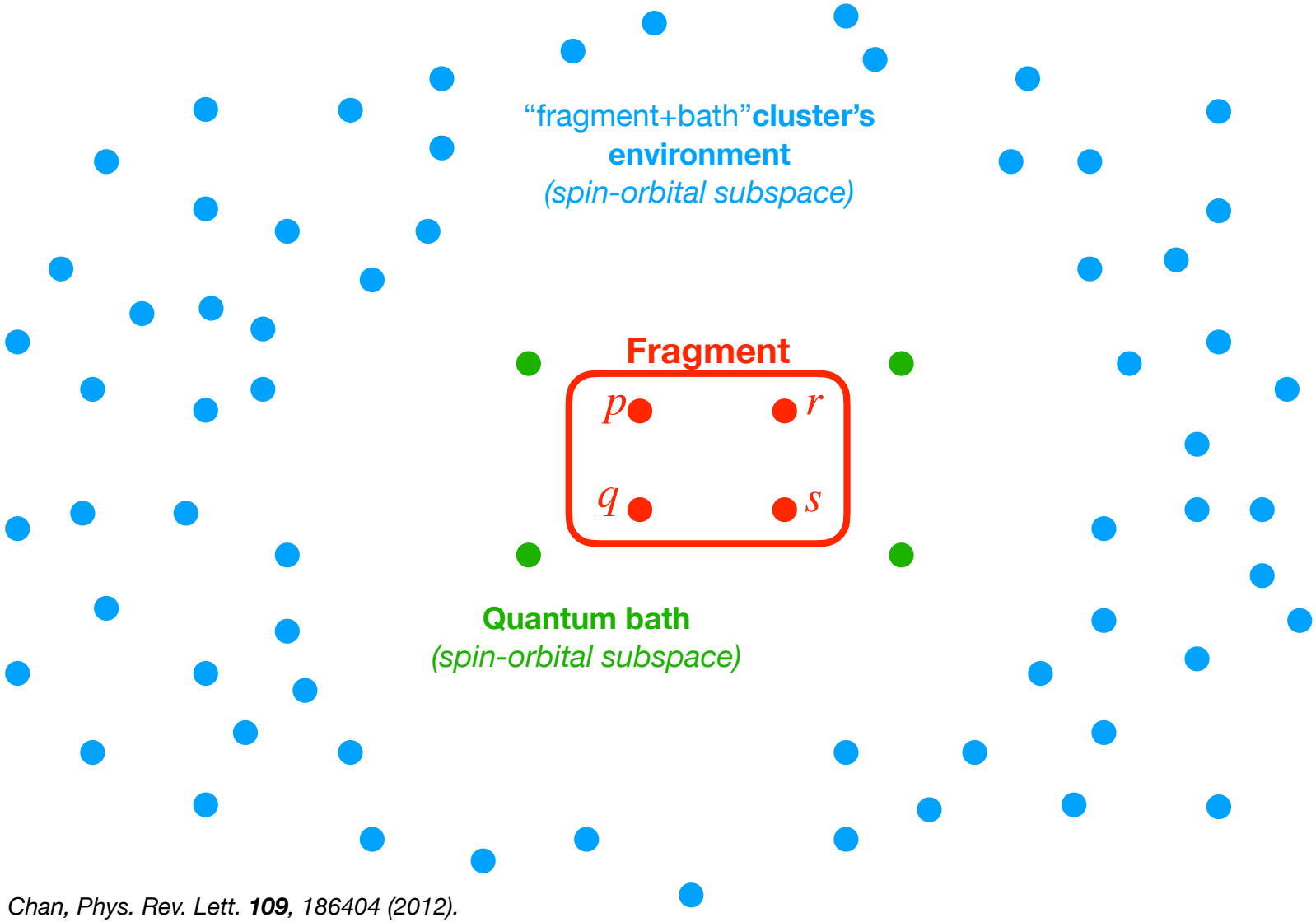
$$|\chi_q\rangle \rightarrow \sum_{p}^{lattice} \mathcal{U}_{pq} |\chi_p\rangle$$



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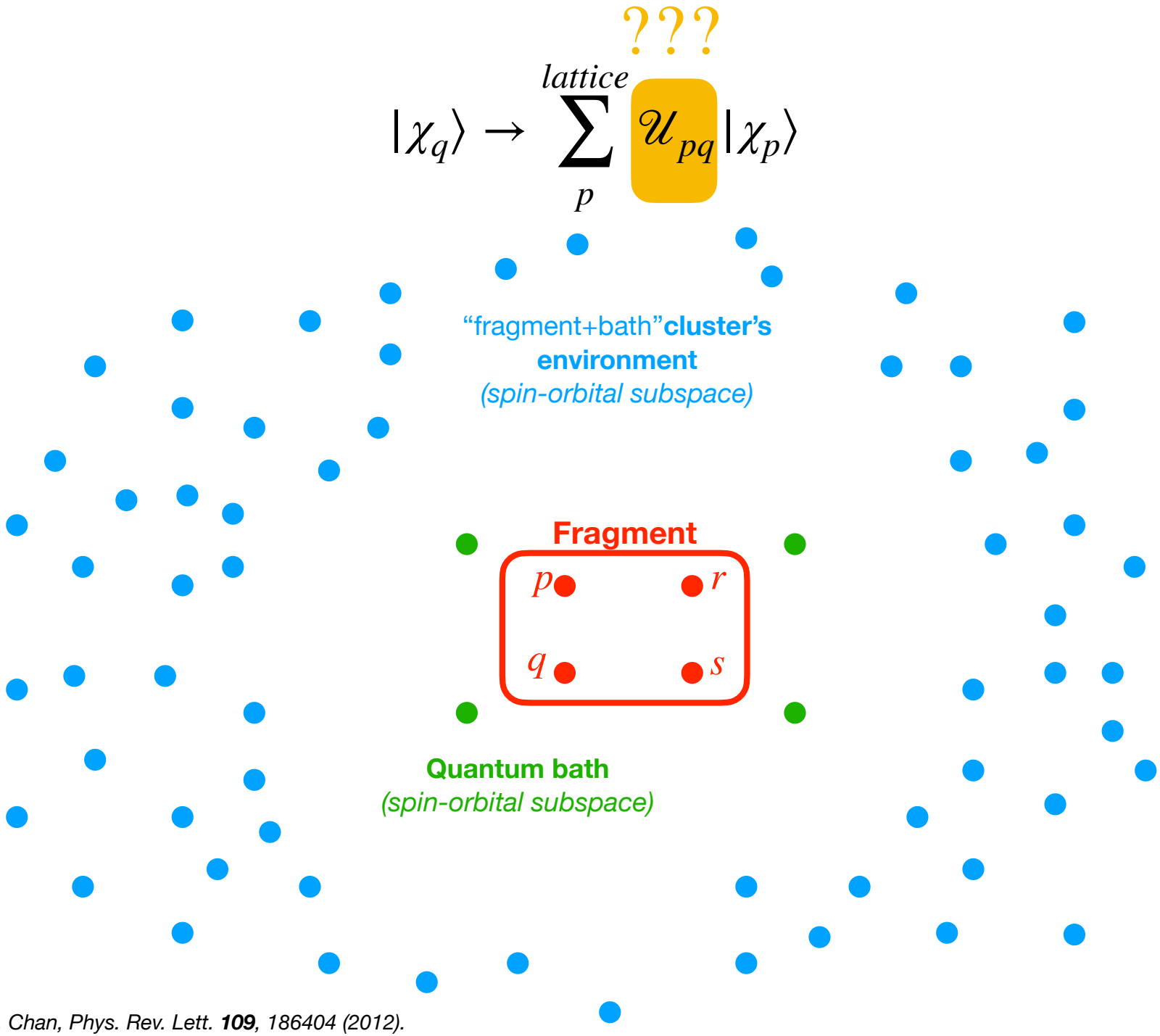

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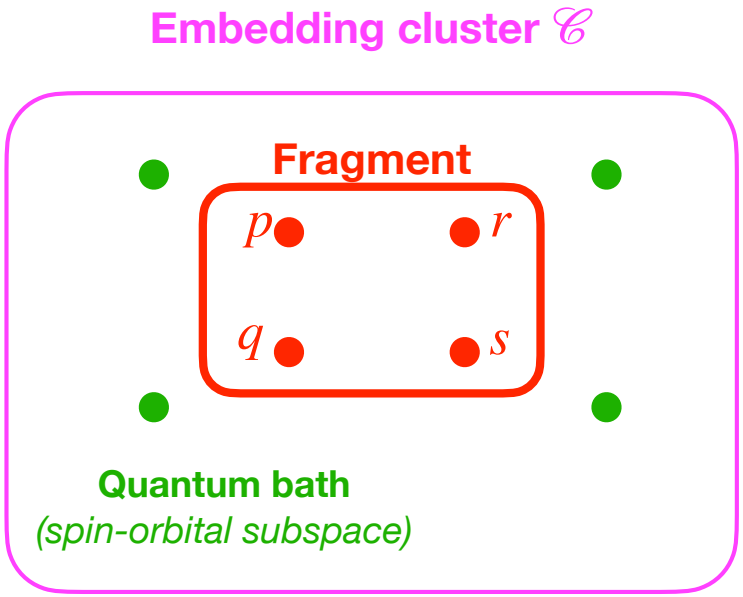

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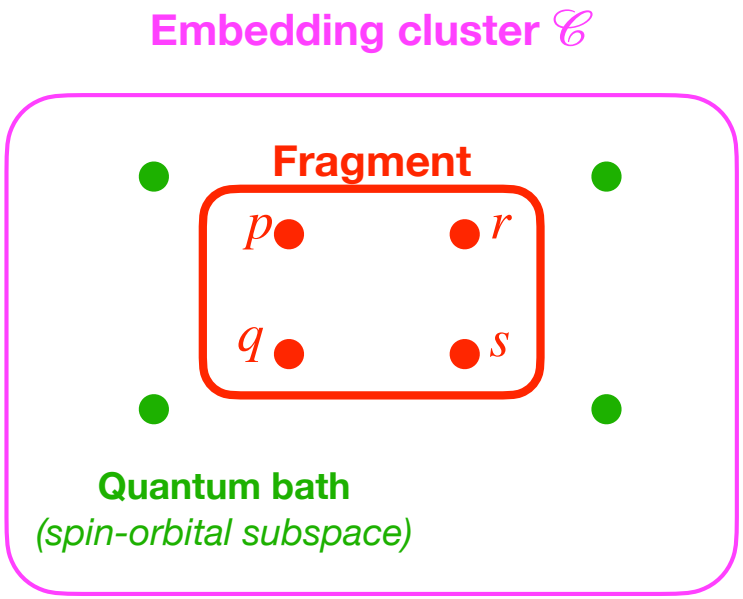


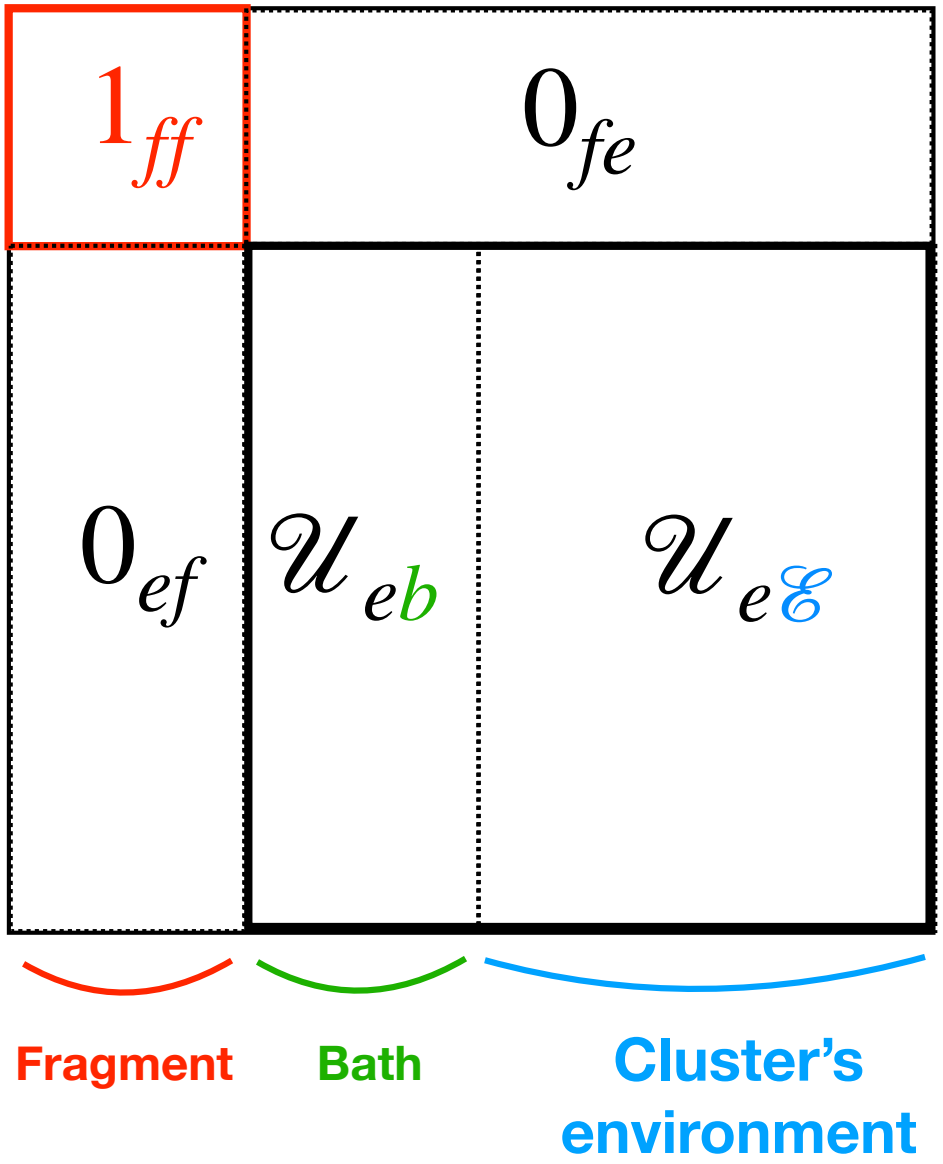
How much information do we loose?

G. Knizia and G. K.-L. Chan, Phys. Rev. Lett. ***109****, 186404 (2012).*
S. Wouters, C. A. Jiménez-Hoyos, Q. Sun, and G. K.-L. Chan, J. Chem. Theory Comput. 12, 2706 (2016).

Mathematical construction of the quantum bath

Quantum bath seen as a functional of the density matrix (1RDM)

$$\mathcal{U} =$$



$$|\chi_q\rangle \rightarrow \sum_{p}^{lattice} \mathcal{U}_{pq} |\chi_p\rangle$$

S. Sekaran, O. Bindech, and E. Fromager, J. Chem. Phys. **159**, 034107 (2023).

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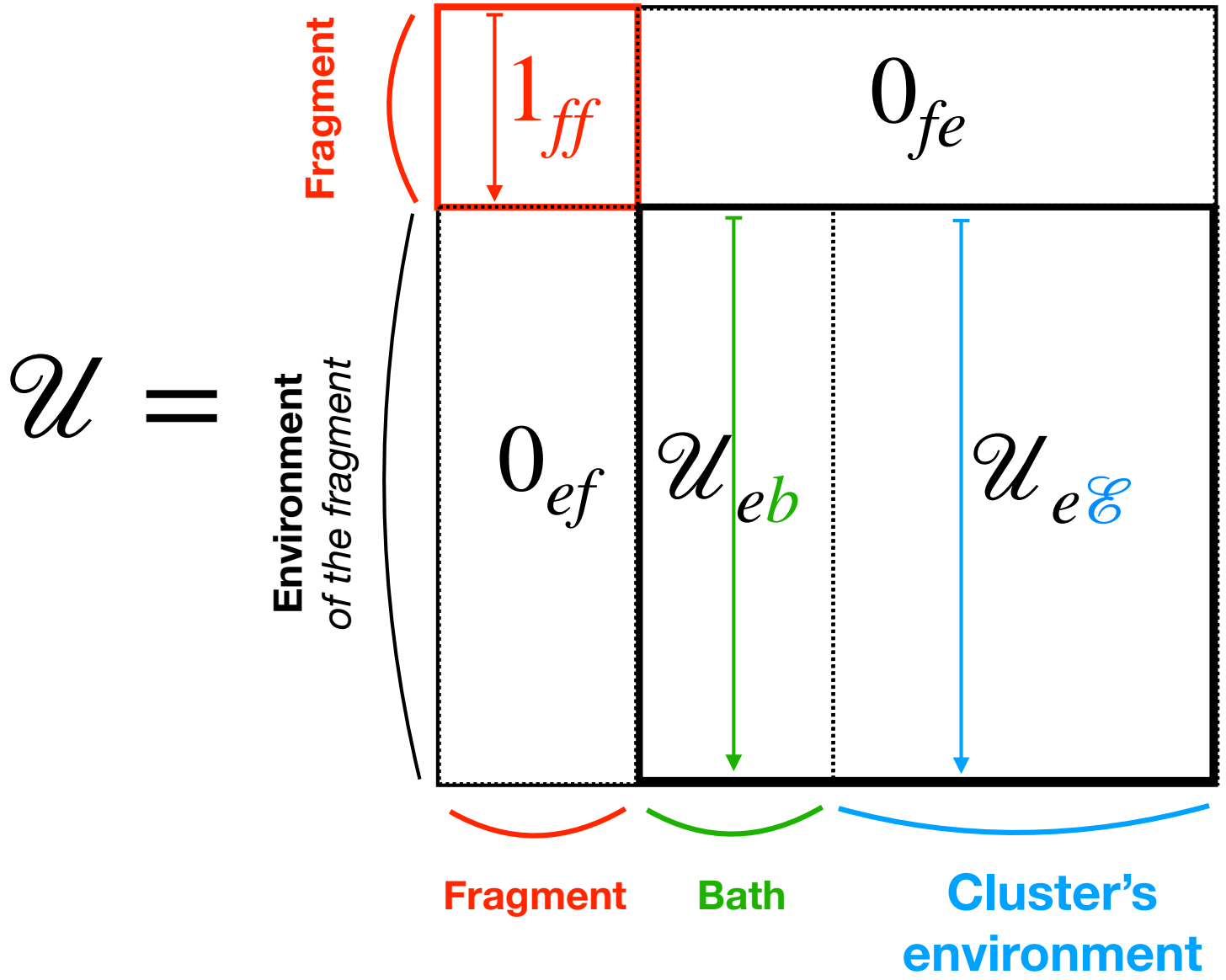

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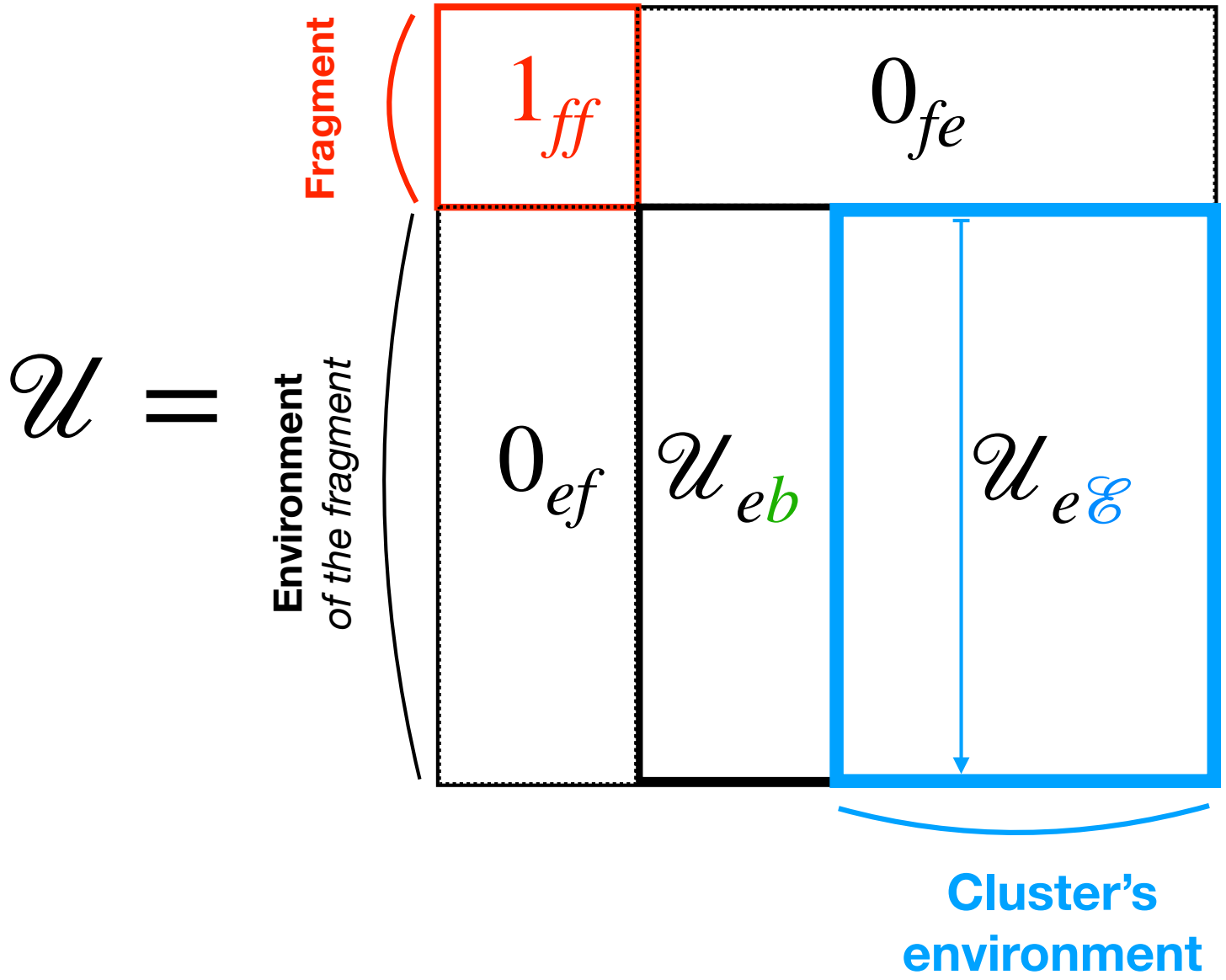
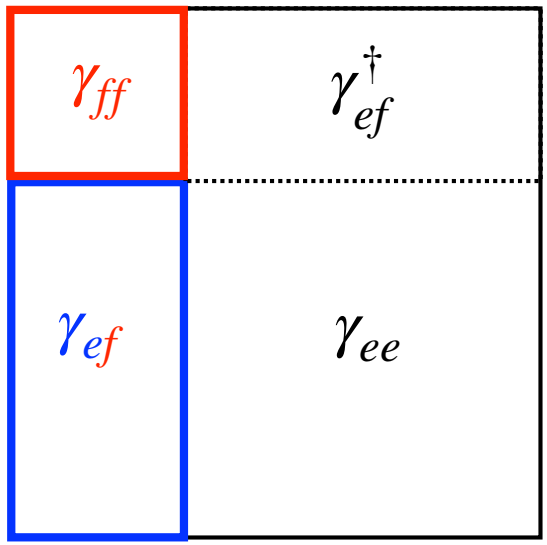


S. Sekaran, O. Bindech, and E. Fromager, J. Chem. Phys. **159**, 034107 (2023).

Quantum bath seen as a functional of the density matrix (1RDM)

$$\gamma \equiv \langle \Psi | \hat{c}_p^\dagger \hat{c}_q | \Psi \rangle = \langle \hat{c}_p^\dagger \hat{c}_q \rangle \equiv$$



← **Lattice representation!**

S. Sekaran, M. Tsuchiizu, M. Saubanère, and E. Fromager, Phys. Rev. B **104**, 035121 (2021).
S. Yalouz, S. Sekaran, E. Fromager, and M. Saubanère, J. Chem. Phys. **157**, 214112 (2022).
S. Sekaran, O. Bindech, and E. Fromager, J. Chem. Phys. **159**, 034107 (2023).

Quantum bath seen as a functional of the density matrix (1RDM)

$$\gamma = \begin{pmatrix} \gamma_{ff} & \gamma_{ef}^{\dagger} \\ \gamma_{ef} & \gamma_{ee} \end{pmatrix}$$

Env.-fragment block

$$\mathcal{U} = \begin{pmatrix} 1_{ff} & 0_{fe} \\ 0_{ef} & \mathcal{U}_{eb} \quad \mathcal{U}_{e\mathscr{E}} \end{pmatrix}$$

Cluster's environment

Implicit (but much simpler) ***definition of the cluster's environment:***

$$\gamma_{ef}^{\dagger}\, \mathcal{U}_{e\mathscr{E}} \equiv 0$$

Will be justified later on…

S. Sekaran, O. Bindech, and E. Fromager, J. Chem. Phys. **159**, 034107 (2023).

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Orthogonality constraint

S. Sekaran, O. Bindech, and E. Fromager, J. Chem. Phys. **159**, 034107 (2023).

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Spin-orbital subspace →

Quantum bath $\equiv \left\{ \sum_{e}^{environment} \gamma_{ef} |\chi_e\rangle \right\}_f$

S. Sekaran, O. Bindech, and E. Fromager, J. Chem. Phys. **159**, 034107 (2023).

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Env.-fragment block

In principle ***as many bath spin-orbitals as the dimension of the fragment*** *(number of "impurities")*

Quantum bath $\equiv \left\{ \sum_{e}^{environment} \gamma_{ef} |\chi_e\rangle \right\}_f$

S. Sekaran, O. Bindech, and E. Fromager, J. Chem. Phys. **159**, 034107 (2023).

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Env.-fragment block

To-be orthonormalized
(SVD, Householder transformation, …)

$$\textbf{Quantum bath} \equiv \left\{ \sum_{e}^{environment} \gamma_{ef} |\chi_e\rangle \right\}_f$$

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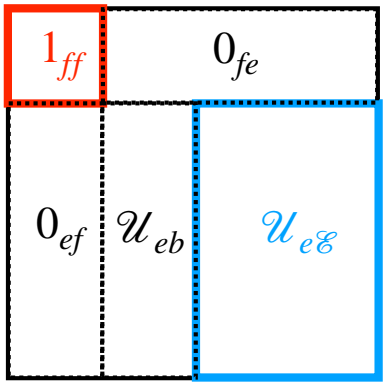
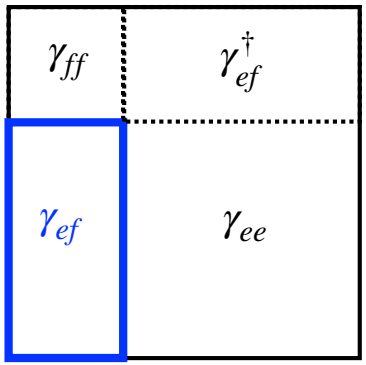
Unitary transformed density matrix



$$\tilde{\gamma} = \mathcal{U}^{\dagger}\gamma\mathcal{U} \equiv$$



Let's visualize the ***clusterization in the 1RDM…***

S. Sekaran, O. Bindech, and E. Fromager, J. Chem. Phys. **159**, 034107 (2023).

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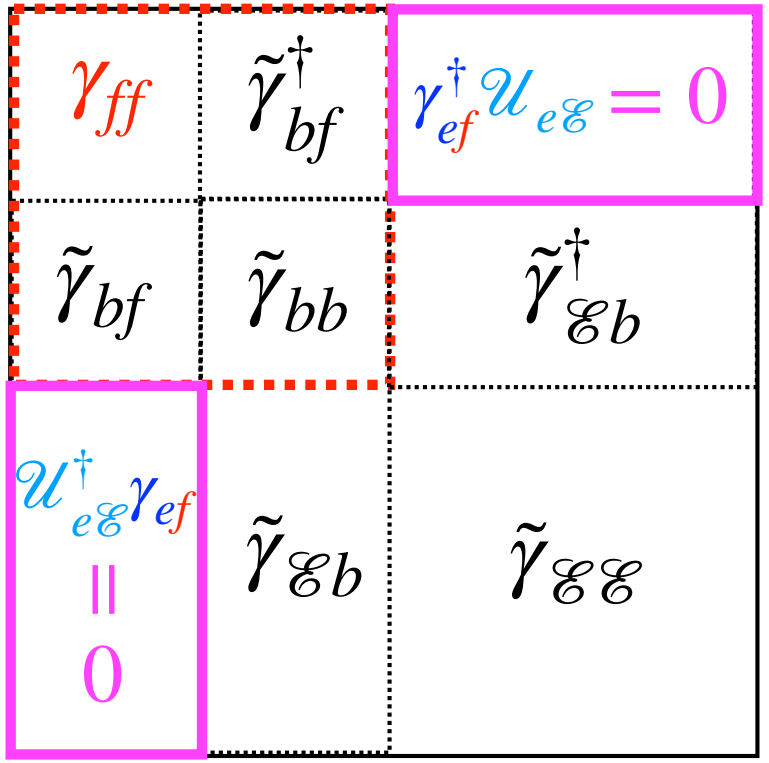
"fragment+bath" embedding cluster

Orthogonality constraint



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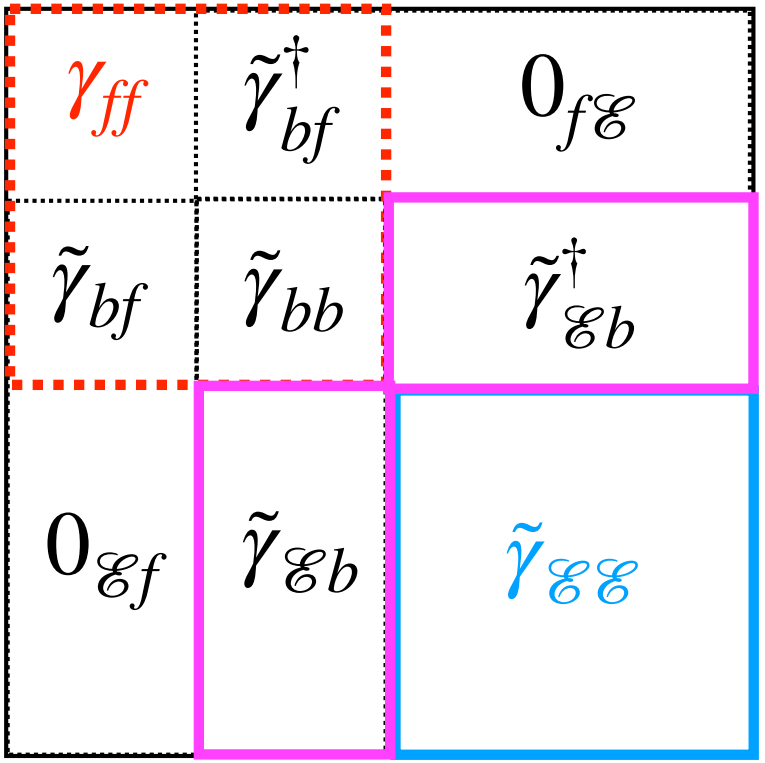


Cluster's environment

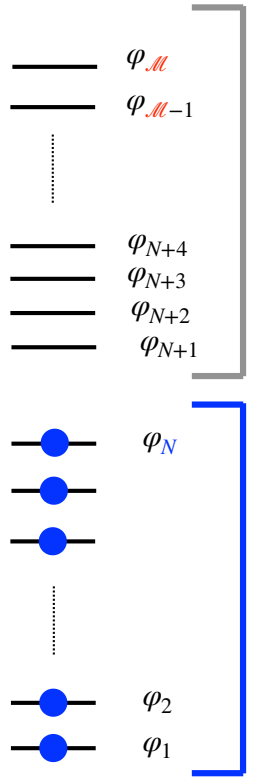
Entanglement

S. Sekaran, O. Bindech, and E. Fromager, J. Chem. Phys. **159**, 034107 (2023).

What if the full-system density matrix is idempotent?

$$\gamma \equiv \begin{bmatrix} 1 & & & & & \\ & 1 & & & & \\ & & 1 & & & \\ & & & \ddots & & \\ & & & & 0 & \\ & & & & & \ddots \\ & & & & & & 0 \end{bmatrix}$$

← **Molecular orbital representation!**



Mean-field (HF)
or Kohn-Sham DFT

S. Sekaran, O. Bindech, and E. Fromager, J. Chem. Phys. **159**, 034107 (2023).

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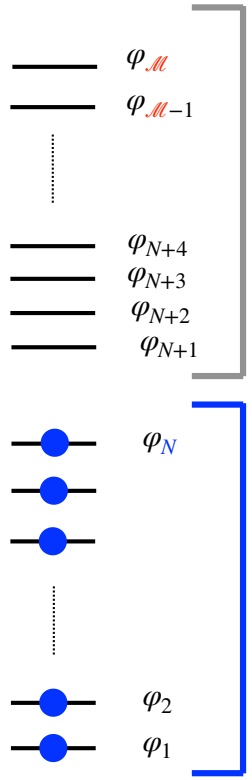

Note that $\mathrm{Tr}\,\gamma = N$ ← *Total number of electrons (in the full system)*

Mean-field (HF) or Kohn-Sham DFT

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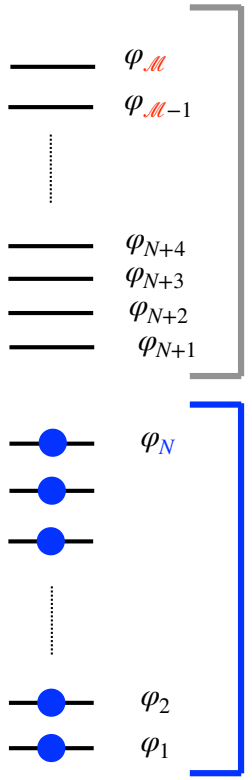
$$\| $$

$$\gamma^2$$

Molecular orbital representation!



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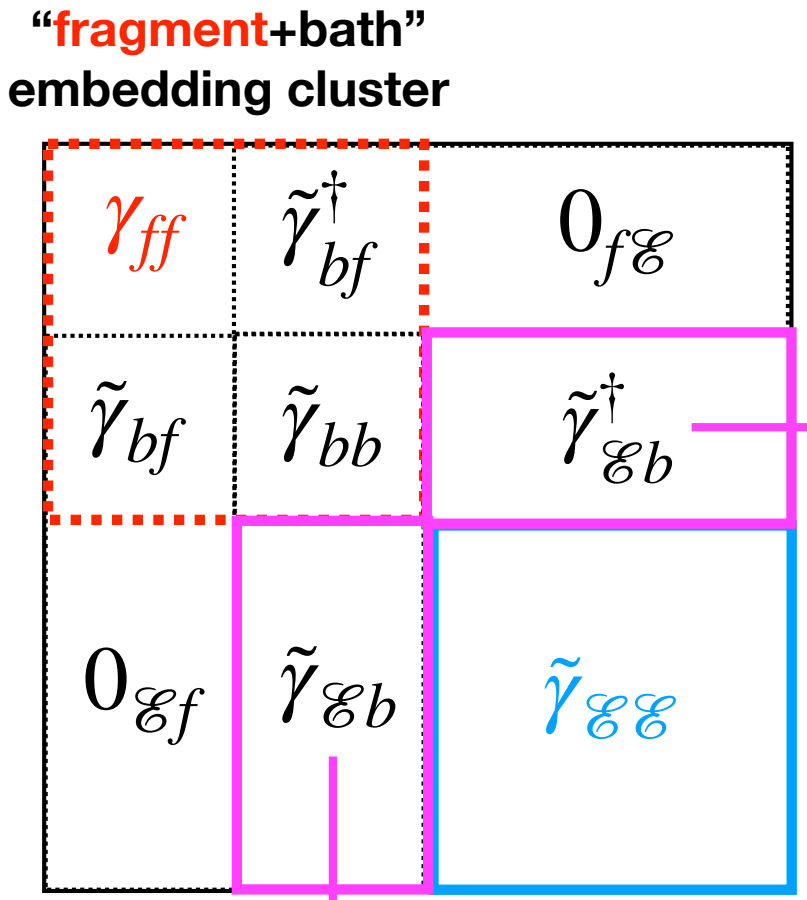
Unitary transformed density matrix

$$\tilde{\gamma} = \mathcal{U}^{\dagger}\gamma\mathcal{U} \equiv$$



if $\gamma^2 = \gamma$ then

idempotency

S. Sekaran, O. Bindech, and E. Fromager, J. Chem. Phys. **159**, 034107 (2023).

Unitary transformed density matrix

Disconnected embedding cluster ✅

$$\tilde{\gamma}^2 = \tilde{\gamma} = \mathcal{U}^\dagger \gamma \mathcal{U} \equiv$$

$$\begin{pmatrix} \gamma_{ff} & \tilde{\gamma}^\dagger_{bf} & 0 \\ \tilde{\gamma}_{bf} & \tilde{\gamma}_{bb} & \\ 0 & & \tilde{\gamma}_{\mathscr{E}\mathscr{E}} \end{pmatrix}$$

Cluster's environment

idempotency

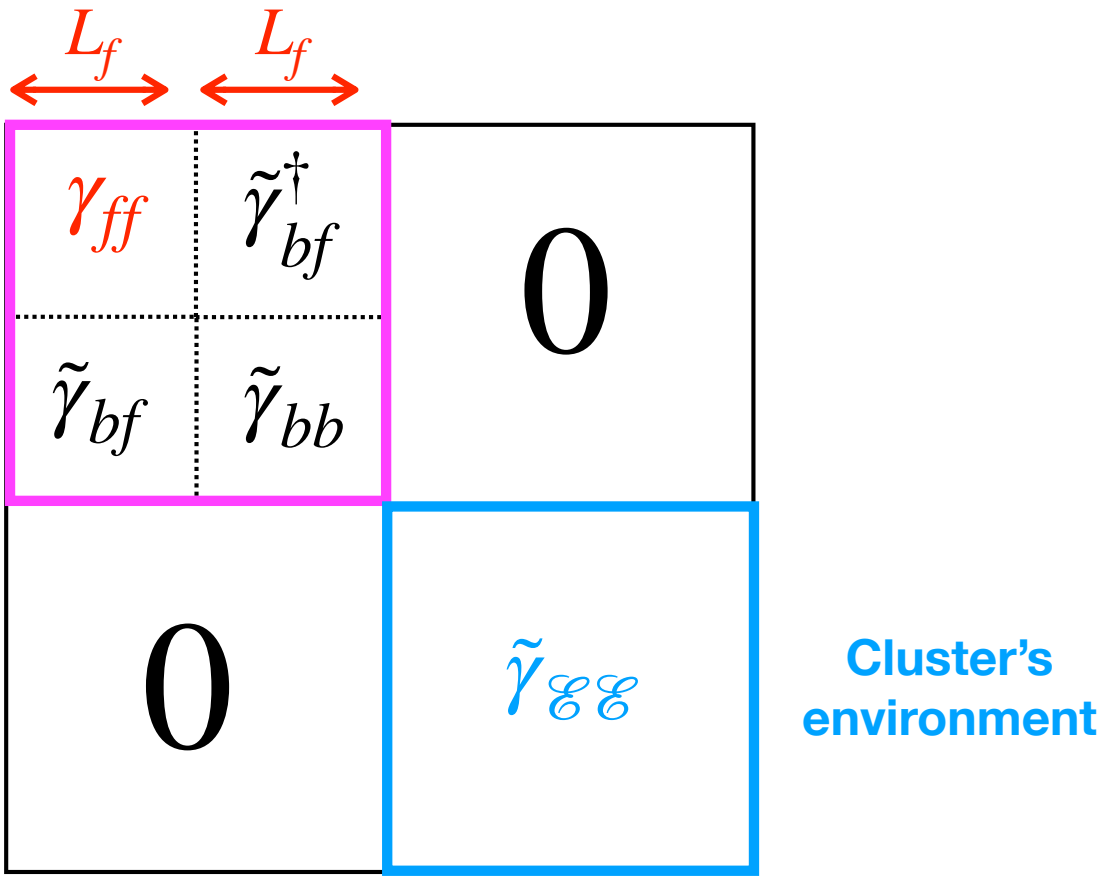
S. Sekaran, O. Bindech, and E. Fromager, J. Chem. Phys. **159**, 034107 (2023).

Unitary transformed density matrix

$$\gamma_{ff} + \tilde{\gamma}_{bf}^{-1}\tilde{\gamma}_{bb}\tilde{\gamma}_{bf} = 1_{ff}$$

$\gamma^2 = \gamma$

idempotency



Cluster's environment

S. Sekaran, O. Bindech, and E. Fromager, J. Chem. Phys. **159**, 034107 (2023).

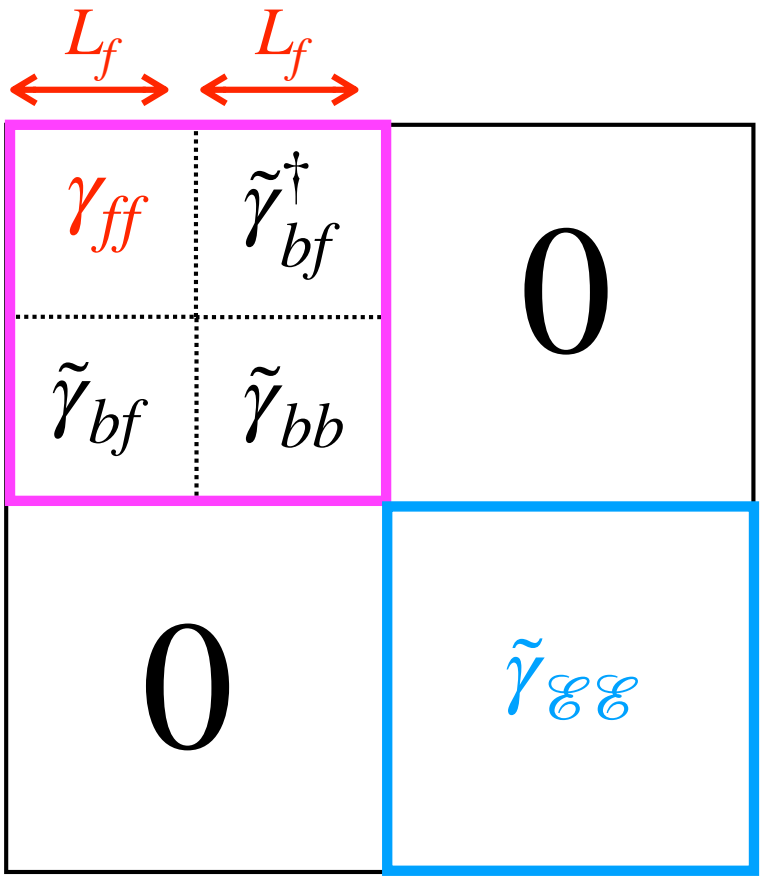
Unitary transformed density matrix

$$\gamma_{ff} + \tilde{\gamma}_{bf}^{-1}\tilde{\gamma}_{bb}\tilde{\gamma}_{bf} = 1_{ff}$$

$\gamma^2 = \gamma$

idempotency

$$\mathrm{Tr}[\gamma_{ff}] + \mathrm{Tr}\left[\tilde{\gamma}_{bb}\right] = L_f$$



Cluster's environment

S. Sekaran, O. Bindech, and E. Fromager, J. Chem. Phys. **159**, 034107 (2023).

Unitary transformed density matrix

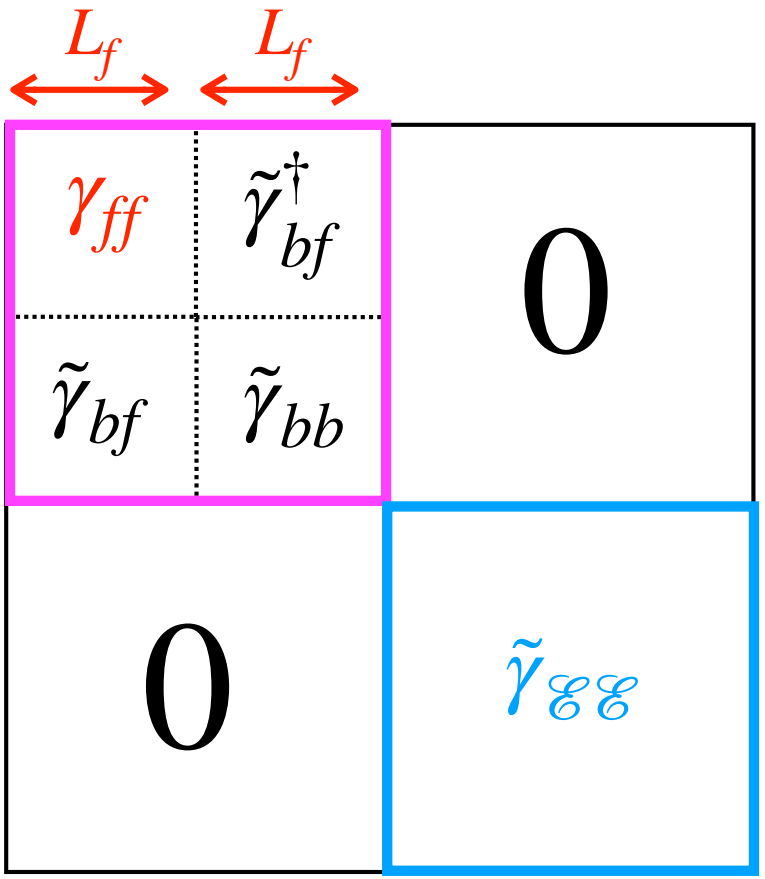
$$\gamma_{ff} + \tilde{\gamma}_{bf}^{-1}\tilde{\gamma}_{bb}\tilde{\gamma}_{bf} = 1_{ff}$$

$\gamma^2 = \gamma$

idempotency

$$\mathrm{Tr}[\gamma_{ff}] + \mathrm{Tr}\left[\tilde{\gamma}_{bb}\right] = L_f$$

The **number of electrons in the cluster** equals the number of embedded impurities



Cluster's environment

S. Sekaran, O. Bindech, and E. Fromager, J. Chem. Phys. **159**, 034107 (2023).

Starting a DMET calculation…

Density matrix of the **full system**

$$\gamma = \begin{array}{|c|c|} \hline \gamma_{ff} & \gamma_{ef}^{\dagger} \\ \hline \gamma_{ef} & \gamma_{ee} \\ \hline \end{array} = ???$$

S. Wouters, C. A. Jiménez-Hoyos, Q. Sun, and G. K.-L. Chan, J. Chem. Theory Comput. 12, 2706 (2016).

Starting a DMET calculation…

Density matrix of the **full system**

$$\gamma = \begin{array}{|c|c|} \hline \gamma_{ff} & \gamma_{ef}^{\dagger} \\ \hline \gamma_{ef} & \gamma_{ee} \\ \hline \end{array}$$

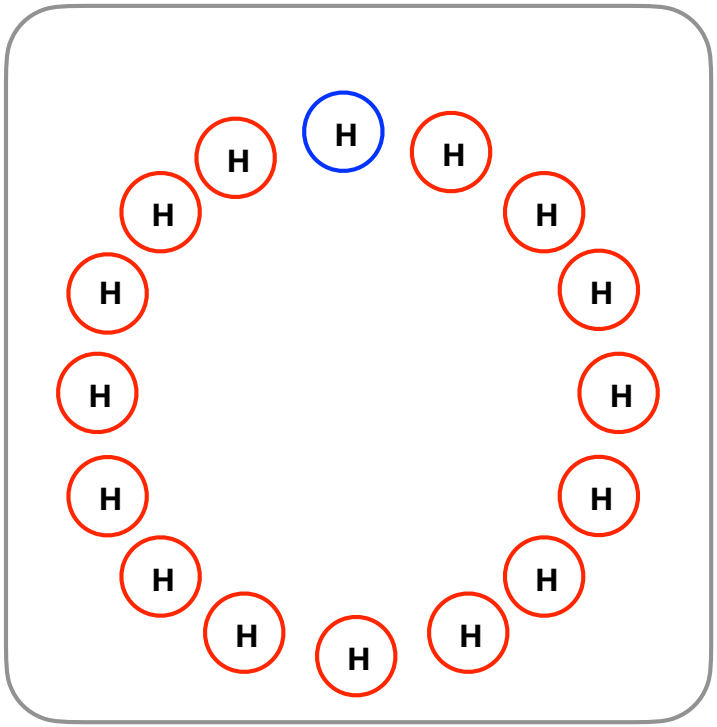
Mean-field evaluation in practice

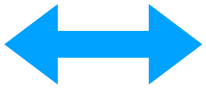
Idempotent $(\gamma^2 = \gamma)$

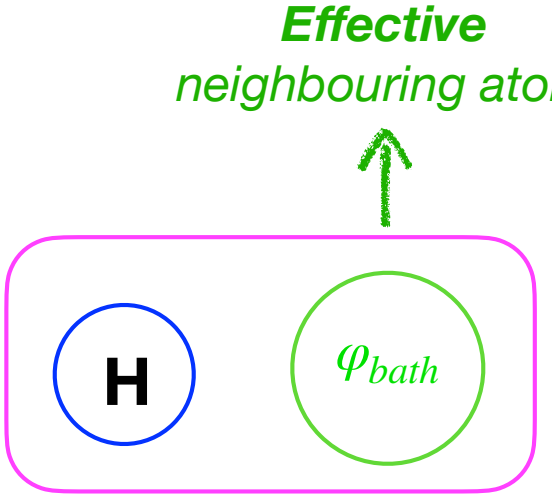
S. Wouters, C. A. Jiménez-Hoyos, Q. Sun, and G. K.-L. Chan, J. Chem. Theory Comput. 12, 2706 (2016).

Illustrative example

Hubbard model for rings of hydrogen atoms







Two-electron system

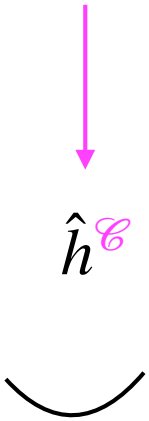
N-electron system

$$\hat{H} = \sum_{\sigma=\uparrow,\downarrow} \sum_{i=0}^{L-1} -t \left(\hat{c}^{\dagger}_{i\sigma} \hat{c}_{(i+1)\sigma} + \hat{c}^{\dagger}_{(i+1)\sigma} \hat{c}_{i\sigma} \right) + U \sum_{i=0}^{L-1} \hat{c}^{\dagger}_{i\uparrow} \hat{c}^{\dagger}_{i\downarrow} \hat{c}_{i\downarrow} \hat{c}_{i\uparrow}$$

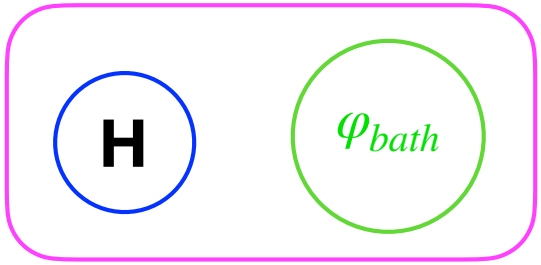
G. Knizia and G. K.-L. Chan, Phys. Rev. Lett. ***109****, 186404 (2012).*
S. Sekaran, M. Tsuchiizu, M. Saubanère, and E. Fromager, Phys. Rev. B ***104****, 035121 (2021).*
S. Sekaran, M. Saubanère, and E. Fromager, Computation **2022***, 10,* 45.

Approximate embedding of interacting Hamiltonians

One-electron Hamiltonian of the cluster



$\hat{h}^{\mathscr{C}}$



Exact non-interacting (*i.e., for* $U = 0$)
embedding

S. Wouters, C. A. Jiménez-Hoyos, Q. Sun, and G. K.-L. Chan, J. Chem. Theory Comput. ***12****, 2706 (2016).*
S. Sekaran, M. Tsuchiizu, M. Saubanère, and E. Fromager, Phys. Rev. B ***104****, 035121 (2021).*
S. Sekaran, M. Saubanère, and E. Fromager, Computation **2022***, 10,* 45.

Approximate embedding of interacting Hamiltonians

One-electron Hamiltonian of the cluster

Two-electron repulsion on the impurity

$$\hat{h}^{\mathscr{C}} \xrightarrow{single\ impurity} \hat{h}^{\mathscr{C}} + \langle pp\,|\,pp\rangle\, \hat{c}^{\dagger}_{p\uparrow}\hat{c}^{\dagger}_{p\downarrow}\hat{c}_{p\downarrow}\hat{c}_{p\uparrow}$$

Exact non-interacting embedding

S. Wouters, C. A. Jiménez-Hoyos, Q. Sun, and G. K.-L. Chan, J. Chem. Theory Comput. ***12****, 2706 (2016).*
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Approximate embedding of interacting Hamiltonians

One-electron Hamiltonian of the cluster

$$\hat{h}^{\mathscr{C}} \xrightarrow{single\ impurity} \hat{h}^{\mathscr{C}} + \overbrace{\langle pp\,|\,pp\rangle}^{U} \hat{c}^{\dagger}_{p\uparrow}\hat{c}^{\dagger}_{p\downarrow}\hat{c}_{p\downarrow}\hat{c}_{p\uparrow}$$

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S. Sekaran, M. Saubanère, and E. Fromager, Computation **2022***, 10,* 45.

Approximate embedding of interacting Hamiltonians

One-electron Hamiltonian of the cluster

Chemical potential on the impurity

$$\hat{h}^{\mathscr{C}} \xrightarrow{single\ impurity} \hat{h}^{\mathscr{C}} + \overbrace{\langle pp|pp\rangle}^{U} \hat{c}^{\dagger}_{p\uparrow}\hat{c}^{\dagger}_{p\downarrow}\hat{c}_{p\downarrow}\hat{c}_{p\uparrow} - \tilde{\mu}^{imp} \sum_{\sigma=\uparrow,\downarrow} \hat{c}^{\dagger}_{p\sigma}\hat{c}_{p\sigma}$$

Exact non-interacting embedding

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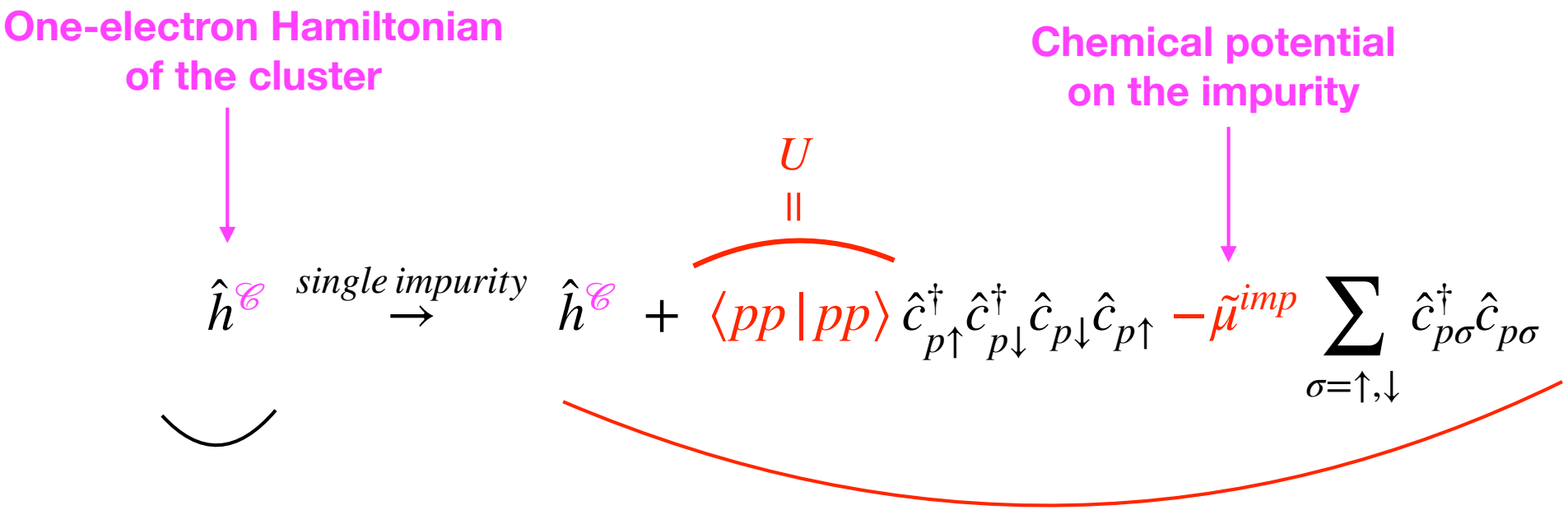

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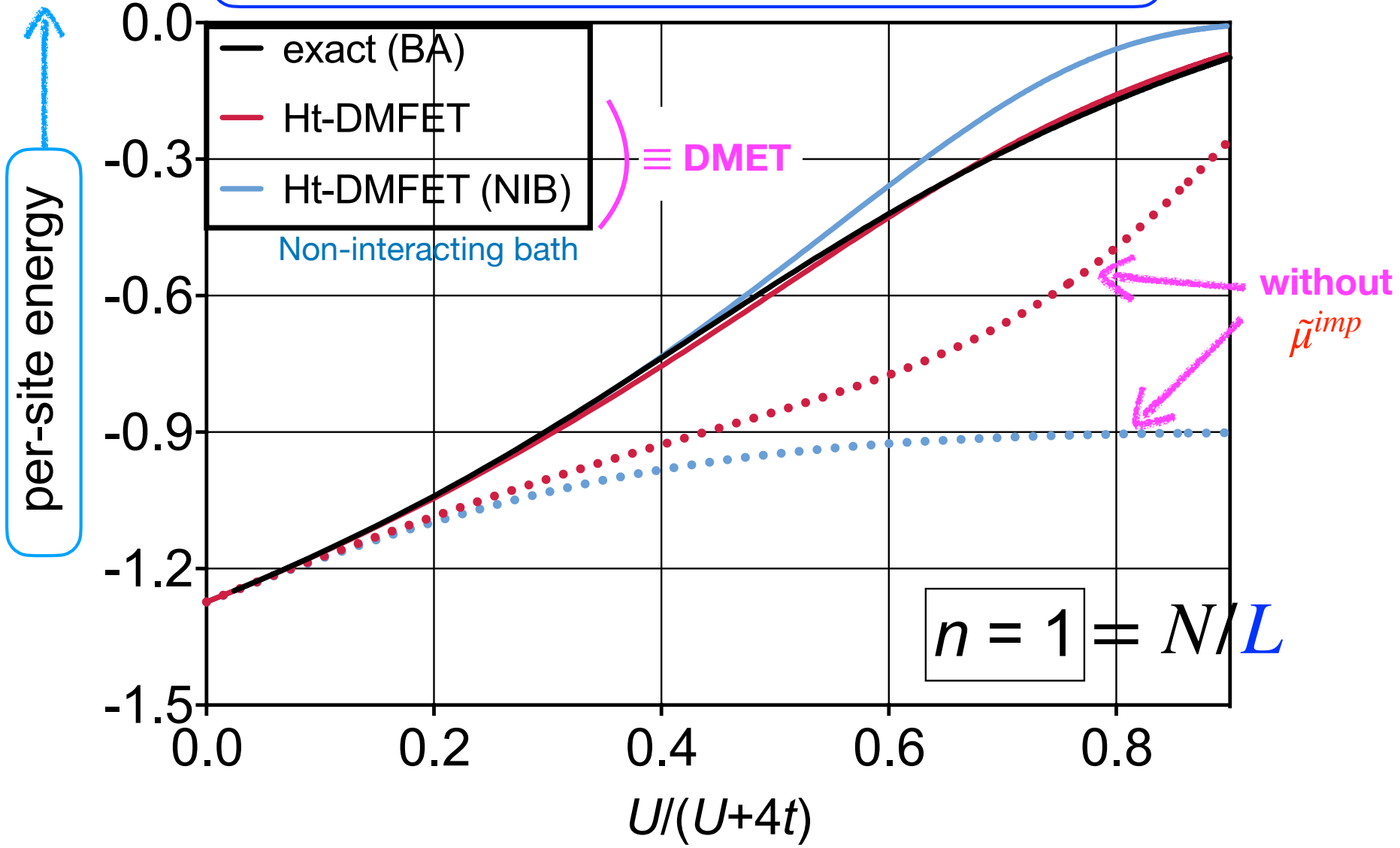
S. Sekaran, M. Saubanère, and E. Fromager, Computation **2022***, 10,* 45.

Half-filled uniform Hubbard ring with $L = 400$ atomic sites

$$E/L \qquad \hat{H} = \sum_{\sigma=\uparrow,\downarrow} \sum_{i=0}^{L-1} -t \left(\hat{c}^{\dagger}_{i\sigma} \hat{c}_{(i+1)\sigma} + \hat{c}^{\dagger}_{(i+1)\sigma} \hat{c}_{i\sigma} \right) + U \sum_{i=0}^{L-1} \hat{c}^{\dagger}_{i\uparrow} \hat{c}^{\dagger}_{i\downarrow} \hat{c}_{i\downarrow} \hat{c}_{i\uparrow}$$



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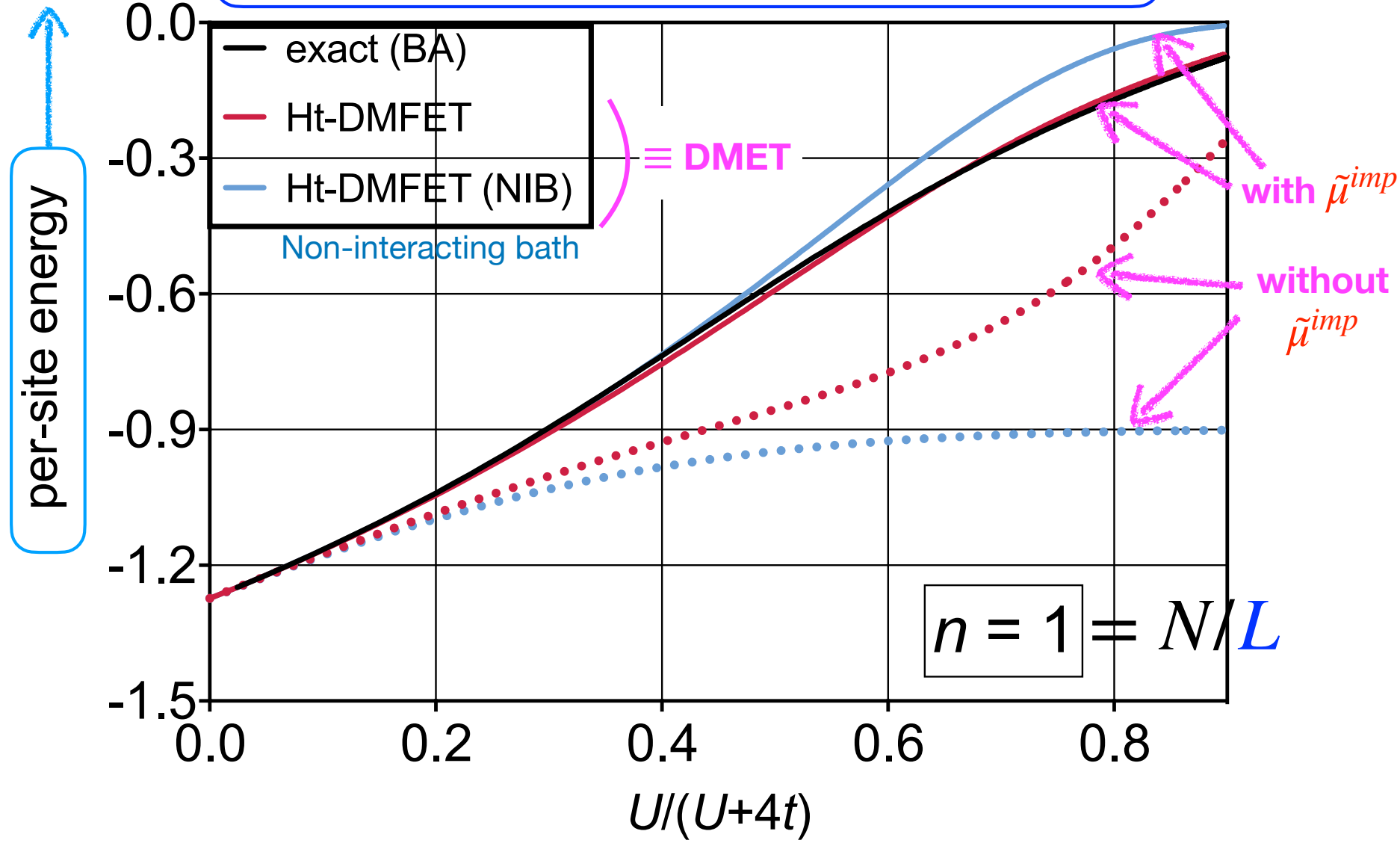

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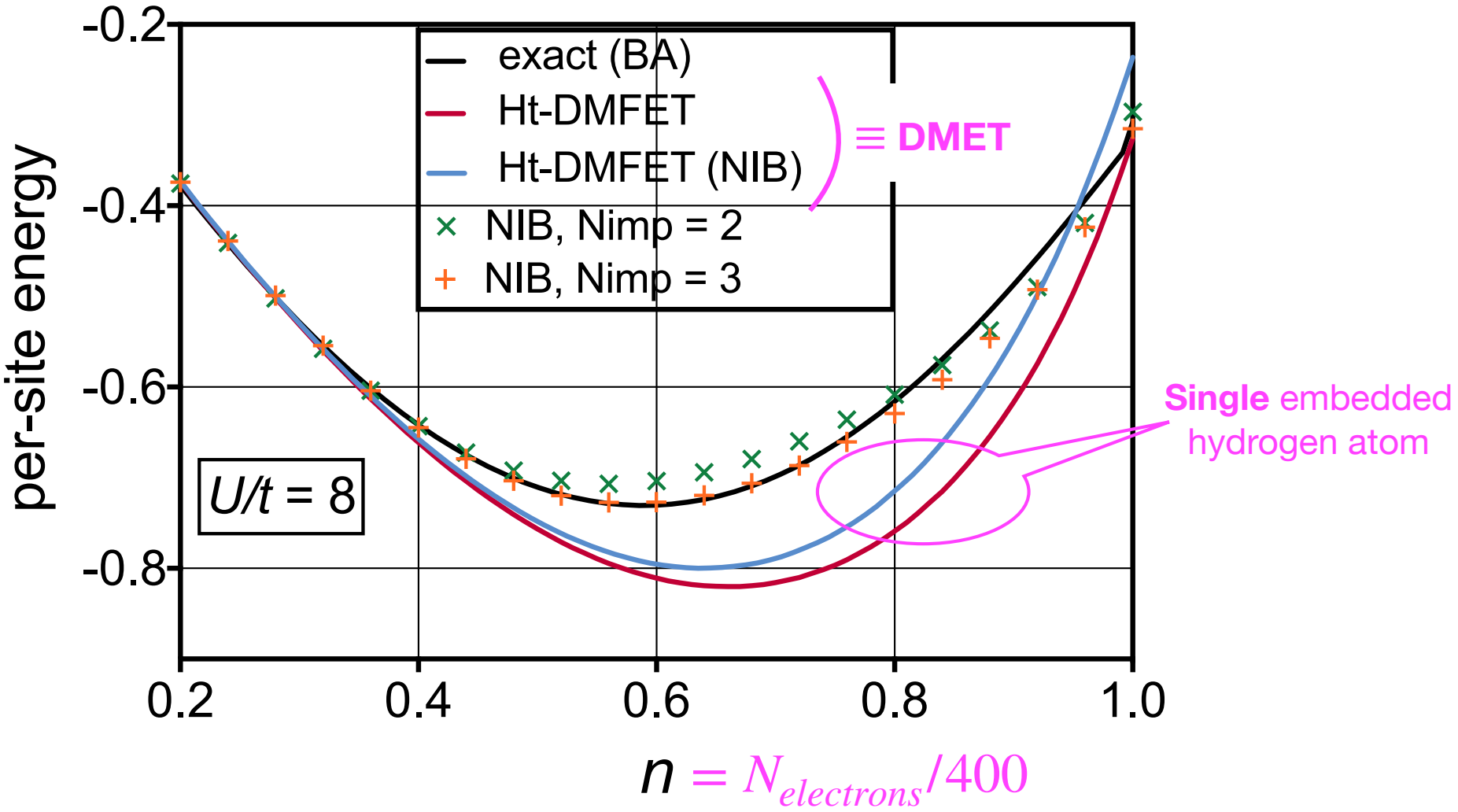
(Hubbard) model of a stretched 400-atom hydrogen ring



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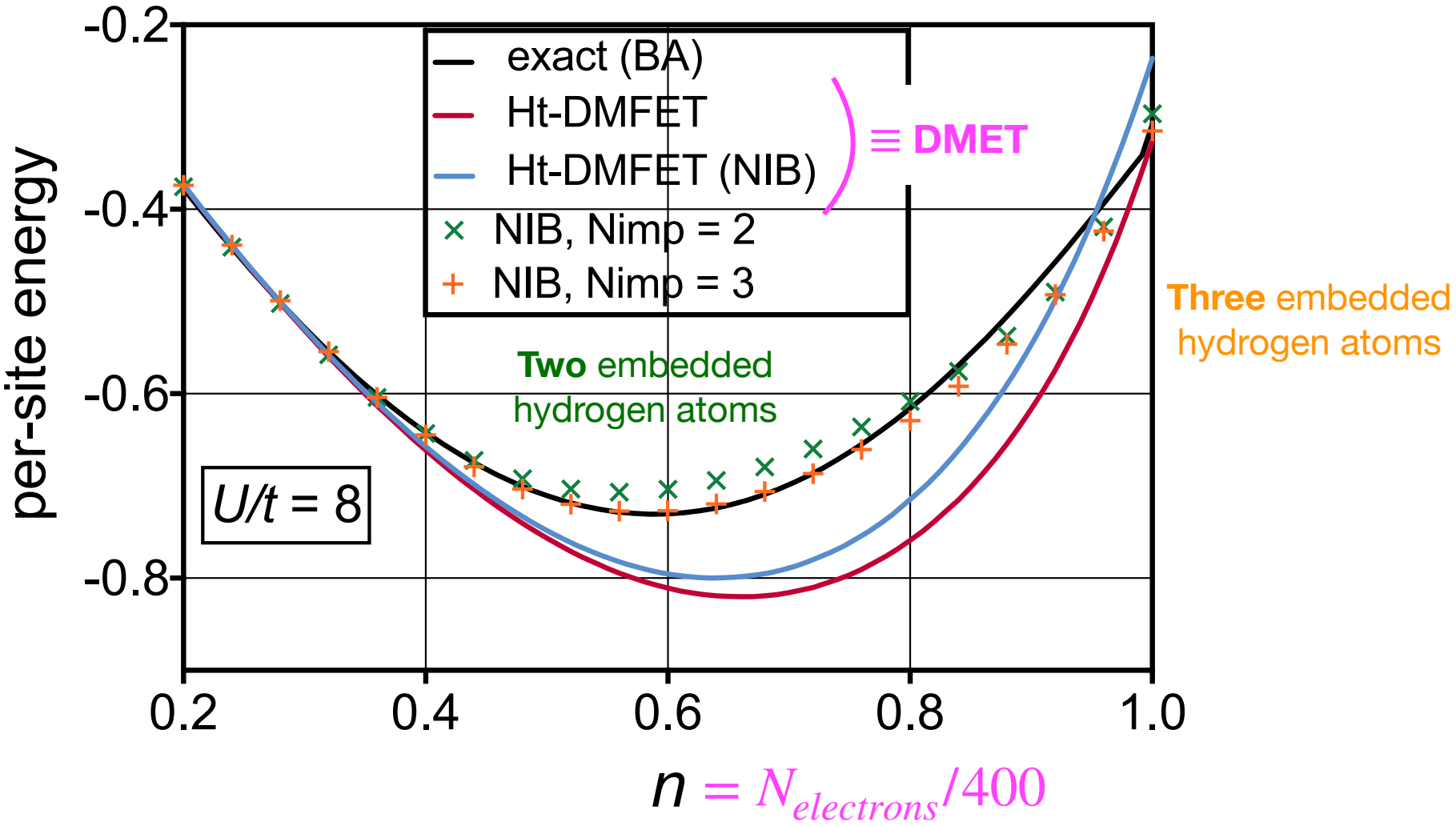
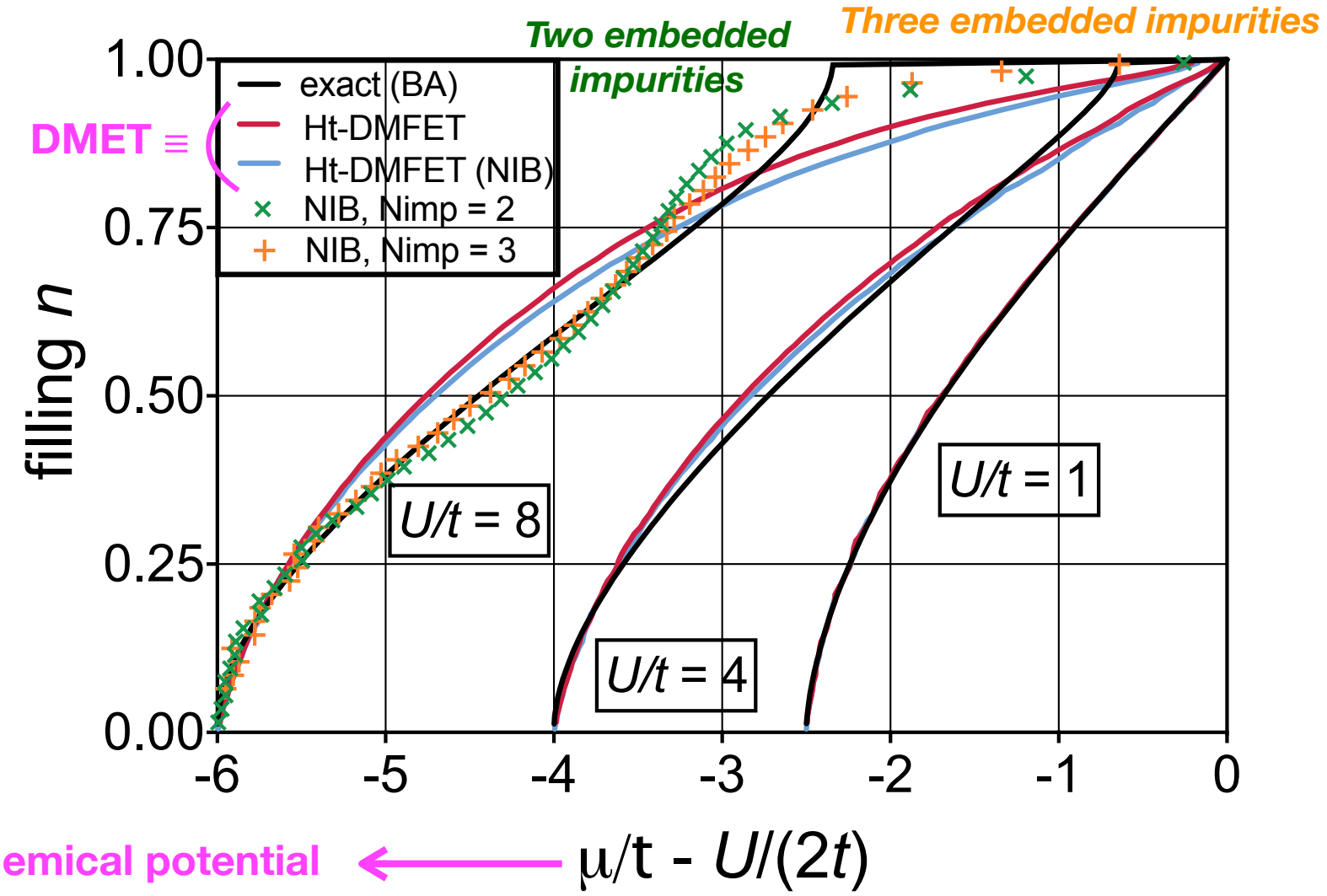
(Hubbard) model of a stretched 400-atom hydrogen ring



S. Sekaran, M. Tsuchiizu, M. Saubanère, and E. Fromager, Phys. Rev. B **104**, 035121 (2021).

Mott-Hubbard density-driven transition and multiple impurities



$$\mu \equiv \mu(n) = \frac{1}{L}\frac{\partial E(n)}{\partial n}$$

*S. Sekaran, M. Tsuchiizu, M. Saubanère, and E. Fromager, Phys. Rev. B **104**, 035121 (2021).*

Recent developments and open questions

Self-consistency and formal connection with DFT

Density-functional exactification of DMET (for Hubbard)

computation

MDPI

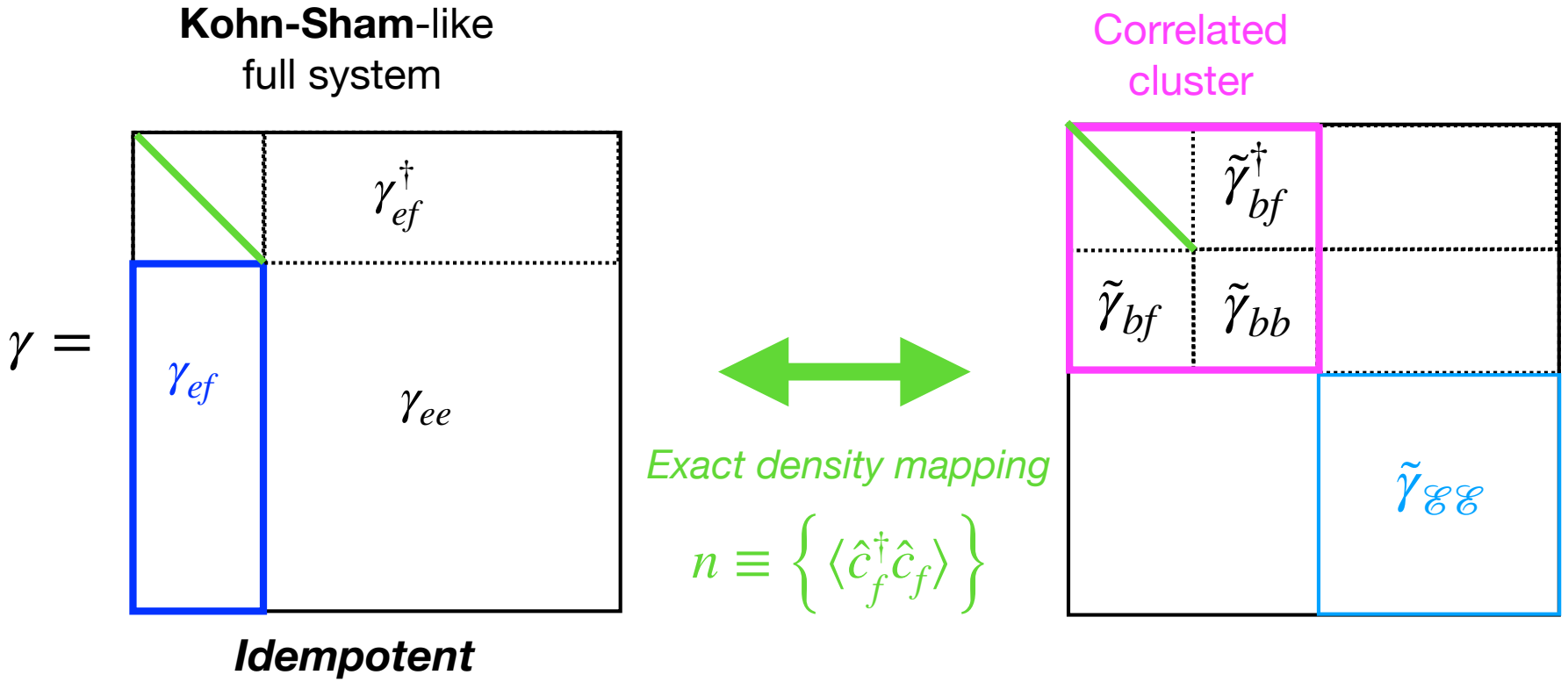
check for updates

Citation: Sekaran, S.; Saubanère, M.; Fromager, E. Local Potential Functional Embedding Theory: A Self-Consistent Flavor of Density Functional Theory for Lattices without Density Functionals. *Computation* **2022**, *10*, 45. https://doi.org/10.3390/computation10030045

Article

Local Potential Functional Embedding Theory: A Self-Consistent Flavor of Density Functional Theory for Lattices without Density Functionals

Sajanthan Sekaran [1,*], Matthieu Saubanère [2] and Emmanuel Fromager [1]



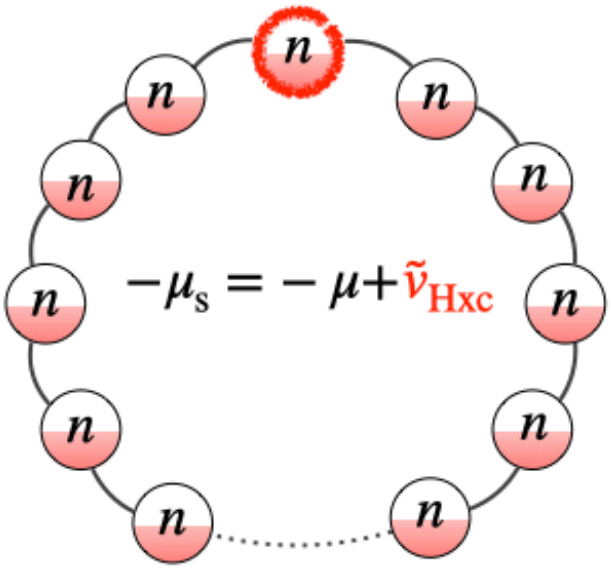
W. Bulik, G. E. Scuseria, and J. Dukelsky, Phys. Rev. B ***89****, 035140 (2014).*
U. Mordovina, T. E. Reinhard, I. Theophilou, H. Appel, and A. Rubio, J. Chem. Theory Comput. ***15****, 5209 (2019).*

Local potential-functional embedding theory (LPFET)

$$v_{\mathrm{Hxc}}(n) \approx \tilde{\mu}^{\mathrm{imp}}(n)$$

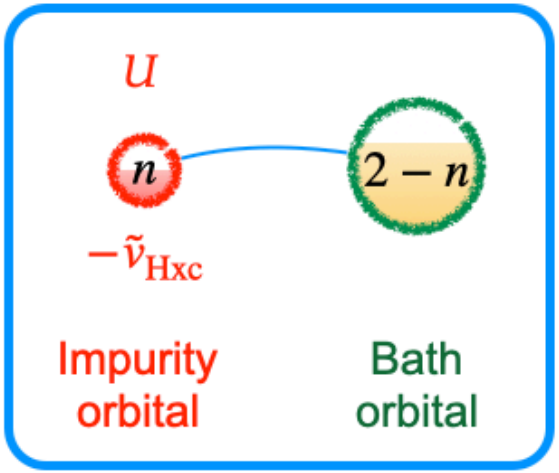
Self-consistency loop

Kohn-Sham lattice

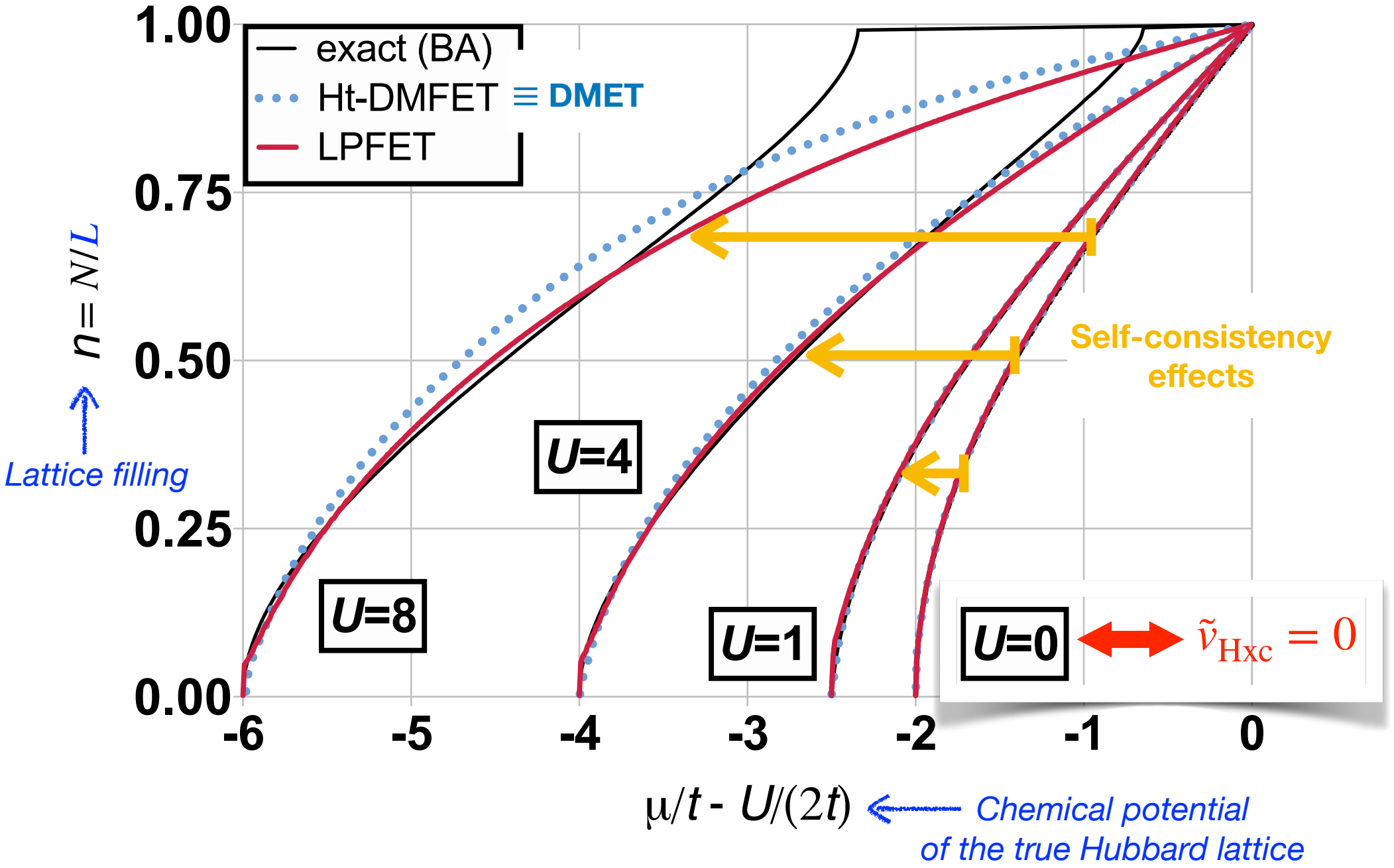


$$n_{\Phi_0^{\mathrm{KS}}[\tilde{v}_{\mathrm{Hxc}}]} = n_{\Psi_0^{cluster}[\tilde{v}_{\mathrm{Hxc}}]}$$

Embedding cluster



Local potential-functional embedding theory (LPFET)



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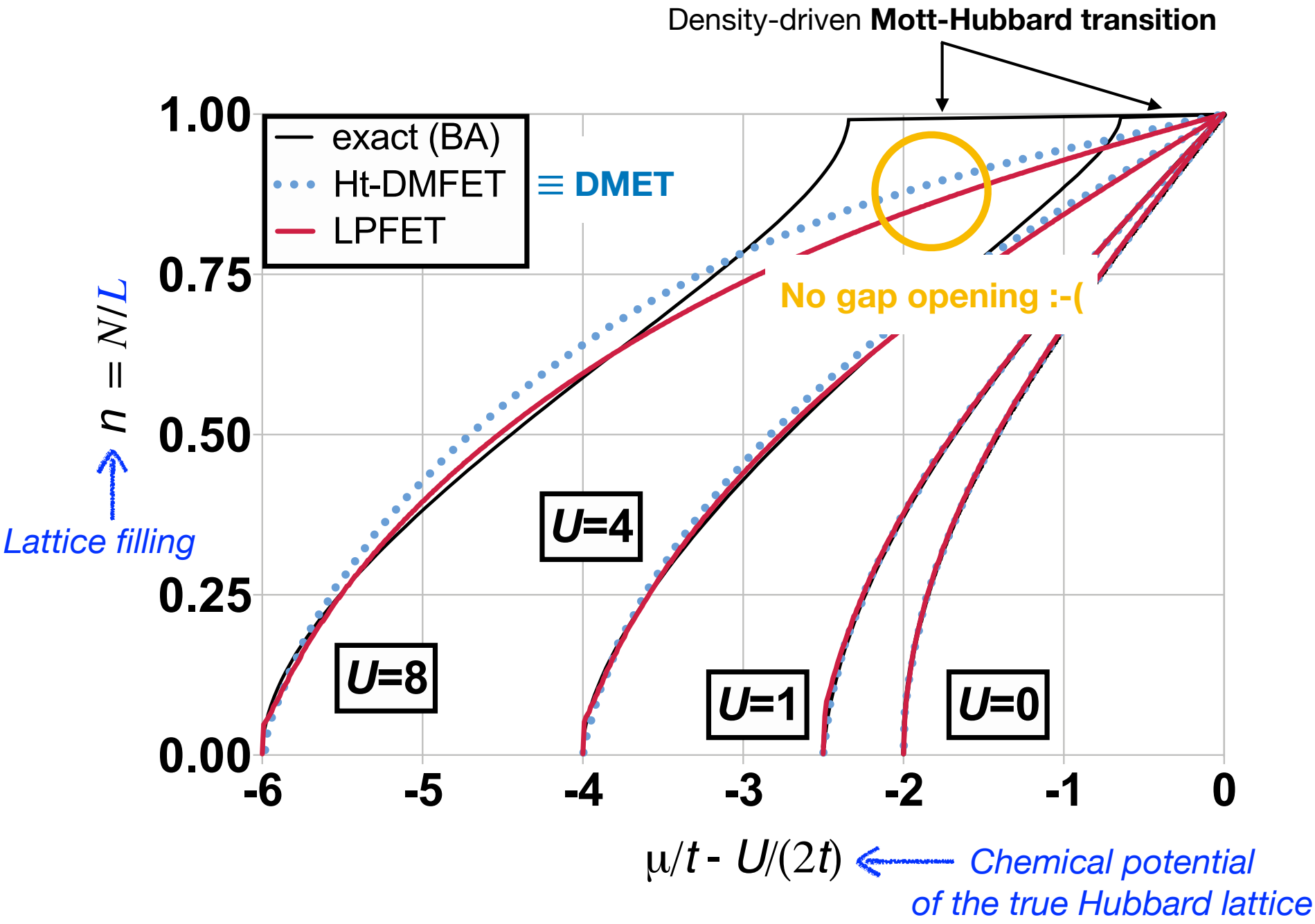


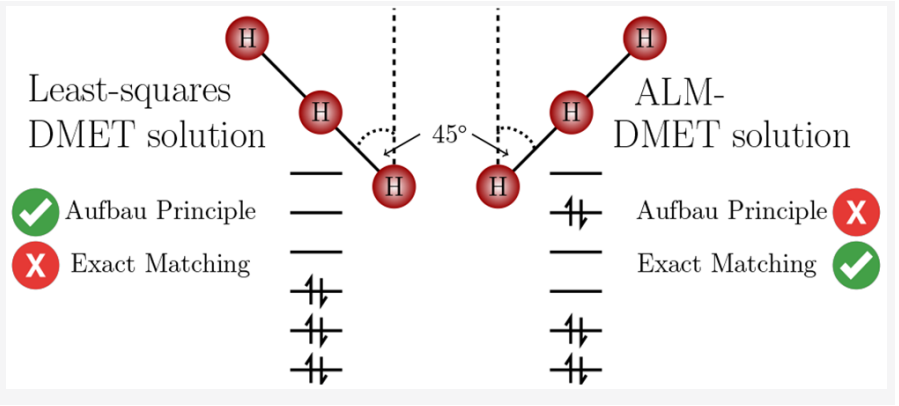
S. Sekaran, M. Saubanère, and E. Fromager, Computation **2022**, *10*, 45.

The “idempotency” problem

Pure State *v*-Representability of Density Matrix Embedding Theory

Fabian M. Faulstich,[⊥] Raehyun Kim,[⊥] Zhi-Hao Cui, Zaiwen Wen, Garnet Kin-Lic Chan, and Lin Lin*

Cite This: *J. Chem. Theory Comput.* 2022, 18, 851–864



Kohn-Sham-like
full system?

$\gamma =$

γ_{ff} $\gamma_{ef}^{\dagger}$

γ_{ef} γ_{ee}

Idempotent

?

Density matrix mapping

Correlated
cluster

γ_{ff} $\tilde{\gamma}_{bf}^{\dagger}$

$\tilde{\gamma}_{bf}$ $\tilde{\gamma}_{bb}$

$\tilde{\gamma}_{\mathscr{E}\mathscr{E}}$

Non-idempotent

Non-Hermitian quantum mechanics?

Non-Hermitian but idempotent density matrix, static self-energy, …

https://www.youtube.com/watch?v=8zgMa-MhoZg
https://www.youtube.com/watch?v=mDkzmSJwwkQ&t=726s

Using an enlarged bath *(ghost orbitals)*?

N. Lanatà, Phys. Rev. B 108, 235112 (2023).

The N-representability problem

JCTC Journal of Chemical Theory and Computation

pubs.acs.org/JCTC Article

Effective Reconstruction of Expectation Values from Ab Initio Quantum Embedding

Max Nusspickel, Basil Ibrahim, and George H. Booth*

Cite This: *J. Chem. Theory Comput.* 2023, 19, 2769–2791

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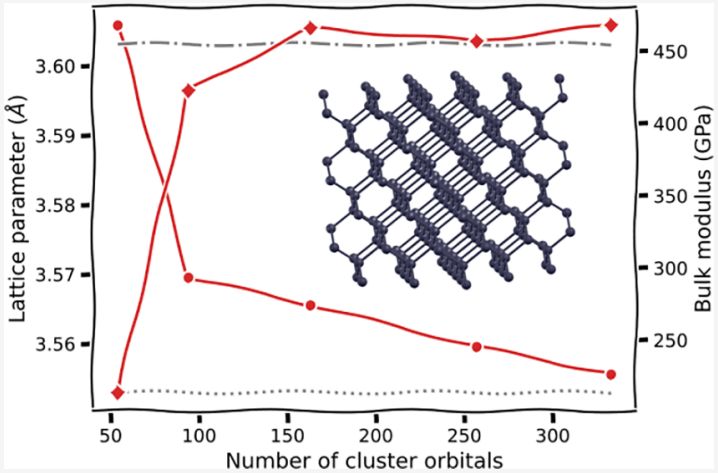
ABSTRACT: Quantum embedding is an appealing route to fragment a large interacting quantum system into several smaller auxiliary "cluster" problems to exploit the locality of the correlated physics. In this work, we critically review approaches to recombine these fragmented solutions in order to compute nonlocal expectation values, including the total energy. Starting from the democratic partitioning of expectation values used in density matrix embedding theory, we motivate and develop a number of alternative approaches, numerically demonstrating their efficiency and improved accuracy as a function of increasing cluster size for both energetics and nonlocal two-body observables in molecular and solid state systems. These approaches consider the *N*-representability of the resulting expectation values via an implicit global wave function across the clusters, as well as the importance of including contributions to expectation values spanning multiple fragments simultaneously, thereby alleviating the fundamental locality approximation of the embedding. We clearly demonstrate the value of these introduced functionals for reliable extraction of observables and robust and systematic convergence as the cluster size increases, allowing for significantly smaller clusters to be used for a desired accuracy compared to traditional approaches in *ab initio* wave function quantum embedding.

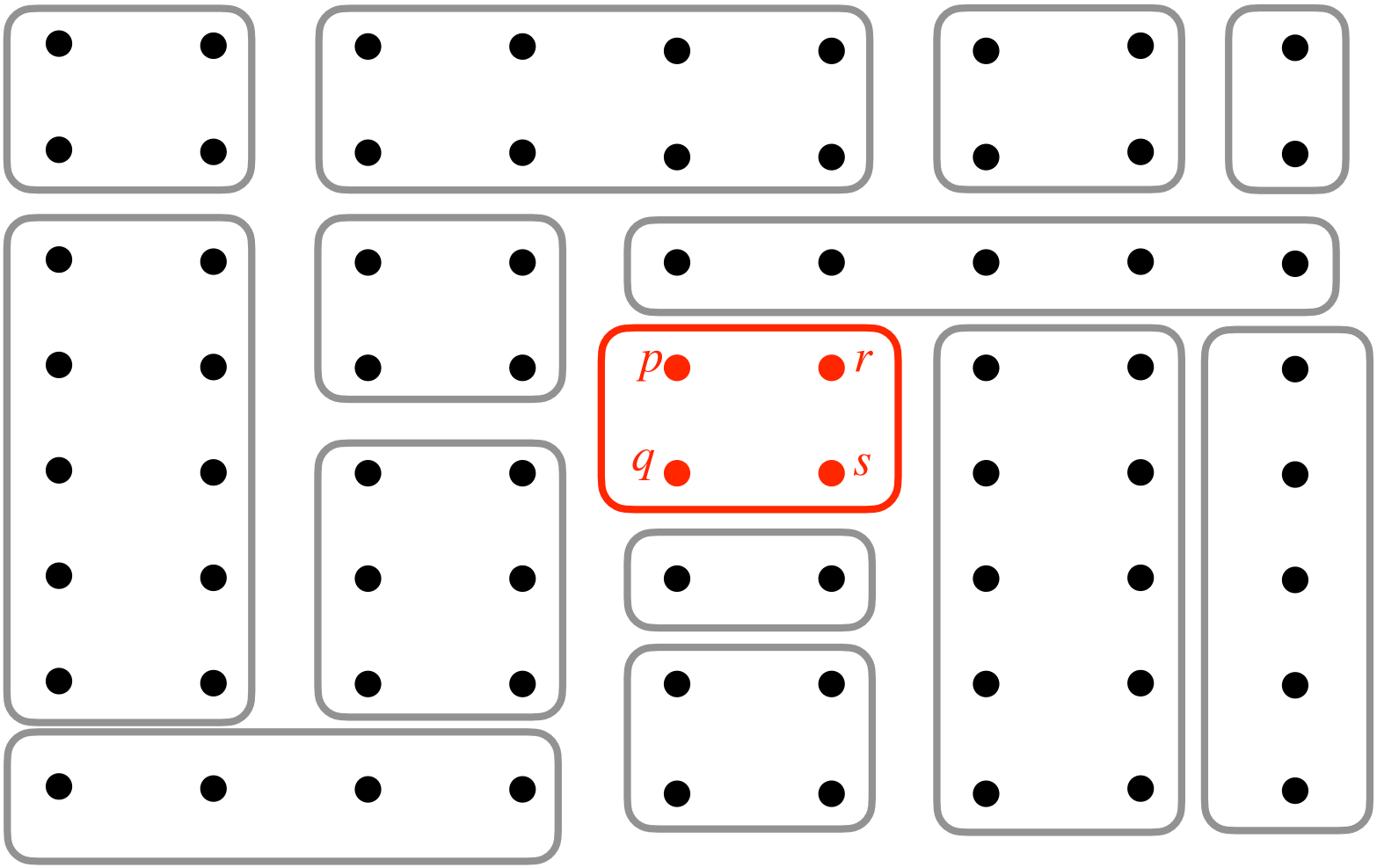


Local evaluation of the energy (in a localised spin-orbital basis)

So-called "lattice representation"

$$\langle \hat{H} \rangle = \sum_{pq} h_{pq} \underbrace{\langle \hat{c}_p^\dagger \hat{c}_q \rangle}_{\text{One-electron density matrix (1RDM)}} + \frac{1}{2} \sum_{pqrs} \langle pq \,|\, rs \rangle \underbrace{\langle \hat{c}_p^\dagger \hat{c}_q^\dagger \hat{c}_s \hat{c}_r \rangle}_{\text{Two-electron density matrix (2RDM)}}$$

Fragmentation

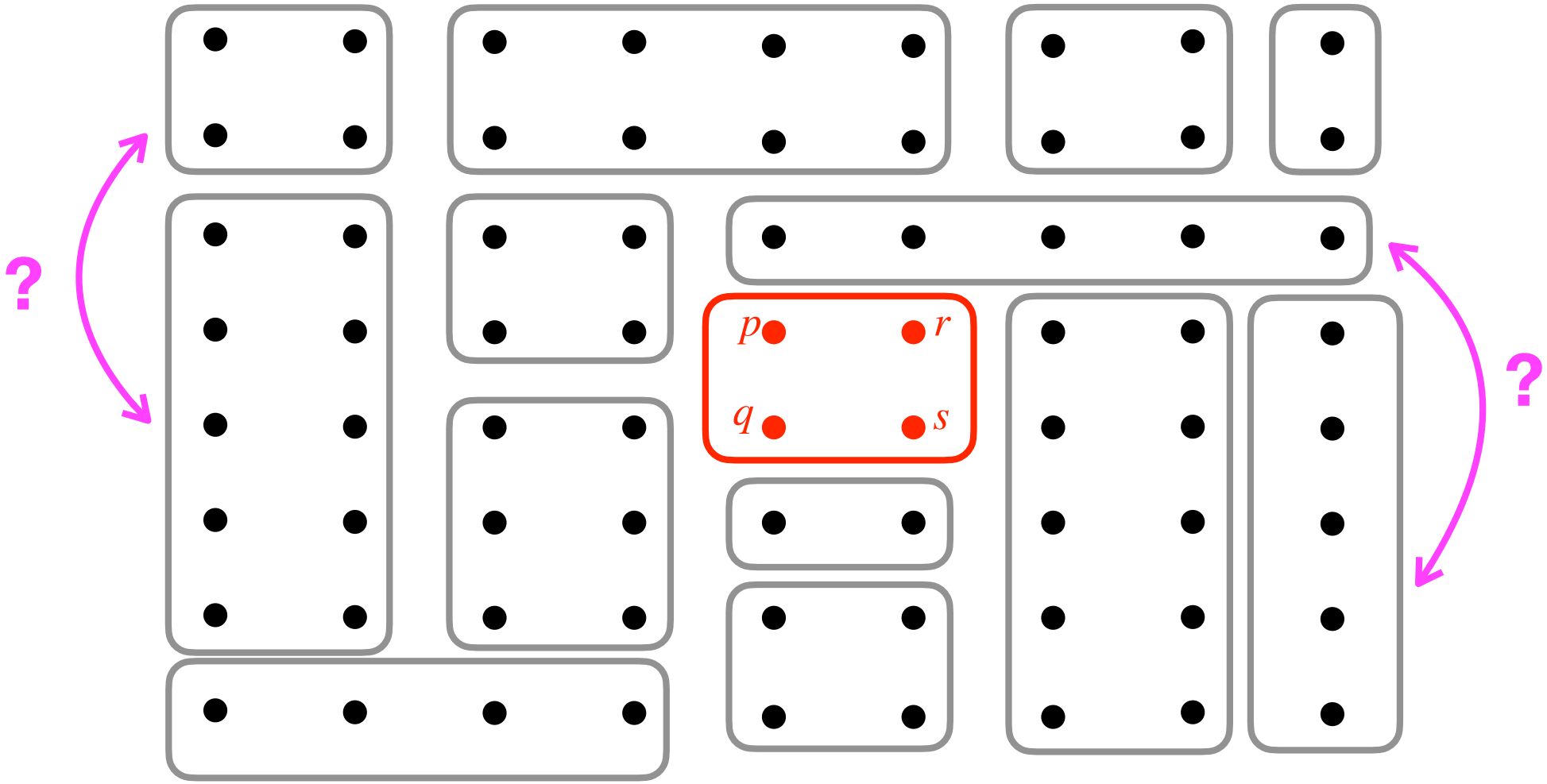


G. Knizia and G. K.-L. Chan, Phys. Rev. Lett. ***109****, 186404 (2012).*
S. Wouters, C. A. Jiménez-Hoyos, Q. Sun, and G. K.-L. Chan, J. Chem. Theory Comput. 12, 2706 (2016).

$$\langle \hat{H} \rangle = \sum_{pq} h_{pq} \langle \hat{c}_p^\dagger \hat{c}_q \rangle + \frac{1}{2} \sum_{pqrs} \langle pq \,|\, rs \rangle \langle \hat{c}_p^\dagger \hat{c}_q^\dagger \hat{c}_s \hat{c}_r \rangle$$

One-electron density matrix (1RDM)

Two-electron density matrix (2RDM)



N-representability problem

$$\langle \hat{c}_p^\dagger \hat{c}_q \rangle_{clusters} \stackrel{?}{=} \langle \Psi | \hat{c}_p^\dagger \hat{c}_q | \Psi \rangle$$

$$\langle \hat{c}_p^\dagger \hat{c}_q^\dagger \hat{c}_r \hat{c}_s \rangle_{clusters} \stackrel{?}{=} \langle \Psi | \hat{c}_p^\dagger \hat{c}_q^\dagger \hat{c}_r \hat{c}_s | \Psi \rangle$$