An introduction to density matrix embedding theory

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https://lcqs.unistra.fr/wordpress/wp-content/uploads/dlm_uploads/2025/02/DMET_lecture_workshop_Austria_2025_Fromager-5.pdf

Workshop on Theoretical Chemistry, Quantum Embedding, Bad Hofgastein, Austria **February 2025**

Back in 2012…

Multiconfigurational extension of the Kohn-Sham optimized effective potential scheme based on range separation

Multiconfigurational extension of the Kohn-Sham optimized effective potential scheme based on range separation

Alexandrina Stoyanova, Andrew Teale, Emmanuel Fromager, and Trygve Helgaker

UNIVERSITÉ DE STRASBOURG

cnrs advancing the frontiers

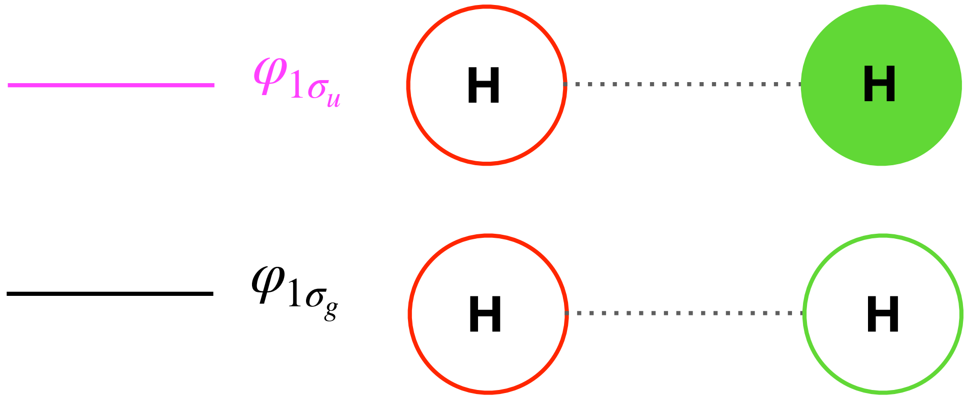
Institut de Chimie de Strasbourg - Laboratoire de Chimie Quantique - Université de Strasbourg /CNRS

Workshop on Theoretical Chemistry, Mariapfarr, Austria, 17.02.12

17.02.2012 Workshop on Theoretical Chemistry, Mariapfarr, Austria Page 1

A few words about strong electron correlation

A brief reminder: *Multi-configurational description of the* ***stretched hydrogen molecule***



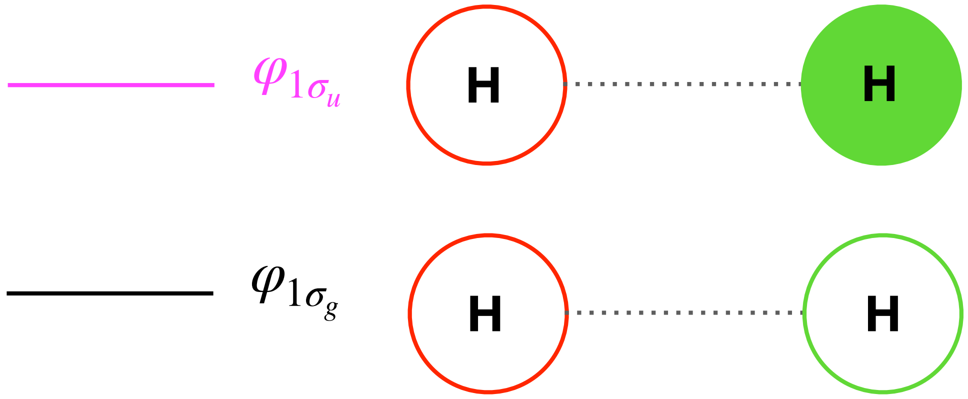
Anti-bonding orbital

$$\varphi_{1\sigma_u}(\mathbf{r}) = \frac{1}{\sqrt{2}}\left(\chi_{s_A}(\mathbf{r}) - \chi_{s_B}(\mathbf{r})\right)$$

$$\varphi_{1\sigma_g}(\mathbf{r}) = \frac{1}{\sqrt{2}}\left(\chi_{s_A}(\mathbf{r}) + \chi_{s_B}(\mathbf{r})\right)$$

Bonding orbital

Multi-configurational description of the ***stretched hydrogen molecule***



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Bonding orbital

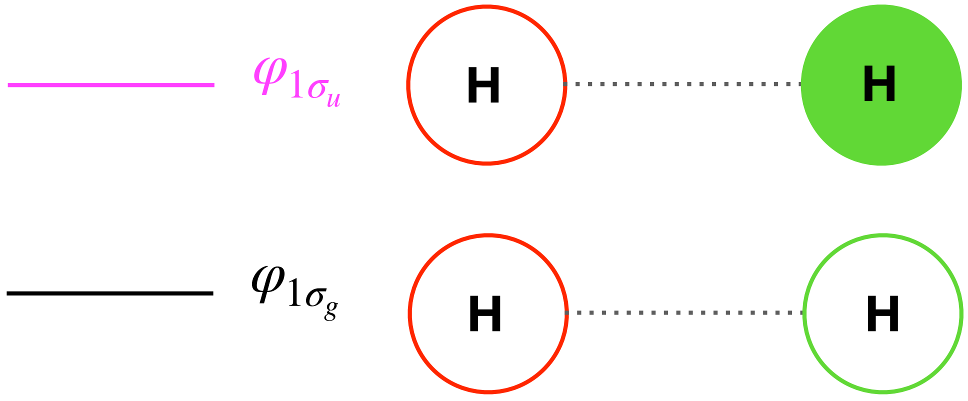
$$\Psi \equiv \frac{1}{\sqrt{2}}\left(\varphi_{1\sigma_g}(\mathbf{r}_1)\varphi_{1\sigma_g}(\mathbf{r}_2) - \varphi_{1\sigma_u}(\mathbf{r}_1)\varphi_{1\sigma_u}(\mathbf{r}_2)\right)$$

←

Delocalised picture
(Chemistry)

Multi-configurational description of the ***stretched hydrogen molecule***

Anti-bonding orbital



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Bonding orbital

$$\Psi \equiv \frac{1}{\sqrt{2}}\left(\overbrace{\varphi_{1\sigma_g}(\mathbf{r}_1)\varphi_{1\sigma_g}(\mathbf{r}_2)}^{\sigma_g^2} - \overbrace{\varphi_{1\sigma_u}(\mathbf{r}_1)\varphi_{1\sigma_u}(\mathbf{r}_2)}^{\sigma_u^2}\right)$$

←

Delocalised picture
(Chemistry)

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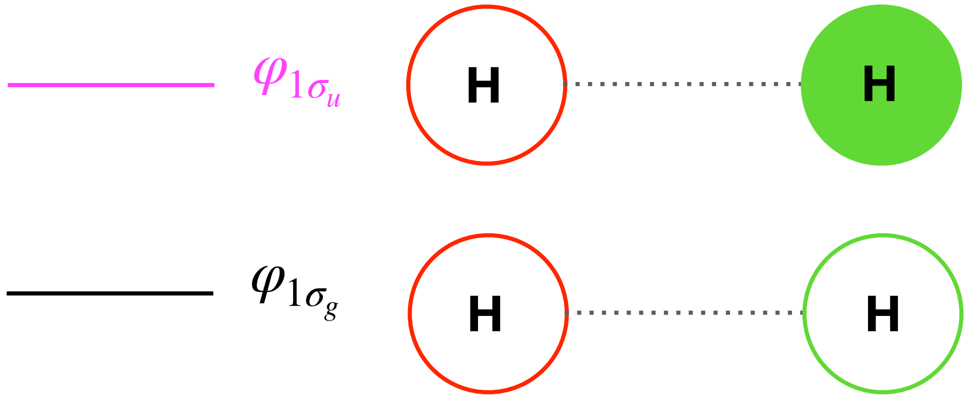

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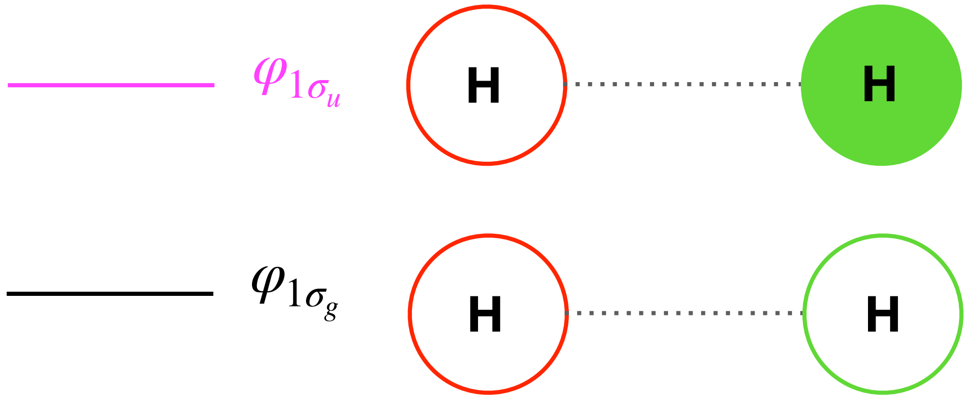
← **Delocalised picture (Chemistry)**

$$= \frac{1}{\sqrt{2}}\Big(\chi_{s_A}(\mathbf{r}_1)\chi_{s_B}(\mathbf{r}_2) + \chi_{s_A}(\mathbf{r}_2)\chi_{s_B}(\mathbf{r}_1)\Big)$$

← **Localised picture (Physics)**

H ······· **H** **H** ······· **H**

Multi-configurational description of the ***stretched hydrogen molecule***



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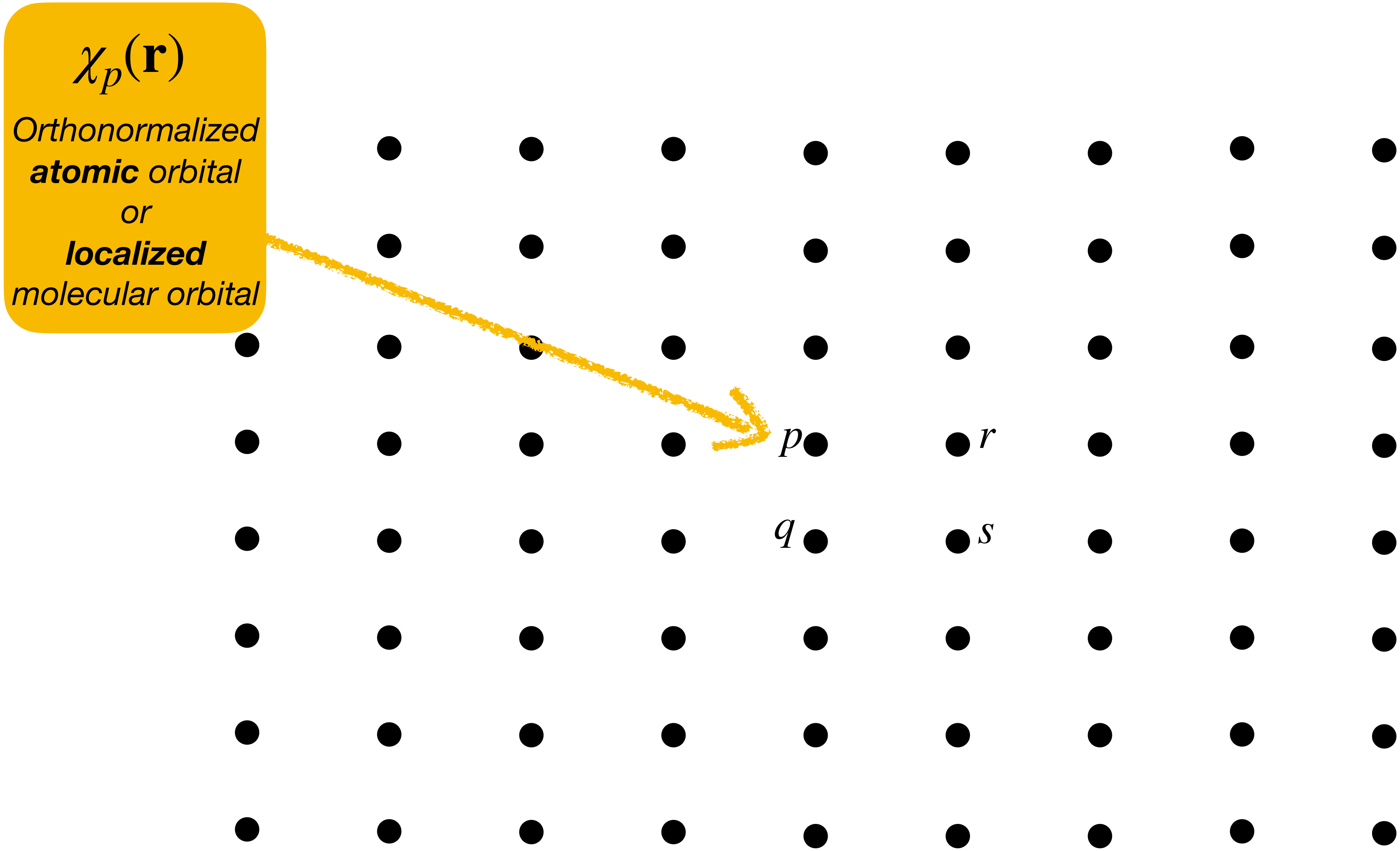
$$= \frac{1}{\sqrt{2}}\Big(\chi_{s_A}(\mathbf{r}_1)\chi_{s_B}(\mathbf{r}_2) + \chi_{s_A}(\mathbf{r}_2)\chi_{s_B}(\mathbf{r}_1)\Big)$$

← **Localised picture (Physics)**

H .... **H** **H** .... **H**

Consequence of the electronic repulsion on each atom!

“Lattice” representation of a molecular or extended system



$\chi_p(\mathbf{r})$

Orthonormalized
atomic orbital
or
localized
molecular orbital

Second quantization, reduced density matrices, and quantum entanglement

Schrödinger equation in second quantization

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

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

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Step 2: Write the Hamiltonian in second quantization in that basis

$$\hat{H} \equiv \sum_{PQ} \langle\varphi_P|\hat{h}|\varphi_Q\rangle\, \hat{c}^\dagger_P \hat{c}_Q + \frac{1}{2}\sum_{PQRS} \langle\varphi_P\varphi_Q|\hat{g}|\varphi_R\varphi_S\rangle\, \hat{c}^\dagger_P \hat{c}^\dagger_Q \hat{c}_S \hat{c}_R$$

See the video* for further explanations

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

Schrödinger equation in second quantization

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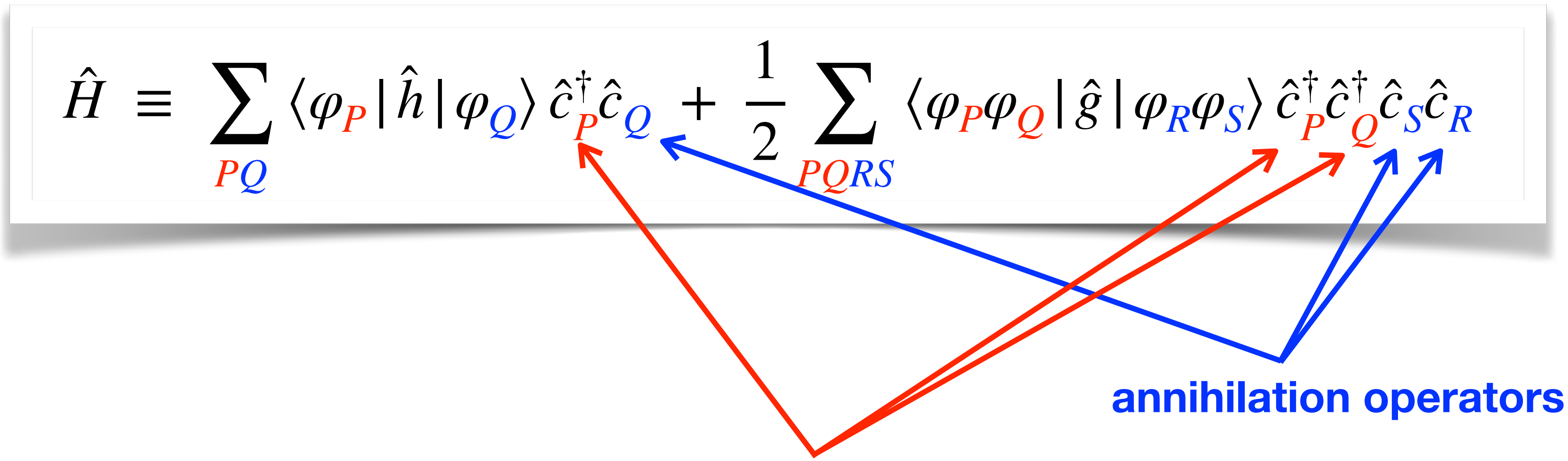

$$\hat{H} \equiv \sum_{PQ} \langle \varphi_P | \hat{h} | \varphi_Q \rangle \, \hat{c}^{\dagger}_{P} \hat{c}_{Q} + \frac{1}{2} \sum_{PQRS} \langle \varphi_P \varphi_Q | \hat{g} | \varphi_R \varphi_S \rangle \, \hat{c}^{\dagger}_{P} \hat{c}^{\dagger}_{Q} \hat{c}_{S} \hat{c}_{R}$$

annihilation operators

creation operators

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

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

One-electron integrals

(Kinetic energy+nuclear attraction)

Schrödinger equation in second quantization

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

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

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Two-electron integrals

(electronic repulsion)

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

Evaluation of the energy from the reduced density matrices

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

Evaluation of the energy from the reduced density matrices

$$E_0 = \langle \hat{H} \rangle_{\Psi_0}$$

$$= \sum_{PQ} h_{PQ} \langle \hat{c}^{\dagger}_{P} \hat{c}_{Q} \rangle_{\Psi_0} + \frac{1}{2} \sum_{PQRS} g_{PQRS} \langle \hat{c}^{\dagger}_{P} \hat{c}^{\dagger}_{Q} \hat{c}_{S} \hat{c}_{R} \rangle_{\Psi_0}$$

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One-electron reduced density matrix (1RDM)

$$\gamma_{PQ} = \langle \hat{c}^{\dagger}_{P} \hat{c}_{Q} \rangle_{\Psi_0}$$

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One-electron reduced density matrix (1RDM)

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

*Often referred to as **"density matrix"**,*
like in density matrix embedding theory (DMET)

Evaluation of the energy from the reduced density matrices

$$E_0 = \langle \hat{H} \rangle_{\Psi_0}$$

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

One-electron reduced density matrix (1RDM)

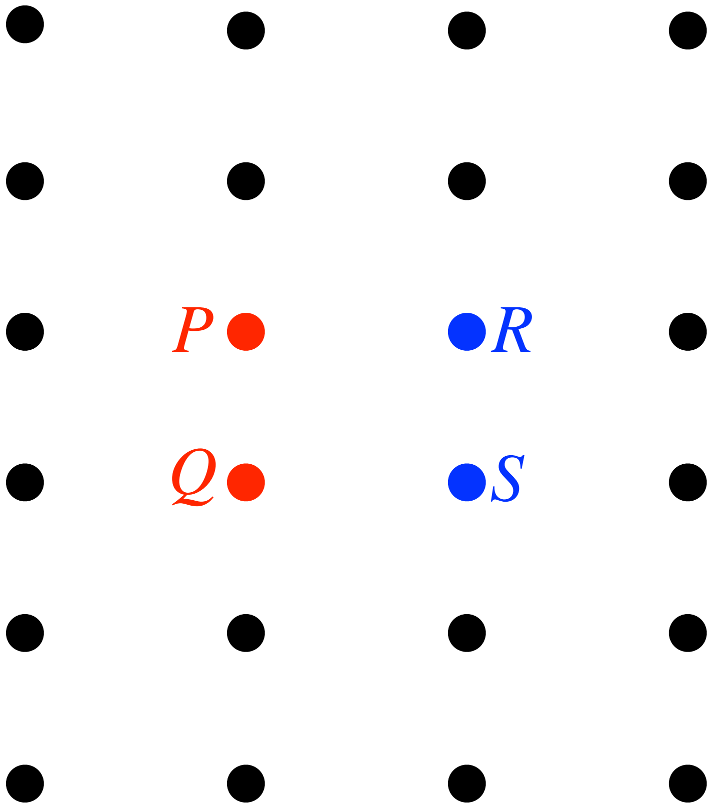
Two-electron reduced density matrix (2RDM)

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

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

Meaning of the reduced density matrices

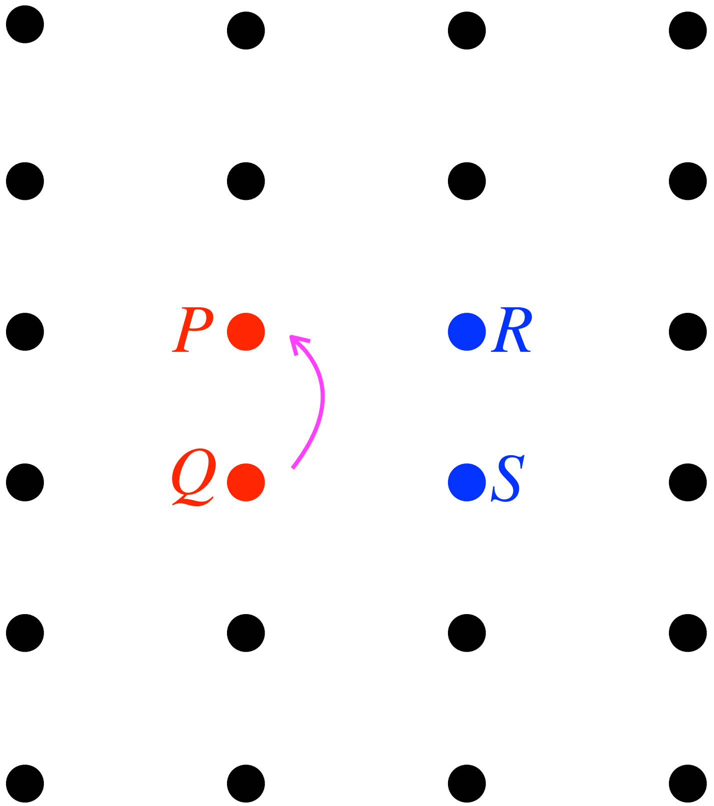
Let’s consider a 2D lattice of localised spin-orbitals



Meaning of the reduced density matrices

$$\gamma_{PQ} = \langle \Psi_0 | \underset{\longleftarrow}{\boxed{\hat{c}^\dagger_P \hat{c}_Q | \Psi_0 \rangle}}$$

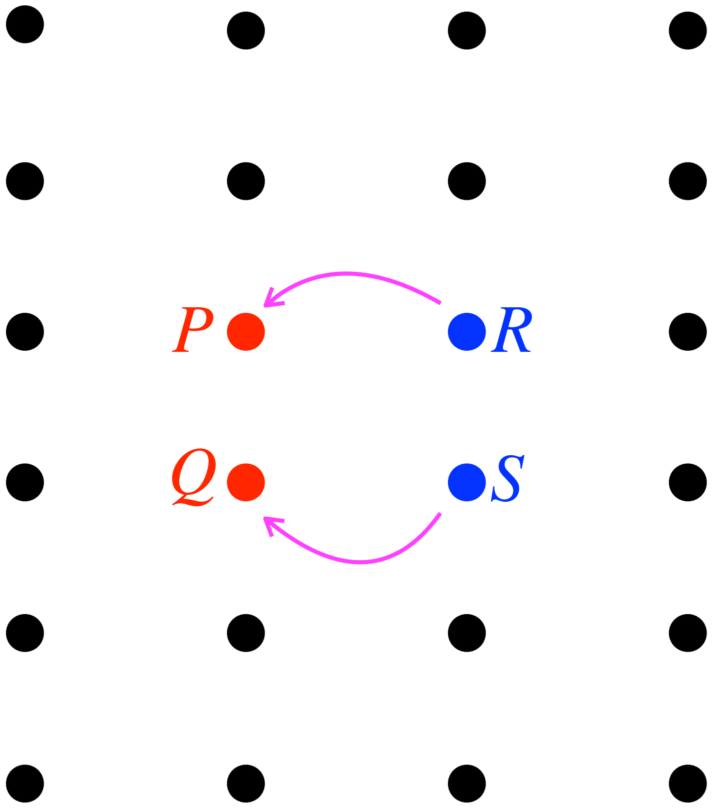
1RDM



Meaning of the reduced density matrices

$$\Gamma_{PQSR} = \langle \Psi_0 | \boxed{\hat{c}^\dagger_P \hat{c}^\dagger_Q \hat{c}_S \hat{c}_R | \Psi_0 \rangle} \quad \xleftarrow{\hspace{3cm}}$$

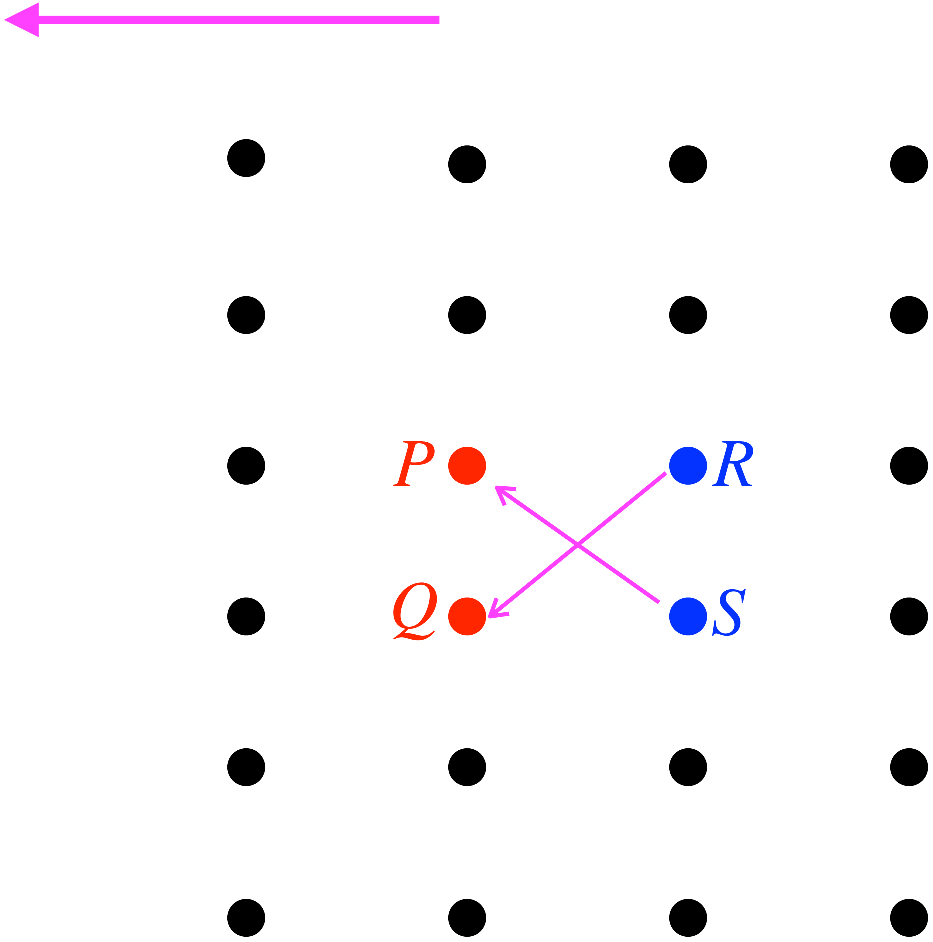
2RDM



Meaning of the reduced density matrices

$$\Gamma_{PQSR} = \langle \Psi_0 | \boxed{\hat{c}^\dagger_P \hat{c}^\dagger_Q \hat{c}_S \hat{c}_R | \Psi_0 \rangle}$$

2RDM



Evaluation of the energy from the reduced density matrices

$$
\begin{aligned}
E_0 &= \langle \hat{H} \rangle_{\Psi_0} \\
&= \sum_{PQ} h_{PQ} \boxed{\langle \hat{c}^\dagger_P \hat{c}_Q \rangle_{\Psi_0}} + \frac{1}{2} \sum_{PQRS} g_{PQRS} \boxed{\langle \hat{c}^\dagger_P \hat{c}^\dagger_Q \hat{c}_S \hat{c}_R \rangle_{\Psi_0}}
\end{aligned}
$$

One-electron reduced density matrix (1RDM)

Two-electron reduced density matrix (2RDM)

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

$$\Gamma_{PQSR} = \langle \hat{c}^\dagger_P \hat{c}^\dagger_Q \hat{c}_S \hat{c}_R \rangle_{\Psi_0}$$

The energy is an ***explicit functional*** of the 1 and 2RDMs!

Evaluation of the energy from the reduced density matrices

In fact...

$$\gamma_{PQ} = -\frac{\sum_R \Gamma_{PRQR}}{N-1}$$

$$\hat{c}^\dagger_R \hat{c}_Q = \delta_{RQ} - \hat{c}_Q \hat{c}^\dagger_R$$

Number of electrons

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

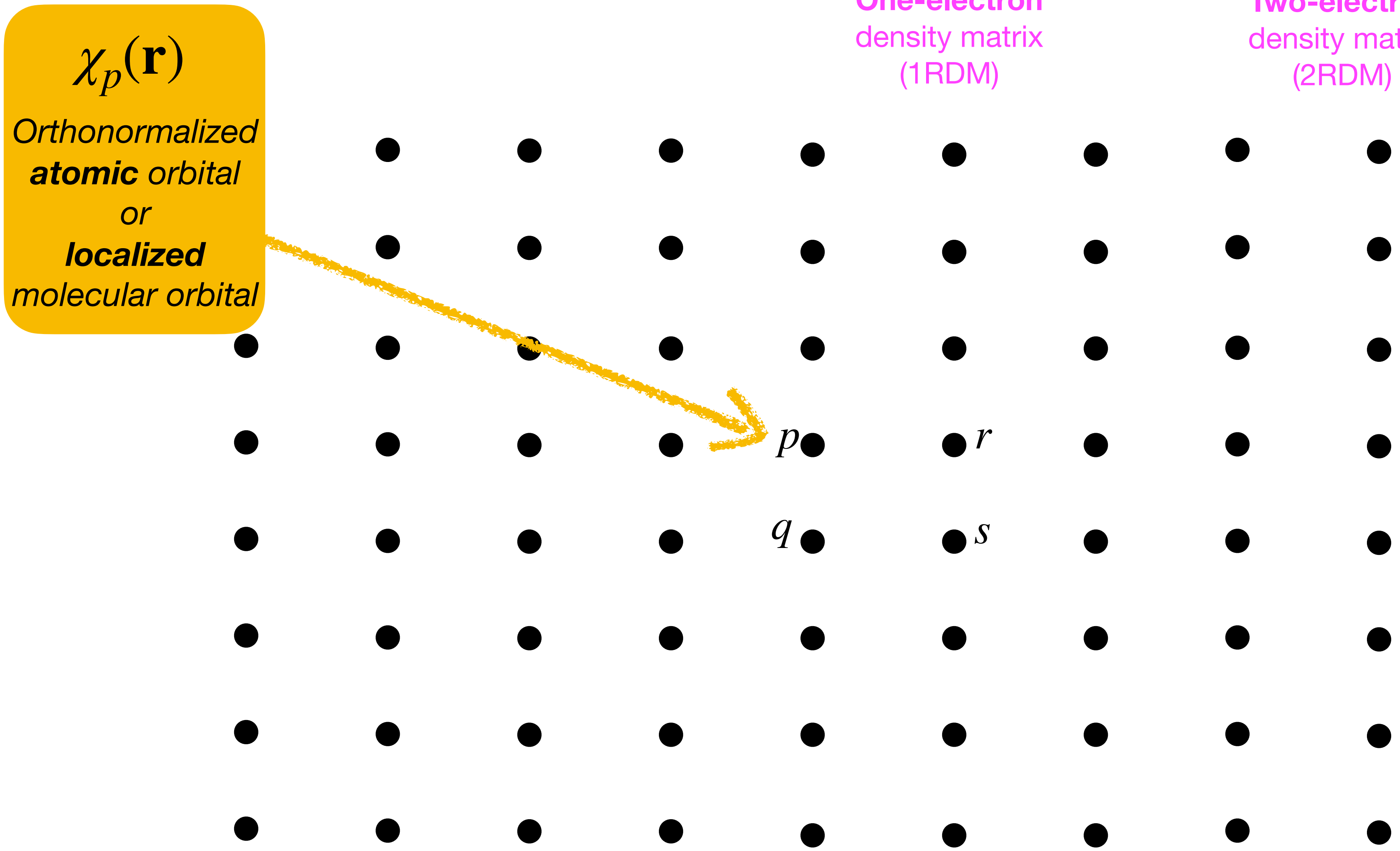
$$\Gamma_{PQSR} = \langle \hat{c}^\dagger_P \hat{c}^\dagger_Q \hat{c}_S \hat{c}_R \rangle_{\Psi_0}$$

The energy is an ***explicit functional*** of the 1 and 2RDMs!

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

So-called "lattice" representation

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



$\chi_p(\mathbf{r})$

Orthonormalized ***atomic*** *orbital*
or
localized
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G. Knizia and G. K.-L. Chan, Phys. Rev. Lett. ***109****, 186404 (2012).*
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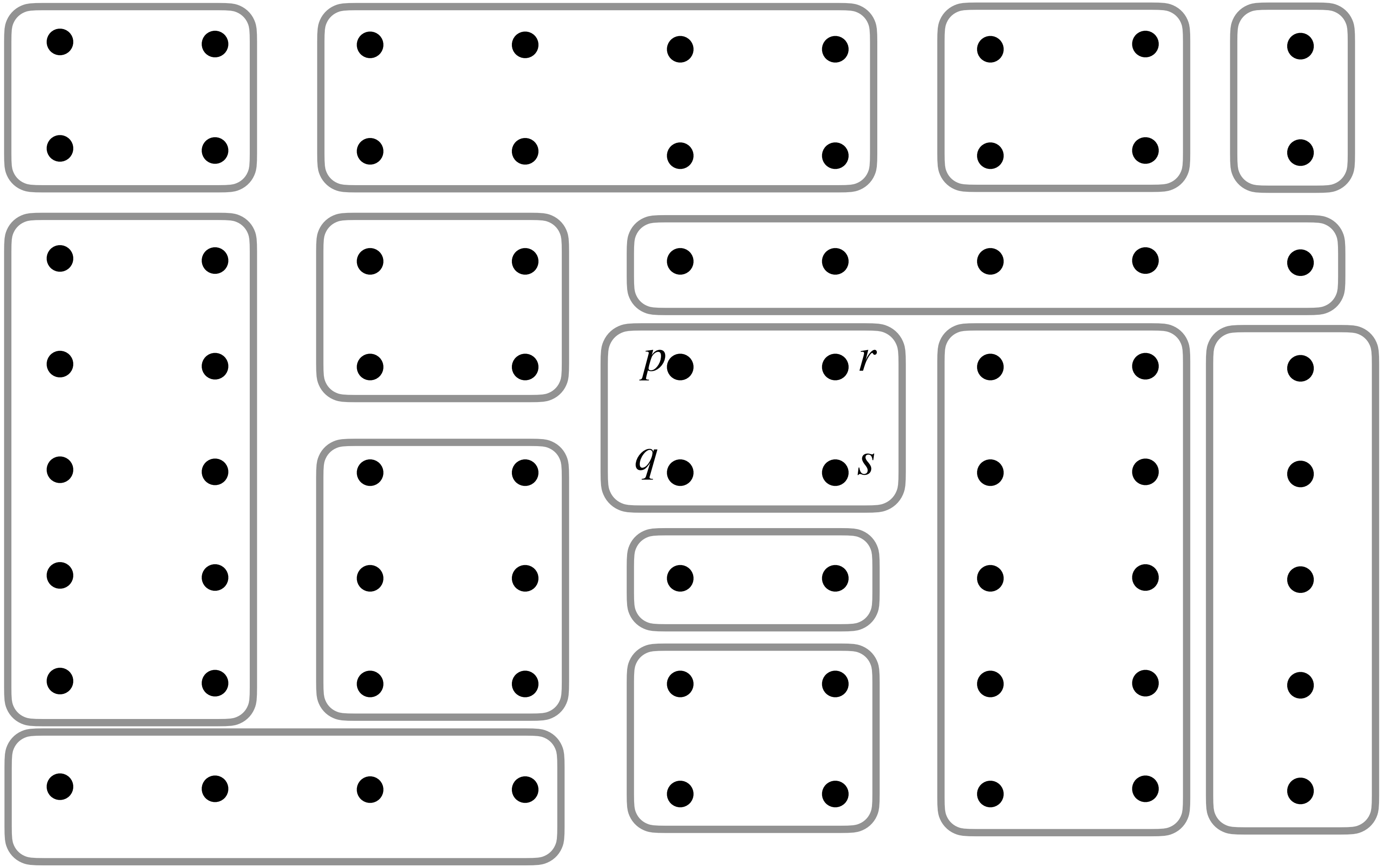
Local evaluation of the energy (in a localised spin-orbital basis)

Fragmentation

for treating strong local electron correlations

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



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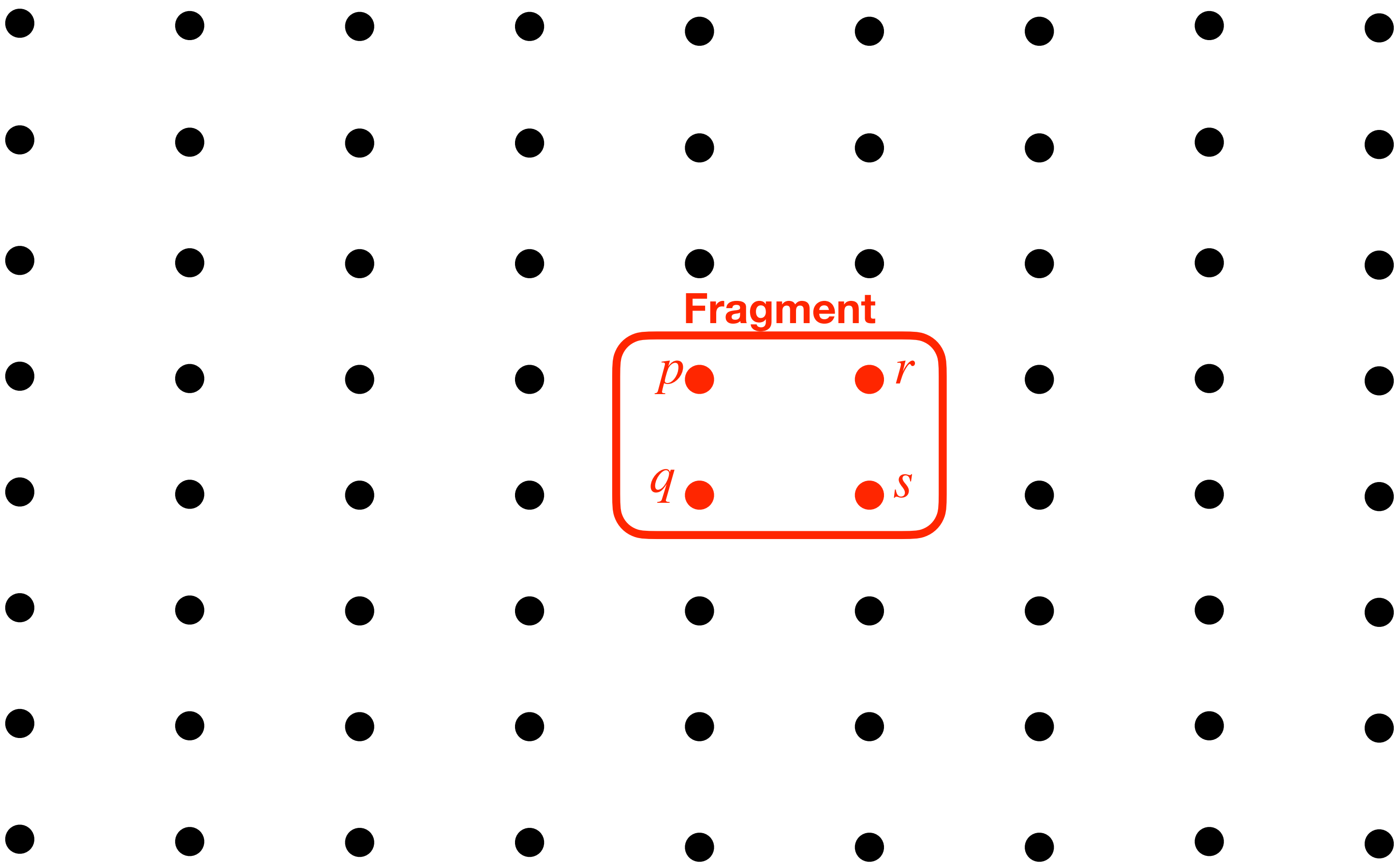

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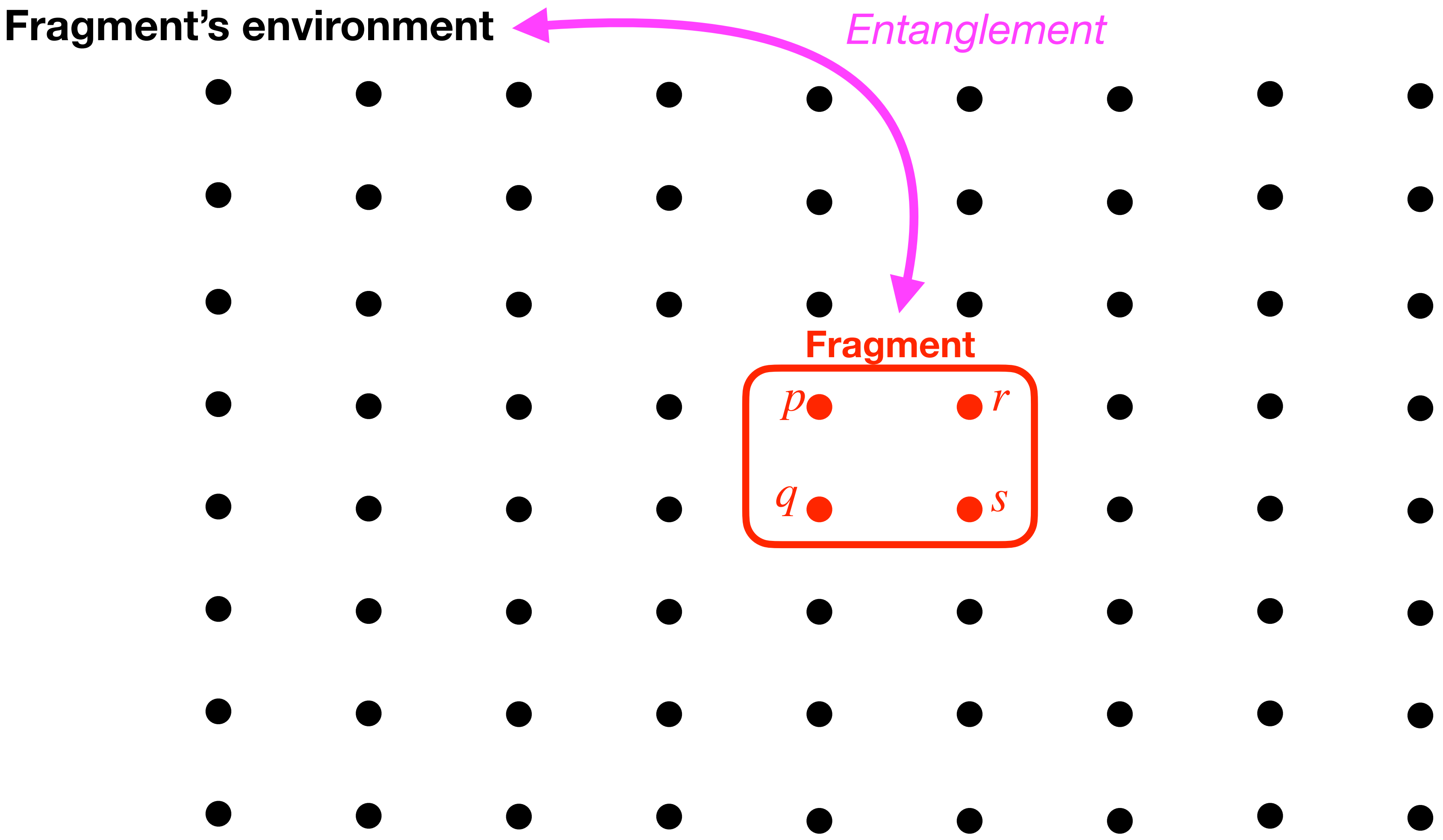

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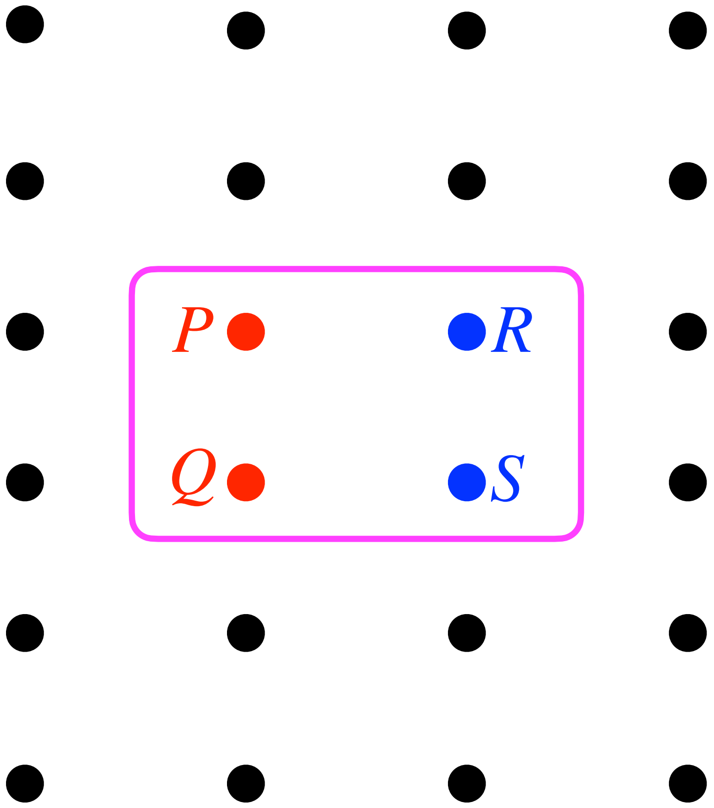
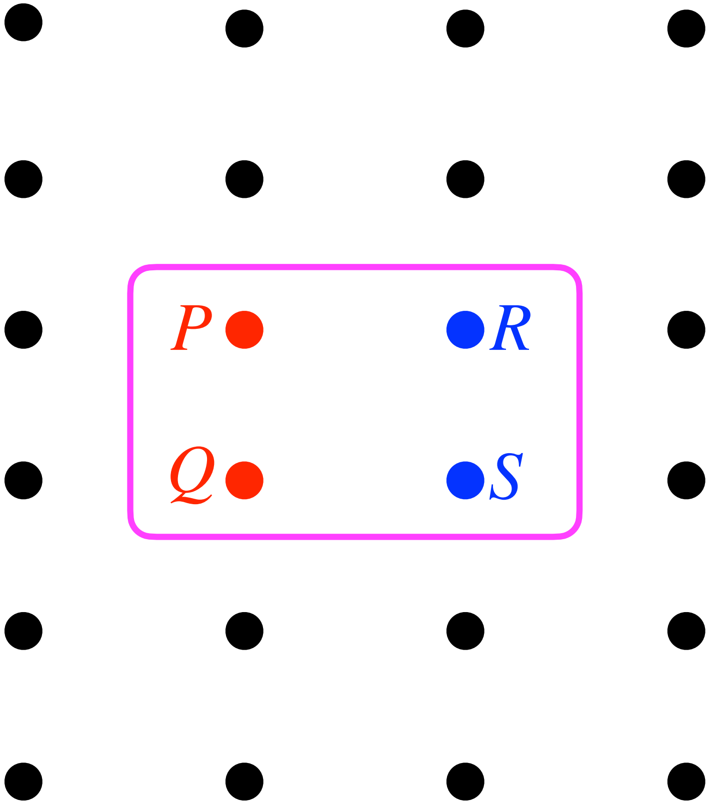
Quantum entanglement of a fragment with its environment

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



Quantum entanglement of a fragment with its environment

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



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:

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

Quantum entanglement of a fragment with its environment

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

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

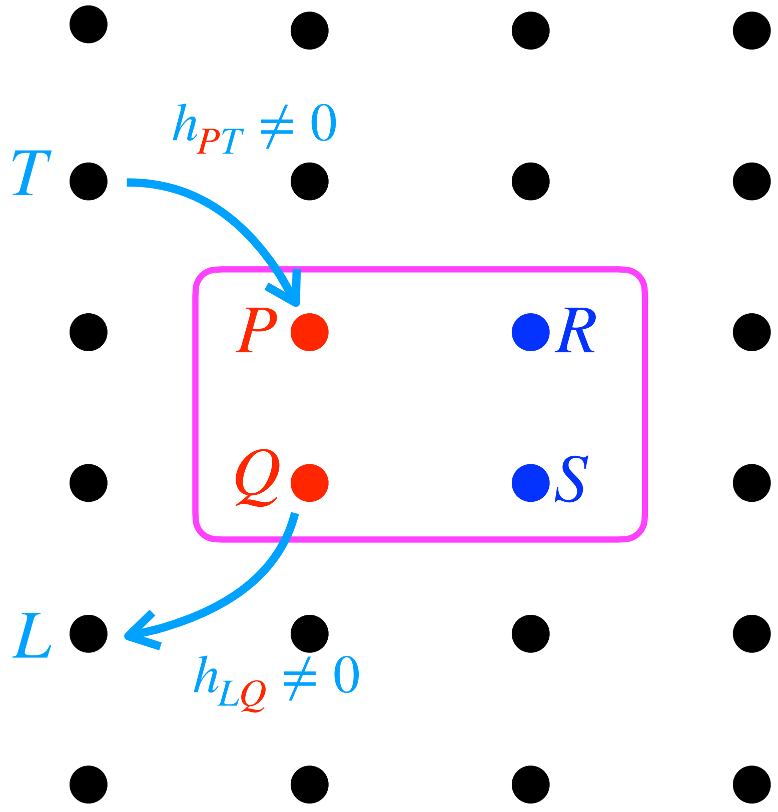
$$\hat{H}|\Psi_0\rangle = E_0|\Psi_0\rangle$$

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

Quantum entanglement of a fragment with its environment

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

Summation running
over the **full lattice!**



Entanglement

Quantum entanglement of a fragment with its environment

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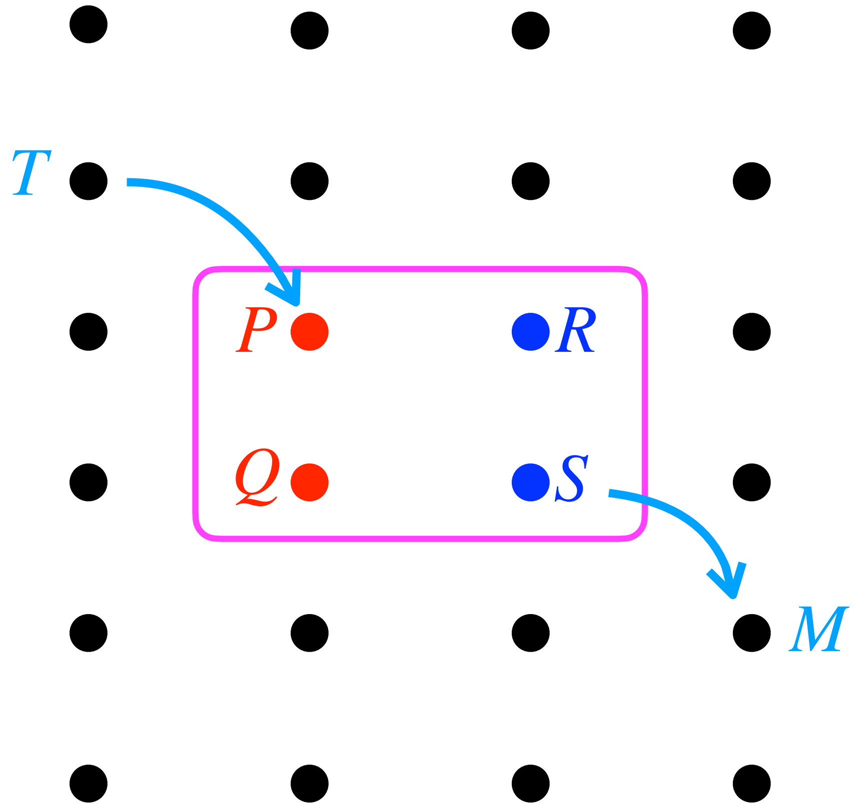
Summation running over the **full lattice!**



$$g_{PMTS} \neq 0$$

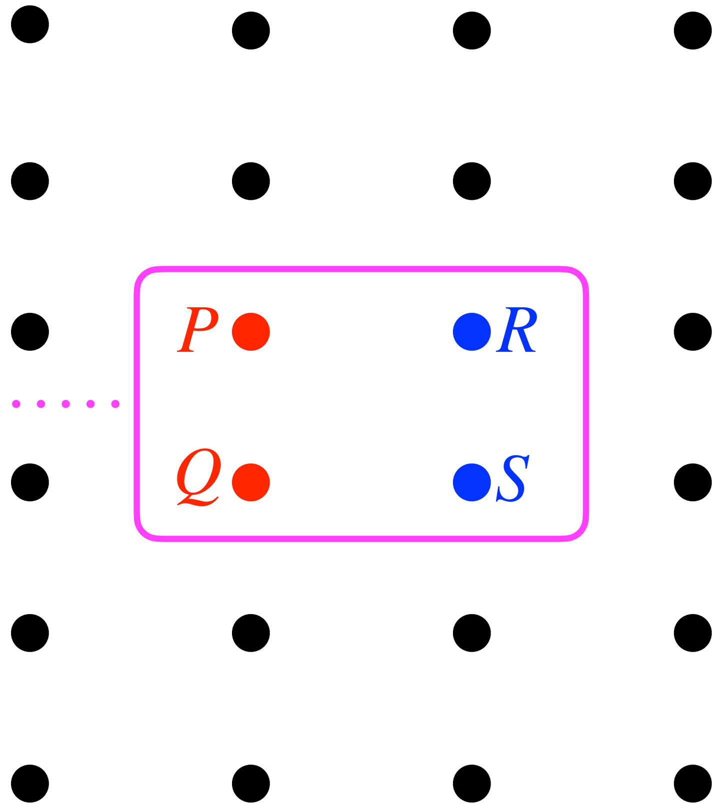
Entanglement

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***

$$\gamma_{PQ} = \langle \hat{c}^{\dagger}_{P} \hat{c}_{Q} \rangle_{\Psi_0}$$

$$\Gamma_{PQSR} = \langle \hat{c}^{\dagger}_{P} \hat{c}^{\dagger}_{Q} \hat{c}_{S} \hat{c}_{R} \rangle_{\Psi_0}$$



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

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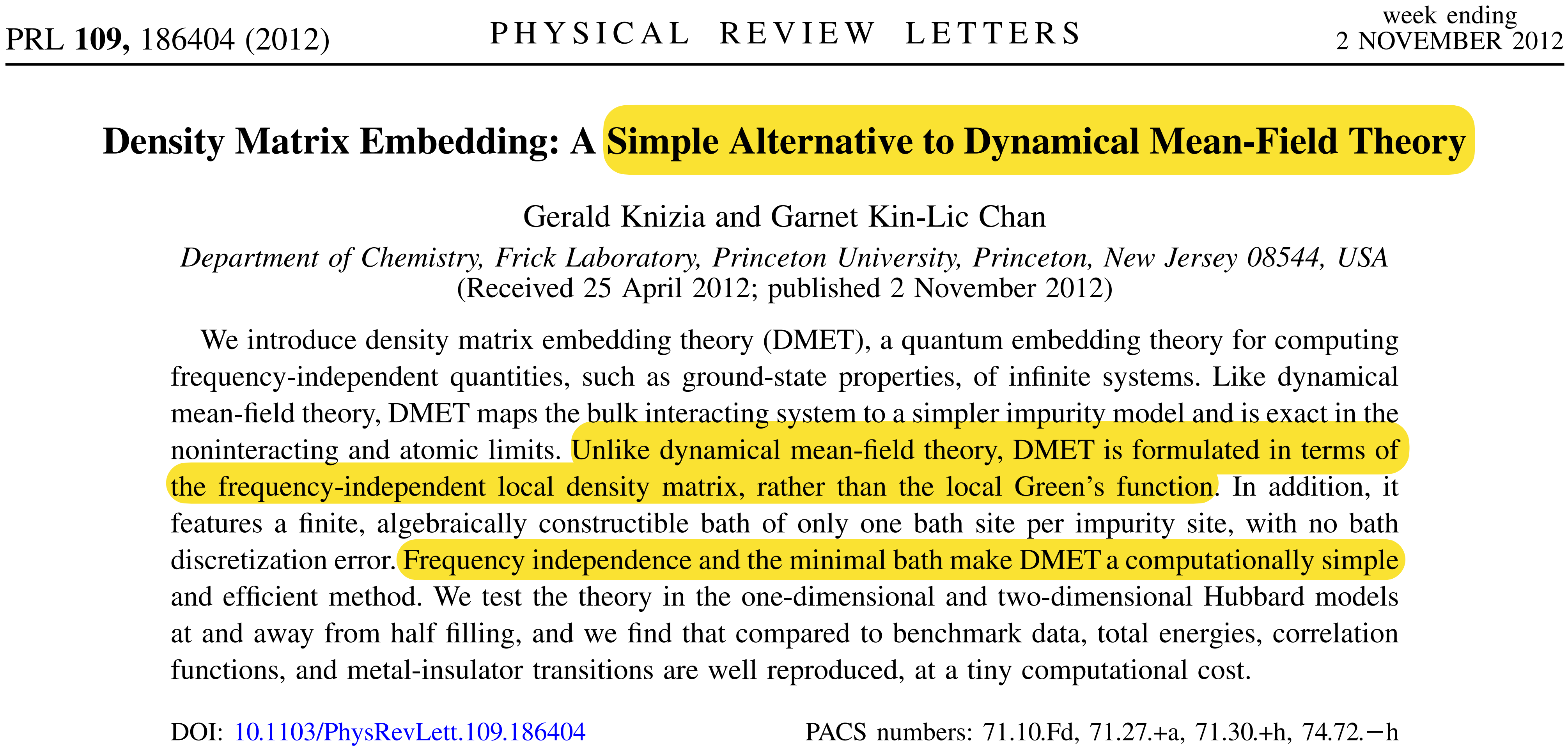

PRL **109,** 186404 (2012) PHYSICAL REVIEW LETTERS week ending 2 NOVEMBER 2012

Density Matrix Embedding: A Simple Alternative to Dynamical Mean-Field Theory

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(Received 25 April 2012; published 2 November 2012)

We introduce density matrix embedding theory (DMET), a quantum embedding theory for computing frequency-independent quantities, such as ground-state properties, of infinite systems. Like dynamical mean-field theory, DMET maps the bulk interacting system to a simpler impurity model and is exact in the noninteracting and atomic limits. Unlike dynamical mean-field theory, DMET is formulated in terms of the frequency-independent local density matrix, rather than the local Green's function. In addition, it features a finite, algebraically constructible bath of only one bath site per impurity site, with no bath discretization error. Frequency independence and the minimal bath make DMET a computationally simple and efficient method. We test the theory in the one-dimensional and two-dimensional Hubbard models at and away from half filling, and we find that compared to benchmark data, total energies, correlation functions, and metal-insulator transitions are well reproduced, at a tiny computational cost.

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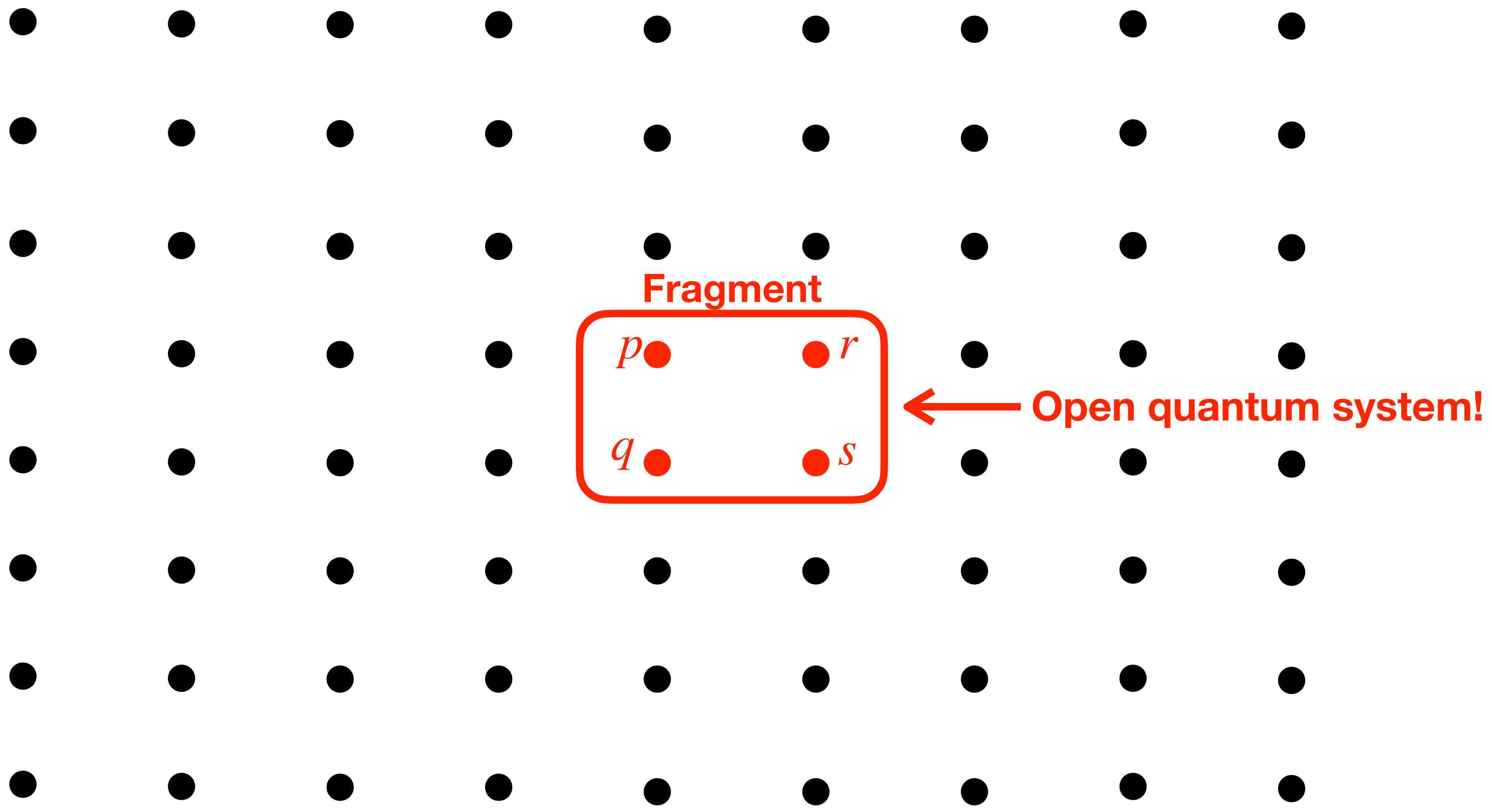
Local evaluation of the energy (in a localised spin-orbital basis)

So-called "lattice" representation



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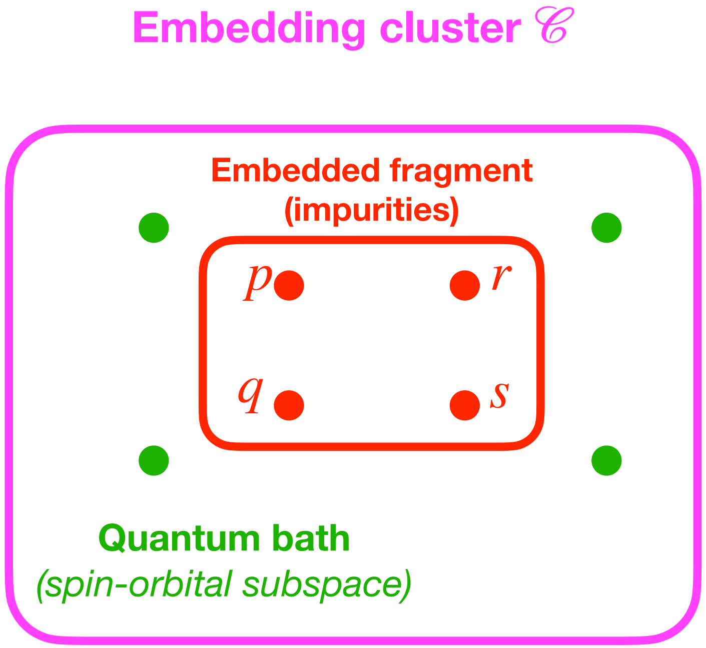
Clusterization procedure



Embedding cluster $\mathscr{C}$

Embedded fragment (impurities)

Quantum bath

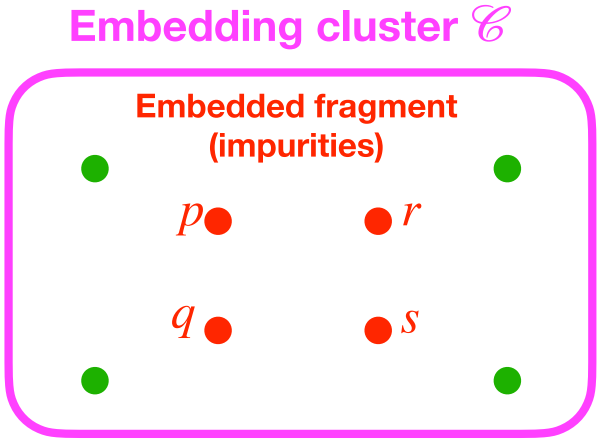
(spin-orbital subspace)

Clusterization procedure

Reduction in size of the problem to be solved:

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

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


Embedding cluster $\mathscr{C}$

Embedded fragment (impurities)

p r q s

Quantum bath
≡ electronic reservoir

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

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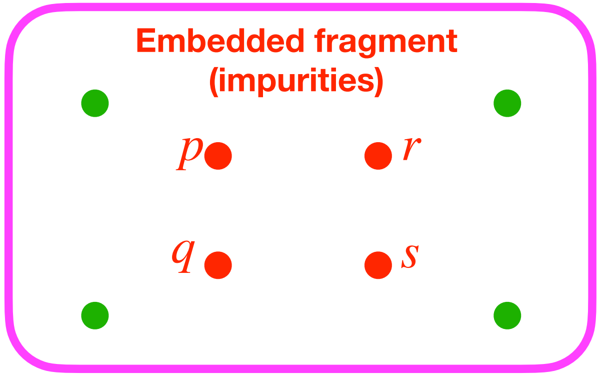
How many bath orbitals?

↓

Quantum bath

≡ electronic reservoir

Embedding cluster $\mathscr{C}$



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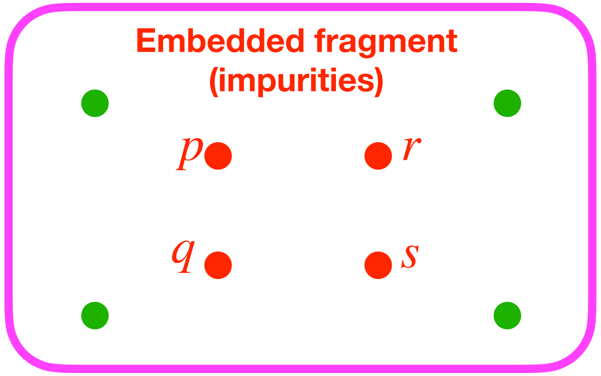
↓

Quantum bath

≡ electronic reservoir

Embedding cluster $\mathscr{C}$



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

As many as the number of orbitals in the fragment…

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Clusterization procedure

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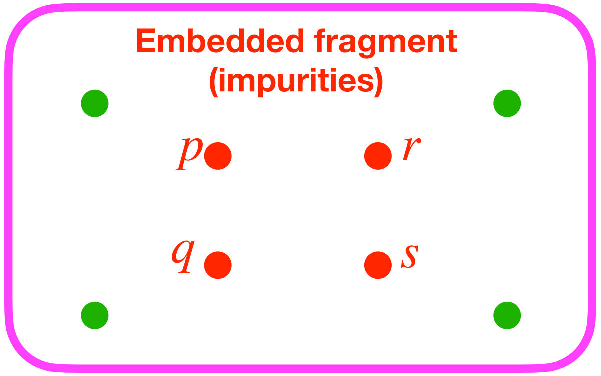
4 orbitals here:
Why and how?

↓

Quantum bath
≡ electronic reservoir

Embedding cluster $\mathscr{C}$



Embedded fragment
(impurities)

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

How many?

↓

Few-electron
correlated wave function

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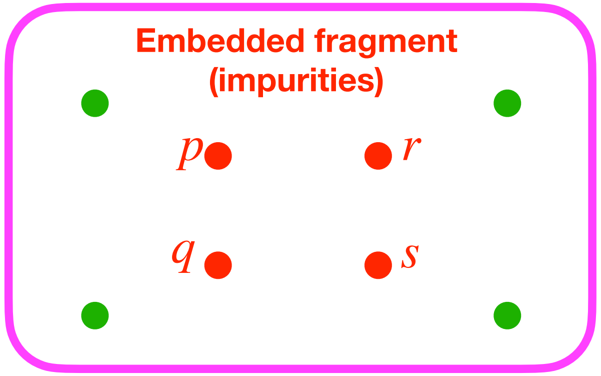
4 orbitals here:
Why and how?

↓

Quantum bath
≡ electronic reservoir

Embedding cluster $\mathscr{C}$



Embedded fragment
(impurities)

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

How many?

↓

Few-electron
correlated wave function

As many as the number of spin-orbitals
in the fragment
(***half-filled embedding cluster***)…

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Mathematical construction and justification of the DMET quantum bath

Clusterization through a unitary one-electron transformation

Original lattice representation

Resolution of the identity (RI)

$$|\chi_p\rangle \quad \rightarrow \boxed{|\phi_p\rangle} = \left(\sum_q |\chi_q\rangle\langle\chi_q|\right)\boxed{|\phi_p\rangle} = \sum_q \langle\chi_q\boxed{|\phi_p\rangle}|\chi_q\rangle$$

Embedding representation

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Clusterization through a unitary one-electron transformation

$$|\chi_p\rangle \quad \to |\phi_p\rangle = \left(\sum_q |\chi_q\rangle\langle\chi_q|\right)|\phi_p\rangle = \sum_q \langle\chi_q|\phi_p\rangle\,|\chi_q\rangle$$

Original lattice representation

Embedding representation

$$\left\{|\chi_p\rangle\right\} \quad \equiv$$

↑

Same space, different basis

$$|\phi_p\rangle \overset{p\in\text{Fragment}}{=} |\chi_p\rangle$$

Fragment

$$\left\{|\phi_b\rangle\right\}$$

Bath subspace *(not defined yet)*

$$\left\{|\phi_{\mathscr{E}}\rangle\right\}$$

Cluster's environment *(not defined yet)*

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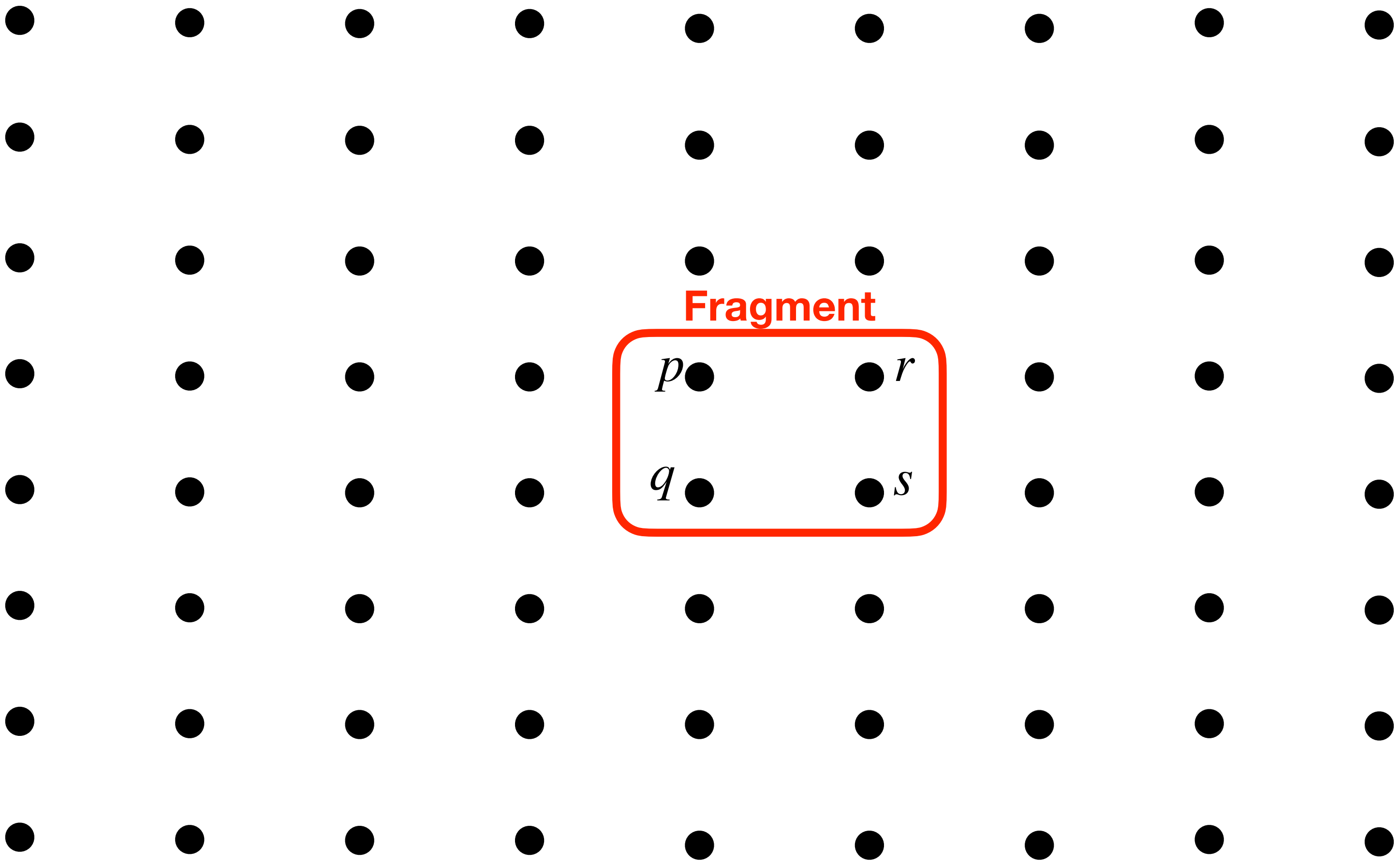
Clusterization through a unitary one-electron transformation

So-called "lattice representation"



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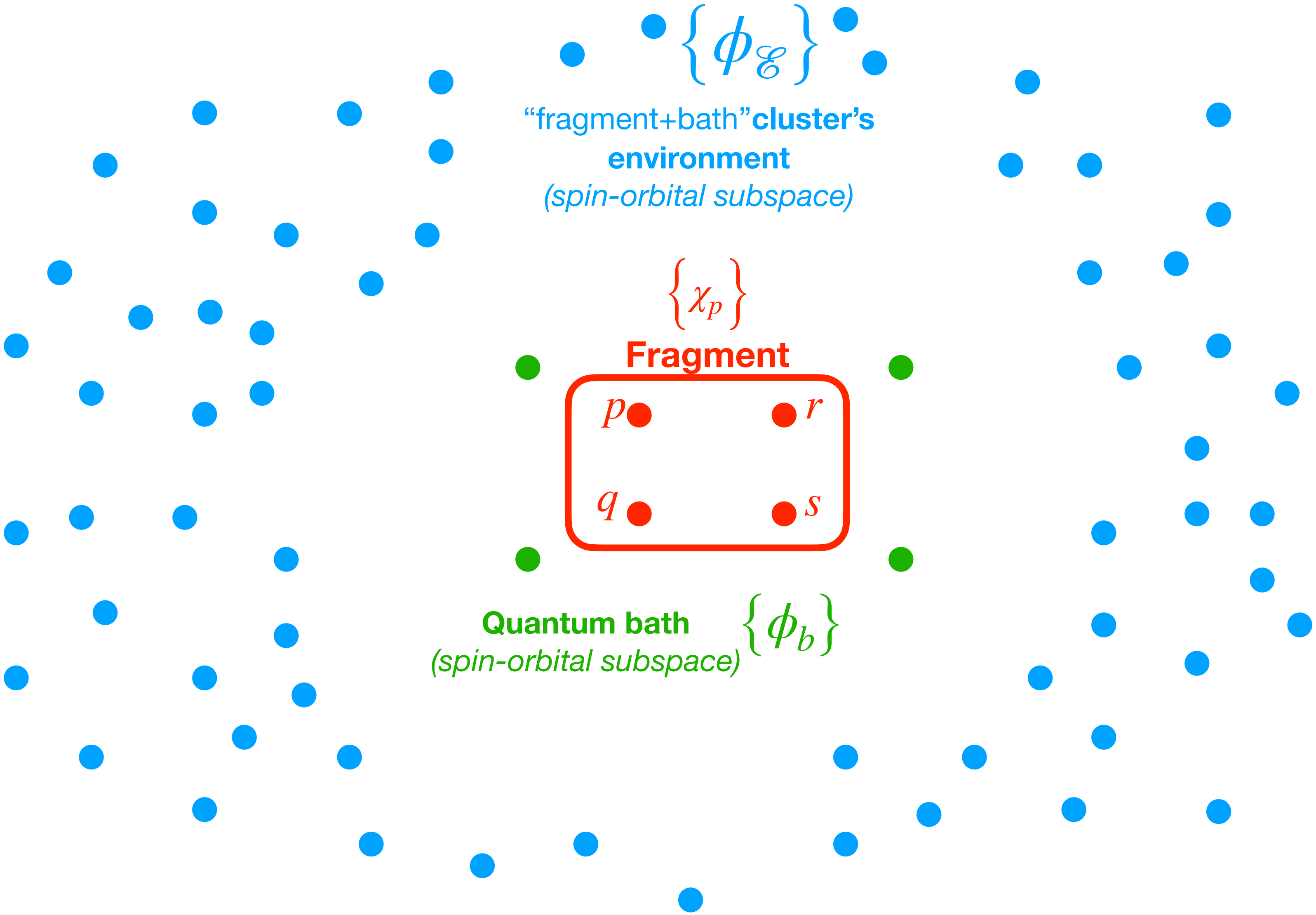
Clusterization through a unitary one-electron transformation



$\left\{\phi_{\mathscr{E}}\right\}$

“fragment+bath”**cluster’s environment**
(spin-orbital subspace)

$\left\{\chi_p\right\}$

Fragment

Quantum bath $\left\{\phi_b\right\}$
(spin-orbital subspace)

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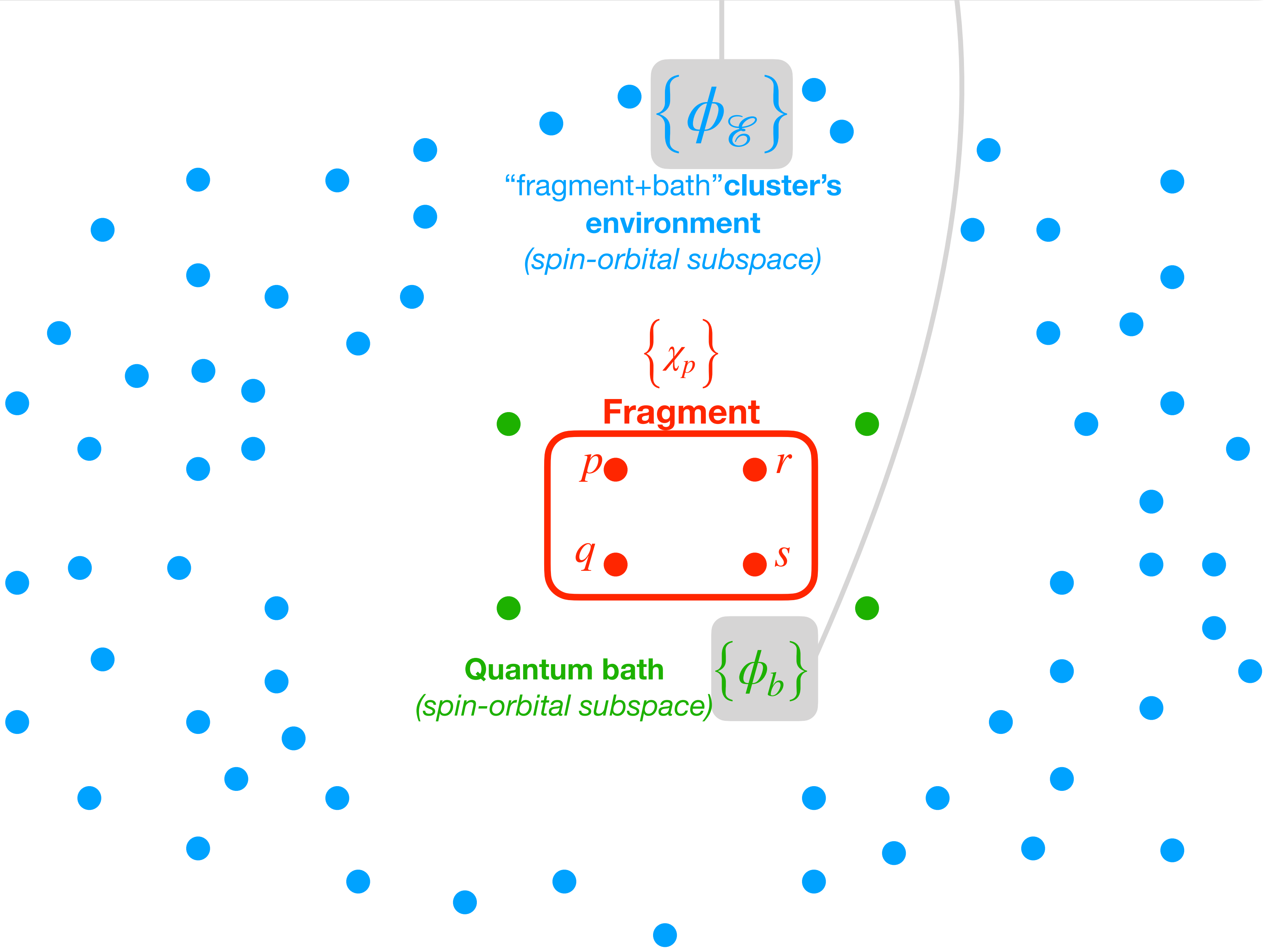
Clusterization through a unitary one-electron transformation

Span the **original lattice** without overlapping with the fragment



$\{\phi_{\mathscr{E}}\}$

"fragment+bath"**cluster's environment**

(spin-orbital subspace)

$\{\chi_p\}$

Fragment

Quantum bath

(spin-orbital subspace)

$\{\phi_b\}$

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Unitary one-electron transformation in second quantization

$$|\chi_p\rangle \rightarrow |\phi_p\rangle = \sum_q \langle \chi_q | \phi_p \rangle |\chi_q\rangle$$

$$\Updownarrow$$

$$|\chi_p\rangle \rightarrow |\phi_p\rangle \equiv \hat{d}_p^\dagger |\text{vac}\rangle = \sum_q \langle \chi_q | \phi_p \rangle \underbrace{\hat{c}_q^\dagger |\text{vac}\rangle}_{|\chi_q\rangle}$$

Unitary one-electron transformation in second quantization

$$|\chi_p\rangle \rightarrow |\phi_p\rangle \equiv \hat{d}_p^\dagger|\mathrm{vac}\rangle = \sum_q \langle\chi_q|\phi_p\rangle \hat{c}_q^\dagger|\mathrm{vac}\rangle$$

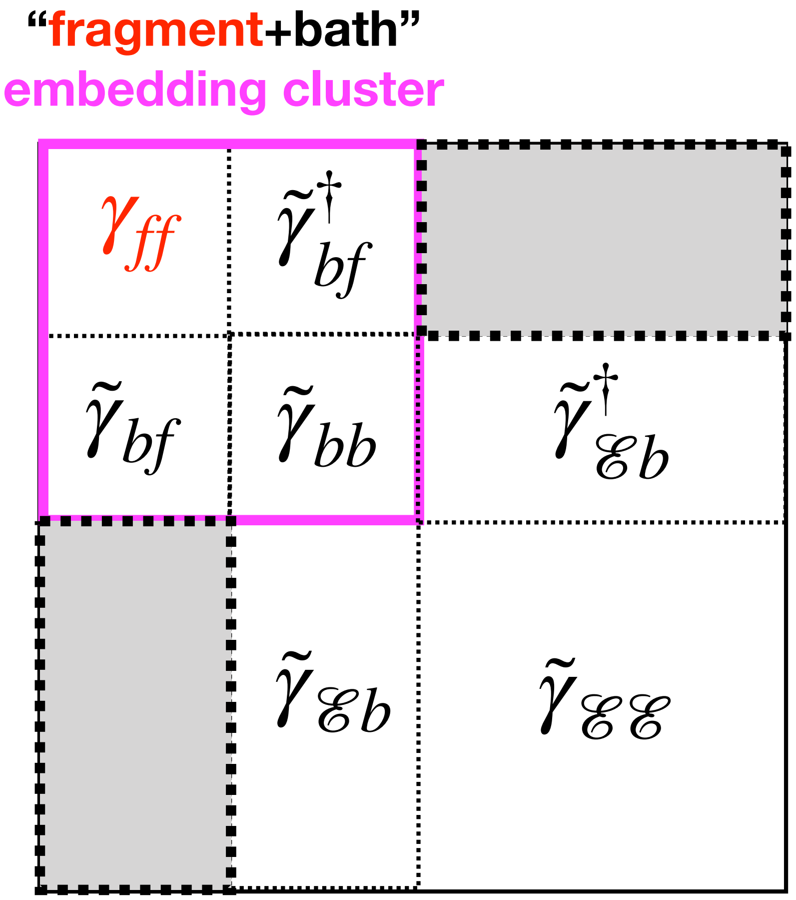
$$\boxed{\hat{d}_p^\dagger = \sum_q \langle\chi_q|\phi_p\rangle \hat{c}_q^\dagger}$$

Embedding representation

Lattice representation

Unitary transformed density matrix

$$\tilde{\gamma} = \langle \hat{d}_p^{\dagger} \hat{d}_q \rangle \equiv$$



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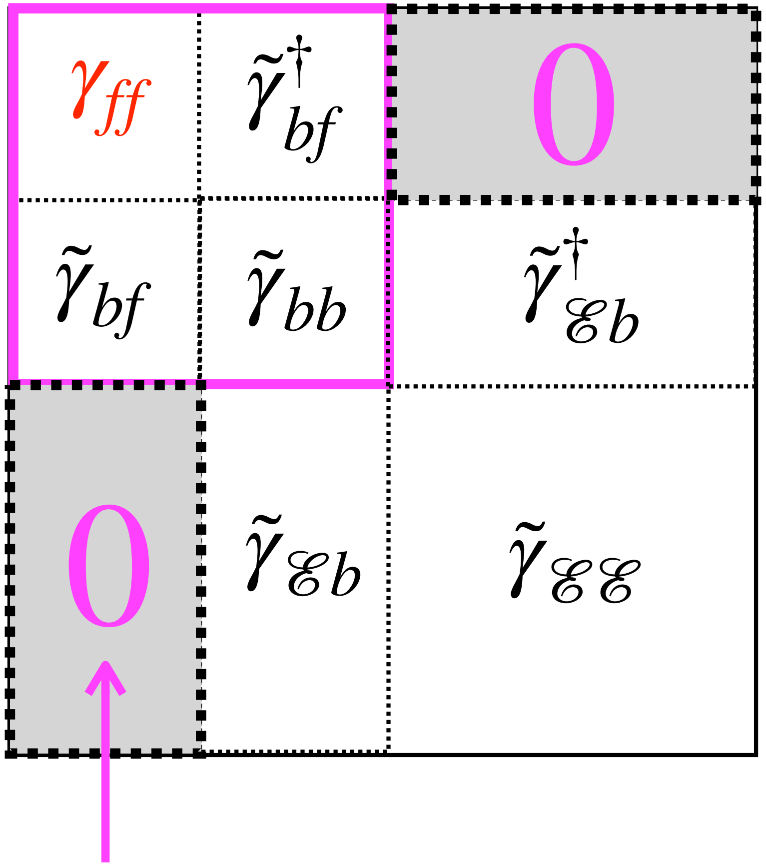
Unitary transformed density matrix



“**fragment**+bath”

embedding cluster

$$\tilde{\gamma} = \langle \hat{d}_p^\dagger \hat{d}_q \rangle \equiv \begin{pmatrix} \gamma_{ff} & \tilde{\gamma}_{bf}^\dagger & 0 \\ \tilde{\gamma}_{bf} & \tilde{\gamma}_{bb} & \tilde{\gamma}_{\mathscr{E}b}^\dagger \\ 0 & \tilde{\gamma}_{\mathscr{E}b} & \tilde{\gamma}_{\mathscr{E}\mathscr{E}} \end{pmatrix}$$

We impose that constraint (this is what we want!)

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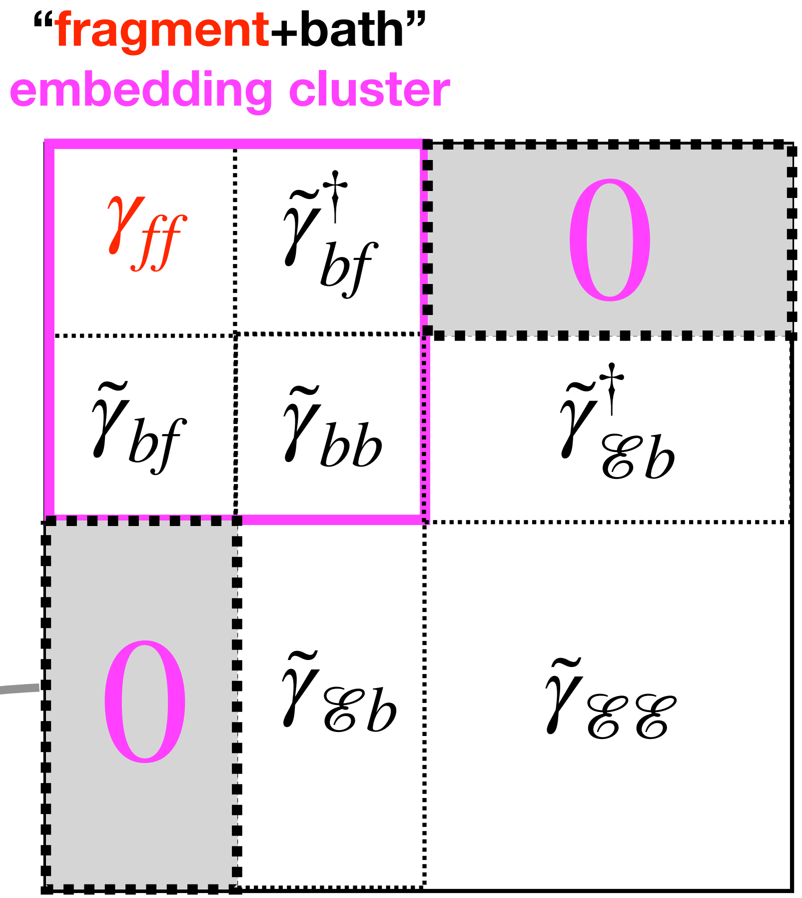
Unitary transformed density matrix

$$\tilde{\gamma} = \langle \hat{d}^\dagger_p \hat{d}_q \rangle \equiv \begin{pmatrix} \gamma_{ff} & \tilde{\gamma}^\dagger_{bf} & 0 \\ \tilde{\gamma}_{bf} & \tilde{\gamma}_{bb} & \tilde{\gamma}^\dagger_{\mathscr{E}b} \\ 0 & \tilde{\gamma}_{\mathscr{E}b} & \tilde{\gamma}_{\mathscr{E}\mathscr{E}} \end{pmatrix}$$



$$\langle \hat{d}^\dagger_{\mathscr{E}} \hat{c}_f \rangle = \sum_{e \notin \text{Fragment}}^{\text{lattice}} \langle \chi_e | \phi_{\mathscr{E}} \rangle \underbrace{\langle \hat{c}^\dagger_e \hat{c}_f \rangle}_{\gamma_{ef}}$$

Density matrix in the original lattice representation ***(supposed to be known!)***

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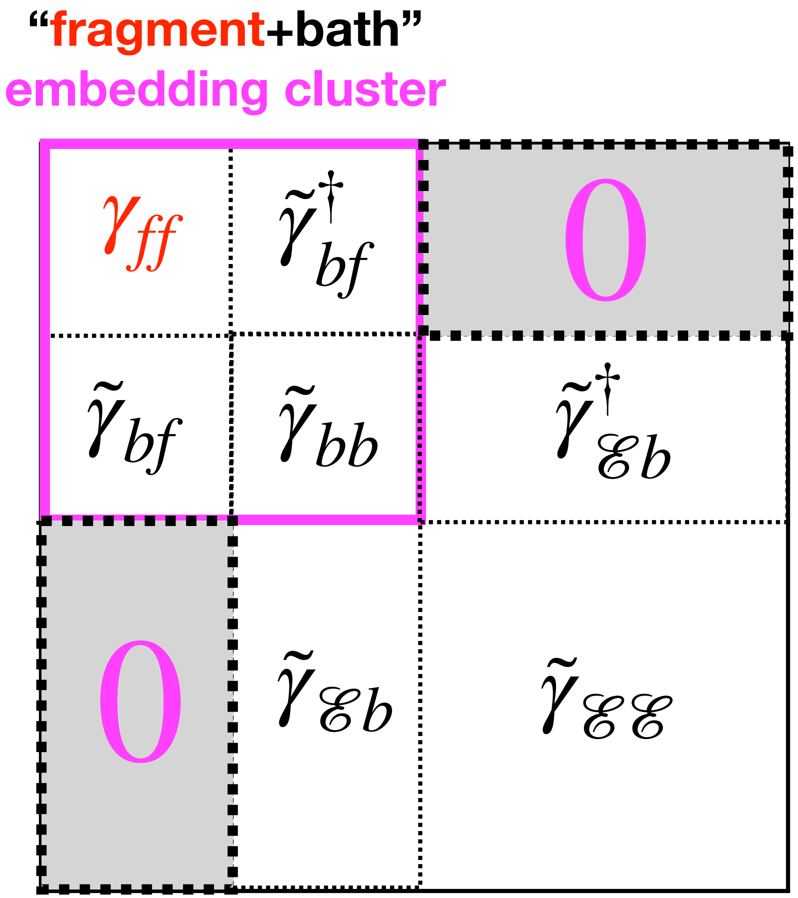
Unitary transformed density matrix



$$\tilde{\gamma} = \langle \hat{d}_p^\dagger \hat{d}_q \rangle \equiv \begin{pmatrix} \gamma_{ff} & \tilde{\gamma}_{bf}^\dagger & 0 \\ \tilde{\gamma}_{bf} & \tilde{\gamma}_{bb} & \tilde{\gamma}_{\mathscr{E}b}^\dagger \\ 0 & \tilde{\gamma}_{\mathscr{E}b} & \tilde{\gamma}_{\mathscr{E}\mathscr{E}} \end{pmatrix}$$

$$\langle \hat{d}_{\mathscr{E}}^\dagger \hat{c}_f \rangle = \sum_{e \notin \text{Fragment}} \langle \chi_e | \phi_{\mathscr{E}} \rangle \langle \hat{c}_e^\dagger \hat{c}_f \rangle = \left\langle \sum_{e \notin \text{Fragment}} \gamma_{ef} \chi_e \middle| \phi_{\mathscr{E}} \right\rangle \overset{!}{=} 0, \quad \forall f$$

Orthogonality constraint

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The bath is a functional of the density matrix

$$\left\langle \sum_{e\notin \text{Fragment}} \gamma_{ef}\chi_e \middle| \phi_{\mathscr{E}} \right\rangle \overset{!}{=} 0, \quad \forall f$$

Embedding
cluster's environment

The **bath** is a **functional** of the full-system **density matrix** $\gamma \equiv \langle \hat{c}_p^\dagger \hat{c}_q \rangle$

$$\left\{ \sum_{e\notin \text{Fragment}}^{lattice} \gamma_{ef} |\chi_e\rangle \right\}_{f\in\text{Fragment}} \equiv \mathscr{B}$$

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The bath is a functional of the density matrix

$$\dim \mathscr{B} = \dim \text{Fragment}$$ ✅

The **bath** is a **functional** of the full-system **density matrix** $\gamma \equiv \langle \hat{c}_p^\dagger \hat{c}_q \rangle$

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The bath is a functional of the density matrix

*The bath orbital basis needs to be **orthonormalized***
(SVD, Householder transformation, …)

The **bath** is a **functional** of the full-system **density matrix** $\gamma \equiv \langle \hat{c}_p^\dagger \hat{c}_q \rangle$

$$\left\{ \sum_{e \notin \text{Fragment}}^{lattice} \gamma_{ef} \, |\chi_e\rangle \right\}_{f \in \text{Fragment}} \equiv \mathscr{B}$$

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Orthonormalisation of the bath orbitals

$$|u_f\rangle = \sum_{e \notin \text{Fragment}} \gamma_{ef} |\chi_e\rangle$$

$$S_{ff'} = \langle u_f | u_{f'} \rangle =: [\mathbf{S}]_{ff'}$$

Overlap matrix

Orthonormalisation of the bath orbitals

$$|u_f\rangle = \sum_{e \notin \text{Fragment}} \gamma_{ef} |\chi_e\rangle$$

$$S_{ff'} = \langle u_f | u_{f'} \rangle =: [\mathbf{S}]_{ff'}$$

Overlap matrix

$$\mathbf{SX} = \lambda \mathbf{X} \rightarrow \lambda = \sum_{ff'} X_f S_{ff'} X_{f'} = \left\langle \sum_f X_f u_f \middle| \sum_{f'} X_{f'} u_{f'} \right\rangle > 0$$

Normalised eigenvector

Eigenvalue

If the $|u_f\rangle$ are linearly independent
(usually the case)

Orthonormalisation of the bath orbitals

$$|u_f\rangle = \sum_{e \notin \text{Fragment}} \gamma_{ef} |\chi_e\rangle$$

$$S_{ff'} = \langle u_f | u_{f'} \rangle =: \left[\mathbf{S}\right]_{ff'}$$

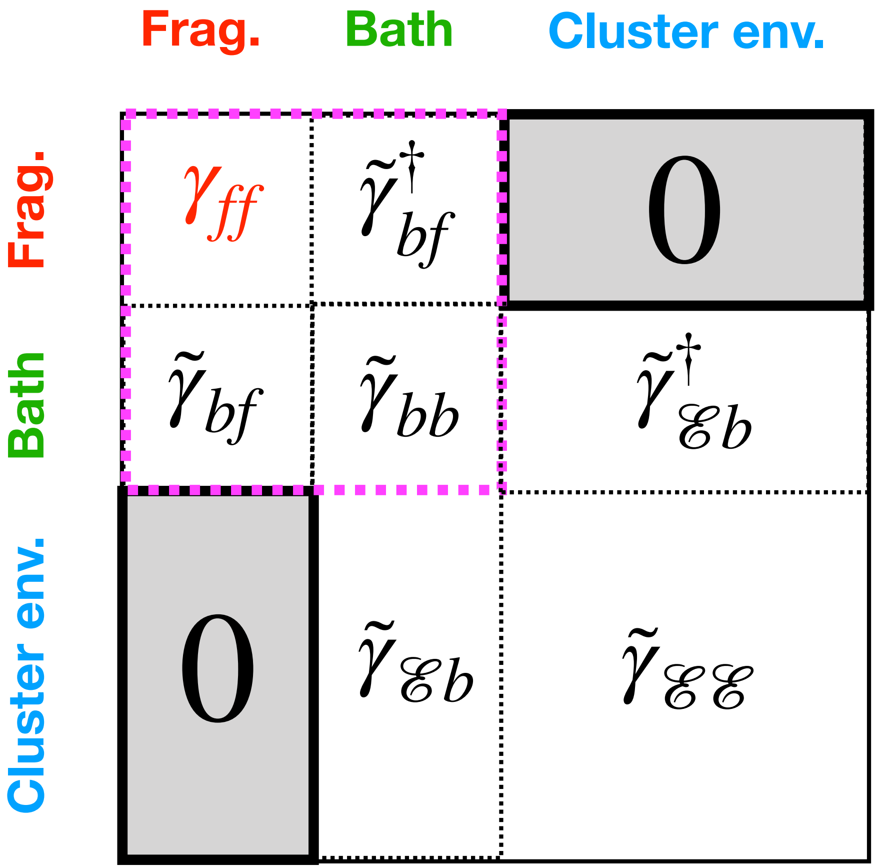
Overlap matrix

$$\mathscr{B} \equiv \left\{ |\phi_b\rangle = \sum_f \left[\mathbf{S}^{-1/2}\right]_{bf} |u_f\rangle \right\}$$

✅

$$\langle \phi_b | \phi_{b'} \rangle = \sum_{ff'} \left[\mathbf{S}^{-1/2}\right]_{bf} \left[\mathbf{S}^{-1/2}\right]_{b'f'} \left[\mathbf{S}\right]_{ff'} = \delta_{bb'}$$

Unitary transformed density matrix



$$\tilde{\gamma} = \langle \hat{d}_p^\dagger \hat{d}_q \rangle \equiv \begin{array}{c|ccc} & \text{Frag.} & \text{Bath} & \text{Cluster env.} \\ \hline \text{Frag.} & \gamma_{ff} & \tilde{\gamma}_{bf}^\dagger & 0 \\ \text{Bath} & \tilde{\gamma}_{bf} & \tilde{\gamma}_{bb} & \tilde{\gamma}_{\mathscr{E}b}^\dagger \\ \text{Cluster env.} & 0 & \tilde{\gamma}_{\mathscr{E}b} & \tilde{\gamma}_{\mathscr{E}\mathscr{E}} \end{array}$$

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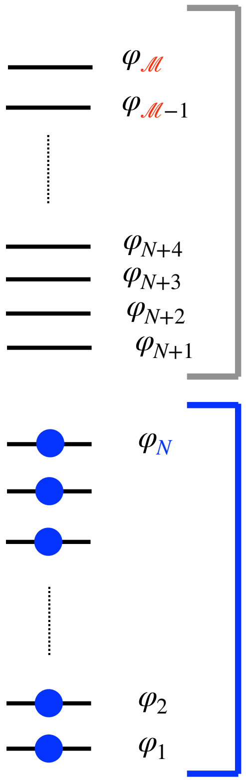
What if the full-system density matrix is idempotent?

$$\langle \hat{a}_p^\dagger \hat{a}_q \rangle \equiv \boxed{\begin{matrix} 1 & & & & & & & \\ & 1 & & & & \mathbf{0} & & \\ & & 1 & & & & & \\ & & & \ddots & & & & \\ & & & & 1 & & & \\ & \mathbf{0} & & & & 0 & & \\ & & & & & & \ddots & \\ & & & & & & & 0 \end{matrix}}$$

←

Molecular orbital representation!

$$|\varphi_p\rangle = \hat{a}_p^\dagger |\mathrm{vac}\rangle$$



Mean-field (HF)
or Kohn-Sham DFT

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What if the full-system density matrix is idempotent?

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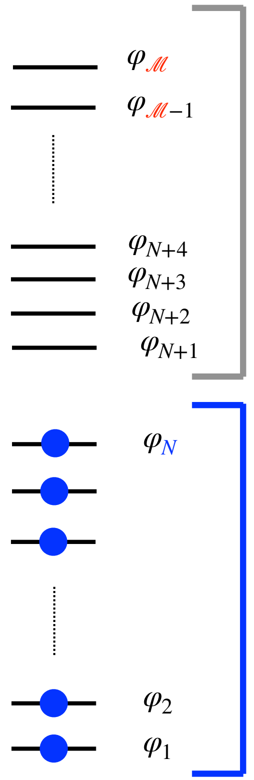
← **Molecular orbital representation!**



Mean-field (HF)
or Kohn-Sham DFT

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

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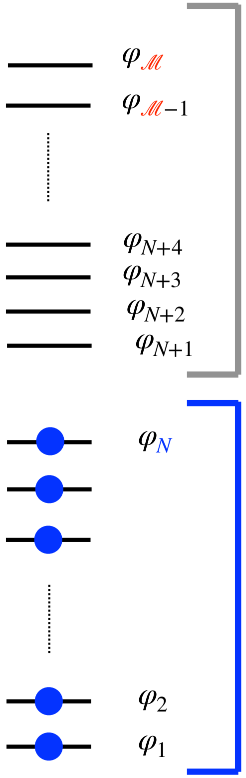
What if the full-system density matrix is idempotent?

$$\bar{\gamma} \equiv \boxed{\begin{matrix} 1 & & & & & & & \\ & 1 & & & & & \mathbf{0} & \\ & & 1 & & & & & \\ & & & \ddots & & & & \\ & & & & 1 & & & \\ & \mathbf{0} & & & & 0 & & \\ & & & & & & \ddots & \\ & & & & & & & 0 \end{matrix}} = \bar{\gamma}^2$$

← **Molecular orbital representation!**



Mean-field (HF)
or Kohn-Sham DFT

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Unitary transformed idempotent density matrix

$$\tilde{\gamma}^2 = \tilde{\gamma} \equiv \left[\begin{array}{c:c:c} \gamma_{ff} & \tilde{\gamma}^{\dagger}_{bf} & 0_{f\mathscr{E}} \\ \hdashline \tilde{\gamma}_{bf} & \tilde{\gamma}_{bb} & \tilde{\gamma}^{\dagger}_{\mathscr{E}b} \\ \hline \underset{\tilde{\gamma}_{\mathscr{E}b}\tilde{\gamma}_{bf}}{\underset{\parallel}{0_{\mathscr{E}f}}} & \tilde{\gamma}_{\mathscr{E}b} & \tilde{\gamma}_{\mathscr{E}\mathscr{E}} \end{array}\right]$$

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

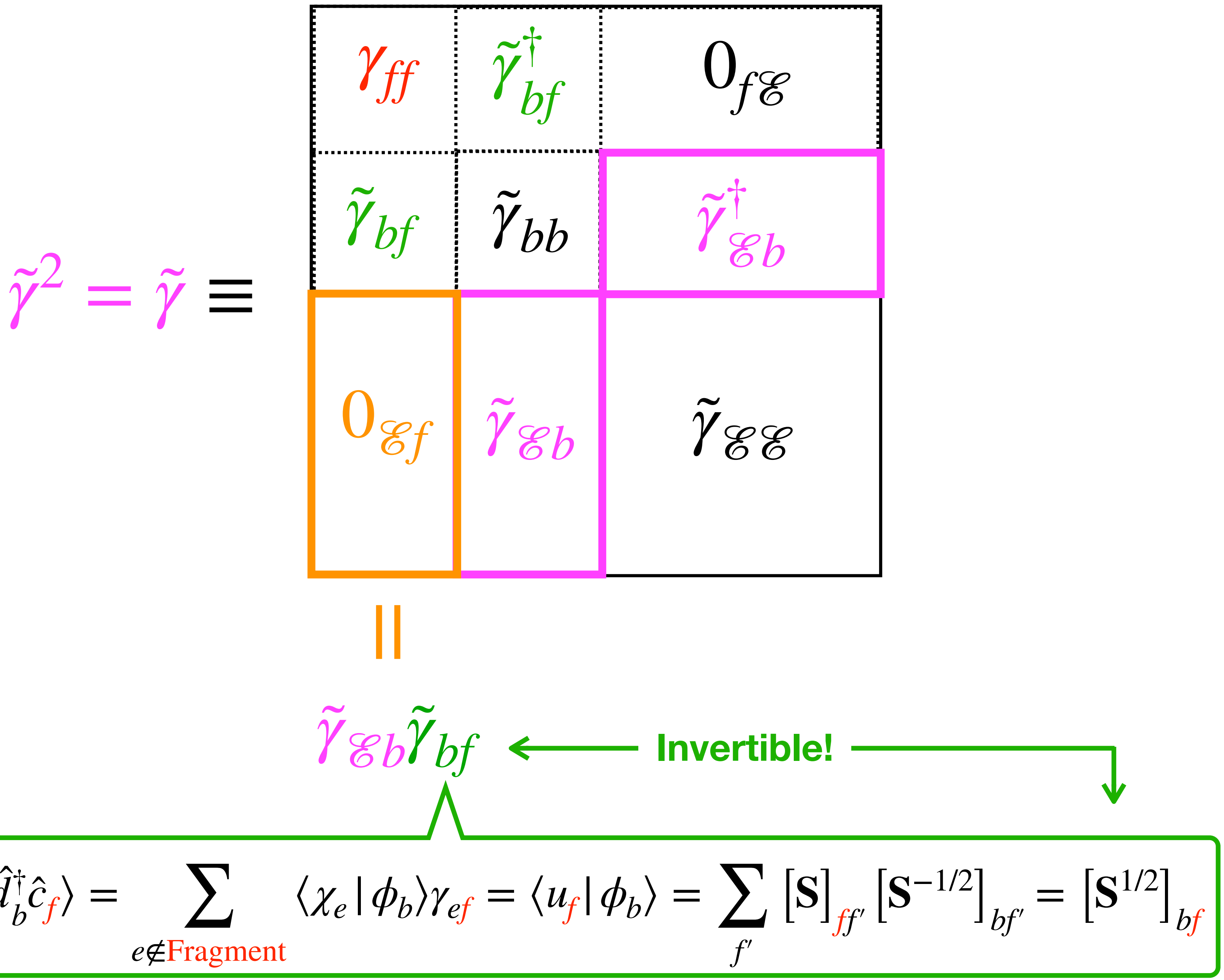
Unitary transformed idempotent density matrix

$$\tilde{\gamma}^2 = \tilde{\gamma} \equiv \begin{pmatrix} \gamma_{ff} & \tilde{\gamma}^\dagger_{bf} & 0_{f\mathscr{E}} \\ \tilde{\gamma}_{bf} & \tilde{\gamma}_{bb} & \tilde{\gamma}^\dagger_{\mathscr{E}b} \\ 0_{\mathscr{E}f} & \tilde{\gamma}_{\mathscr{E}b} & \tilde{\gamma}_{\mathscr{E}\mathscr{E}} \end{pmatrix}$$

$$0_{\mathscr{E}f} = \tilde{\gamma}_{\mathscr{E}b}\tilde{\gamma}_{bf}$$

$$\tilde{\gamma}_{bf} = \langle \hat{d}^\dagger_b \hat{c}_f \rangle = \sum_{e \notin \text{Fragment}} \langle \chi_e | \phi_b \rangle \gamma_{ef} = \langle u_f | \phi_b \rangle = \sum_{f'} \left[\mathbf{S}\right]_{ff'} \left[\mathbf{S}^{-1/2}\right]_{bf'} = \left[\mathbf{S}^{1/2}\right]_{bf}$$

Unitary transformed idempotent density matrix



$$\tilde{\gamma}^2 = \tilde{\gamma} \equiv \begin{pmatrix} \gamma_{ff} & \tilde{\gamma}^{\dagger}_{bf} & 0_{f\mathcal{E}} \\ \tilde{\gamma}_{bf} & \tilde{\gamma}_{bb} & \tilde{\gamma}^{\dagger}_{\mathcal{E}b} \\ 0_{\mathcal{E}f} & \tilde{\gamma}_{\mathcal{E}b} & \tilde{\gamma}_{\mathcal{E}\mathcal{E}} \end{pmatrix}$$

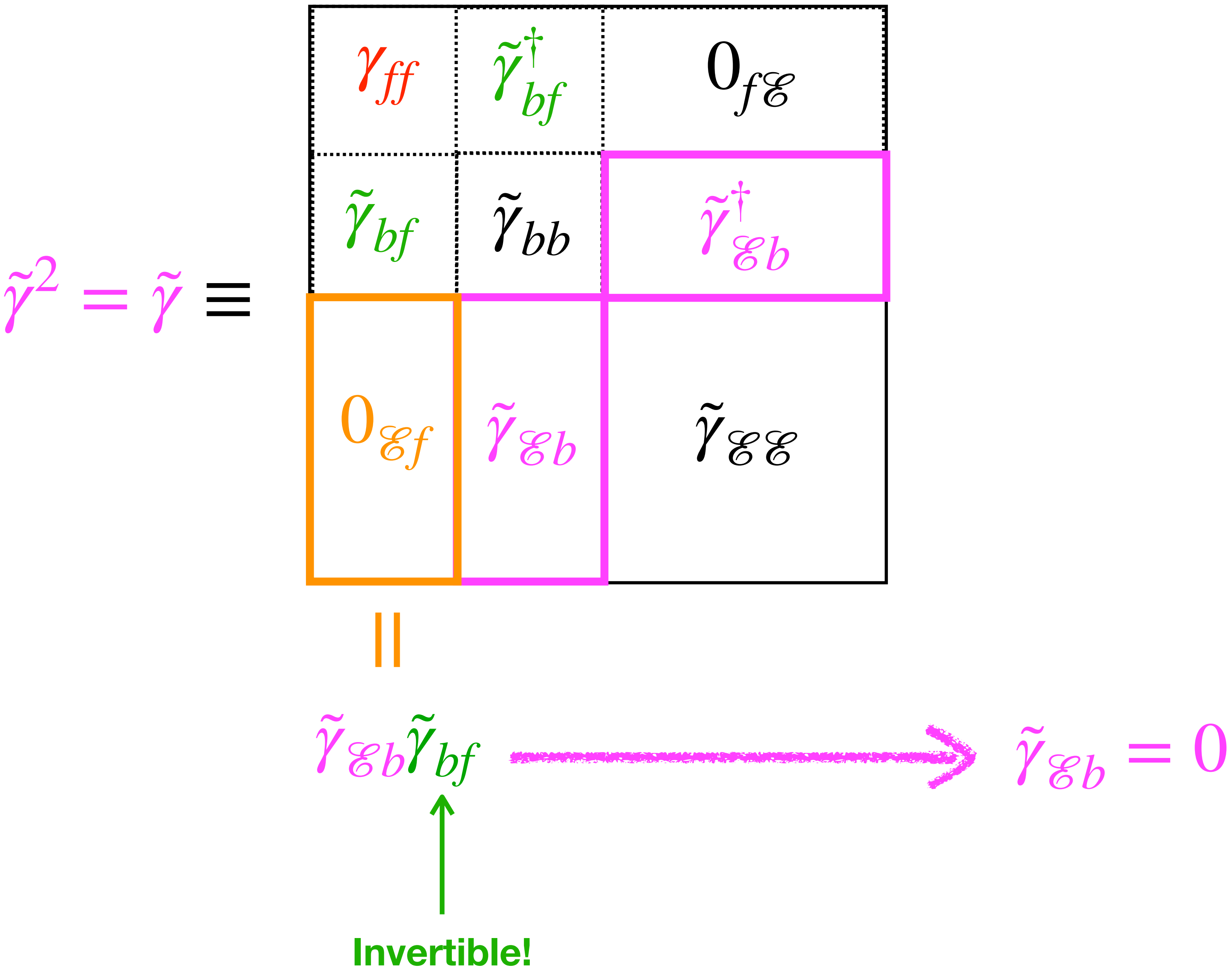
$$\parallel$$

$$\tilde{\gamma}_{\mathcal{E}b}\tilde{\gamma}_{bf}$$

Invertible!

$$\tilde{\gamma}_{bf} = \langle \hat{d}_b^{\dagger}\hat{c}_f \rangle = \sum_{e \notin \text{Fragment}} \langle \chi_e | \phi_b \rangle \gamma_{ef} = \langle u_f | \phi_b \rangle = \sum_{f'} [\mathbf{S}]_{ff'} [\mathbf{S}^{-1/2}]_{bf'} = [\mathbf{S}^{1/2}]_{bf}$$

Unitary transformed idempotent density matrix



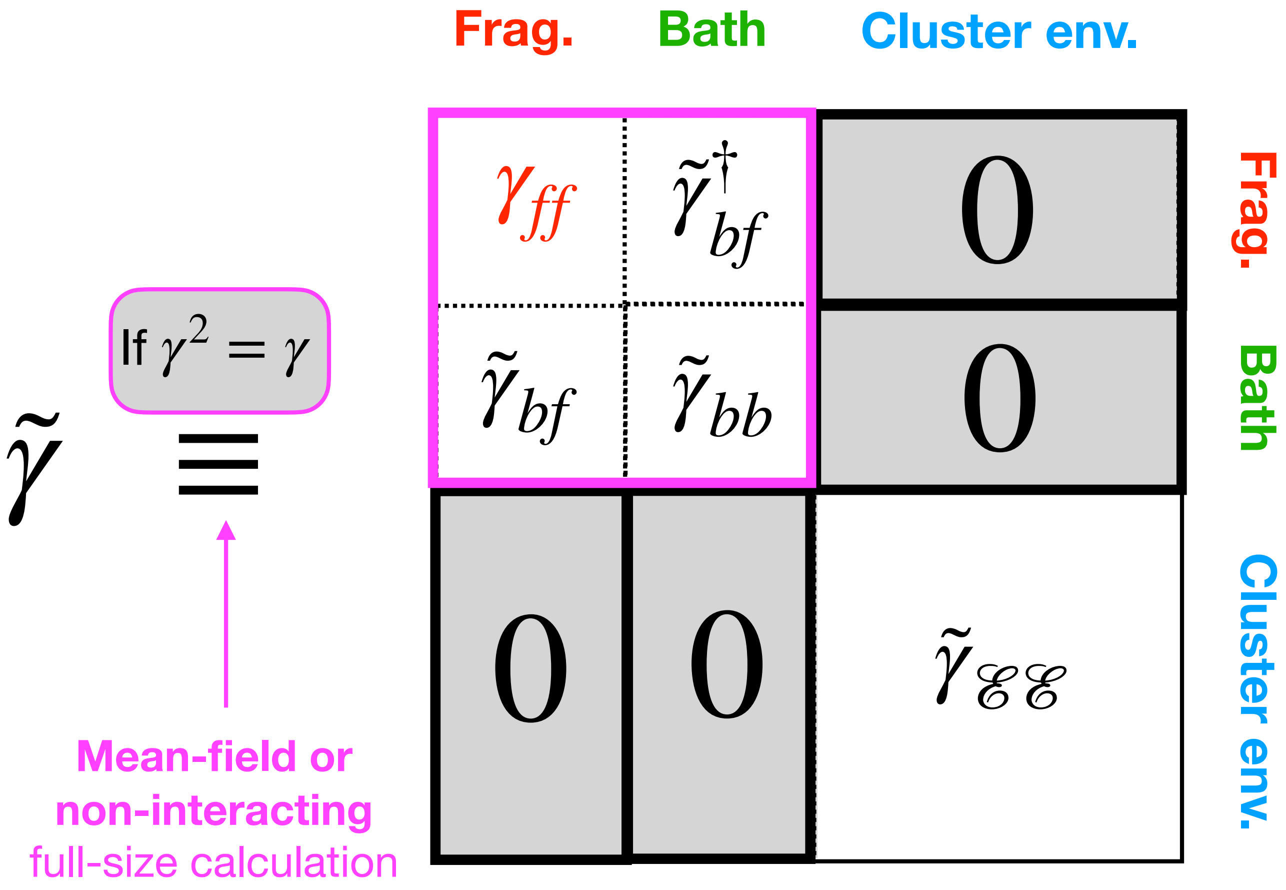
$$\tilde{\gamma}^2 = \tilde{\gamma} \equiv \begin{pmatrix} \gamma_{ff} & \tilde{\gamma}_{bf}^{\dagger} & 0_{f\mathscr{E}} \\ \tilde{\gamma}_{bf} & \tilde{\gamma}_{bb} & \tilde{\gamma}_{\mathscr{E}b}^{\dagger} \\ 0_{\mathscr{E}f} & \tilde{\gamma}_{\mathscr{E}b} & \tilde{\gamma}_{\mathscr{E}\mathscr{E}} \end{pmatrix}$$

$$0_{\mathscr{E}f} = \tilde{\gamma}_{\mathscr{E}b}\tilde{\gamma}_{bf} \Longrightarrow \tilde{\gamma}_{\mathscr{E}b} = 0$$

Invertible!

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

Unitary transformed density matrix



$$\tilde{\gamma} \overset{\text{If } \gamma^2 = \gamma}{\equiv} \begin{array}{ccc|c} \text{Frag.} & \text{Bath} & \text{Cluster env.} & \\ \gamma_{ff} & \tilde{\gamma}^{\dagger}_{bf} & 0 & \text{Frag.} \\ \tilde{\gamma}_{bf} & \tilde{\gamma}_{bb} & 0 & \text{Bath} \\ 0 & 0 & \tilde{\gamma}_{\mathcal{E}\mathcal{E}} & \text{Cluster env.} \end{array}$$

Mean-field or non-interacting
full-size calculation

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

Unitary transformed idempotent density matrix

$$\tilde{\gamma}_{bf}\gamma_{ff}+\tilde{\gamma}_{bb}\tilde{\gamma}_{bf} = \left[\begin{array}{c:c:c} \gamma_{ff} & \tilde{\gamma}^{\dagger}_{bf} & 0_{f\mathscr{E}} \\ \hdashline \boxed{\tilde{\gamma}_{bf}} & \tilde{\gamma}_{bb} & 0_{b\mathscr{E}} \\ \hdashline 0_{\mathscr{E}f} & 0_{\mathscr{E}b} & \tilde{\gamma}_{\mathscr{E}\mathscr{E}} \end{array}\right] \equiv \tilde{\gamma} = \tilde{\gamma}^2$$

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

Unitary transformed *idempotent* density matrix

$$\begin{array}{ccc} \overset{L_f}{\longleftrightarrow} & \overset{L_f}{\longleftrightarrow} & \\ \left.\begin{array}{c|c|c} \gamma_{ff} & \tilde{\gamma}^{\dagger}_{bf} & 0_{f\mathscr{E}} \\ \hline \tilde{\gamma}_{bf} & \tilde{\gamma}_{bb} & 0_{b\mathscr{E}} \\ \hline 0_{\mathscr{E}f} & 0_{\mathscr{E}b} & \tilde{\gamma}_{\mathscr{E}\mathscr{E}} \end{array}\right. & & \end{array} \equiv \tilde{\gamma} = \tilde{\gamma}^2$$

Invertible!

$$\boxed{\tilde{\gamma}_{bf}\gamma_{ff}+\tilde{\gamma}_{bb}\tilde{\gamma}_{bf} = \tilde{\gamma}_{bf}}$$

$$\Downarrow$$

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

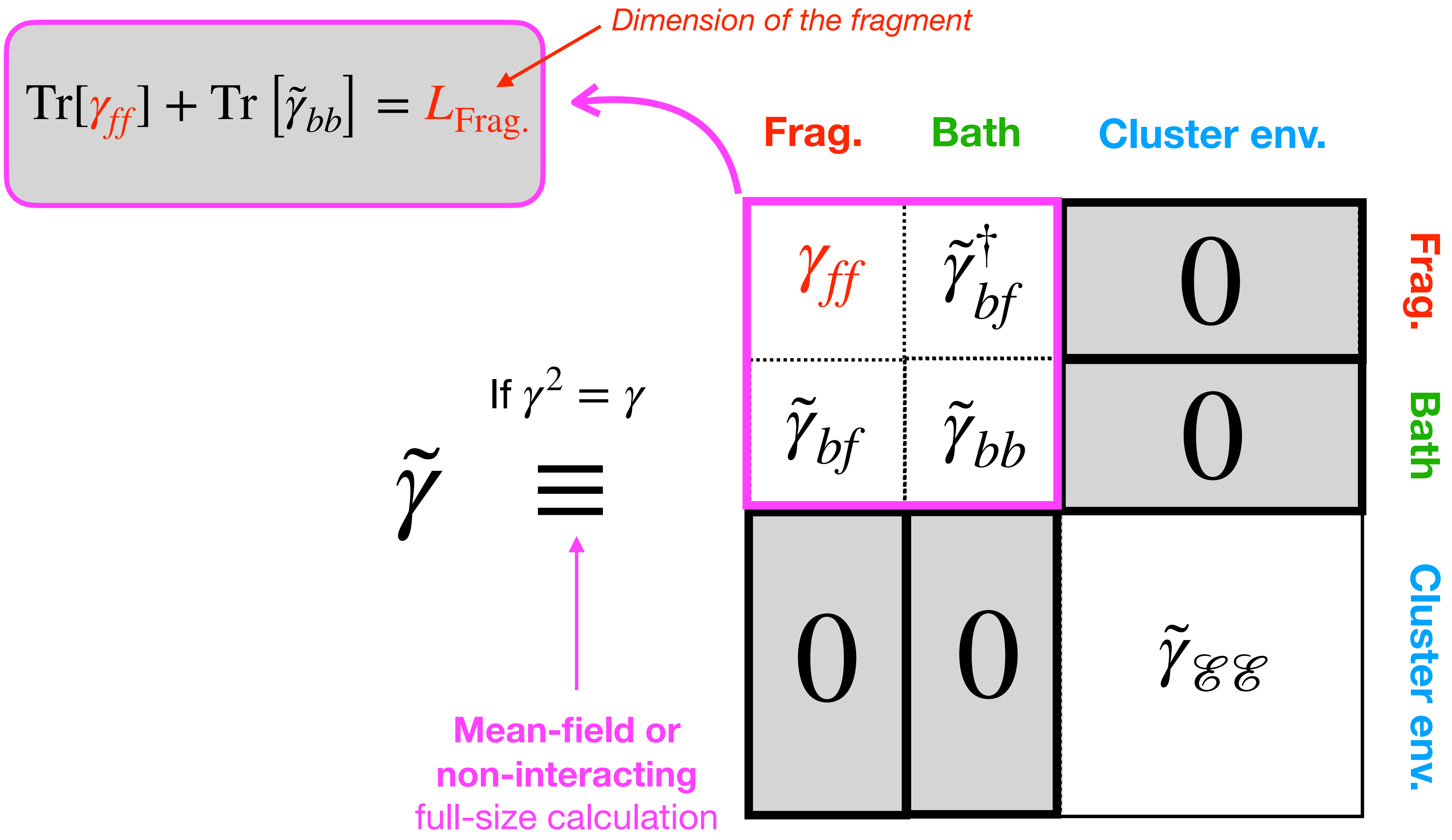
$$\Downarrow$$

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

The embedding cluster contains exactly L_f electrons!

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

Unitary transformed density matrix



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

Dimension of the fragment

If $\gamma^2 = \gamma$

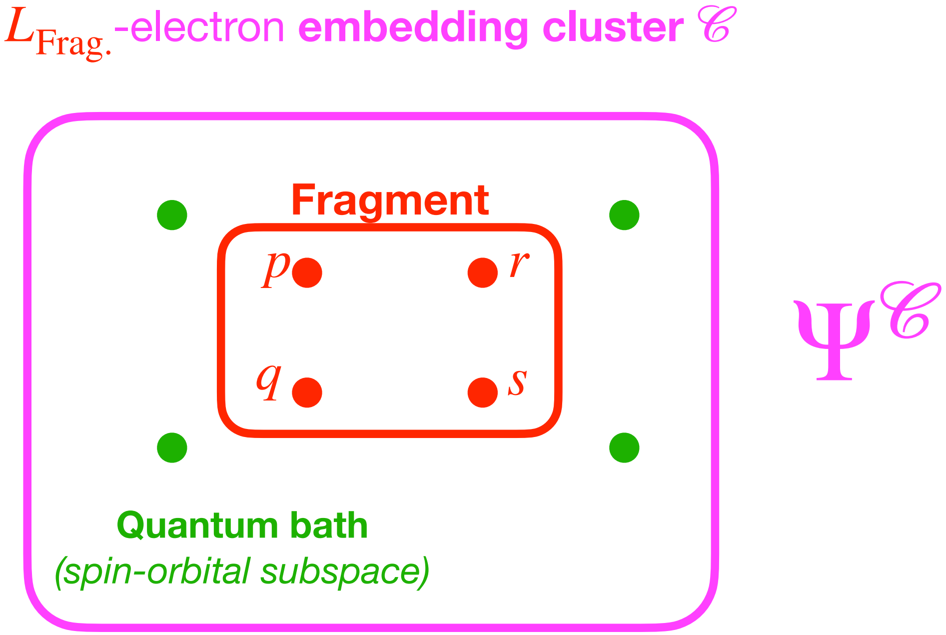
$$\tilde{\gamma} \equiv \begin{array}{cc|c|c}
\text{Frag.} & \text{Bath} & \text{Cluster env.} & \\
\gamma_{ff} & \tilde{\gamma}^{\dagger}_{bf} & 0 & \text{Frag.} \\
\tilde{\gamma}_{bf} & \tilde{\gamma}_{bb} & 0 & \text{Bath} \\
\hline
0 & 0 & \tilde{\gamma}_{\mathcal{E}\mathcal{E}} & \text{Cluster env.}
\end{array}$$

Mean-field or
non-interacting
full-size calculation

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

Clusterization through a unitary one-electron transformation

Exact at the
non-interacting
or
mean-field
level of calculation!



$L_{\text{Frag.}}$-electron **embedding cluster** $\mathscr{C}$

Fragment

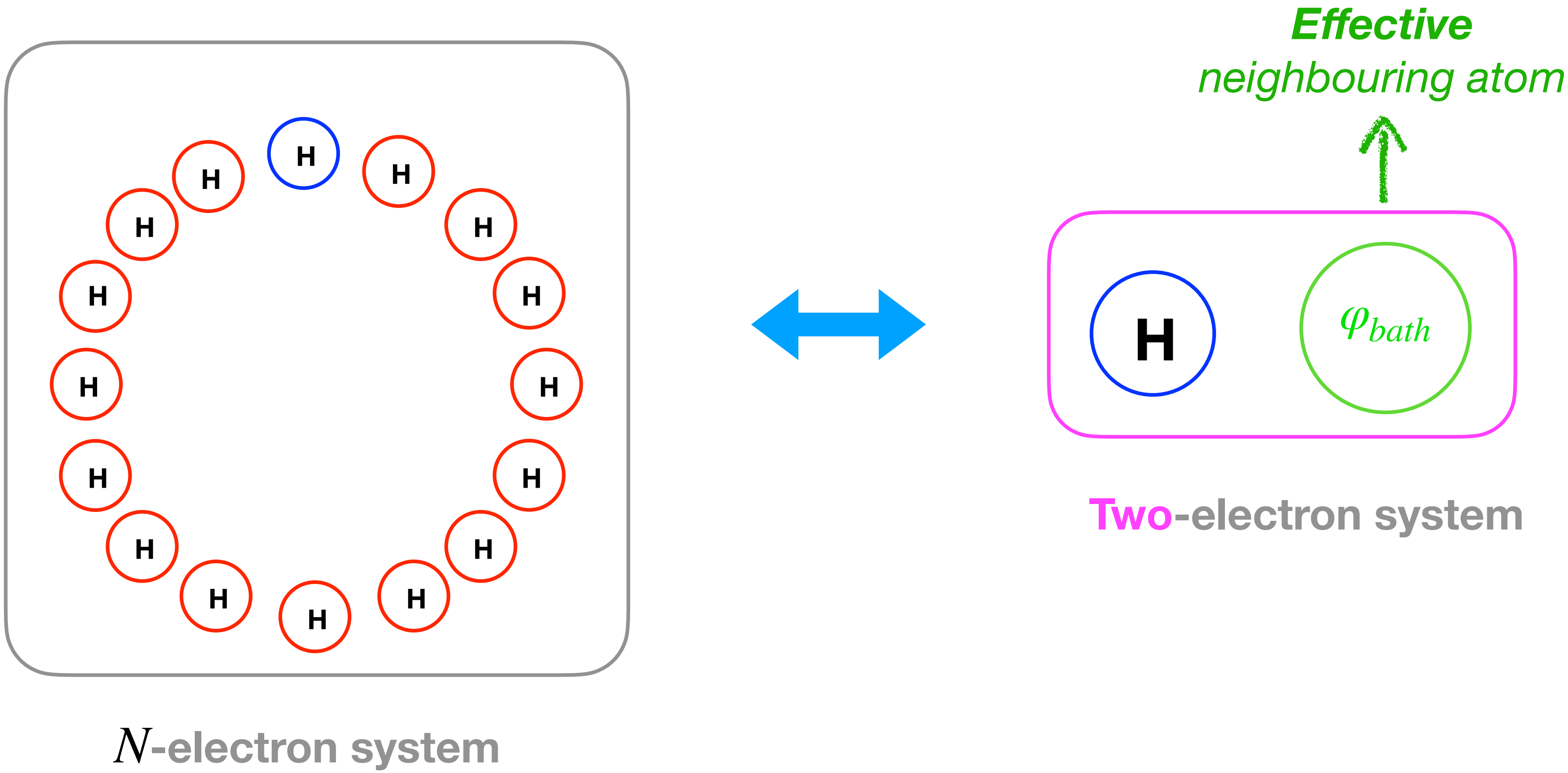
Quantum bath
(spin-orbital subspace)

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

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

Illustrative example

Rings of hydrogen atoms (Hubbard model)



Effective
neighbouring atom

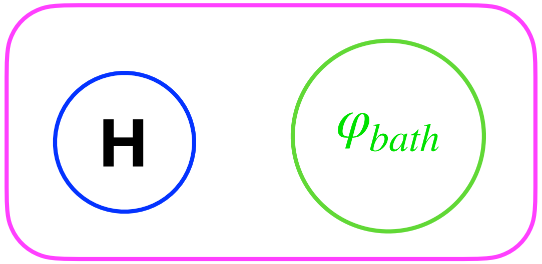
Two-electron system

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

$$\downarrow$$

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

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

$$\underbrace{\hat{h}^{\mathscr{C}}}_{\text{\textbf{Exact non-interacting} embedding}} \xrightarrow{single\ impurity} \hat{h}^{\mathscr{C}} + \overbrace{\langle pp|pp\rangle}^{\text{Two-electron repulsion on the impurity}} \hat{c}^{\dagger}_{p\uparrow}\hat{c}^{\dagger}_{p\downarrow}\hat{c}_{p\downarrow}\hat{c}_{p\uparrow}$$

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

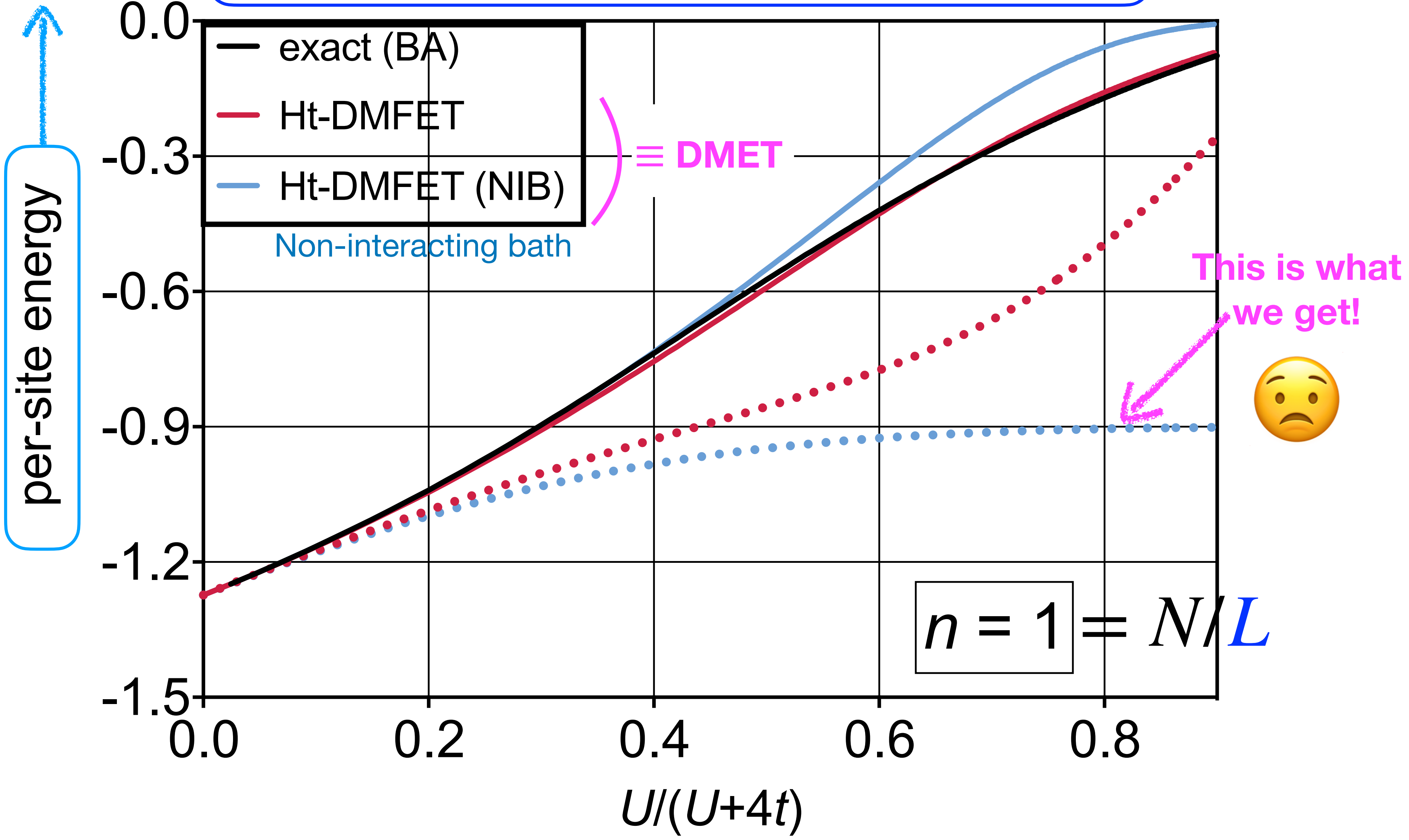
$$\underbrace{\hat{h}^{\mathscr{C}}}_{\textbf{Exact non-interacting}\ \text{embedding}} \xrightarrow{single\ impurity} \hat{h}^{\mathscr{C}} + \overbrace{\langle pp|pp\rangle}^{U\ =}\, \hat{c}^{\dagger}_{p\uparrow}\hat{c}^{\dagger}_{p\downarrow}\hat{c}_{p\downarrow}\hat{c}_{p\uparrow}$$

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.*

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

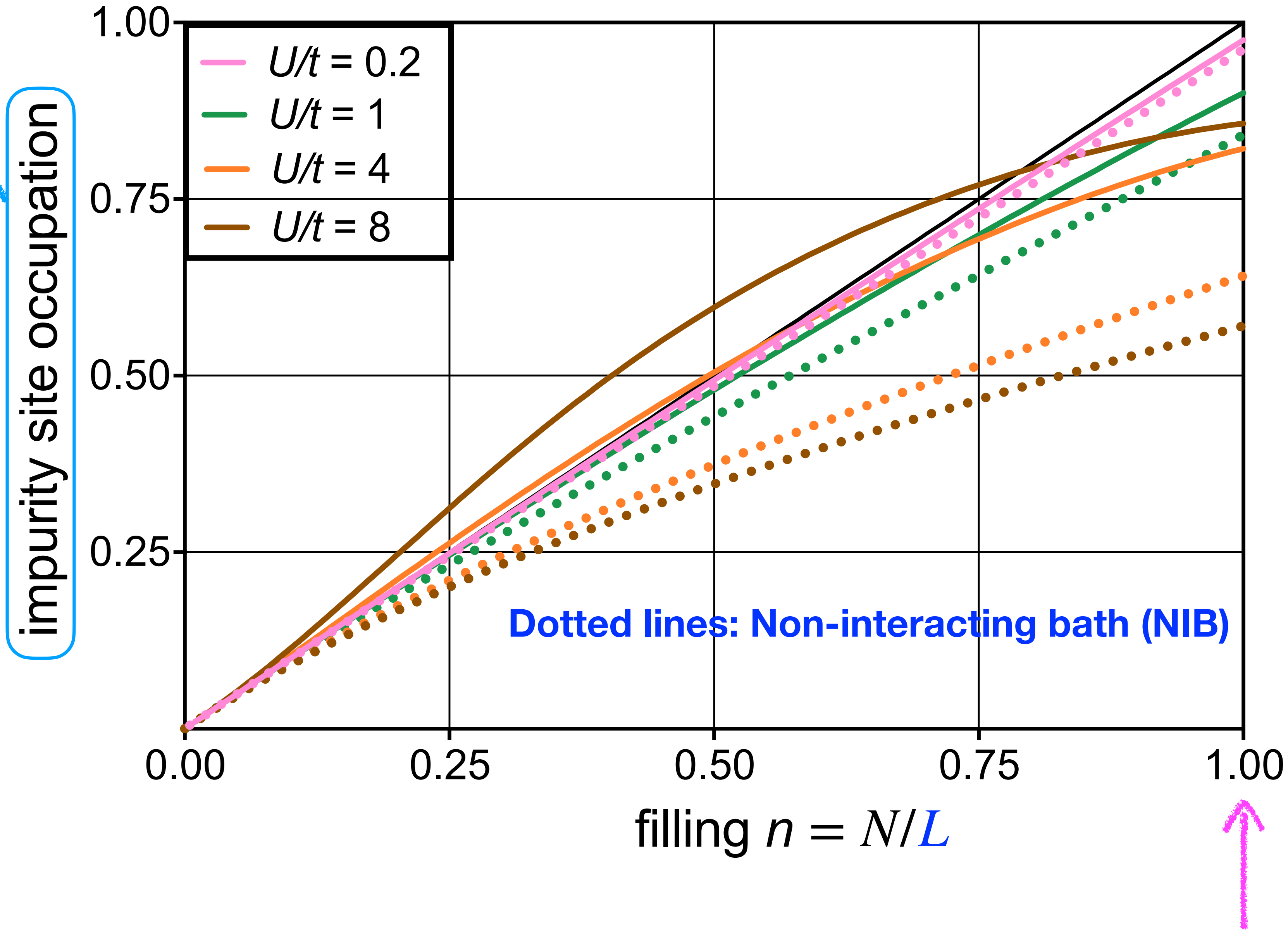
$$\hat{H} = \sum_{\sigma=\uparrow,\downarrow}\sum_{i=0}^{L-1} -t\left(\hat{c}^\dagger_{i\sigma}\hat{c}_{(i+1)\sigma} + \hat{c}^\dagger_{(i+1)\sigma}\hat{c}_{i\sigma}\right) + U\sum_{i=0}^{L-1}\hat{c}^\dagger_{i\uparrow}\hat{c}^\dagger_{i\downarrow}\hat{c}_{i\downarrow}\hat{c}_{i\uparrow}$$

E/L



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

$$\sum_{\sigma=\uparrow,\downarrow} \langle \Psi^{\mathscr{C}} | \hat{c}^{\dagger}_{p\sigma} \hat{c}_{p\sigma} | \Psi^{\mathscr{C}} \rangle$$



Dotted lines: Non-interacting bath (NIB)

$L = 400$ atoms

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

Approximate embedding of interacting Hamiltonians

One-electron Hamiltonian of the cluster

Chemical potential on the impurity

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

Exact non-interacting
embedding

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

Chemical potential
on the impurity

$$\underbrace{\hat{h}^{\mathscr{C}}}_{\text{Exact non-interacting embedding}} \xrightarrow{single\,impurity} \underbrace{\hat{h}^{\mathscr{C}} + \overbrace{\langle pp|pp\rangle}^{\overset{U}{\shortparallel}} \hat{c}^{\dagger}_{p\uparrow}\hat{c}^{\dagger}_{p\downarrow}\hat{c}_{p\downarrow}\hat{c}_{p\uparrow} - \tilde{\mu}^{imp} \sum_{\sigma=\uparrow,\downarrow} \hat{c}^{\dagger}_{p\sigma}\hat{c}_{p\sigma}}_{\text{Approximate interacting embedding}}$$

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.*

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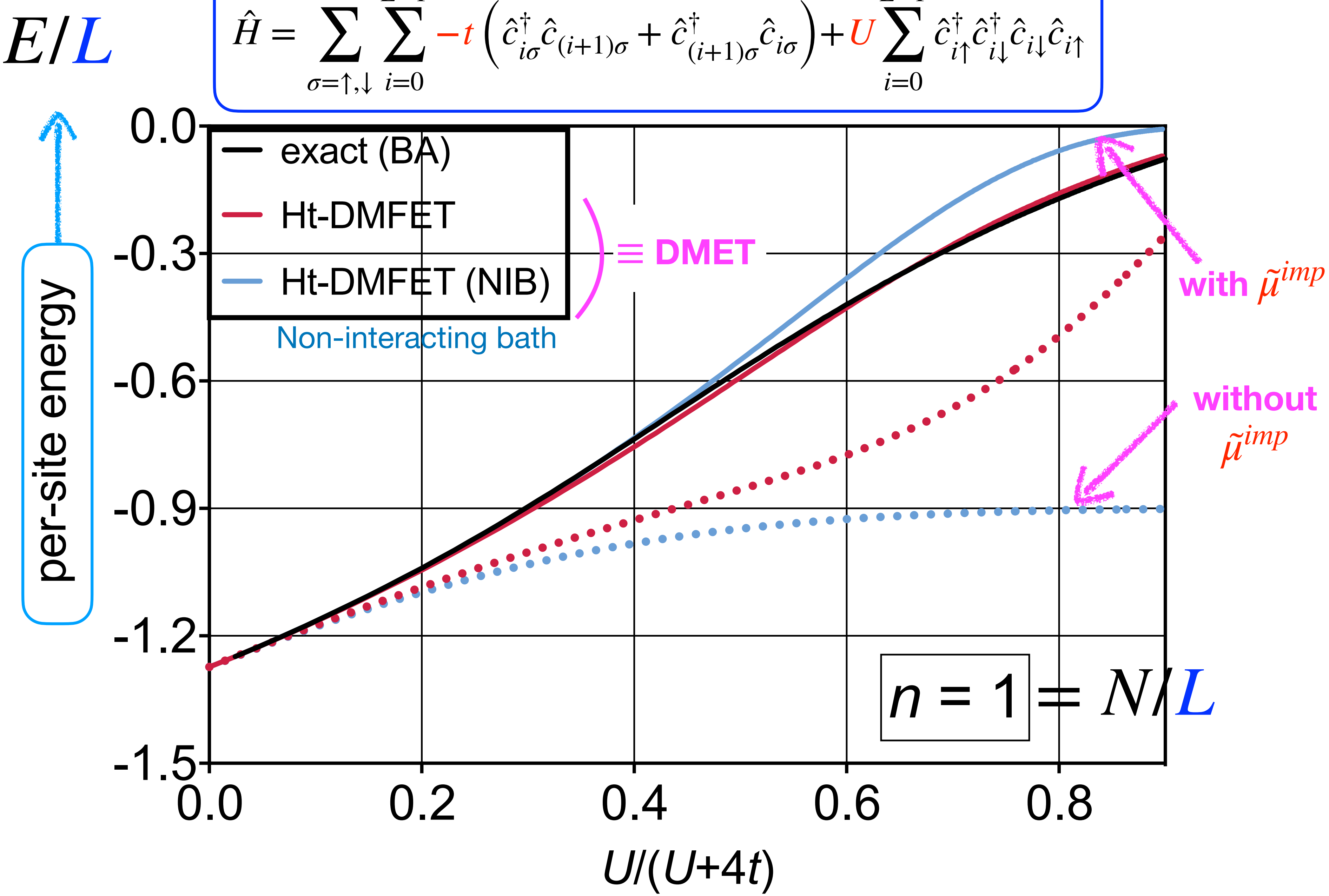
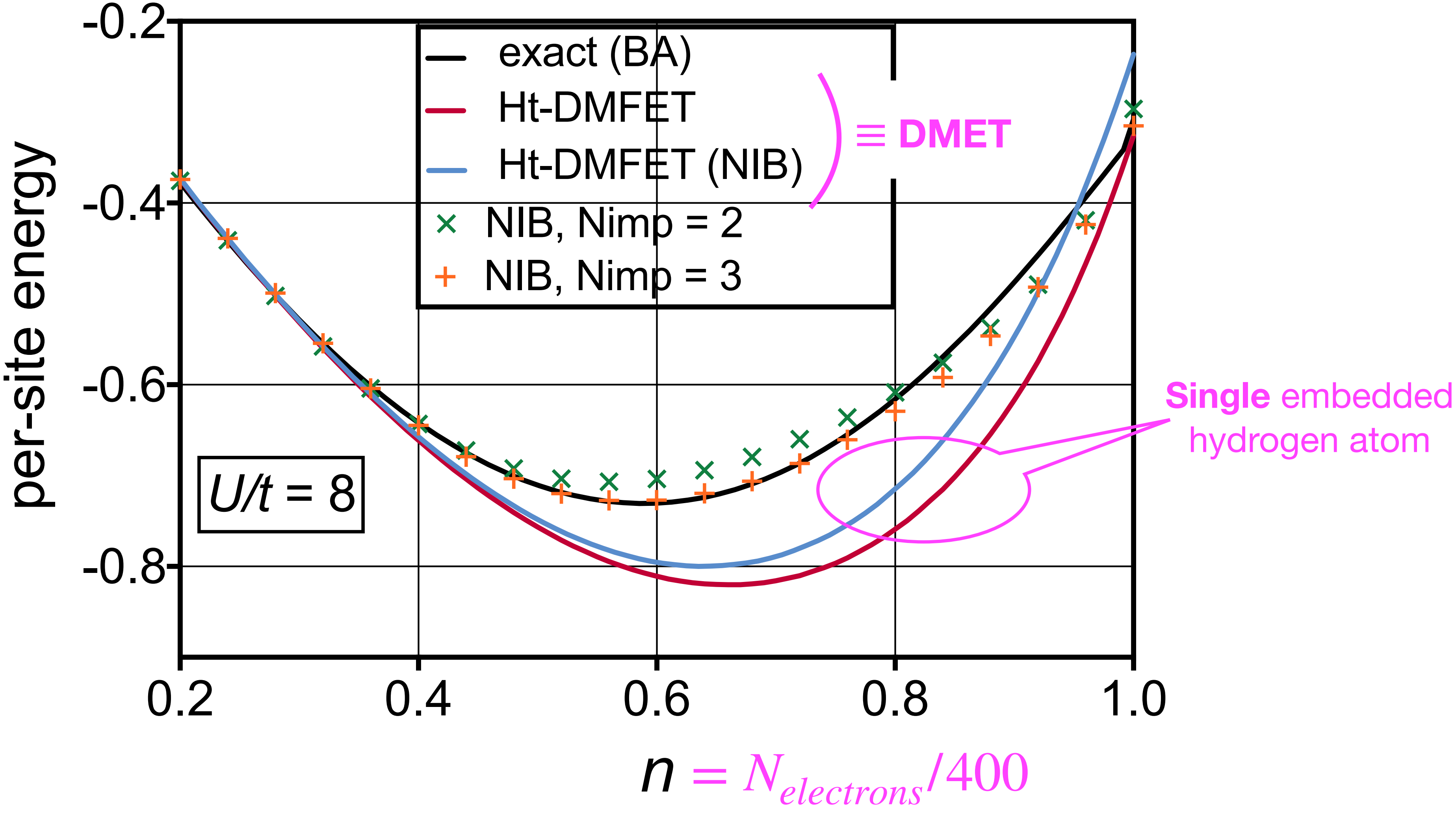


*S. Sekaran, M. Tsuchiizu, M. Saubanère, and E. Fromager, Phys. Rev. B **104**, 035121 (2021).*

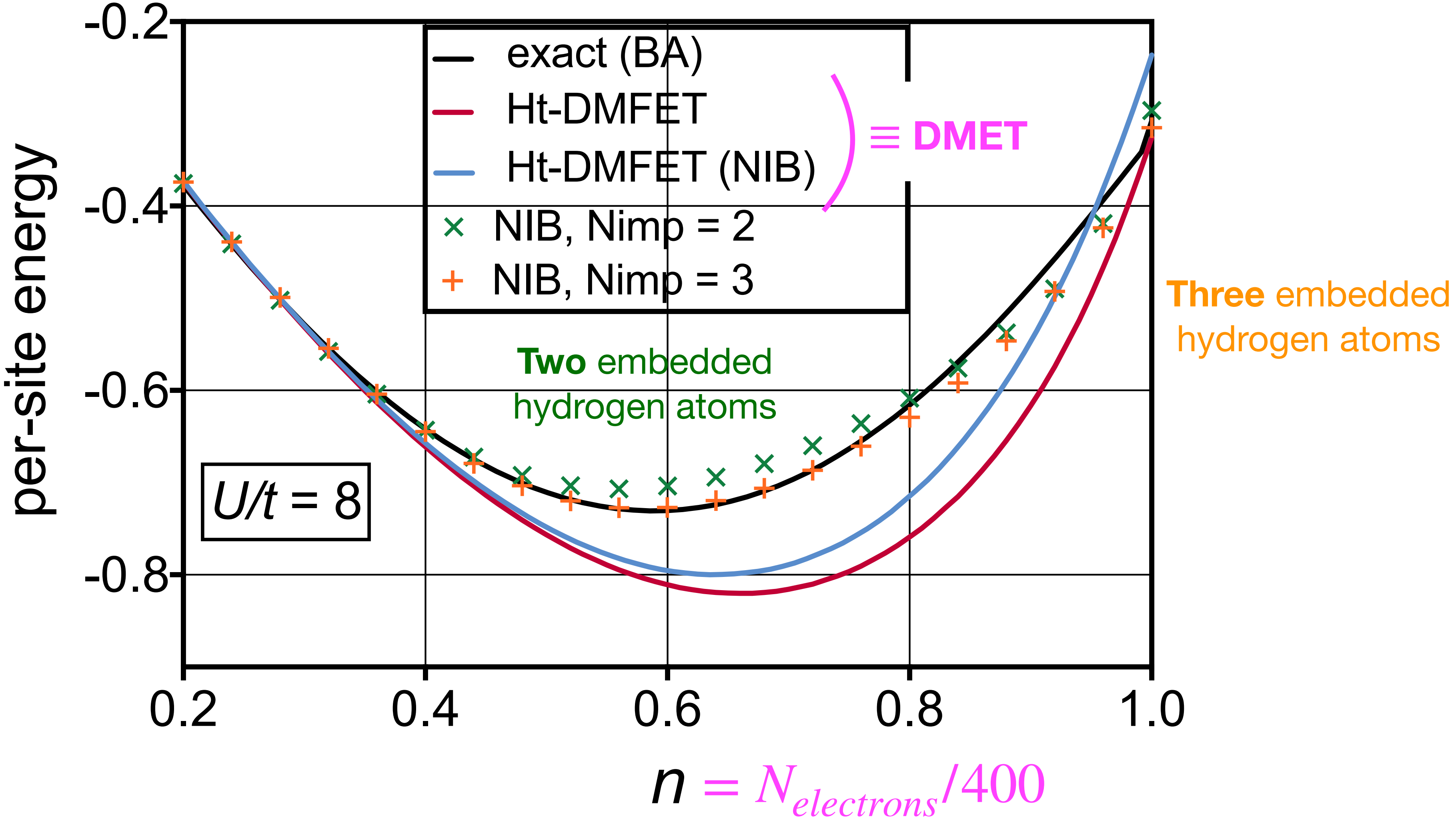
(Hubbard) model of a stretched 400-atom hydrogen ring



$n = N_{electrons}/400$

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

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



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

Self-consistent embedding and connection with DFT

(still for a single impurity and a uniform full-size system)

Fixing the number of electrons versus fixing the chemical potential

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

… and we fix the number of electrons in the system

Fixing the number of electrons versus fixing the chemical potential

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

$$\hat{H} - \mu \sum_{\sigma=\uparrow,\downarrow} \sum_{i=0}^{L-1} \hat{c}^{\dagger}_{i\sigma} \hat{c}_{i\sigma}$$

"Grand-canonical" Hamiltonian

Chemical potential

≡ uniform external potential

Fixing the number of electrons versus fixing the chemical potential

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

$$\hat{H} - \mu \sum_{\sigma=\uparrow,\downarrow}\sum_{i=0}^{L-1}\hat{c}^{\dagger}_{i\sigma}\hat{c}_{i\sigma}$$

“Grand-canonical” Hamiltonian

Chemical potential

≡ uniform external potential

Uniform density profile (twice the filling):

≡ $N(\mu)$: Total number of electrons

$$n = \left\langle \sum_{\sigma=\uparrow,\downarrow}\hat{c}^{\dagger}_{i\sigma}\hat{c}_{i\sigma}\right\rangle = \frac{N}{L}$$

Total number of sites

Self-consistency through a connection with density functional theory

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

True interacting Hamiltonian $(U \neq 0)$

Fixed chemical potential

$$n = n(\mu) = ?$$

Self-consistency through a connection with density functional theory

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

True interacting Hamiltonian $(U \neq 0)$ ✗

Fixed chemical potential

$$n = n(\mu) = ?$$

Self-consistency through a connection with density functional theory

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

True interacting Hamiltonian $(U \neq 0)$

Fixed chemical potential

$$n = n(\mu) = ?$$

$$\hat{H}(U=0) - \mu^{\mathrm{KS}} \sum_{\sigma=\uparrow,\downarrow} \sum_{i=0}^{L-1} \hat{c}^{\dagger}_{i\sigma}\hat{c}_{i\sigma}$$

"Low-level" non-interacting full-size Hamiltonian that generates the bath through its ground-state **idempotent density matrix**

$\Leftrightarrow$ **Kohn—Sham full-size Hamiltonian**

Unknown Kohn—Sham chemical potential

$$-\mu^{\mathrm{KS}} = -\mu + v_{\mathrm{Hxc}} \longleftarrow n^{\mathrm{KS}} = n(\mu) = ?$$

Self-consistency through a connection with density functional theory

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

True interacting Hamiltonian $(U \neq 0)$ ✗

Fixed chemical potential

$$n = n(\mu) = ?$$

$$\hat{H}(U=0) - \mu^{\mathrm{KS}} \sum_{\sigma=\uparrow,\downarrow} \sum_{i=0}^{L-1} \hat{c}^{\dagger}_{i\sigma} \hat{c}_{i\sigma}$$

"Low-level" non-interacting full-size Hamiltonian that generates the bath through its ground-state **idempotent density matrix**

⇔ **Kohn—Sham full-size Hamiltonian**

Unknown Kohn—Sham chemical potential

$$-\mu^{\mathrm{KS}} = -\mu + v_{\mathrm{Hxc}} \longleftarrow n^{\mathrm{KS}} = n(\mu) = ?$$

✓

Self-consistency through a connection with density functional theory

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

True interacting Hamiltonian $(U \neq 0)$ ✗

Fixed chemical potential

$$n = n(\mu) = ?$$

$$\hat{H}(U=0) - \mu^{\mathrm{KS}} \sum_{\sigma=\uparrow,\downarrow} \sum_{i=0}^{L-1} \hat{c}^{\dagger}_{i\sigma}\hat{c}_{i\sigma}$$

"Low-level" non-interacting full-size Hamiltonian that generates the bath through its ground-state **idempotent density matrix**

⇔ **Kohn—Sham full-size Hamiltonian**

Unknown Kohn—Sham chemical potential

$$-\mu^{\mathrm{KS}} = -\mu + v_{\mathrm{Hxc}} \longleftarrow n^{\mathrm{KS}} = n(\mu) = ?$$

✓

$$\hat{H}^{\mathscr{C}} = \hat{h}^{\mathscr{C}} + U \hat{c}^{\dagger}_{p\uparrow}\hat{c}^{\dagger}_{p\downarrow}\hat{c}_{p\downarrow}\hat{c}_{p\uparrow} - \tilde{\mu}^{imp} \sum_{\sigma=\uparrow,\downarrow} \hat{c}^{\dagger}_{p\sigma}\hat{c}_{p\sigma}$$

Impurity-interacting
Hamiltonian
of the two-electron
embedding cluster

Self-consistency through a connection with density functional theory

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

True interacting Hamiltonian $(U \neq 0)$ ✗

Fixed chemical potential

$$n = n(\mu) = ?$$

$$\hat{H}(U=0) - \mu^{\mathrm{KS}} \sum_{\sigma=\uparrow,\downarrow} \sum_{i=0}^{L-1} \hat{c}^{\dagger}_{i\sigma}\hat{c}_{i\sigma}$$

“Low-level” non-interacting full-size Hamiltonian that generates the bath through its ground-state **idempotent density matrix**

Unknown Kohn—Sham chemical potential

⇔ **Kohn—Sham full-size Hamiltonian**

$$-\mu^{\mathrm{KS}} = -\mu + v_{\mathrm{Hxc}} \longleftarrow n^{\mathrm{KS}} = n(\mu) = ?$$

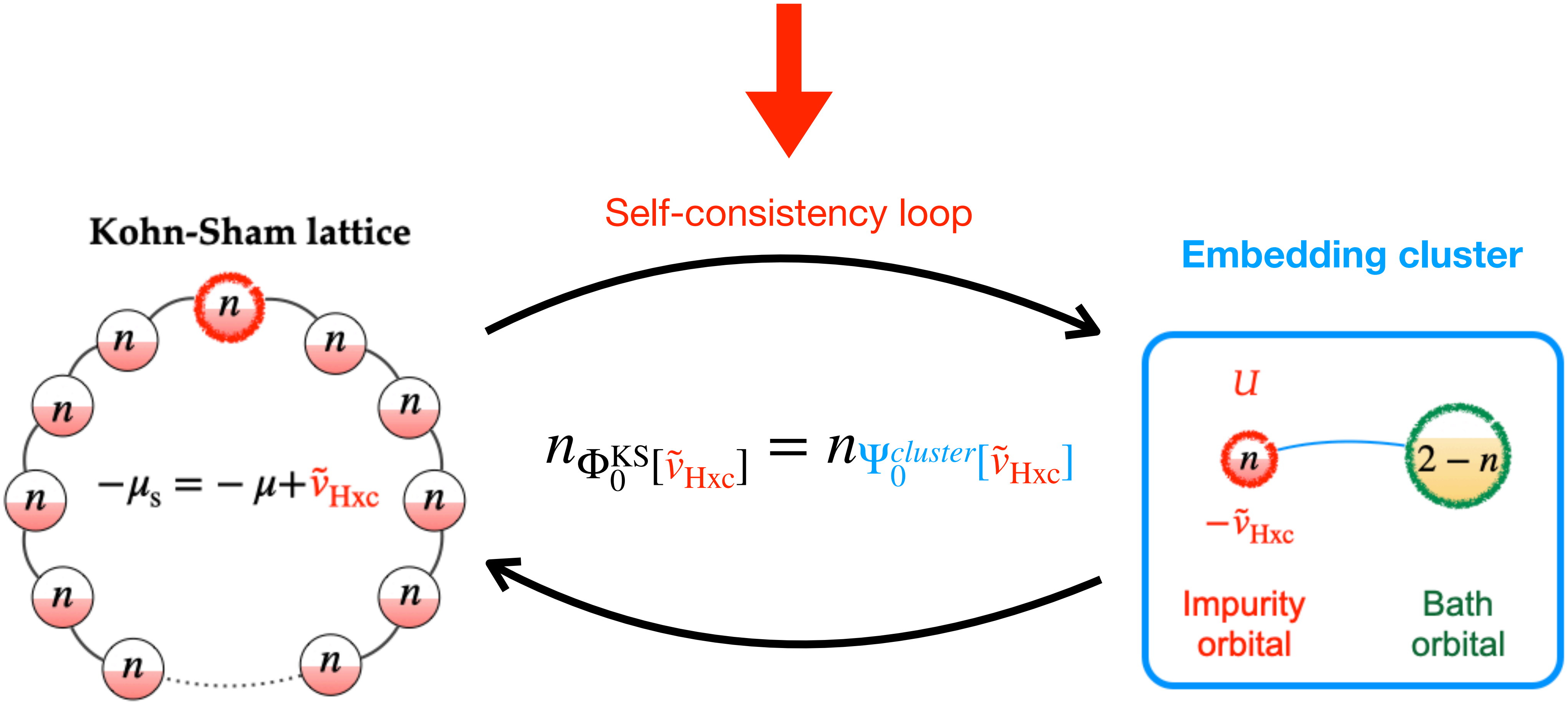
✓

$$\hat{H}^{\mathscr{C}} = \hat{h}^{\mathscr{C}} + U\,\hat{c}^{\dagger}_{p\uparrow}\hat{c}^{\dagger}_{p\downarrow}\hat{c}_{p\downarrow}\hat{c}_{p\uparrow} - \tilde{\mu}^{imp} \sum_{\sigma=\uparrow,\downarrow} \hat{c}^{\dagger}_{p\sigma}\hat{c}_{p\sigma}$$

Impurity-interacting Hamiltonian of the two-electron embedding cluster ✓

Local potential-functional embedding theory (LPFET)

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



Self-consistency loop

Kohn-Sham lattice

$$-\mu_{\rm s} = -\mu + \tilde{v}_{\rm Hxc}$$

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

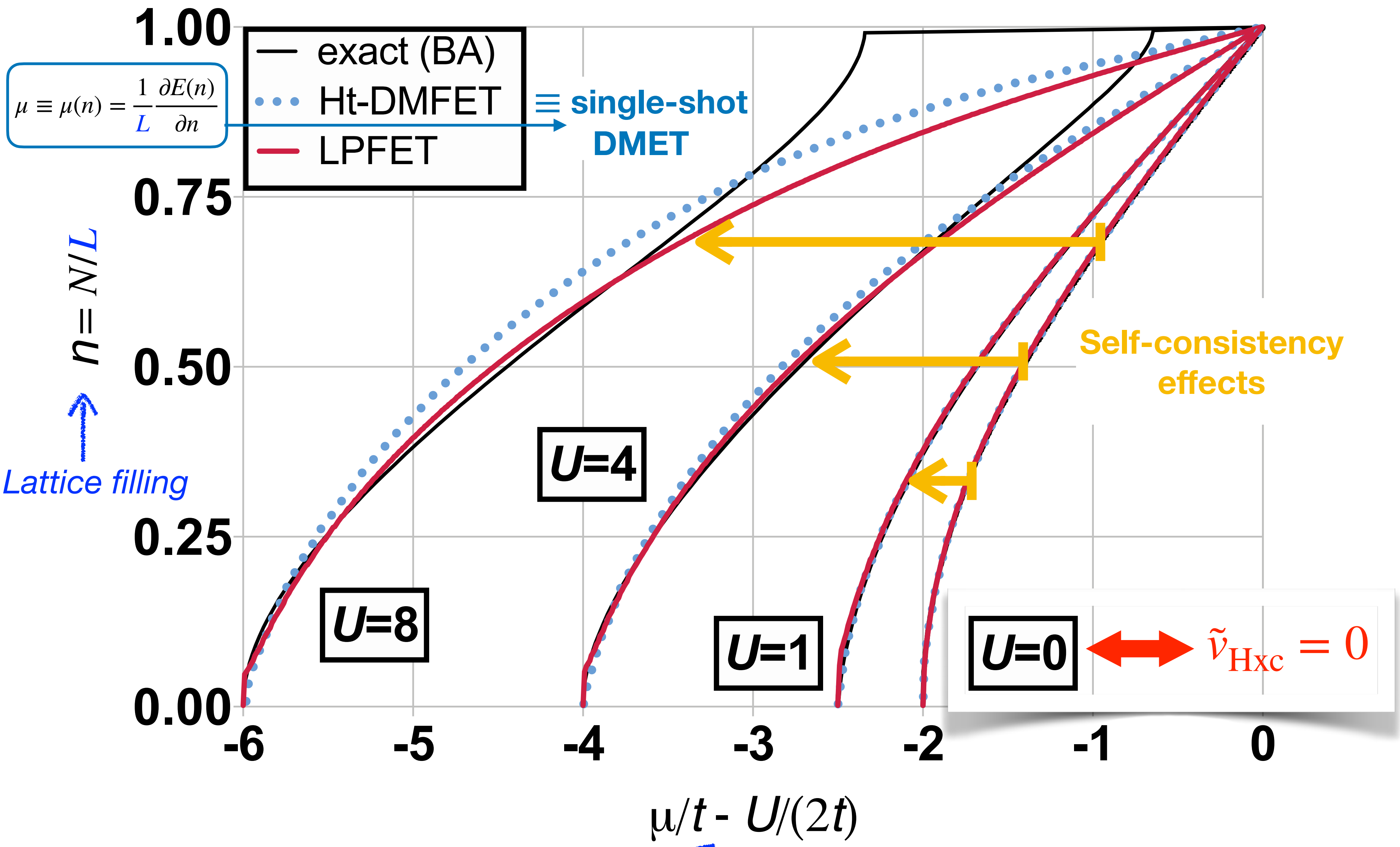
Embedding cluster

Impurity orbital

Bath orbital

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

Local potential-functional embedding theory (LPFET)



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

≡ single-shot DMET

Self-consistency effects

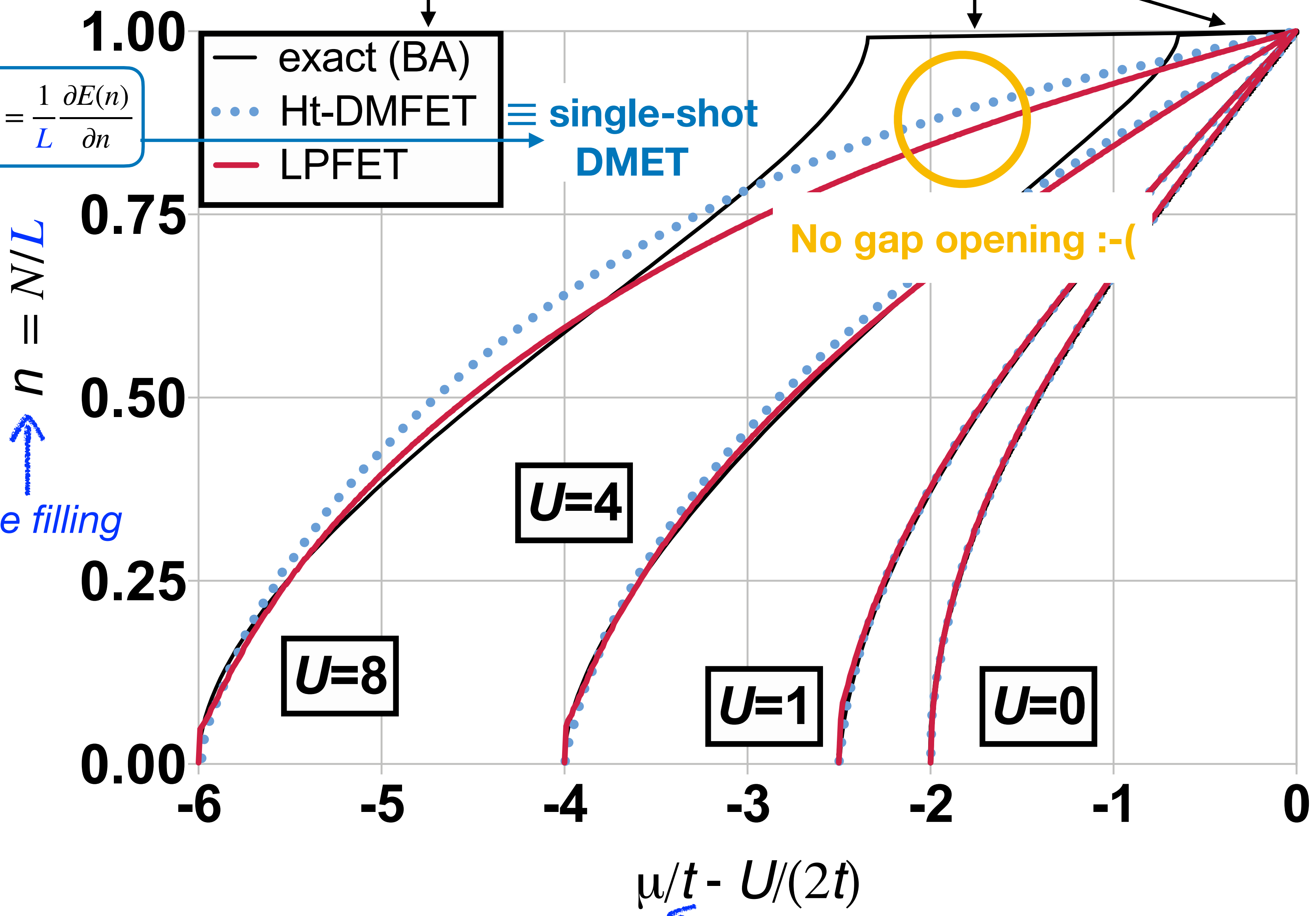
Lattice filling

$$\tilde{v}_{\mathrm{Hxc}} = 0$$

Chemical potential of the true Hubbard lattice

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

Local potential-functional embedding theory (LPFET)



“Bethe Ansatz”

Density-driven **Mott-Hubbard transition**

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

≡ **single-shot DMET**

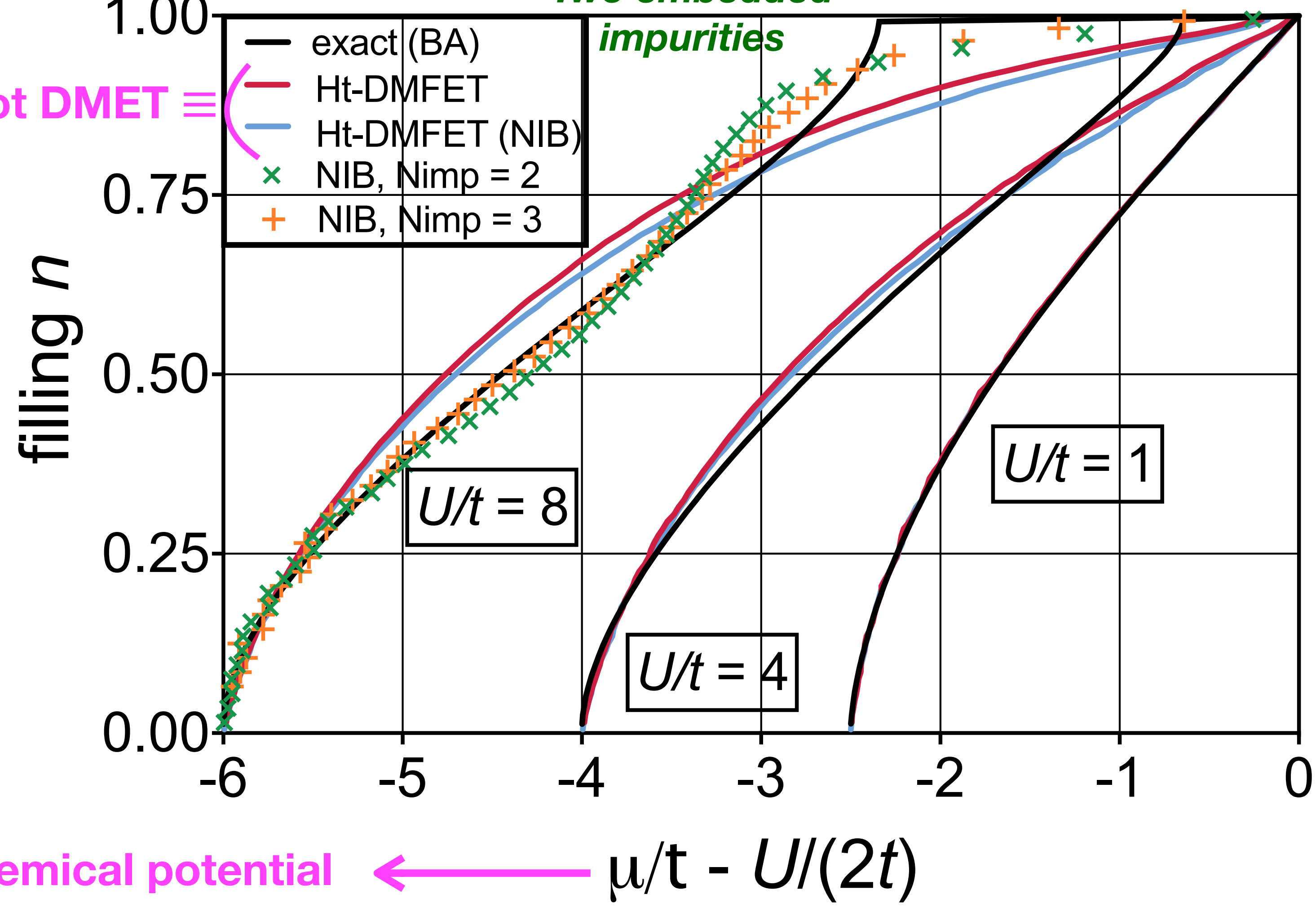
No gap opening :-(

Lattice filling

Chemical potential of the true Hubbard lattice

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

Mott-Hubbard density-driven transition and multiple impurities



Two embedded impurities

Three embedded impurities

Single-shot DMET ≡

Chemical potential ←

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

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

Recent developments and open questions

Density-functional ***exactification***
of
Density *(matrix)* ***Embedding Theory (DET)***

Density-functional exactification of D(M)ET

computation

MDPI

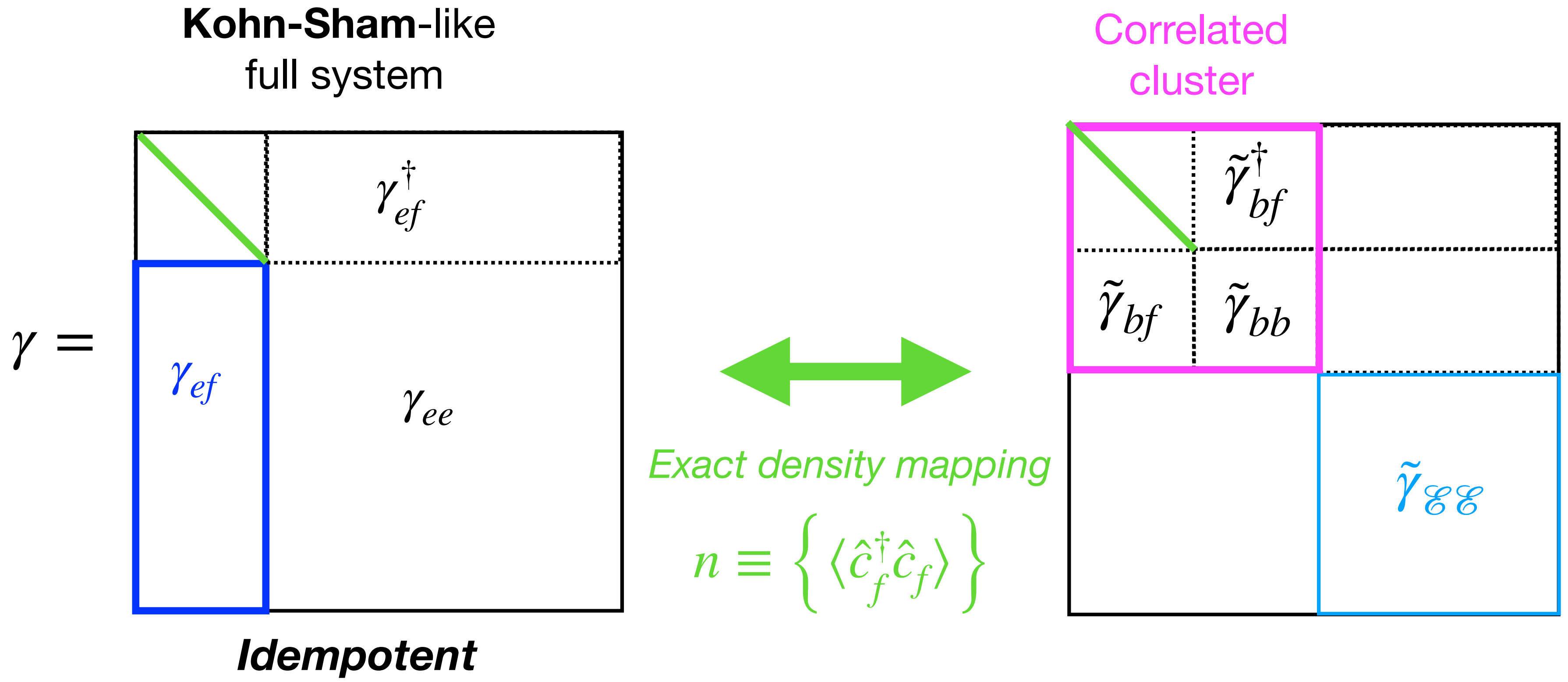
check for updates

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]

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



Kohn-Sham-like
full system

$\gamma =$

Idempotent

Exact density mapping

$$n \equiv \left\{ \langle \hat{c}_f^{\dagger} \hat{c}_f \rangle \right\}$$

Correlated
cluster

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).*

A few words about what “Kohn-Sham DFT” refers to in this context

A few words about what "Kohn-Sham DFT" refers to in this context

Strictly speaking, we are dealing with a

site occupation functional theory (for lattice models)
or
a **localized orbital occupation functional theory** (for *ab initio* Hamiltonians)

K. Capelle and V. L. Campo Jr., Phys. Rep. 528, 91 (2013).
E. Fromager, Mol. Phys. 113, 419 (2015).

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Strictly speaking, we are dealing with a

site occupation functional theory (for lattice models)
or
a **localized orbital occupation functional theory** (for *ab initio* Hamiltonians)

$$\textbf{Density} \equiv \left\{ n_i = \sum_{\sigma=\uparrow,\downarrow} \langle \hat{c}^\dagger_{i\sigma} \hat{c}_{i\sigma} \rangle = \langle \hat{n}_i \rangle \right\}$$

“Density operator”

K. Capelle and V. L. Campo Jr., Phys. Rep. 528, 91 (2013).
E. Fromager, Mol. Phys. 113, 419 (2015).

A few words about what “Kohn-Sham DFT” refers to in this context

Kohn-Sham Hamiltonian in this context:

$$\hat{H}_{\mathrm{KS}} = \overbrace{\sum_{p\neq q} h_{pq} \sum_{\sigma} \hat{c}^{\dagger}_{p\sigma}\hat{c}_{q\sigma} + \sum_{p} h_{pp}\hat{n}_{p}}^{\text{Regular one-electron part of the true Hamiltonian } \hat{H}} + \ldots$$

K. Capelle and V. L. Campo Jr., Phys. Rep. 528, 91 (2013).
E. Fromager, Mol. Phys. 113, 419 (2015).

A few words about what "Kohn-Sham DFT" refers to in this context

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$$\hat{H}_{\mathrm{KS}} = \overbrace{\underbrace{\sum_{p\neq q} h_{pq}\sum_{\sigma} \hat{c}^{\dagger}_{p\sigma}\hat{c}_{q\sigma}}_{\equiv\,\hat{\mathscr{T}}} + \underbrace{\sum_{p} h_{pp}\hat{n}_{p}}_{\equiv\,\hat{\mathscr{V}}_{\mathrm{ext}}}}^{\text{Regular one-electron part of the true Hamiltonian } \hat{H}} + \dots$$

Analogs of the **kinetic energy**
and **external potential** operators

K. Capelle and V. L. Campo Jr., Phys. Rep. 528, 91 (2013).
E. Fromager, Mol. Phys. 113, 419 (2015).

A few words about what "Kohn-Sham DFT" refers to in this context

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$$\downarrow$$

$$\boxed{\langle\hat{n}_p\rangle_{\hat{H}_{\mathrm{KS}}} \overset{!}{=} \langle\hat{n}_p\rangle_{\hat{H}} \quad \forall p}$$

K. Capelle and V. L. Campo Jr., Phys. Rep. 528, 91 (2013).
E. Fromager, Mol. Phys. 113, 419 (2015).

LPFET of finite and non-uniform *(model or ab-initio)* ***systems***

What will be discussed in the following can be recovered (more rigorously)
from
an **exact DFT-like theory***
where
local densities (localised orbital occupations)
are **mapped**
onto **interacting embedding clusters**

E. Fromager, Mol. Phys. 113, 419 (2015).

**W. Makhlouf, B. Senjean, and E. Fromager,* to be submitted (2025).

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Note: Exact means FCI in this context!

E. Fromager, Mol. Phys. 113, 419 (2015).

**W. Makhlouf, B. Senjean, and E. Fromager,* to be submitted (2025).

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local densities (localised orbital occupations)
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onto **interacting embedding clusters**

Kohn-Sham decomposition

$$\mathscr{F}(\underline{n}) = \mathscr{T}_{\rm s}(\underline{n}) + E_{\rm Hxc}(\underline{n})$$

$$\mathscr{F}(\underline{n}) = \min_{\Psi\rightarrow\underline{n}} \left\langle \Psi \middle| \hat{\mathscr{T}} + \hat{W}_{\rm ee} \middle| \Psi \right\rangle$$

$$\mathscr{T}_{\rm s}(\underline{n}) = \min_{\Psi\rightarrow\underline{n}} \left\langle \Psi \middle| \hat{\mathscr{T}} \middle| \Psi \right\rangle$$

Analog of the Hohenberg-Kohn functional

E. Fromager, Mol. Phys. 113, 419 (2015).

**W. Makhlouf, B. Senjean, and E. Fromager,* to be submitted (2025).

LPFET of finite and non-uniform *(model or ab-initio)* ***systems***

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Fragmentation of the Hohenberg-Kohn functional

$$\mathscr{F}(\underline{n}) = \mathscr{T}_{\mathrm{s}}(\underline{n}) + E_{\mathrm{Hxc}}(\underline{n})$$

$$= \sum_i \left\langle \Psi^{\mathscr{C}^i}(\underline{n}) \middle| \sum_{j>i} h_{ij} \sum_\sigma \left(\hat{c}^\dagger_{i\sigma}\hat{c}_{j\sigma} + \hat{c}^\dagger_{j\sigma}\hat{c}_{i\sigma} \right) + \hat{U}_i \middle| \Psi^{\mathscr{C}^i}(\underline{n}) \right\rangle + \overline{E}_{\mathrm{Hxc}}(\underline{n})$$

Single-orbital fragments here

**W. Makhlouf, B. Senjean, and E. Fromager,* to be submitted (2025).

LPFET of finite and non-uniform *(model or ab-initio)* ***systems***

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Single-orbital fragments here

$$\underline{n} \equiv \{n_i\} \quad \text{where} \quad \sum_i n_i = N$$

W. Makhlouf, B. Senjean, and E. Fromager, to be submitted (2025).

LPFET of finite and non-uniform *(model or ab-initio)* ***systems***

Exact relation between $\left\{v_i^{\mathrm{Hxc}}\right\}$

and

the chemical potential value μ_i^{imp} on the embedded impurity

$$\Big\uparrow\ \frac{\partial}{\partial n_i}$$

$$\overbrace{\mathscr{T}_{\mathrm{s}}(\underline{n}) + E_{\mathrm{Hxc}}(\underline{n}) = \sum_i \left\langle \Psi^{\mathscr{C}^i}(\underline{n}) \middle| \sum_{j>i} h_{ij} \sum_{\sigma} \left(\hat{c}^\dagger_{i\sigma}\hat{c}_{j\sigma} + \hat{c}^\dagger_{j\sigma}\hat{c}_{i\sigma}\right) + \hat{U}_i \middle| \Psi^{\mathscr{C}^i}(\underline{n}) \right\rangle + \overline{E}_{\mathrm{Hxc}}(\underline{n})}$$

$$\underline{n} \equiv \left\{n_i\right\} \quad \text{where} \quad \sum_i n_i = N$$

**W. Makhlouf, B. Senjean, and E. Fromager,* to be submitted (2025).

LPFET of finite and non-uniform *(model or ab-initio)* ***systems***

Let’s have a simpler (approximate but practical) individual-cluster-based approach to the problem:

W. Makhlouf, B. Senjean, and E. Fromager, to be submitted (2025).

LPFET of finite and non-uniform** (model or ab-initio) **systems

$$E_{\mathrm{Hxc}}^{\mathscr{C}_i}(n_i) = \left\langle \Psi^{\mathscr{C}_i}(n_i) \middle| \hat{P}^{\mathscr{C}_i}\hat{H}\hat{P}^{\mathscr{C}_i} \middle| \Psi^{\mathscr{C}_i}(n_i) \right\rangle - \left\langle \Phi_{\mathrm{KS}}^{\mathscr{C}_i}(n_i) \middle| \hat{P}^{\mathscr{C}_i}\left(\hat{H}_{\mathrm{KS}} - \hat{V}^{\mathrm{Hxc}}\right)\hat{P}^{\mathscr{C}_i} \middle| \Phi_{\mathrm{KS}}^{\mathscr{C}_i}(n_i) \right\rangle$$

Local density functional evaluation
of the
Hxc energy

W. Makhlouf, B. Senjean, and E. Fromager, to be submitted (2025).

LPFET of finite and non-uniform *(model or ab-initio)* ***systems***

$$E^{\mathscr{C}^i}_{\mathrm{Hxc}}(n_i) = \left\langle \Psi^{\mathscr{C}^i}(n_i) \middle| \hat{P}^{\mathscr{C}^i} \hat{H} \hat{P}^{\mathscr{C}^i} \middle| \Psi^{\mathscr{C}^i}(n_i) \right\rangle - \left\langle \Phi^{\mathscr{C}^i}_{\mathrm{KS}}(n_i) \middle| \hat{P}^{\mathscr{C}^i} \left(\hat{H}_{\mathrm{KS}} - \hat{V}^{\mathrm{Hxc}} \right) \hat{P}^{\mathscr{C}^i} \middle| \Phi^{\mathscr{C}^i}_{\mathrm{KS}}(n_i) \right\rangle$$

Local evaluation
of the
Hxc energy

Exact "projection
onto the cluster"
operator

W. Makhlouf, B. Senjean, and E. Fromager, to be submitted (2025).

LPFET of finite and non-uniform *(model or ab-initio)* ***systems***

$$E^{\mathscr{C}_i}_{\mathrm{Hxc}}(n_i) = \left\langle \Psi^{\mathscr{C}_i}(n_i) \middle| \hat{P}^{\mathscr{C}_i}\hat{H}\hat{P}^{\mathscr{C}_i} \middle| \Psi^{\mathscr{C}_i}(n_i) \right\rangle - \left\langle \Phi^{\mathscr{C}_i}_{\mathrm{KS}}(n_i) \middle| \hat{P}^{\mathscr{C}_i}\left(\hat{H}_{\mathrm{KS}} - \hat{V}^{\mathrm{Hxc}}\right)\hat{P}^{\mathscr{C}_i} \middle| \Phi^{\mathscr{C}_i}_{\mathrm{KS}}(n_i) \right\rangle$$

Local evaluation
of the
Hxc energy

Exact "projection
onto the cluster"
operator **(fixed)**

I can **infinitesimally vary the local density** n_i within the embedding cluster
(while freezing the density in the other clusters)

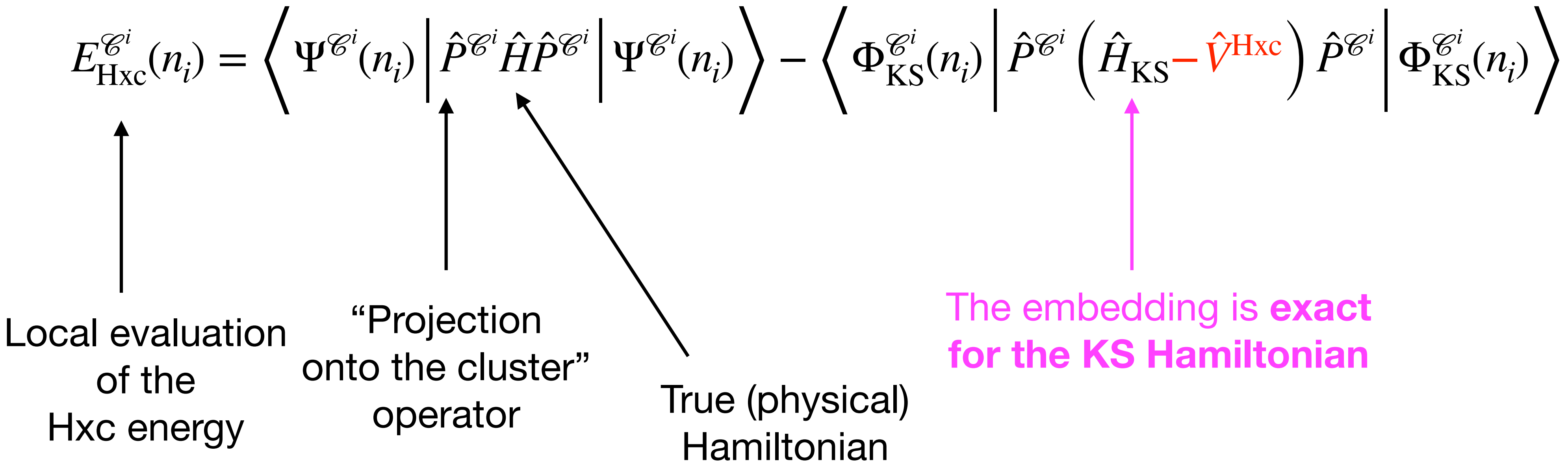
W. Makhlouf, B. Senjean, and E. Fromager, to be submitted (2025).

LPFET of finite and non-uniform *(model or ab-initio)* ***systems***

$$\underset{\substack{\uparrow\\ \text{Local evaluation}\\ \text{of the}\\ \text{Hxc energy}}}{E^{\mathscr{C}i}_{\mathrm{Hxc}}(n_i)} = \left\langle \Psi^{\mathscr{C}i}(n_i) \middle| \underset{\substack{\uparrow\\ \text{“Projection}\\ \text{onto the cluster”}\\ \text{operator}}}{\hat{P}^{\mathscr{C}i}} \underset{\substack{\nwarrow\\ \text{True (physical)}\\ \text{Hamiltonian}}}{\hat{H}} \hat{P}^{\mathscr{C}i} \middle| \Psi^{\mathscr{C}i}(n_i) \right\rangle - \left\langle \Phi^{\mathscr{C}i}_{\mathrm{KS}}(n_i) \middle| \hat{P}^{\mathscr{C}i} \left(\hat{H}_{\mathrm{KS}} - \hat{V}^{\mathrm{Hxc}} \right) \hat{P}^{\mathscr{C}i} \middle| \Phi^{\mathscr{C}i}_{\mathrm{KS}}(n_i) \right\rangle$$

W. Makhlouf, B. Senjean, and E. Fromager, to be submitted (2025).

LPFET of finite and non-uniform** (model or ab-initio) **systems



$$E^{\mathscr{C}^i}_{\rm Hxc}(n_i) = \left\langle \Psi^{\mathscr{C}^i}(n_i) \middle| \hat{P}^{\mathscr{C}^i}\hat{H}\hat{P}^{\mathscr{C}^i} \middle| \Psi^{\mathscr{C}^i}(n_i) \right\rangle - \left\langle \Phi^{\mathscr{C}^i}_{\rm KS}(n_i) \middle| \hat{P}^{\mathscr{C}^i}\left(\hat{H}_{\rm KS} - \hat{V}^{\rm Hxc}\right)\hat{P}^{\mathscr{C}^i} \middle| \Phi^{\mathscr{C}^i}_{\rm KS}(n_i) \right\rangle$$

Local evaluation
of the
Hxc energy

“Projection
onto the cluster”
operator

True (physical)
Hamiltonian

The embedding is **exact**
for the KS Hamiltonian

W. Makhlouf, B. Senjean, and E. Fromager, to be submitted (2025).

LPFET of finite and non-uniform *(model or ab-initio)* ***systems***

$$E^{\mathscr{C}_i}_{\mathrm{Hxc}}(n_i) = \left\langle \Psi^{\mathscr{C}_i}(n_i) \middle| \hat{P}^{\mathscr{C}_i}\hat{H}\hat{P}^{\mathscr{C}_i} \middle| \Psi^{\mathscr{C}_i}(n_i) \right\rangle - \left\langle \Phi^{\mathscr{C}_i}_{\mathrm{KS}}(n_i) \middle| \hat{P}^{\mathscr{C}_i}\left(\hat{H}_{\mathrm{KS}} - \hat{V}^{\mathrm{Hxc}}\right)\hat{P}^{\mathscr{C}_i} \middle| \Phi^{\mathscr{C}_i}_{\mathrm{KS}}(n_i) \right\rangle$$

Local evaluation
of the
Hxc energy

“Projection
onto the cluster”
operator

True (physical)
Hamiltonian

The embedding
is exact
for the KS Hamiltonian

No double counting!

W. Makhlouf, B. Senjean, and E. Fromager, to be submitted (2025).

LPFET of finite and non-uniform *(model or ab-initio)* ***systems***

$$E_{\mathrm{Hxc}}^{\mathscr{C}^i}(n_i) = \left\langle \Psi^{\mathscr{C}^i}(n_i) \middle| \hat{P}^{\mathscr{C}^i}\hat{H}\hat{P}^{\mathscr{C}^i} \middle| \Psi^{\mathscr{C}^i}(n_i) \right\rangle - \left\langle \Phi_{\mathrm{KS}}^{\mathscr{C}^i}(n_i) \middle| \hat{P}^{\mathscr{C}^i}\left(\hat{H}_{\mathrm{KS}} - \hat{V}^{\mathrm{Hxc}}\right)\hat{P}^{\mathscr{C}^i} \middle| \Phi_{\mathrm{KS}}^{\mathscr{C}^i}(n_i) \right\rangle$$

$$\frac{\partial E_{\mathrm{Hxc}}^{\mathscr{C}^i}(n_i)}{\partial n_i} = \mu_i^{\mathrm{imp}} + v_i^{\mathrm{Hxc}} - \sum_k \langle \chi_k | \phi_b^{\mathscr{C}^i} \rangle^2 v_k^{\mathrm{Hxc}}$$

Projection of the Hxc potential
onto the bath (denoted $\phi_b^{\mathscr{C}^i}$ here)

Ensures that the KS cluster reproduces n_i

W. Makhlouf, B. Senjean, and E. Fromager, to be submitted (2025).

LPFET of finite and non-uniform *(model or ab-initio)* ***systems***

$$E^{\mathscr{C}_i}_{\mathrm{Hxc}}(n_i) = \left\langle \Psi^{\mathscr{C}_i}(n_i) \middle| \hat{P}^{\mathscr{C}_i}\hat{H}\hat{P}^{\mathscr{C}_i} \middle| \Psi^{\mathscr{C}_i}(n_i)\right\rangle - \left\langle \Phi^{\mathscr{C}_i}_{\mathrm{KS}}(n_i)\middle|\hat{P}^{\mathscr{C}_i}\left(\hat{H}_{\mathrm{KS}}-\hat{V}^{\mathrm{Hxc}}\right)\hat{P}^{\mathscr{C}_i}\middle|\Phi^{\mathscr{C}_i}_{\mathrm{KS}}(n_i)\right\rangle$$

$$\frac{\partial E^{\mathscr{C}_i}_{\mathrm{Hxc}}(n_i)}{\partial n_i} = \mu_i^{\mathrm{imp}} + v_i^{\mathrm{Hxc}} - \sum_k \langle \chi_k | \phi_b^{\mathscr{C}_i}\rangle^2 v_k^{\mathrm{Hxc}}$$

$$\frac{\partial E^{\mathscr{C}_i}_{\mathrm{Hxc}}(n_i)}{\partial n_i} \approx v_i^{\mathrm{Hxc}}$$

$$\boxed{-\mu_i^{\mathrm{imp}} \approx -\sum_k \langle \chi_k | \phi_b^{\mathscr{C}_i}\rangle^2 v_k^{\mathrm{Hxc}}}$$

W. Makhlouf, B. Senjean, and E. Fromager, to be submitted (2025).

LPFET of finite and non-uniform *(model or ab-initio)* ***systems***

$$E_{\rm Hxc}^{\mathscr{C}^i}(n_i) = \left\langle \Psi^{\mathscr{C}^i}(n_i) \middle| \hat{P}^{\mathscr{C}^i}\hat{H}\hat{P}^{\mathscr{C}^i} \middle| \Psi^{\mathscr{C}^i}(n_i) \right\rangle - \left\langle \Phi_{\rm KS}^{\mathscr{C}^i}(n_i) \middle| \hat{P}^{\mathscr{C}^i}\left(\hat{H}_{\rm KS} - \hat{V}^{\rm Hxc}\right)\hat{P}^{\mathscr{C}^i} \middle| \Phi_{\rm KS}^{\mathscr{C}^i}(n_i) \right\rangle$$

$$\frac{\partial E_{\rm Hxc}^{\mathscr{C}^i}(n_i)}{\partial n_i} = \mu_i^{\rm imp} + v_i^{\rm Hxc} - \sum_k \langle \chi_k | \phi_b^{\mathscr{C}^i} \rangle^2 v_k^{\rm Hxc}$$

$$\frac{\partial E_{\rm Hxc}^{\mathscr{C}^i}(n_i)}{\partial n_i} \approx v_i^{\rm Hxc}$$

$$-\mu_i^{\rm imp} \approx -\sum_k \langle \chi_k | \phi_b^{\mathscr{C}^i} \rangle^2 v_k^{\rm Hxc} \xrightarrow{\text{Uniform case}} \boxed{\mu_i^{\rm imp} \approx v^{\rm Hxc}}$$

😅

W. Makhlouf, B. Senjean, and E. Fromager, to be submitted (2025).

LPFET of finite and non-uniform** (model or ab-initio) **systems

$$E_{\mathrm{Hxc}}^{\mathscr{C}_i}(n_i) = \left\langle \Psi^{\mathscr{C}_i}(n_i) \middle| \hat{P}^{\mathscr{C}_i}\hat{H}\hat{P}^{\mathscr{C}_i} \middle| \Psi^{\mathscr{C}_i}(n_i)\right\rangle - \left\langle \Phi_{\mathrm{KS}}^{\mathscr{C}_i}(n_i) \middle| \hat{P}^{\mathscr{C}_i}\left(\hat{H}_{\mathrm{KS}} - \hat{V}^{\mathrm{Hxc}}\right)\hat{P}^{\mathscr{C}_i} \middle| \Phi_{\mathrm{KS}}^{\mathscr{C}_i}(n_i)\right\rangle$$

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$$\frac{\partial E_{\mathrm{Hxc}}^{\mathscr{C}_i}(n_i)}{\partial n_i} \approx v_i^{\mathrm{Hxc}}$$

$$v_k^{\mathrm{Hxc}} \rightarrow v_k^{\mathrm{Hxc}} + \mu_{\mathrm{glob}}$$

$$-\mu_i^{\mathrm{imp}} \approx -\sum_k \langle \chi_k | \phi_b^{\mathscr{C}_i}\rangle^2 v_k^{\mathrm{Hxc}}$$

$$\boxed{-\mu_i^{\mathrm{imp}} \approx -\mu_{\mathrm{glob}} - \sum_k \langle \chi_k | \phi_b^{\mathscr{C}_i}\rangle^2 v_k^{\mathrm{Hxc}}}$$

W. Makhlouf, B. Senjean, and E. Fromager, to be submitted (2025).

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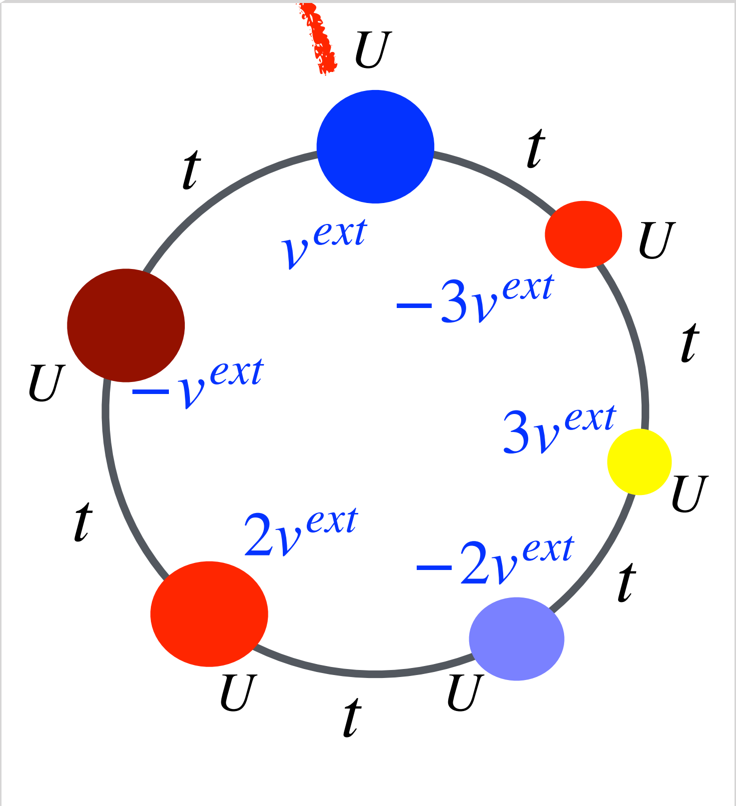
$$\underbrace{-\mu_i^{\rm imp} \approx -\mu_{\rm glob} \overbrace{- \sum_k \langle \chi_k | \phi_b^{\mathscr{C}_i} \rangle^2 v_k^{\rm Hxc}}^{\textbf{Ignored in D(M)ET*}}}_{\textbf{LPFET}}$$

W. Makhlouf, B. Senjean, and E. Fromager, to be submitted (2025).

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

LPFET of finite and non-uniform systems

6-site Hubbard ring



$$t = 1$$

$$v^{ext} = t$$

W. Makhlouf, B. Senjean, and E. Fromager, to be submitted (2025).

Saad Yalouz

|qnb⟩ QuantNBody

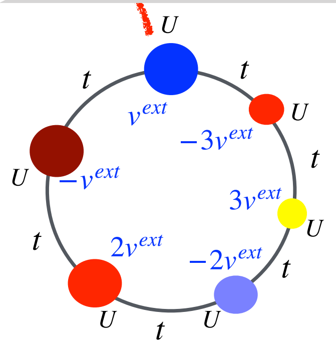
An open access python package for quantum chemistry/physics to manipulate many-body operators and wave functions

Available on : https://github.com/SYalouz/QuantNBody

S. Yalouz, M. R. Gullin, and S. Sekaran, J. Open Source Softw. 7, 4759 (2022).

LPFET of finite and non-uniform systems

6-site Hubbard ring

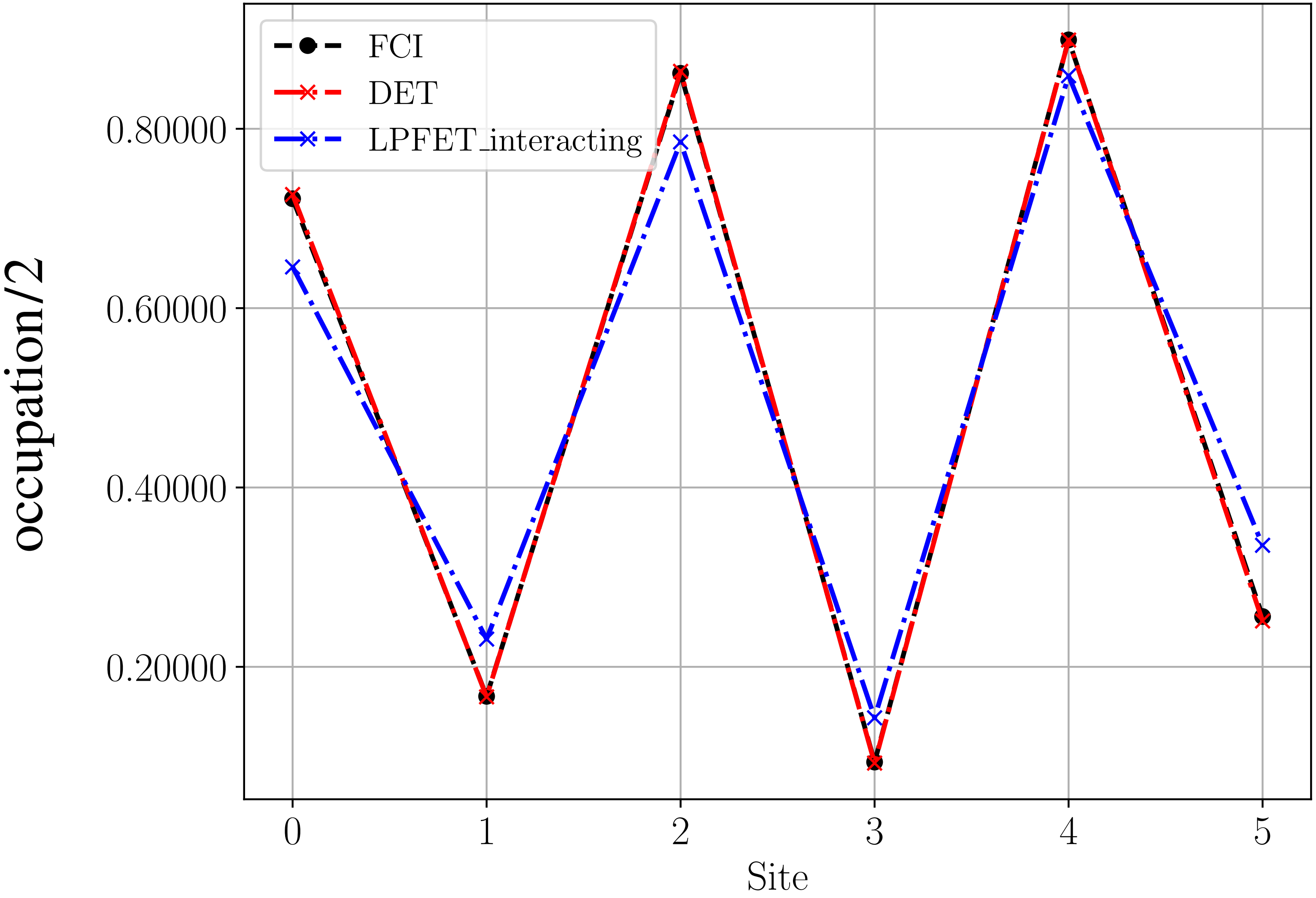


$t = 1$

$v^{ext} = t$

$U = 2$

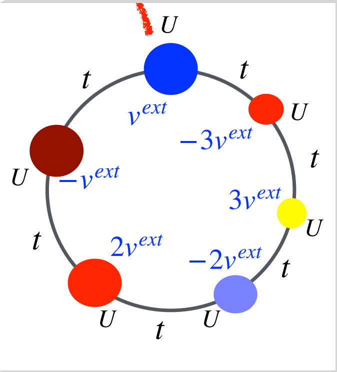
Density profile



W. Makhlouf, *B. Senjean, and E. Fromager,* to be submitted (2025).

LPFET of finite and non-uniform systems

6-site Hubbard ring

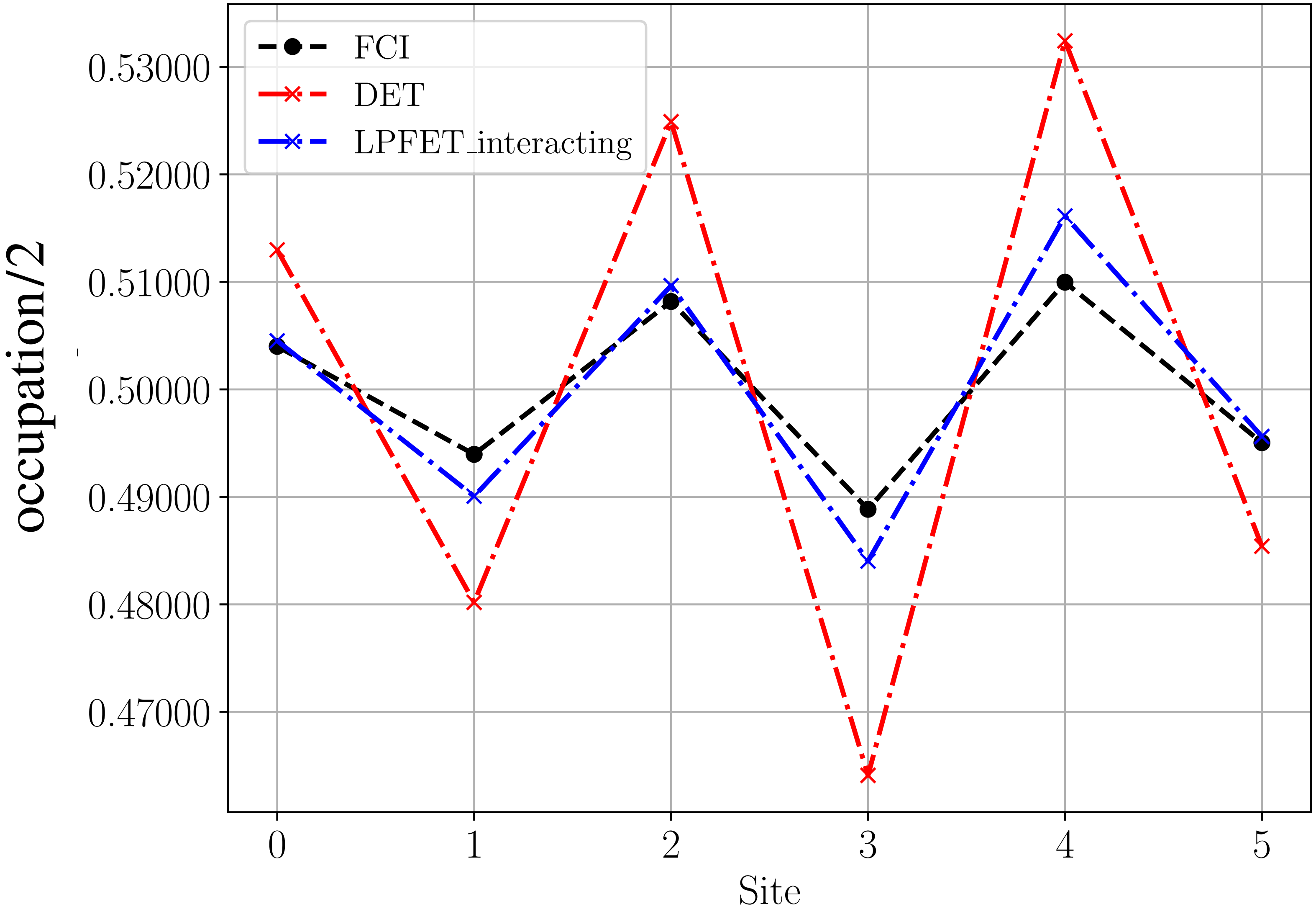


$t = 1$

$v^{ext} = t$

$U = 15$

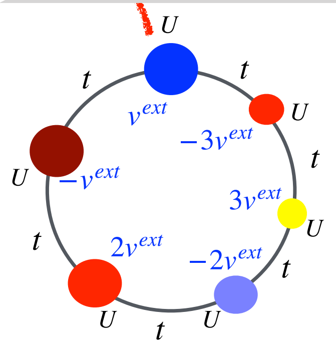
Density profile



W. Makhlouf, B. Senjean, and E. Fromager, to be submitted (2025).

LPFET of finite and non-uniform systems

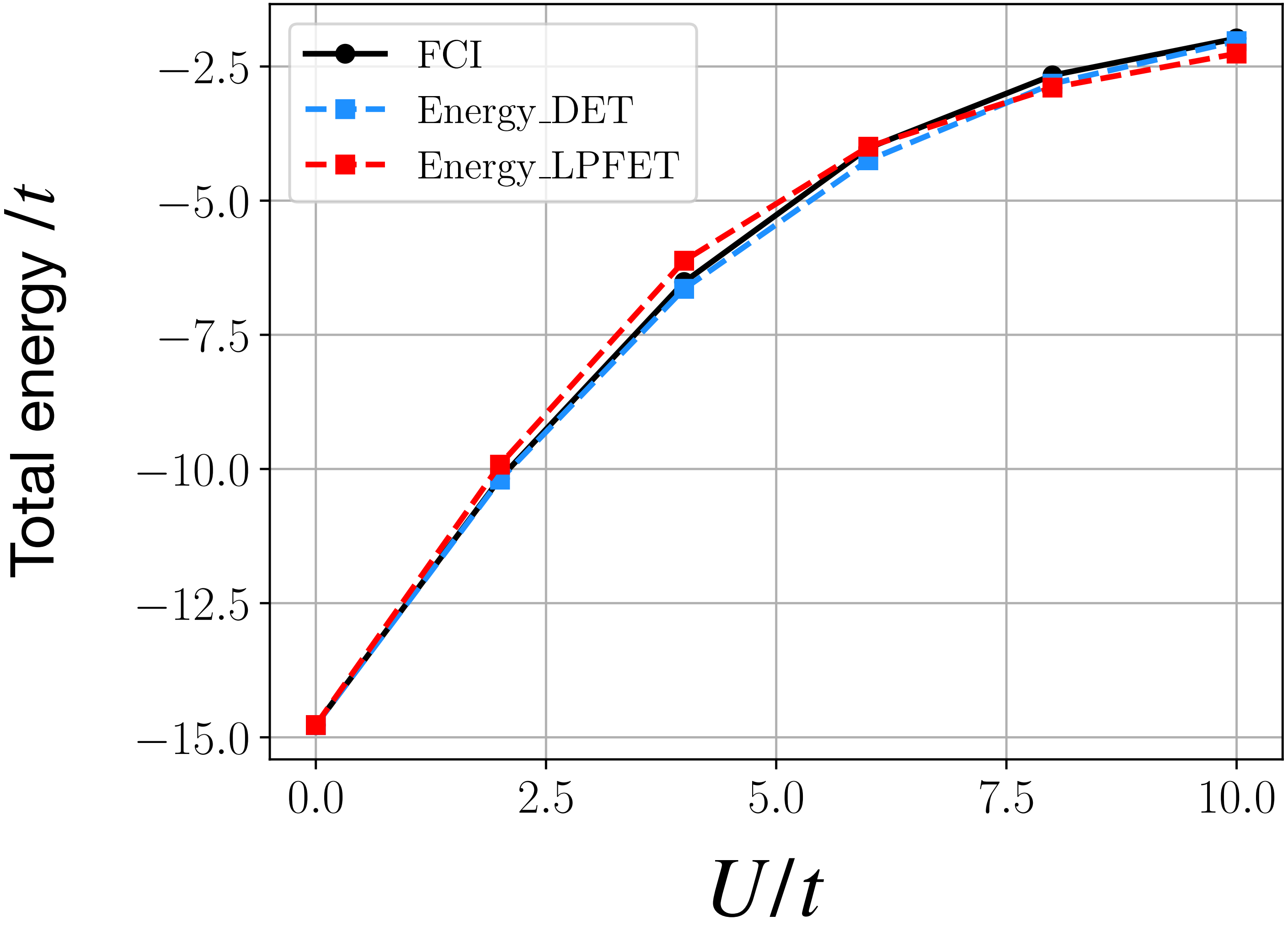
6-site Hubbard ring



$t = 1$

$v^{ext} = t$

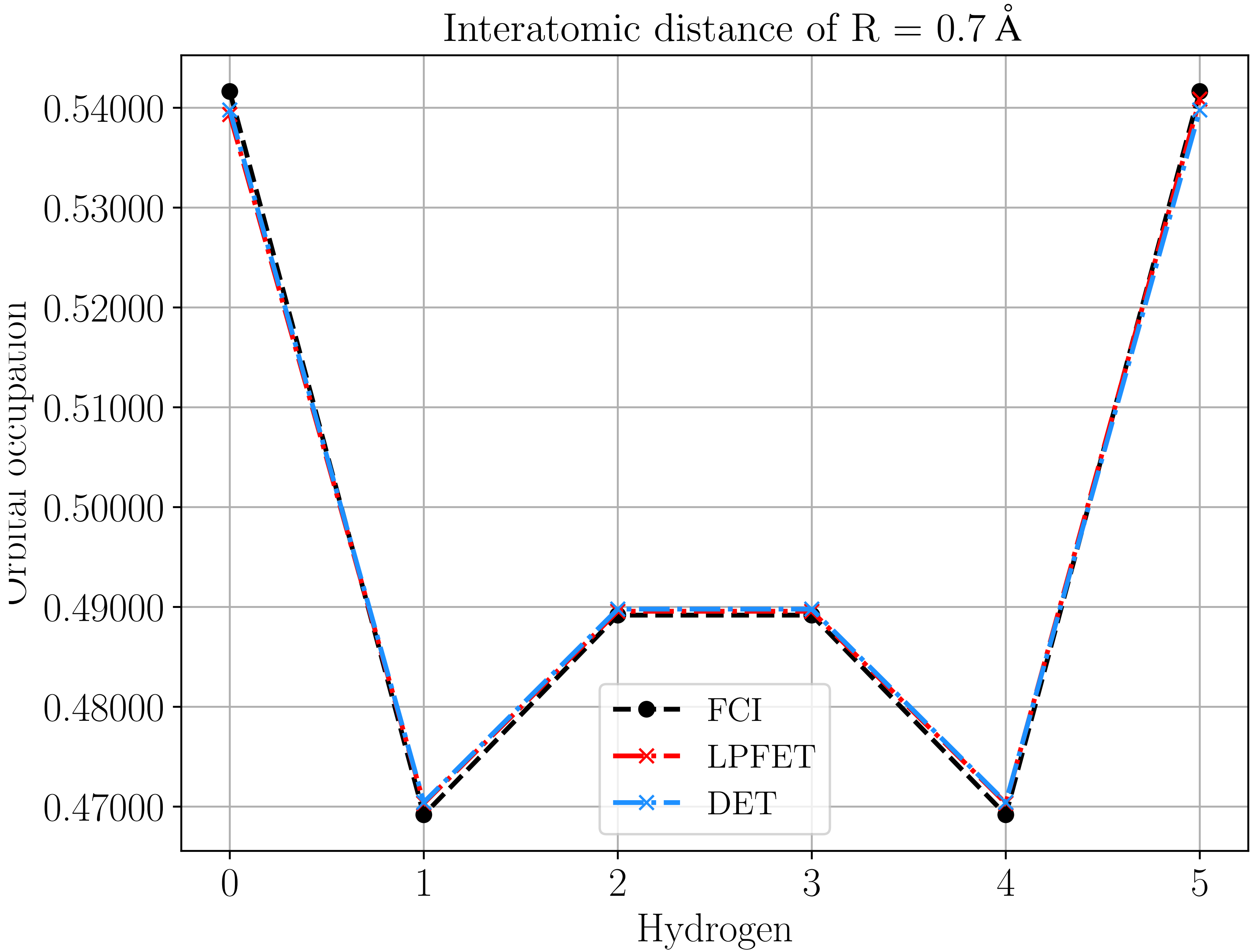
Energy profile



W. Makhlouf, B. Senjean, and E. Fromager, to be submitted (2025).

LPFET of finite and non-uniform systems

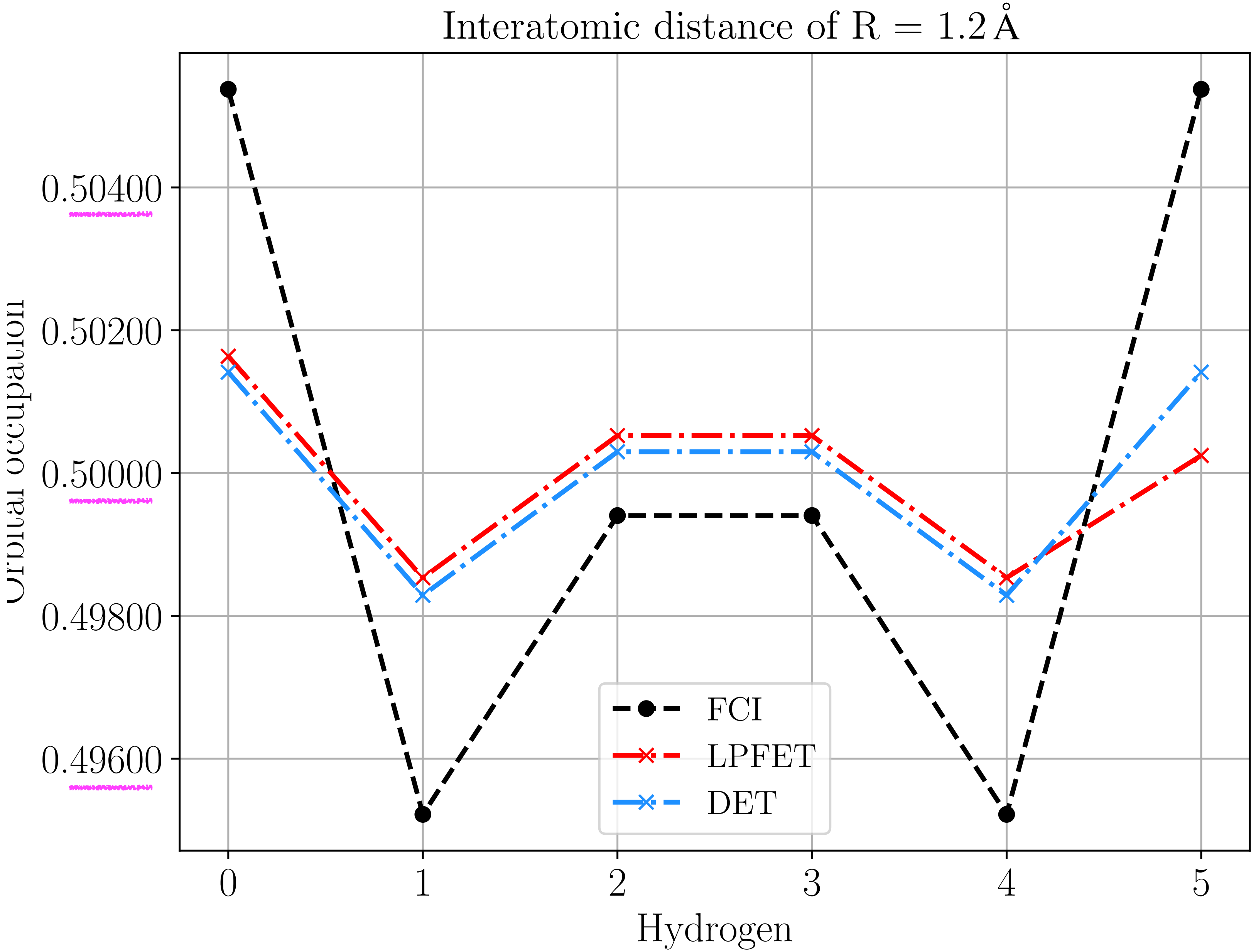
chain of 6 hydrogen atoms (STO-3G)



W. Makhlouf, B. Senjean, and E. Fromager, to be submitted (2025).

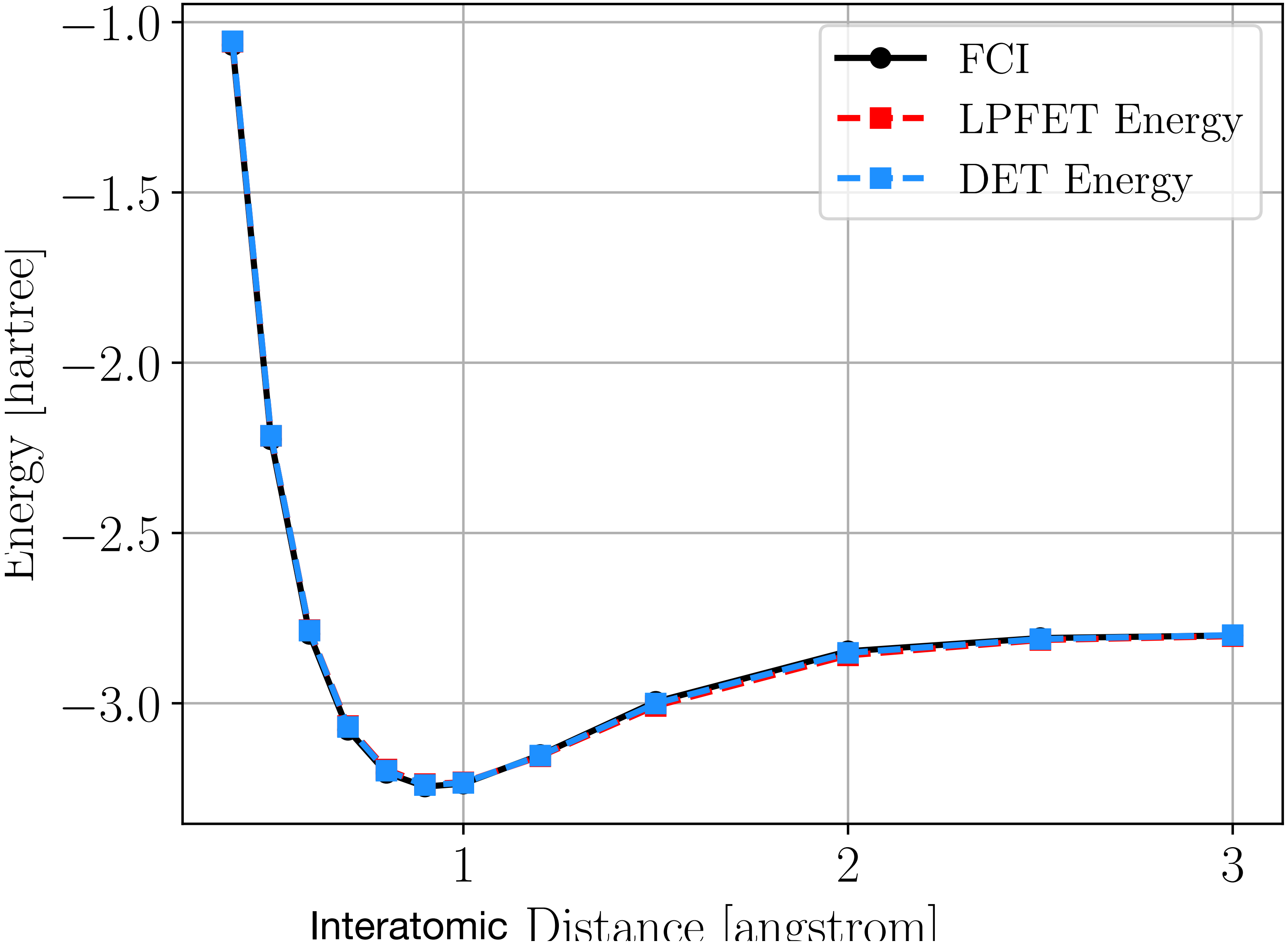
LPFET of finite and non-uniform systems

chain of 6 hydrogen atoms (STO-3G)



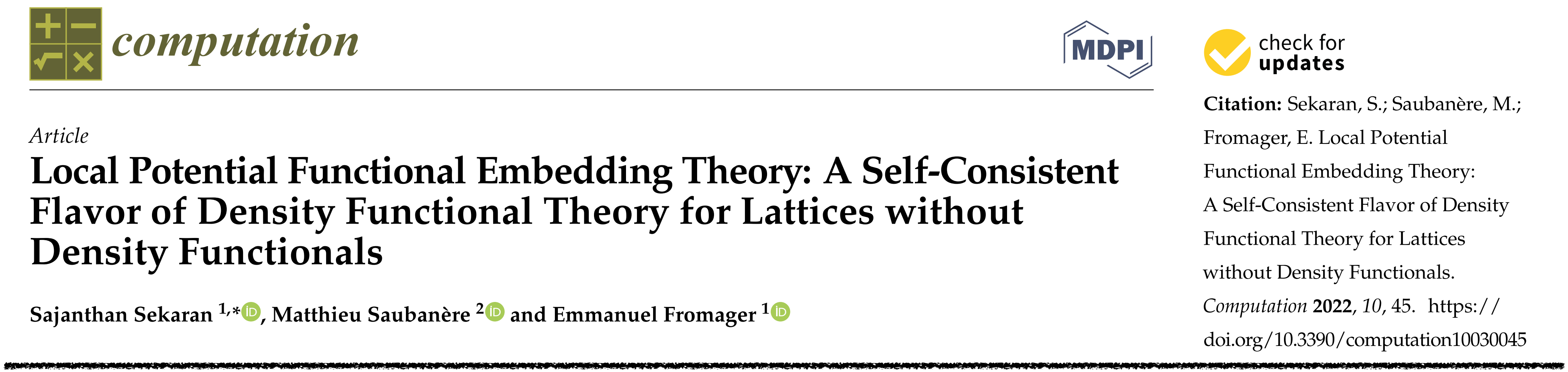
W. Makhlouf, B. Senjean, and E. Fromager, to be submitted (2025).

LPFET of finite and non-uniform systems



W. Makhlouf, B. Senjean, and E. Fromager, to be submitted (2025).

Density-functional exactification of D(M)ET



computation

MDPI

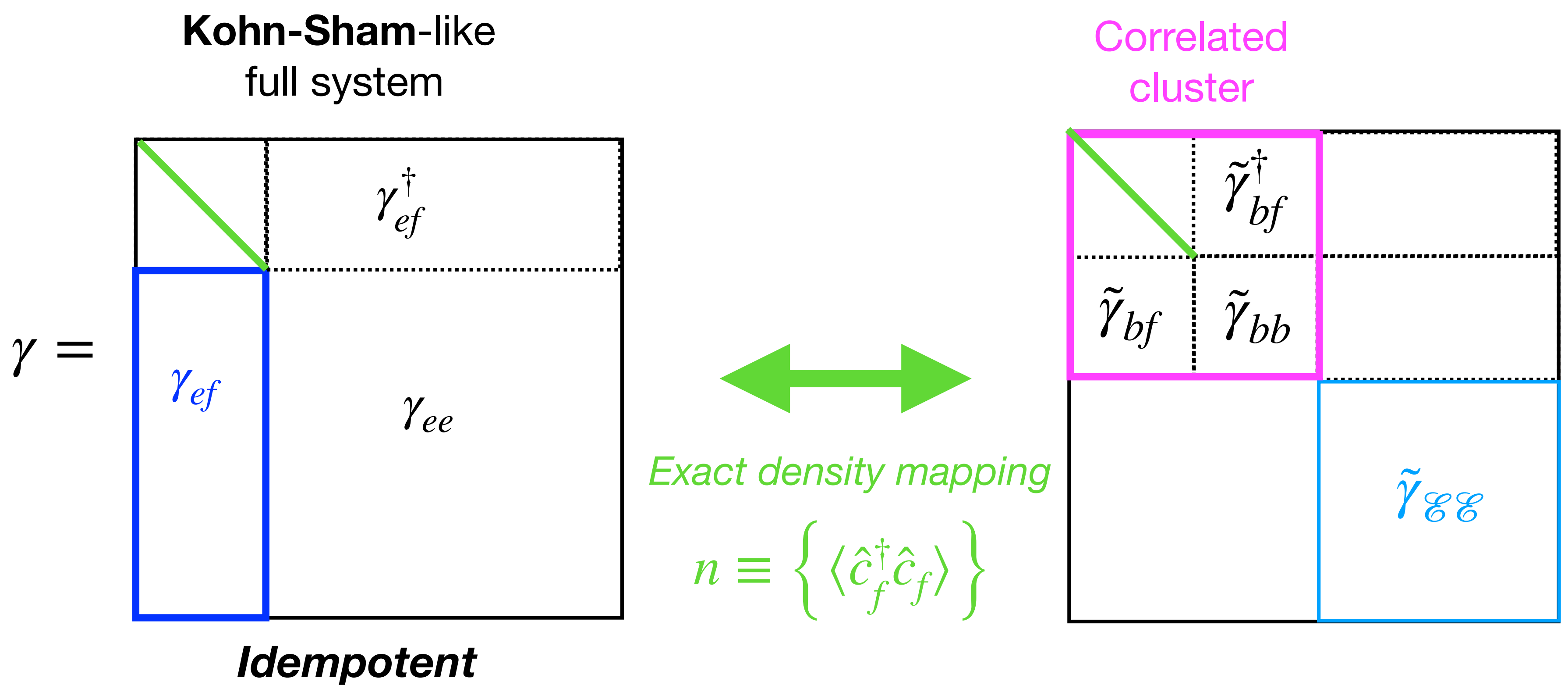
check for updates

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]

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



Kohn-Sham-like full system

Correlated cluster

Exact density mapping

$n \equiv \left\{ \langle \hat{c}_f^\dagger \hat{c}_f \rangle \right\}$

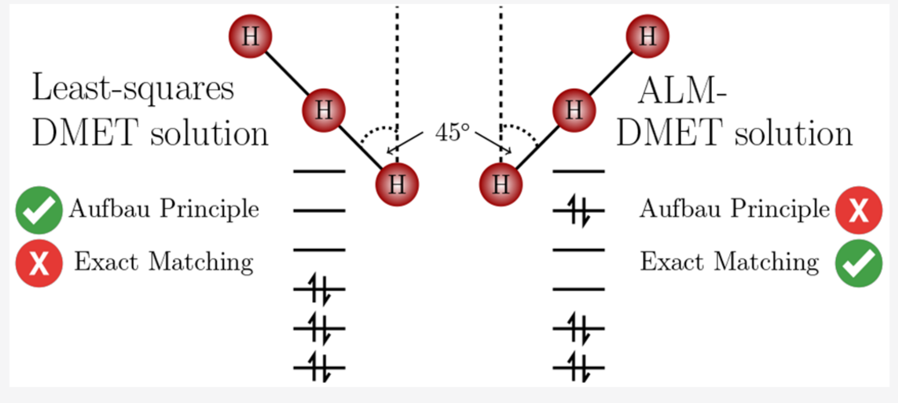
Idempotent

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).*

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

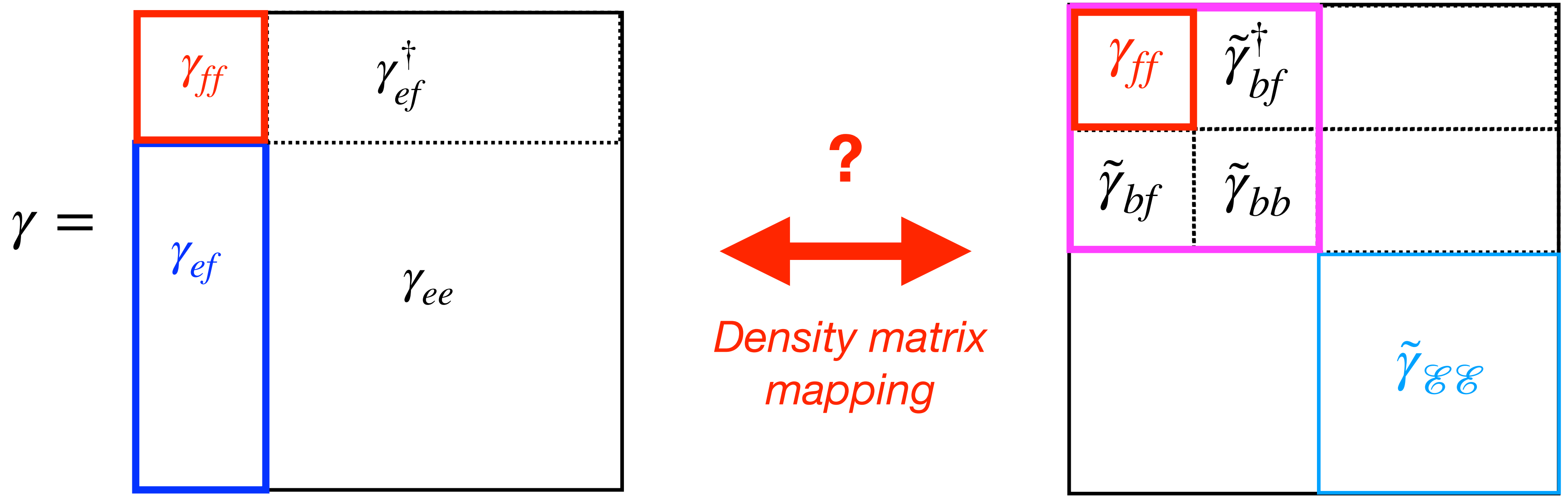
Fabian M. Faulstich,[⊥] Raehyun Kim,[⊥] Zhi-Hao Cui, Zaiwen Wen, Garnet Kin-Lic Chan, and Lin Lin[*]

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



Kohn-Sham-like
full system**?**

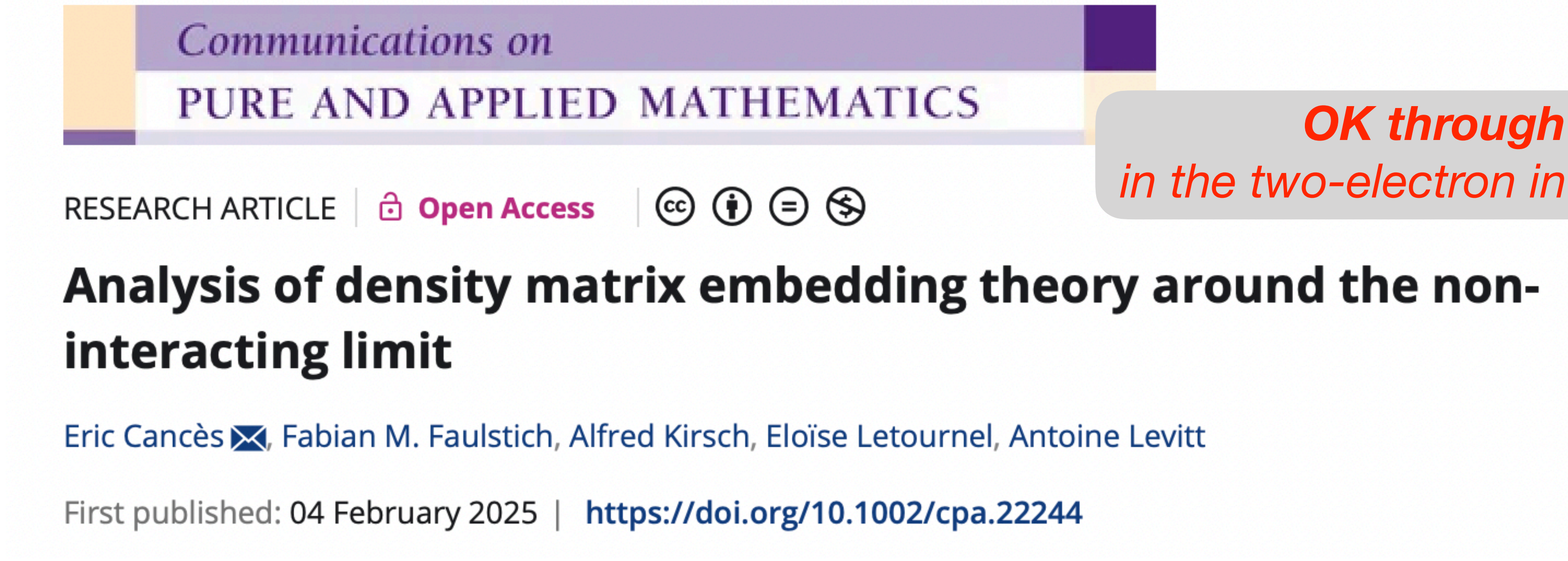
Correlated
cluster



Density matrix
mapping

Idempotent

Non-idempotent



Communications on
PURE AND APPLIED MATHEMATICS

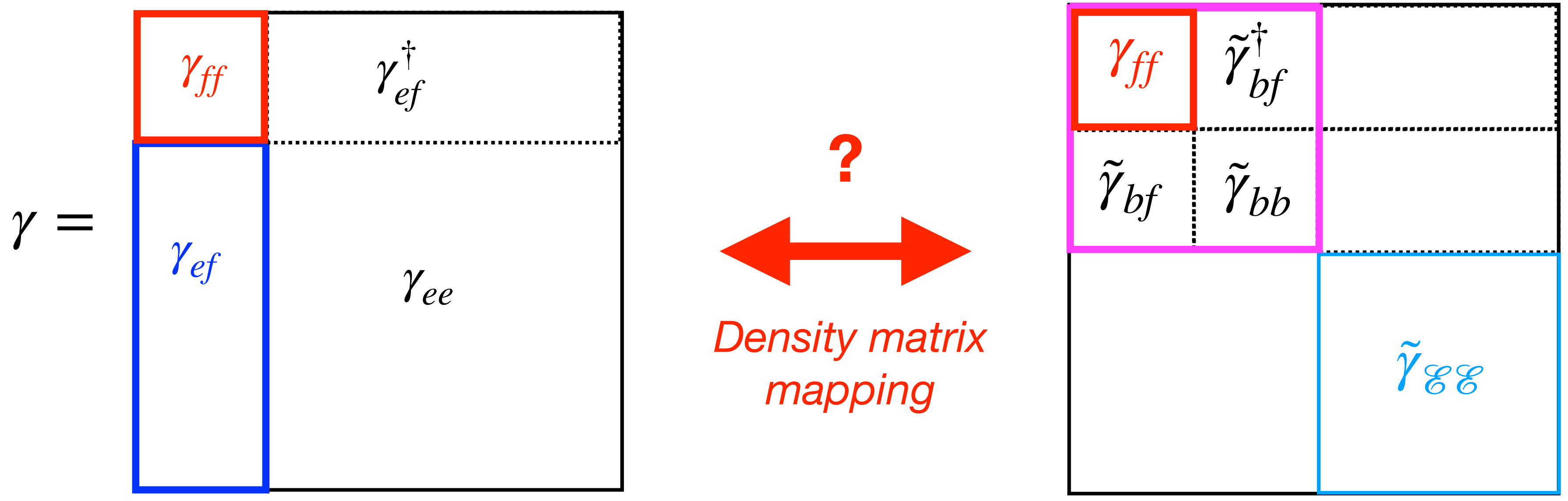
RESEARCH ARTICLE | Open Access

Analysis of density matrix embedding theory around the non-interacting limit

Eric Cancès, Fabian M. Faulstich, Alfred Kirsch, Eloïse Letournel, Antoine Levitt

First published: 04 February 2025 | https://doi.org/10.1002/cpa.22244

OK through first order
in the two-electron interaction strength…



Kohn-Sham-like
full system**?**

Correlated
cluster

Density matrix
mapping

Idempotent

Non-idempotent

JCTC Journal of Chemical Theory and Computation

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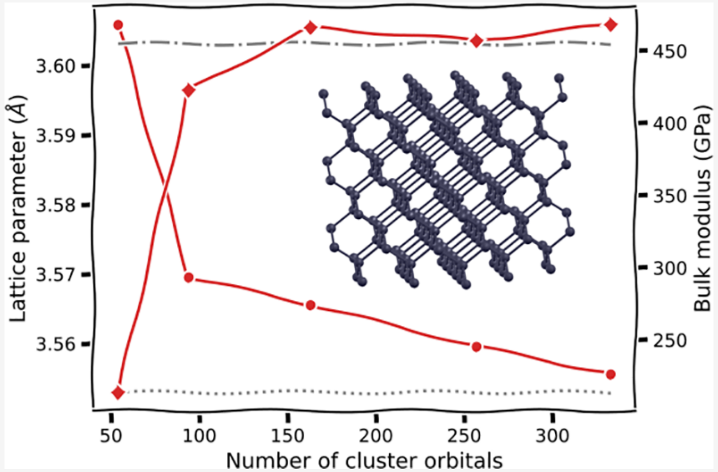
Effective Reconstruction of Expectation Values from Ab Initio Quantum Embedding

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

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

Read Online

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.

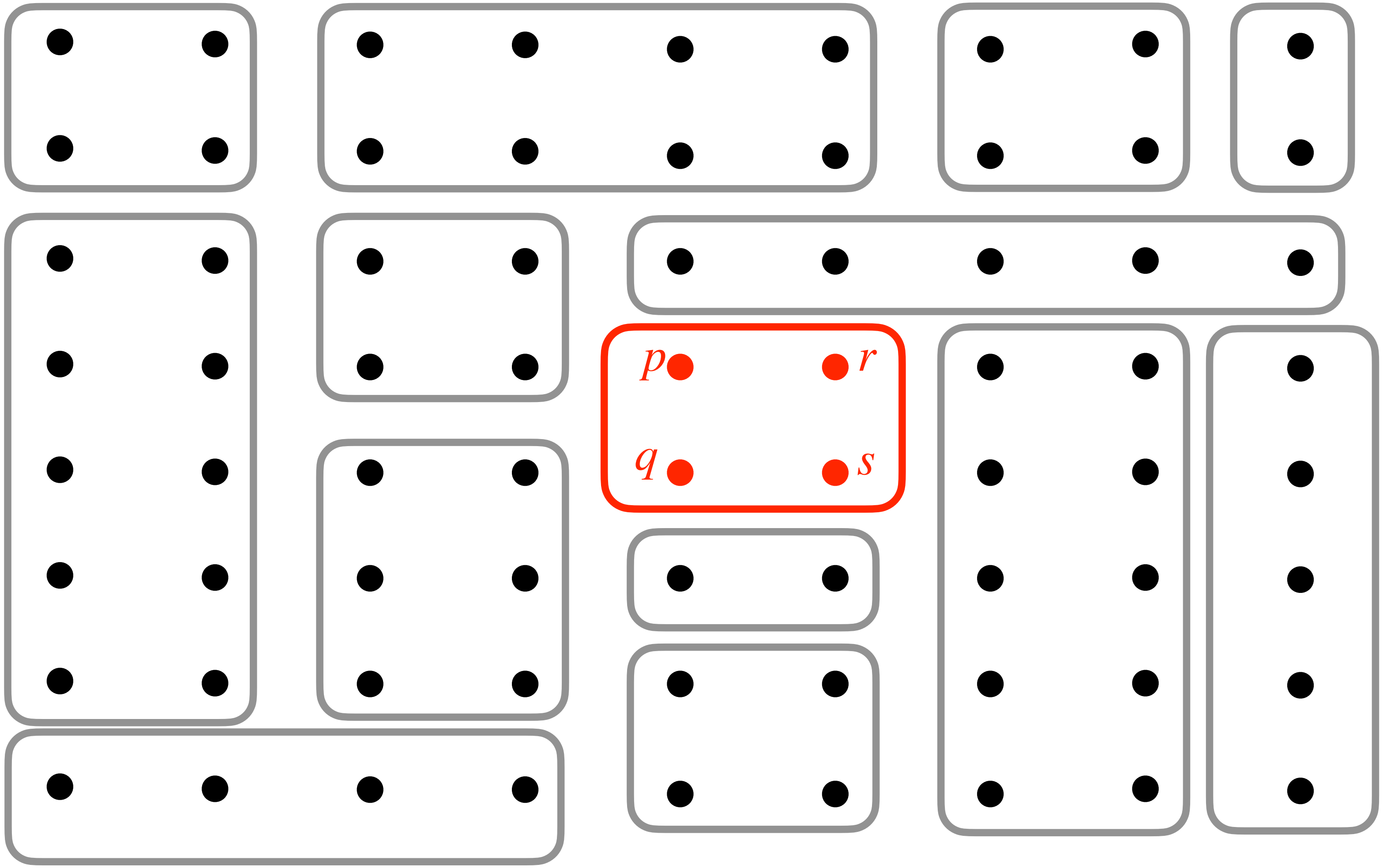


Local evaluation of the energy (in a localised spin-orbital basis)

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

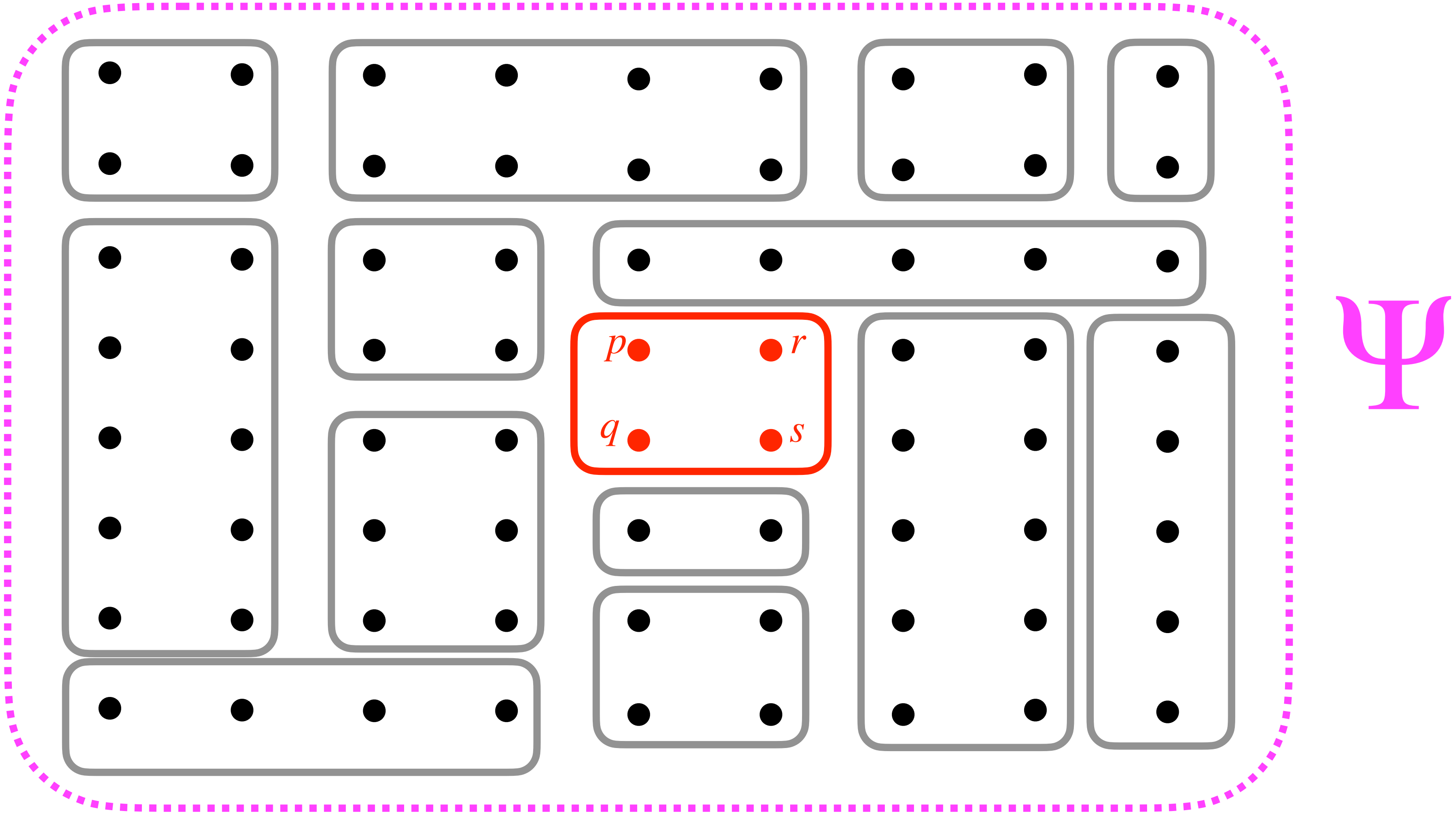


G. Knizia and G. K.-L. Chan, *Phys. Rev. Lett.* ***109***, *186404 (2012).*
S. Wouters, C. A. Jiménez-Hoyos, Q. Sun, and G. K.-L. Chan, J. Chem. Theory Comput. 12, 2706 (2016).

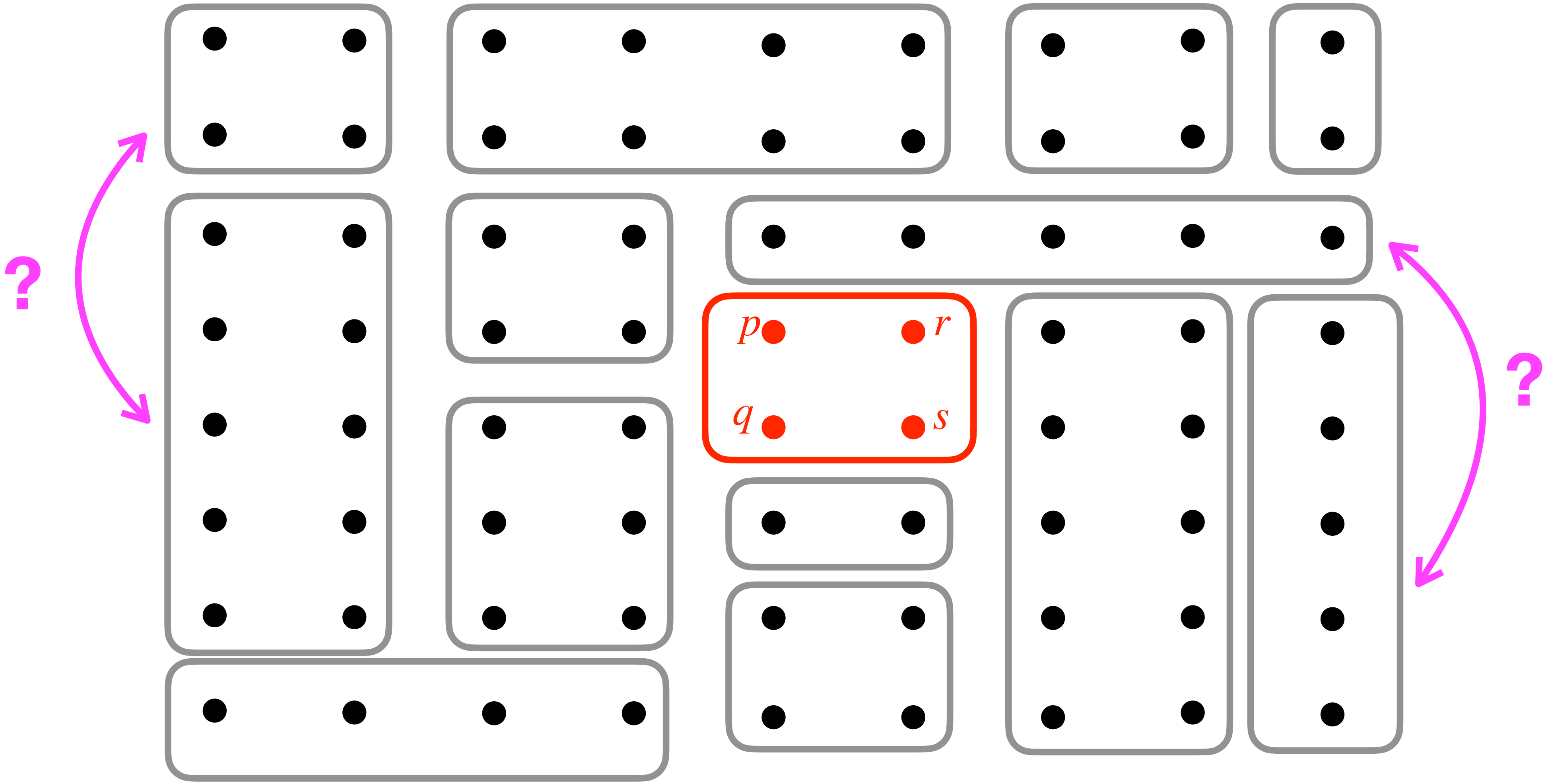
N-representability problem

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

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

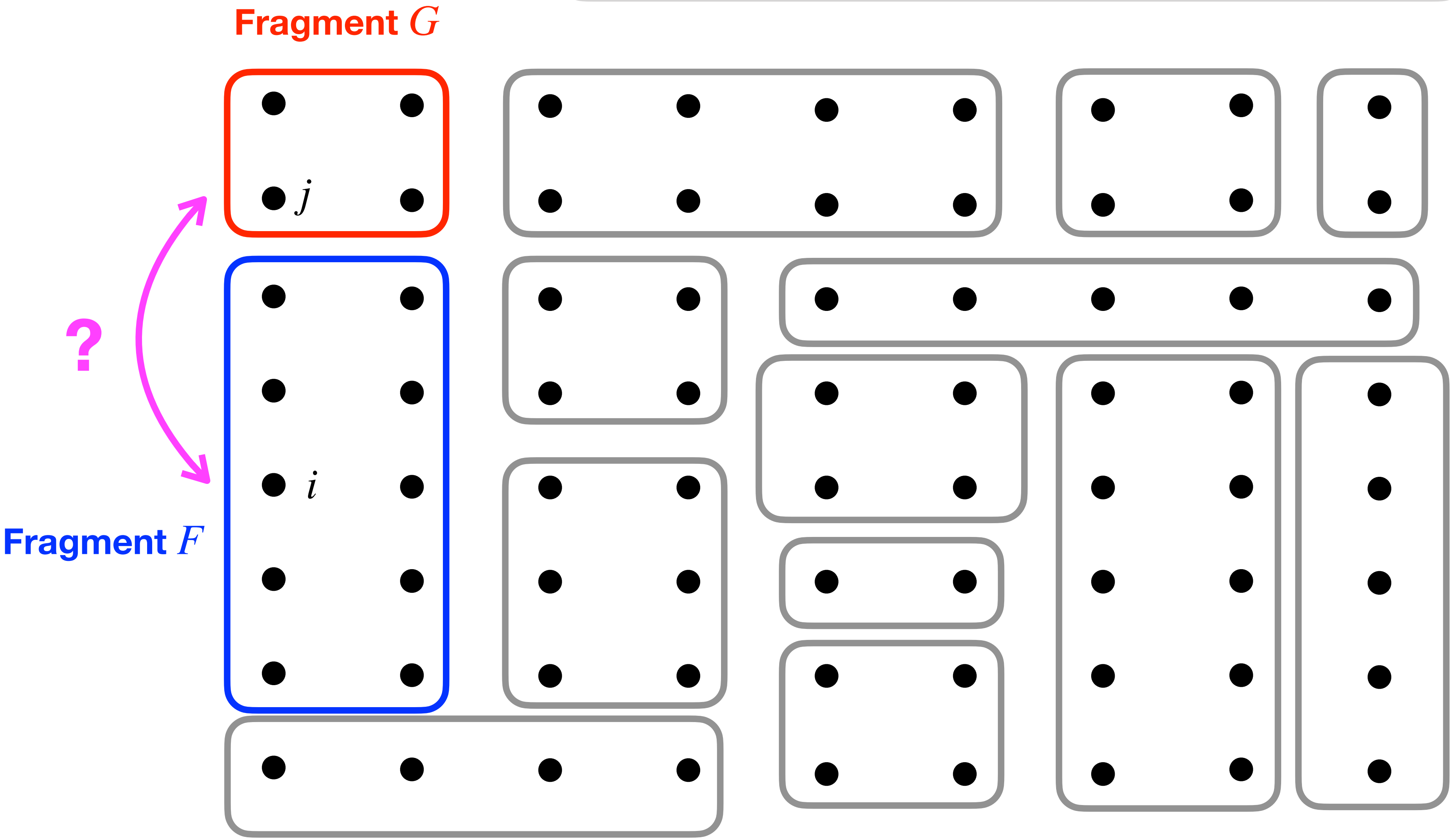


$$\langle \hat{H} \rangle = \sum_{pq} h_{pq} \underbrace{\langle \hat{c}_p^\dagger \hat{c}_q \rangle}_{\substack{\textbf{One-electron}\\ \text{density matrix}\\ \text{(1RDM)}}} + \frac{1}{2} \sum_{pqrs} \langle pq \,|\, rs \rangle \underbrace{\langle \hat{c}_p^\dagger \hat{c}_q^\dagger \hat{c}_s \hat{c}_r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



“Democratic” evaluation of RDMs from embedding clusters

$$\langle \hat{c}_i^\dagger \hat{c}_j \rangle \approx \frac{1}{2}\left(\langle \hat{c}_i^\dagger \hat{c}_j \rangle_{\mathscr{C}^F} + \langle \hat{c}_j^\dagger \hat{c}_i \rangle_{\mathscr{C}^G} \right)$$



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

DMET beyond “low-cost” idempotent ground-state density matrices

Non-idempotent reference 1-RDMs

- Correlated **reference** ground-state **density matrix** (for the full system)

Non-idempotent reference 1-RDMs

- **Correlated reference ground-state density matrix** (for the full system)

- **Multi-state LPFET** (extension to **excited states**)

Non-idempotent reference 1-RDMs

- **Correlated reference ground-state density matrix** (for the full system)

- **Multi-state LPFET** (extension to **excited states**)

Ensemble density matrix

$$\gamma = \sum_{\nu} \mathrm{w}_{\nu}\, \underset{\substack{\uparrow \\ \gamma_{\nu}^{2} = \gamma_{\nu}}}{\gamma_{\nu}} \neq \gamma^{2}$$

Fragment quantum embedding using the Householder transformation: A multi-state extension based on ensembles

Cite as: J. Chem. Phys. 161, 124107 (2024); doi: 10.1063/5.0229787
Submitted: 19 July 2024 • Accepted: 5 September 2024 •
Published Online: 23 September 2024

Filip Cernatic,[a] **Emmanuel Fromager,** **and Saad Yalouz**

AFFILIATIONS

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[a] **Author to whom correspondence should be addressed:** filip.cernatic@gmail.com

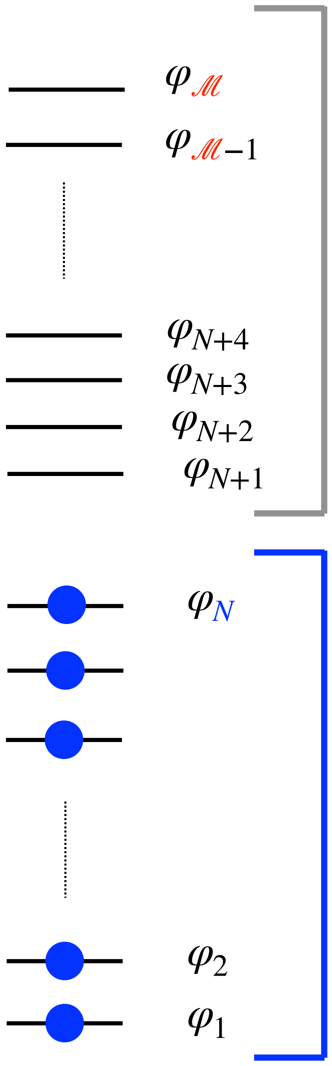
It is possible to design successive (Householder) unitary transformations

that **disentangle exactly** the embedding cluster from its environment!

But …

… the **bath is larger** and the cluster contains **more electrons**.

Quantum embedding from a wave function perspective



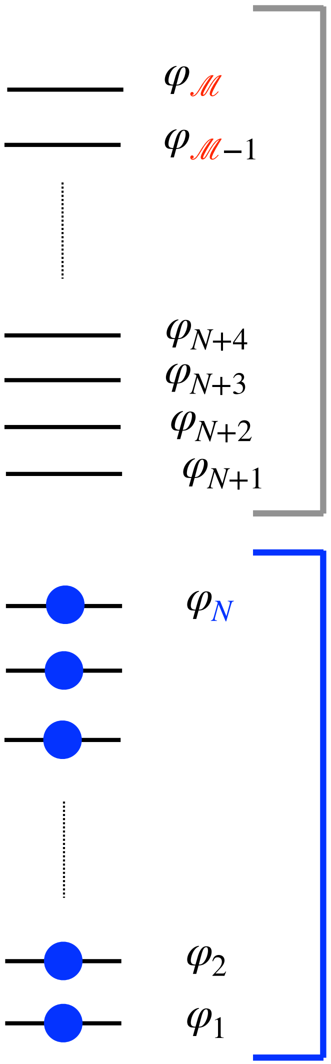
Mean-field (HF)
or Kohn-Sham DFT

$$|\Phi_0\rangle = \prod_{i=1}^{N} \hat{a}_i^{\dagger} |\mathrm{vac}\rangle \equiv |\varphi_1 \ldots \varphi_N|$$

$$|v_f\rangle = \left(\sum_{i=1}^{N} |\varphi_i\rangle\langle\varphi_i| \right) |\chi_f\rangle$$

***Projection** of each fragment spin-orbital*
onto the occupied spin-orbital space

Quantum embedding from a wave function perspective



Mean-field (HF)
or Kohn-Sham DFT

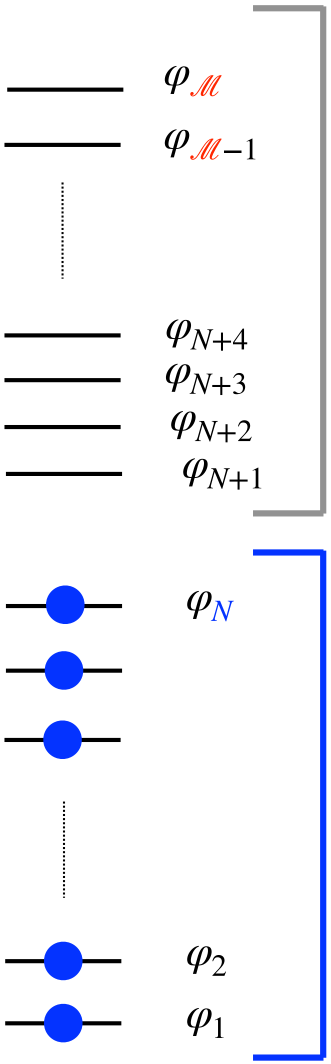
$$|\Phi_0\rangle = \prod_{i=1}^{N} \hat{a}_i^\dagger |\mathrm{vac}\rangle \equiv |\varphi_1 \ldots \varphi_N|$$

$$|v_f\rangle = \left(\sum_{i=1}^{N} |\varphi_i\rangle\langle\varphi_i| \right) |\chi_f\rangle$$

Orthonormalisation procedure

$$\langle v_f | v_{f'} \rangle = \left[\mathbf{T}\right]_{ff'}$$

Quantum embedding from a wave function perspective



Mean-field (HF)
or Kohn-Sham DFT

$$|\Phi_0\rangle = \prod_{i=1}^{N} \hat{a}_i^\dagger |\text{vac}\rangle \equiv |\varphi_1 \ldots \varphi_N|$$

$$|v_f\rangle = \left(\sum_{i=1}^{N} |\varphi_i\rangle\langle\varphi_i| \right) |\chi_f\rangle$$

$$\langle v_f | v_{f'}\rangle = \left[\mathbf{T}\right]_{ff'}$$

“Fragment-occupied” orthonormal spin-orbitals

$$\left\{ |\tilde{\varphi}_f\rangle = \sum_{f'} \left[\mathbf{T}^{-1/2}\right]_{ff'} |v_{f'}\rangle \right\}_{1\leq f\leq L_{\text{frag}}}$$

Quantum embedding from a wave function perspective

Orthogonal complement within the occupied spin-orbital space:

$$\underbrace{\Big\{|\tilde{\varphi}_i\rangle\Big\}_{L_{\rm frag}<i\leq N}}_{\text{“Core” spin-orbitals}} = \Big\{\underset{\substack{\Big\downarrow\\ \text{“Fragment-occupied”}\\ \text{spin-orbitals}}}{|\tilde{\varphi}_f\rangle}\Big\}^{\perp}_{1\leq f\leq L_{\rm frag}}$$

Quantum embedding from a wave function perspective

Orthogonal complement within the occupied spin-orbital space:

$$\underbrace{\left\{|\tilde{\varphi}_i\rangle\right\}_{L_{\mathrm{frag}}<i\leq N}}_{\text{“Core” spin-orbitals}} = \left\{|\tilde{\varphi}_f\rangle\right\}^{\perp}_{1\leq f\leq L_{\mathrm{frag}}}$$

$$\downarrow$$

“Fragment-occupied”
spin-orbitals

$$|\Phi_0\rangle \equiv |\tilde{\varphi}_1\ldots\tilde{\varphi}_{L_{\mathrm{Frag}}}\ \ \tilde{\varphi}_{L_{\mathrm{Frag}}+1}\ldots\tilde{\varphi}_N|$$

$$\equiv |\tilde{\varphi}_1\ldots\tilde{\varphi}_{L_{\mathrm{Frag}}}\Phi_{\mathrm{core}}|$$

Quantum embedding from a wave function perspective

Orthogonal complement within the occupied spin-orbital space:

$$\underbrace{\left\{|\tilde{\varphi}_i\rangle\right\}_{L_{\text{frag}}<i\leq N}}_{\textbf{“Core” spin-orbitals}} = \left\{\underset{\substack{\Big\downarrow\\ \text{“Fragment-occupied”}\\ \text{spin-orbitals}}}{|\tilde{\varphi}_f\rangle}\right\}^{\perp}_{1\leq f\leq L_{\text{frag}}}$$

$$|\Phi_0\rangle \equiv |\tilde{\varphi}_1\ldots\tilde{\varphi}_{L_{\text{Frag}}}\ \ \tilde{\varphi}_{L_{\text{Frag}}+1}\ldots\tilde{\varphi}_N|$$

$$\equiv |\tilde{\varphi}_1\ldots\tilde{\varphi}_{L_{\text{Frag}}}\Phi_{\text{core}}|$$

The core spin-orbitals have **no overlap with the fragment!**

$$\langle\tilde{\varphi}_i|\chi_f\rangle \overset{L_{\text{frag}}<i\leq N}{=} \left\langle\left(\sum_{i=1}^{N}|\varphi_i\rangle\langle\varphi_i|\right)\tilde{\varphi}_i\middle|\chi_f\right\rangle = \langle\tilde{\varphi}_i|v_f\rangle \overset{L_{\text{frag}}<i\leq N}{=} 0$$

Quantum embedding from a wave function perspective

Orthogonal complement within the occupied spin-orbital space:

$$\underbrace{\left\{|\tilde{\varphi}_i\rangle\right\}_{L_{\mathrm{frag}}<i\leq N}}_{\text{“Core” spin-orbitals}} = \left\{|\underset{\downarrow}{\tilde{\varphi}_f}\rangle\right\}^{\perp}_{1\leq f\leq L_{\mathrm{frag}}}$$

“Fragment-occupied”
spin-orbitals

$$|\Phi_0\rangle \equiv |\tilde{\varphi}_1\ldots\tilde{\varphi}_{L_{\mathrm{Frag}}} \;\; \tilde{\varphi}_{L_{\mathrm{Frag}}+1}\ldots\tilde{\varphi}_N|$$

$$\equiv \boxed{|\tilde{\varphi}_1\ldots\tilde{\varphi}_{L_{\mathrm{Frag}}}}\,\Phi_{\mathrm{core}}|$$

We can calculate the 1RDM with only L_{Frag} electrons!

Quantum embedding from a wave function perspective

The fragment-occupied spin-orbitals **overlap both with the fragment and its environment:**

$$\left\{ |\tilde{\varphi}_f\rangle \right\}_{1\leq f\leq L_{\text{frag}}} = \left\{ \sum_{i=1}^{N} \langle \varphi_i | \chi_f \rangle \, |\varphi_i\rangle \right\}$$

Quantum embedding from a wave function perspective

The fragment-occupied spin-orbitals overlap both with the fragment and its environment:

$$\left\{ |\tilde{\varphi}_f\rangle \right\}_{1\leq f\leq L_{\rm frag}} = \left\{ \sum_{i=1}^{N} \langle \varphi_i | \chi_f \rangle \, |\varphi_i\rangle \right\}$$

In order to recover them variationally, we can distribute the $L_{\rm Frag}$ electrons among the $L_{\rm Frag}$ spin-orbitals of the fragment

+

the $L_{\rm Frag}$ fragment-occupied spin-orbitals projected onto the fragment's **environment:**

$$\underbrace{\left\{ |\chi_f\rangle \right\}_{1\leq f\leq L_{\rm frag}}}_{\textbf{Fragment}} \oplus \left\{ \sum_{e\notin {\rm Fragment}} \underbrace{\sum_{i=1}^{N} \langle \chi_e | \varphi_i \rangle \langle \varphi_i | \chi_f \rangle}_{\gamma_{ef}} \, |\chi_e\rangle \right\}$$

Quantum embedding from a wave function perspective

Embedding cluster

$$\underbrace{\left\{|\chi_f\rangle\right\}_{1\leq f\leq L_{\text{frag}}}}_{\textbf{Fragment}} \oplus \underbrace{\left\{\sum_{e\notin\text{Fragment}} \underbrace{\sum_{i=1}^{N}\langle\chi_e|\varphi_i\rangle\langle\varphi_i|\chi_f\rangle}_{\gamma_{ef}}|\chi_e\rangle\right\}}_{\textbf{Bath one-electron subspace!}}$$

$$|\Phi_0\rangle = \sum_\lambda \boxed{C_\lambda \boxed{\left(\hat{d}_1^\dagger\right)^{n_1^\lambda}\ldots\left(\hat{d}_{L_{\text{frag}}}^\dagger\right)^{n_{L_{\text{frag}}}^\lambda}}\boxed{\left(\hat{d}^\dagger_{L_{\text{frag}}+1}\right)^{n^\lambda_{L_{\text{frag}}+1}}\ldots\left(\hat{d}^\dagger_{2L_{\text{frag}}}\right)^{n^\lambda_{2L_{\text{frag}}}}}}|\Phi_{\text{core}}\rangle$$

$$\sum_{i=1}^{2L_{\text{Frag}}} n_i^\lambda = L_{\text{Frag}}, \quad \forall\lambda$$

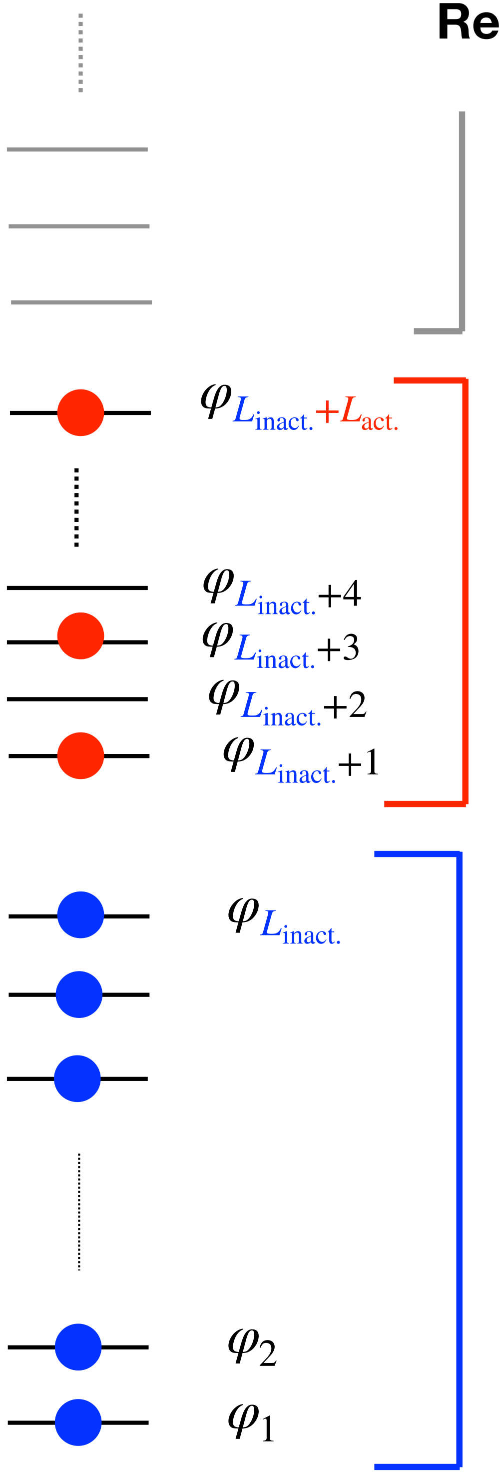
Quantum embedding from a wave function perspective

“Schmidt decomposition of Φ_0”

$$|\Phi_0\rangle = \sum_\lambda C_\lambda \boxed{\left(\hat{d}_1^\dagger\right)^{n_1^\lambda} \ldots \left(\hat{d}_{L_{\text{frag}}}^\dagger\right)^{n_{L_{\text{frag}}}^\lambda}} \boxed{\left(\hat{d}_{L_{\text{frag}}+1}^\dagger\right)^{n_{L_{\text{frag}}+1}^\lambda} \ldots \left(\hat{d}_{2L_{\text{frag}}}^\dagger\right)^{n_{2L_{\text{frag}}}^\lambda}} |\Phi_{\text{core}}\rangle$$

$$\sum_{i=1}^{2L_{\text{Frag}}} n_i^\lambda = L_{\text{Frag}}, \quad \forall \lambda$$

Reference full-system molecular orbital representation



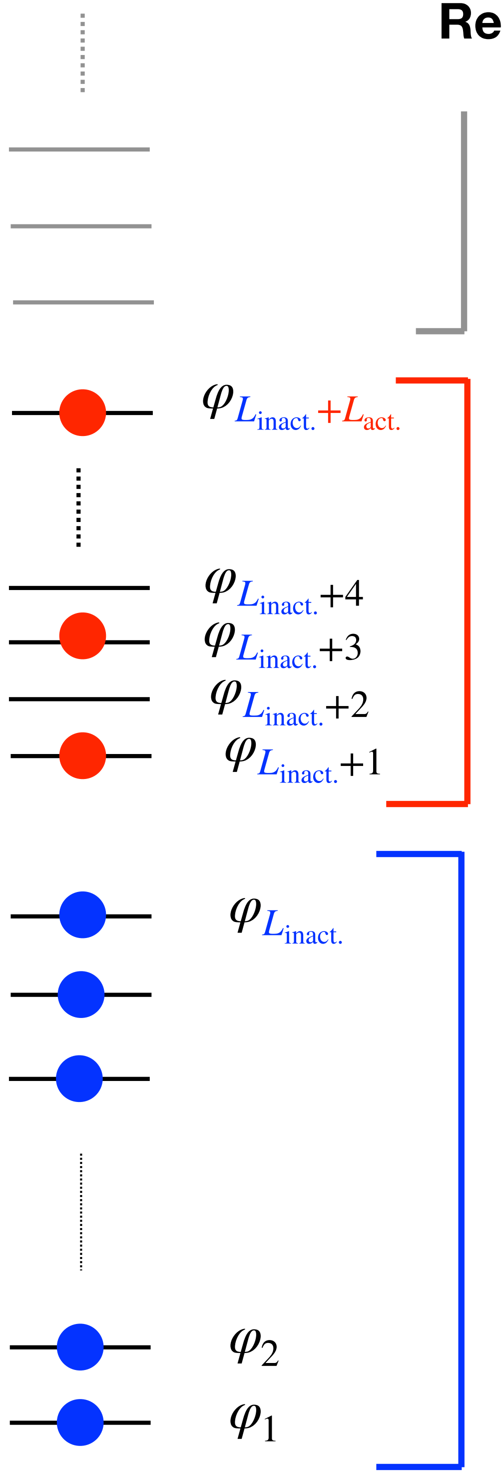
Virtuals

$N_{\text{act.}}$ electrons in
$L_{\text{act.}}$ active spin-orbitals

Inactive (core) spin-orbitals

F. Cernatic, E. Fromager, and S. Yalouz, J. Chem. Phys. **161**, 124107 (2024).

Reference full-system molecular orbital representation



Virtuals

$N_{\text{act.}}$ electrons in
$L_{\text{act.}}$ active spin-orbitals

Inactive (core) spin-orbitals →

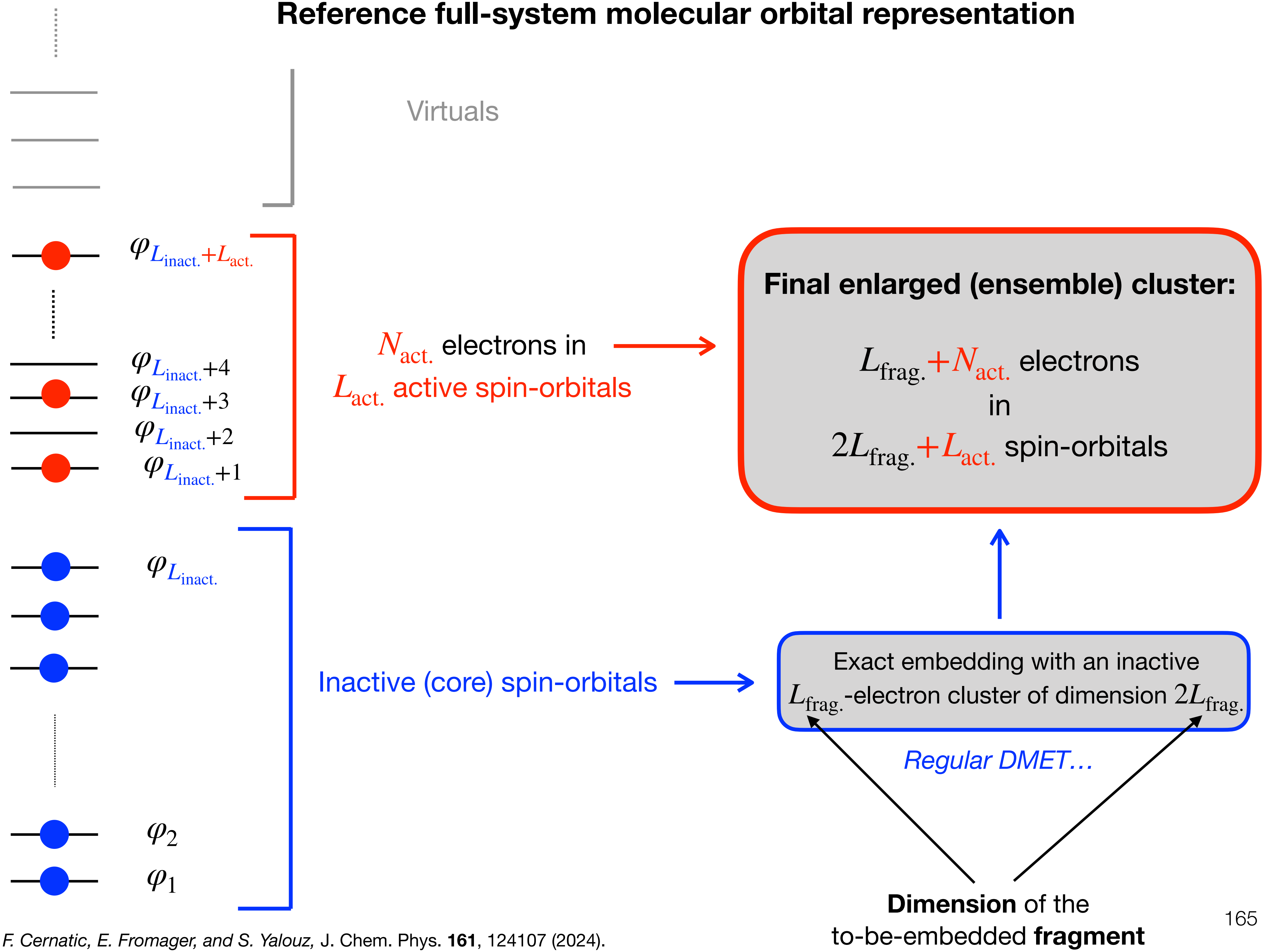
Exact embedding with an inactive
$L_{\text{frag.}}$-electron cluster of dimension $2L_{\text{frag.}}$

Regular DMET…

Dimension of the
to-be-embedded **fragment**

F. Cernatic, E. Fromager, and S. Yalouz, J. Chem. Phys. **161**, 124107 (2024).

Reference full-system molecular orbital representation



Virtuals

$\varphi_{L_{\text{inact.}}+L_{\text{act.}}}$

$\varphi_{L_{\text{inact.}}+4}$

$\varphi_{L_{\text{inact.}}+3}$

$\varphi_{L_{\text{inact.}}+2}$

$\varphi_{L_{\text{inact.}}+1}$

$\varphi_{L_{\text{inact.}}}$

φ_2

φ_1

$N_{\text{act.}}$ electrons in
$L_{\text{act.}}$ active spin-orbitals

Final enlarged (ensemble) cluster:

$L_{\text{frag.}}+N_{\text{act.}}$ electrons
in
$2L_{\text{frag.}}+L_{\text{act.}}$ spin-orbitals

Inactive (core) spin-orbitals

Exact embedding with an inactive $L_{\text{frag.}}$-electron cluster of dimension $2L_{\text{frag.}}$

Regular DMET…

Dimension of the
to-be-embedded **fragment**

F. Cernatic, E. Fromager, and S. Yalouz, J. Chem. Phys. **161**, 124107 (2024).

Ensemble DMET

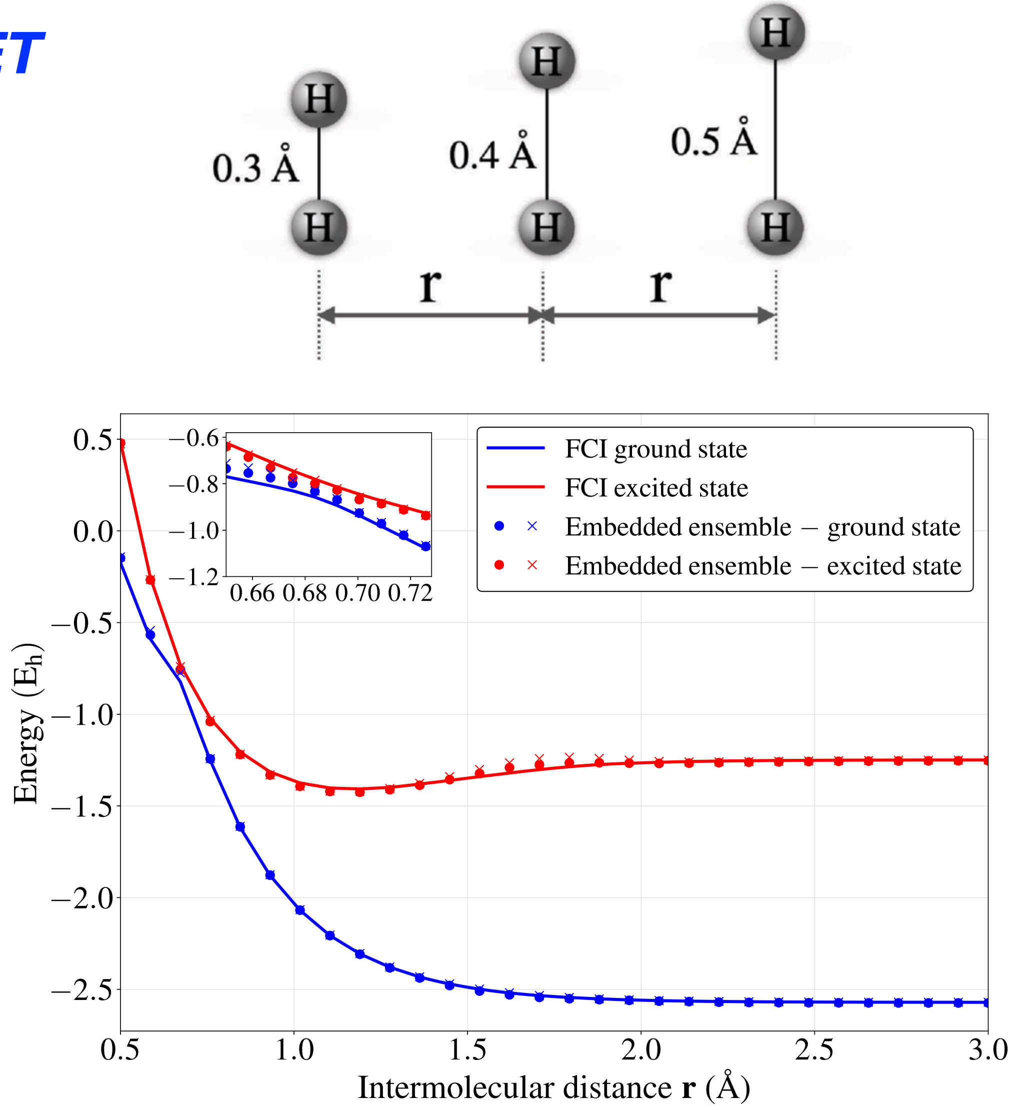


FIG. 5. Top: a schematic picture of the system of hydrogen atoms by Tran *et al.*[24] **Bottom**: dissociation curves of the FCI ground and first excited singlet states (blue and red lines, respectively), and the embedding results for the ground and first excited state (blue and red markers, respectively) for the system of hydrogen atoms. The embedding results are plotted with and without chemical potential optimization [dot (●) and cross (×) markers, respectively].

F. Cernatic, E. Fromager, and S. Yalouz, J. Chem. Phys. **161**, 124107 (2024).
[24] *H. K. Tran, T. Van Voorhis, and A. J. W. Thom,* J. Chem. Phys. **151**, 034112 (2019).