An introduction to density matrix embedding theory

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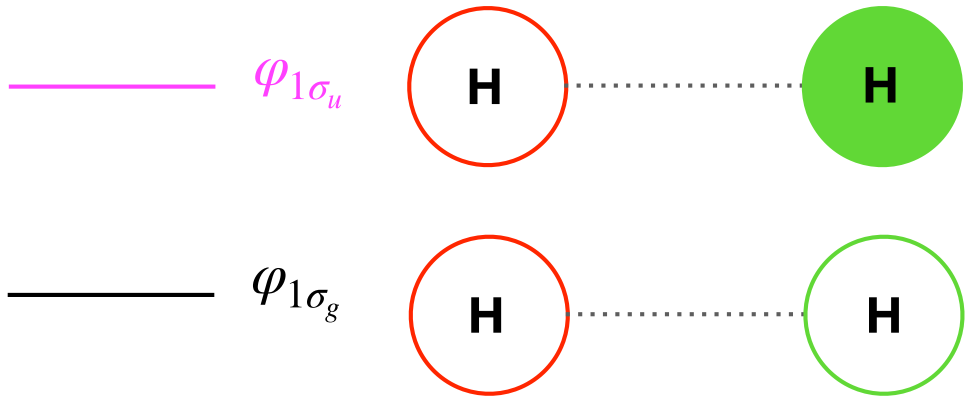
https://lcqs.unistra.fr/wordpress/wp-content/uploads/dlm_uploads/2025/02/DMET_lecture_workshop_Austria_2025_Fromager-2.pdf

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

A few words about strong electron correlation

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



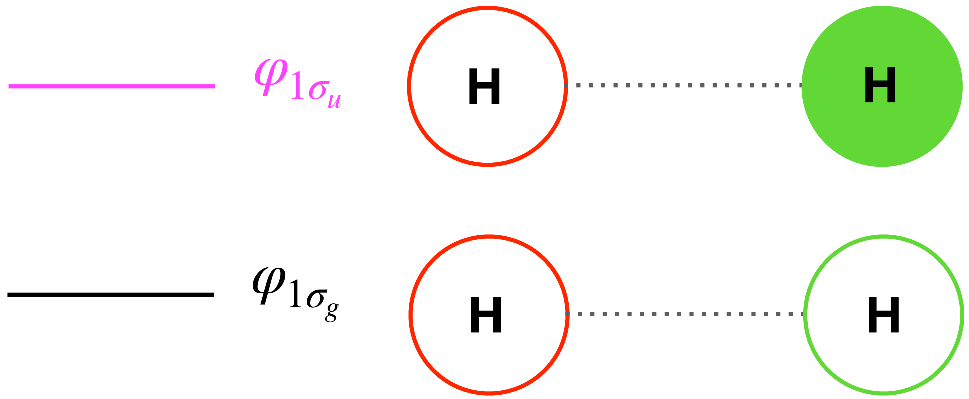
Anti-bonding orbital

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

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

Bonding orbital

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



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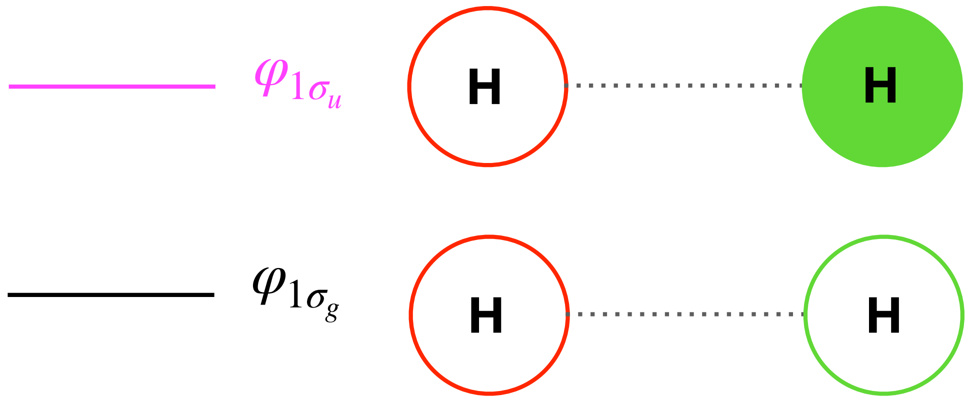
Bonding orbital

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

← **Delocalised picture (Chemistry)**

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

Anti-bonding orbital



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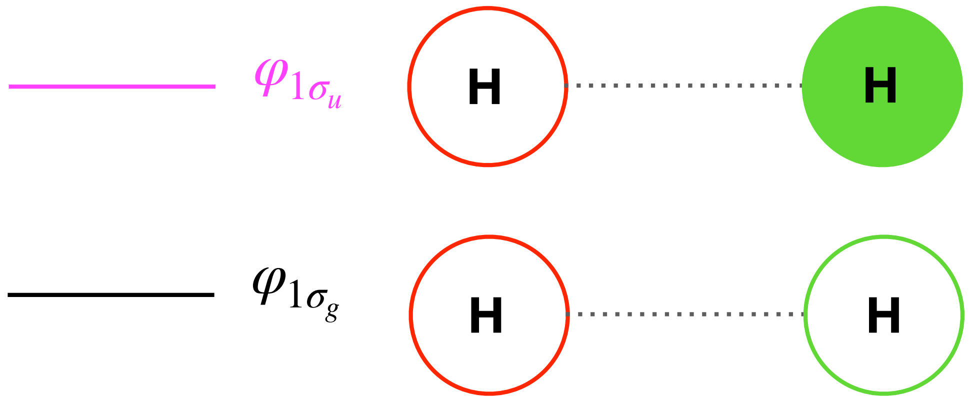
$$= \frac{1}{\sqrt{2}}\left(\chi_{s_A}(\mathbf{r}_1)\chi_{s_B}(\mathbf{r}_2) + \chi_{s_A}(\mathbf{r}_2)\chi_{s_B}(\mathbf{r}_1)\right)$$

← **Localised picture (Physics)**

H ······· **H**   **H** ······· **H**

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

Anti-bonding orbital



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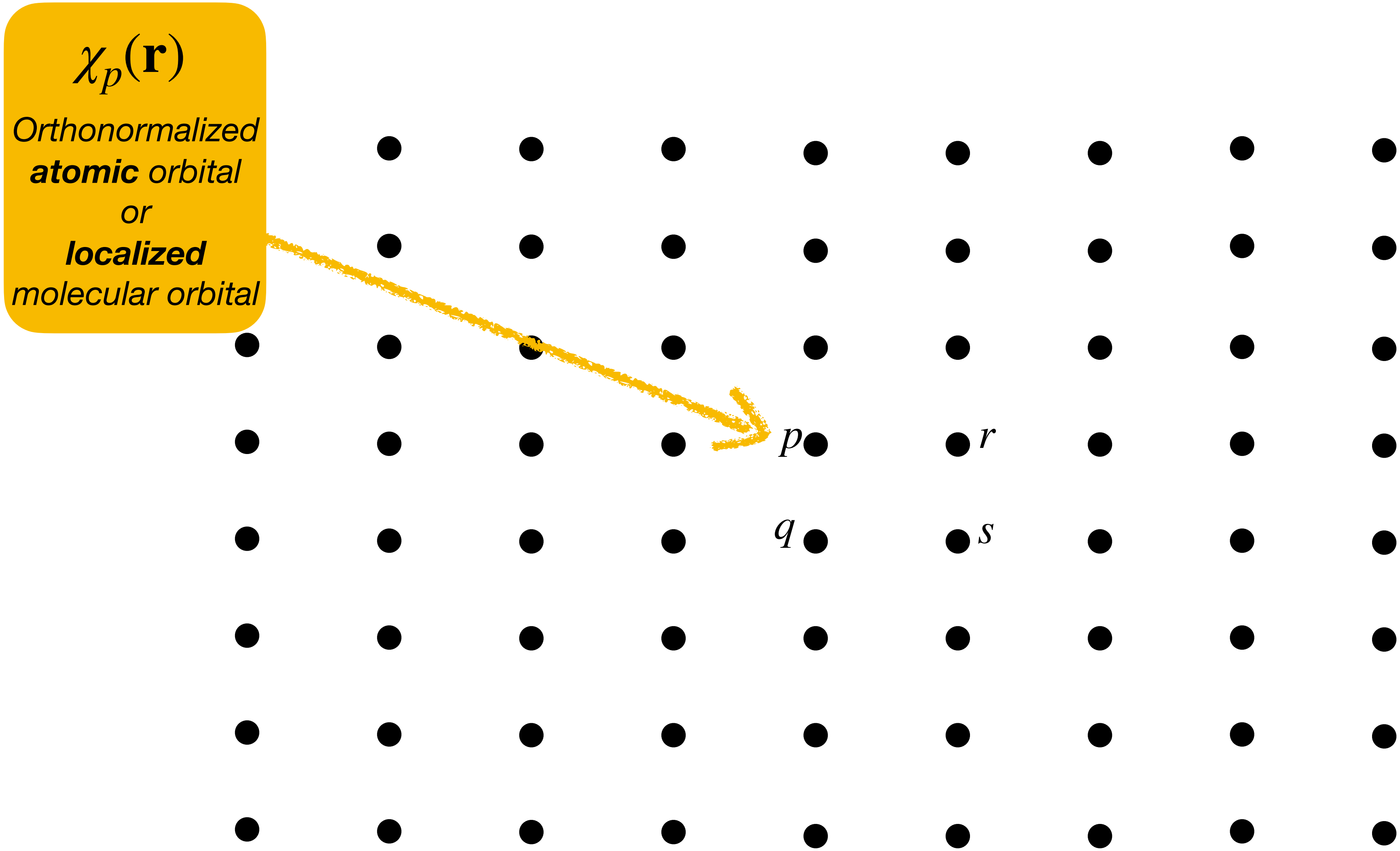
← **Localised picture (Physics)**

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

Consequence of the electronic repulsion on each atom!

“Lattice” representation of a molecular or extended system



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 basis of molecular spin orbitals* $\{\varphi_P\}_{P=1,2,3,\ldots,\mathscr{M}}$

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

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

See the video for further explanations*

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

Schrödinger equation in second quantization

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annihilation operators

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

creation operators

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

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 basis of molecular spin orbitals* $\{\varphi_P\}_{P=1,2,3,\ldots,\mathcal{M}}$

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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

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

Evaluation of the energy from the reduced density matrices

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

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One-electron reduced density matrix (1RDM)

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

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One-electron reduced density matrix (1RDM)

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

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

Evaluation of the energy from the reduced density matrices

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One-electron reduced density matrix (1RDM)

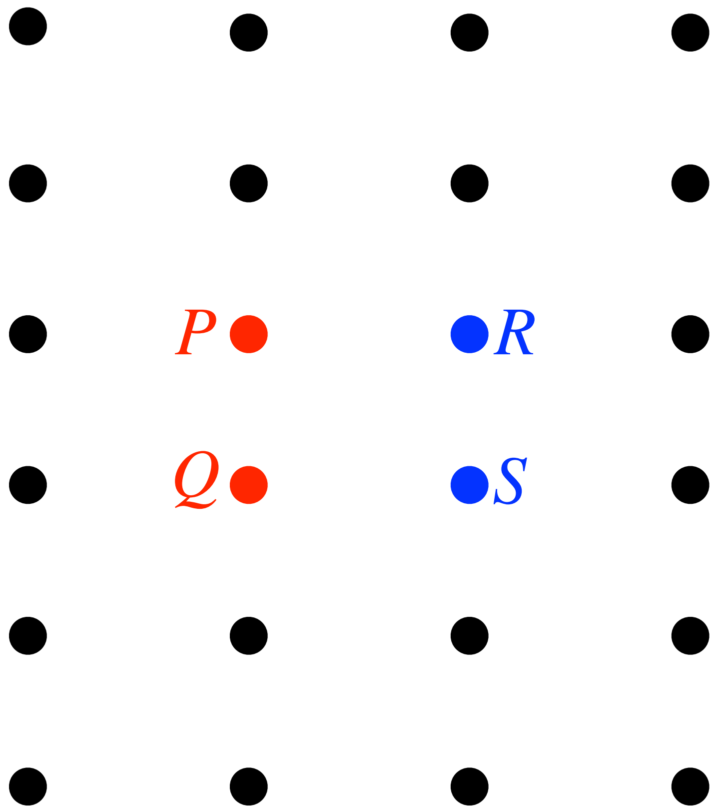
Two-electron reduced density matrix (2RDM)

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

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

Meaning of the reduced density matrices

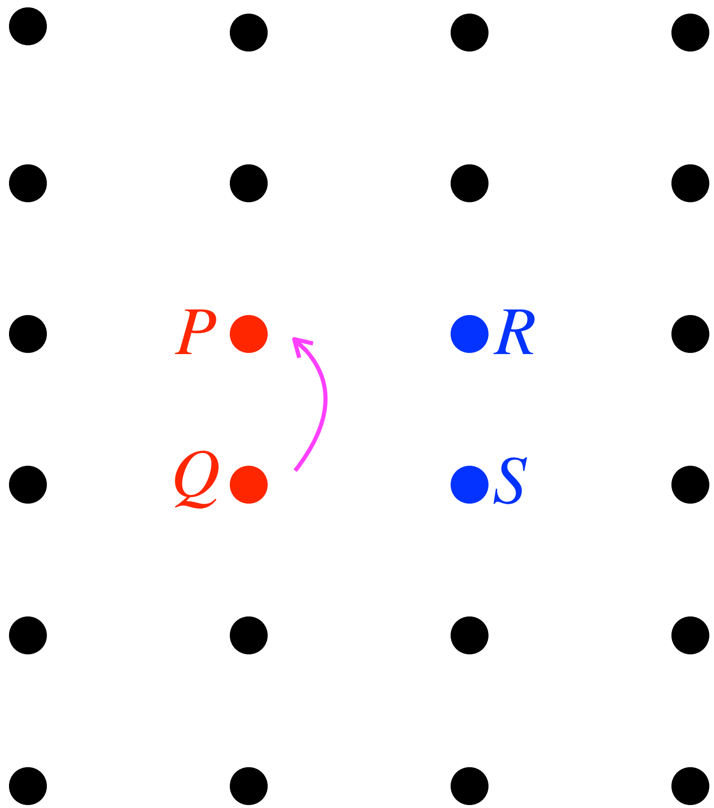
Let's consider a 2D lattice of localised spin-orbitals



Meaning of the reduced density matrices

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

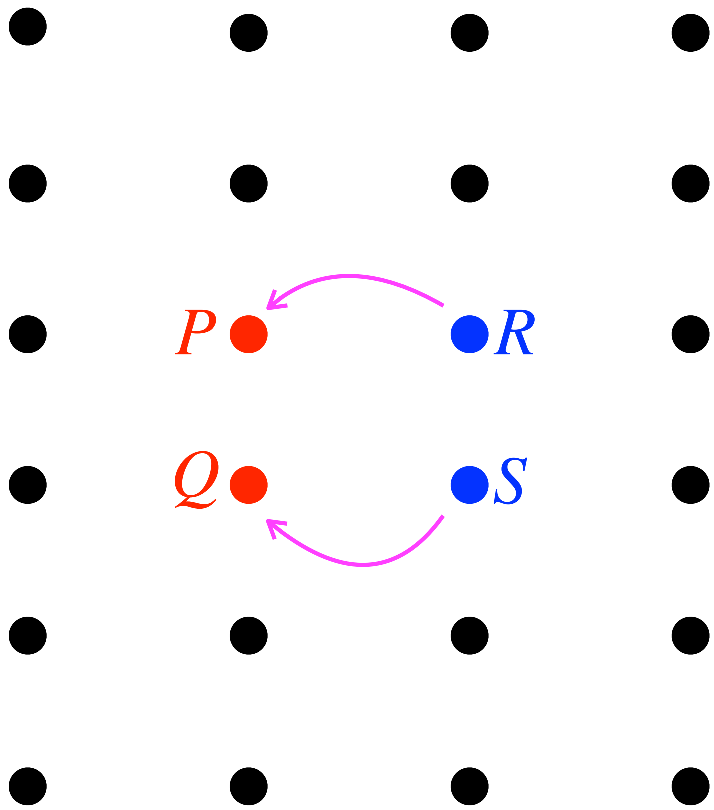
1RDM



Meaning of the reduced density matrices

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

2RDM



Meaning of the reduced density matrices

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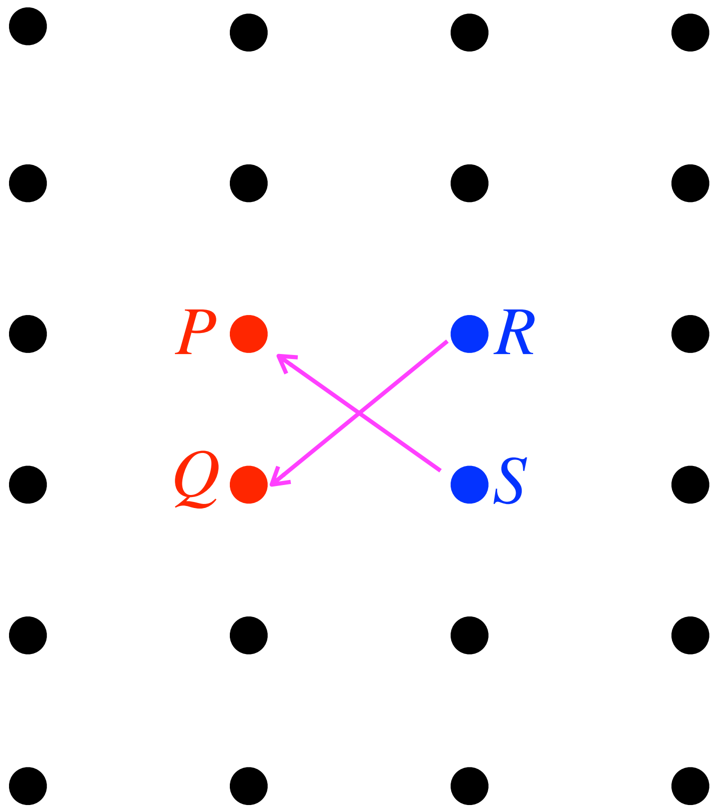
2RDM



Evaluation of the energy from the reduced density matrices

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

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One-electron reduced density matrix (1RDM)

Two-electron reduced density matrix (2RDM)

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

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

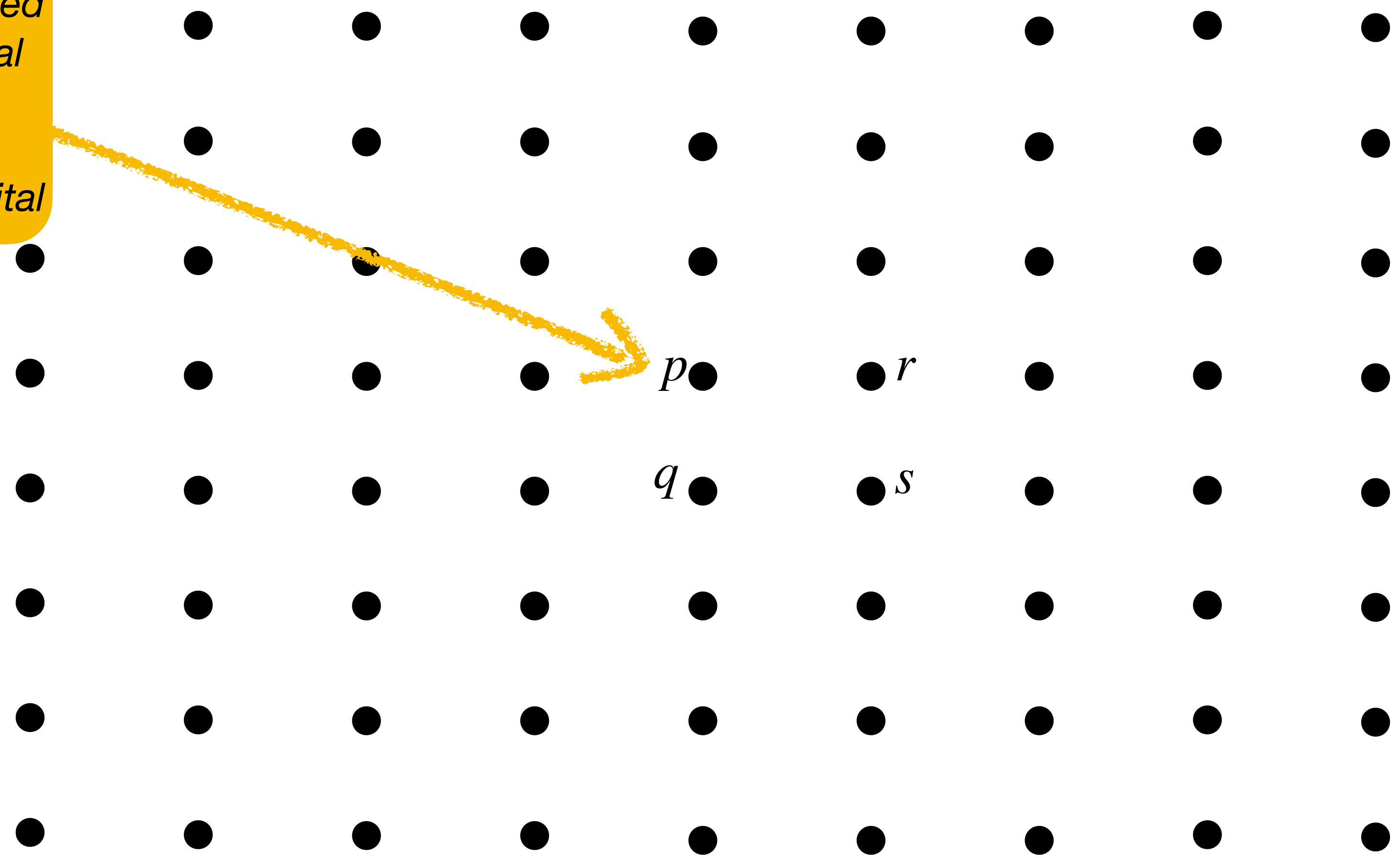
Local evaluation of the energy (in a localised spin-orbital basis)

So-called "lattice" representation

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

$\chi_p(\mathbf{r})$

Orthonormalized
atomic *orbital*
or
localized
molecular orbital



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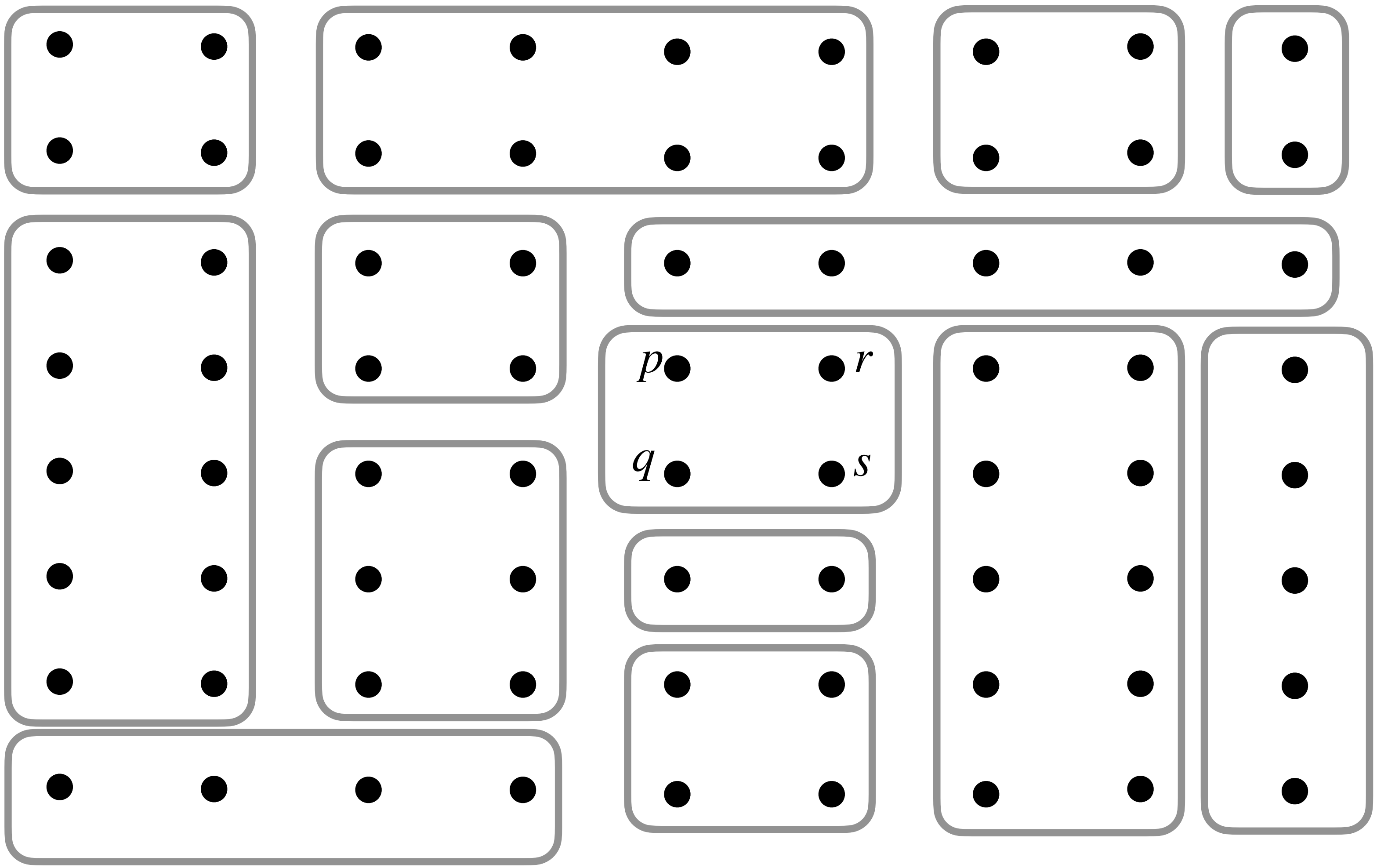
Fragmentation

for treating strong local electron correlations



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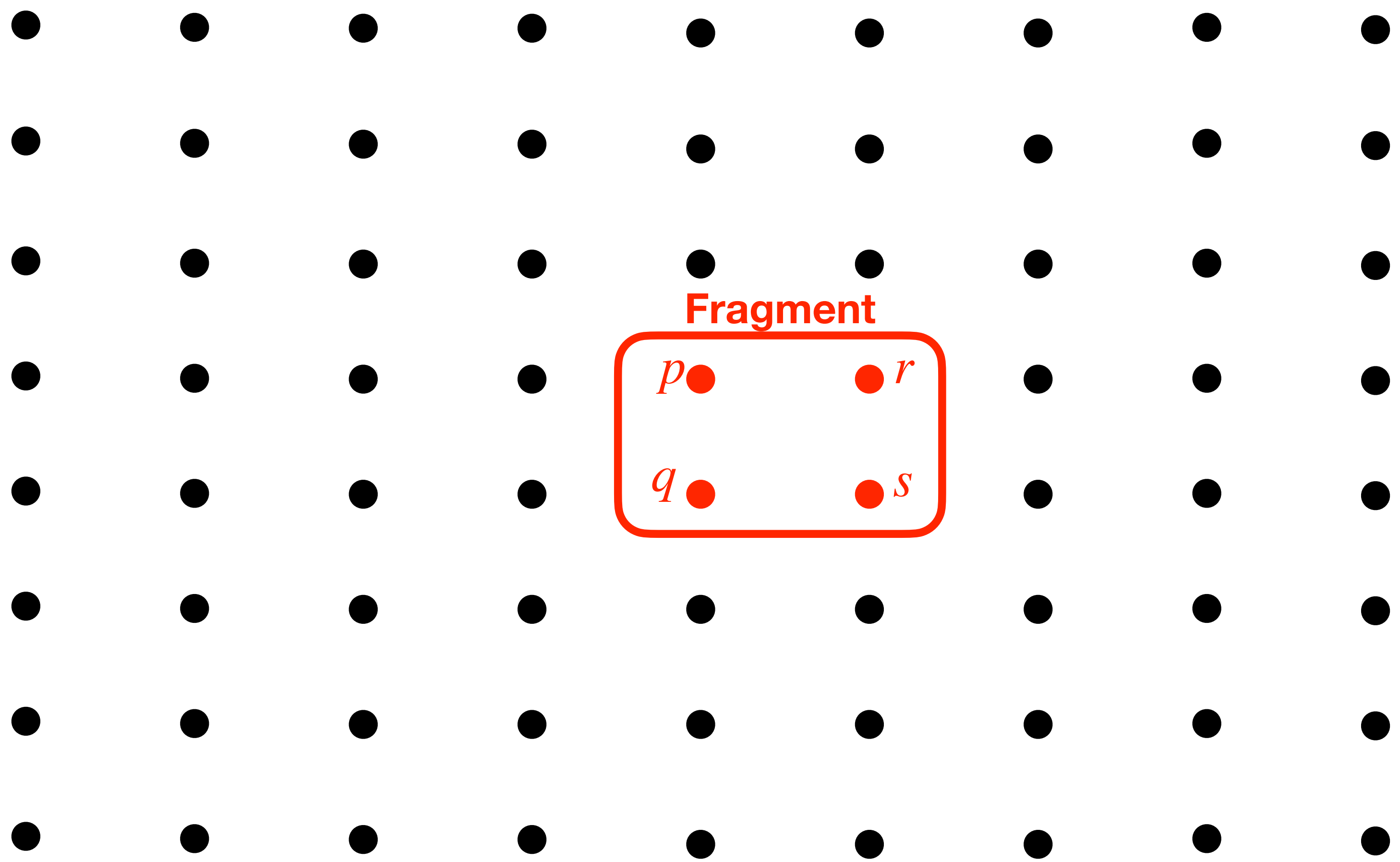

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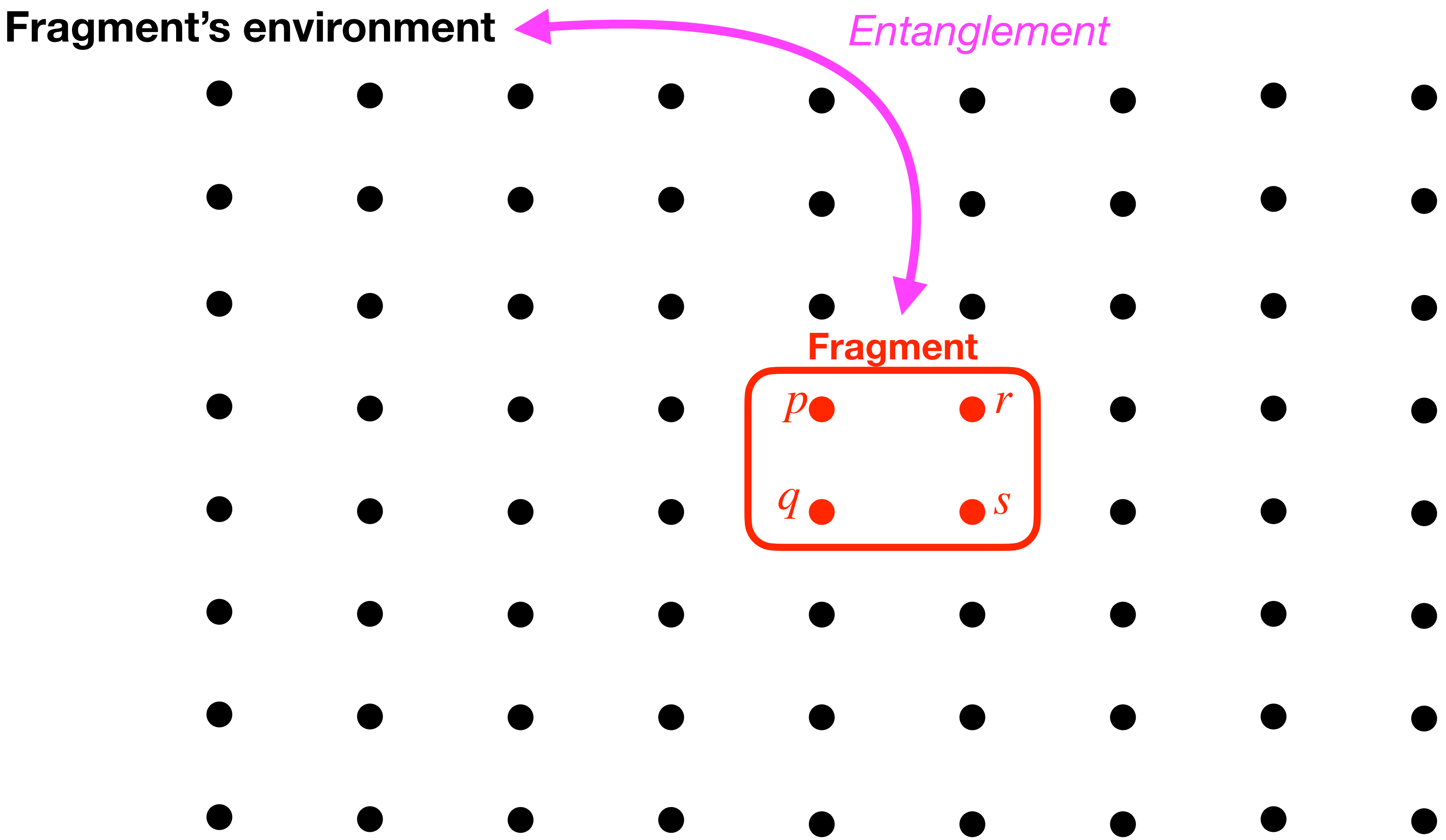

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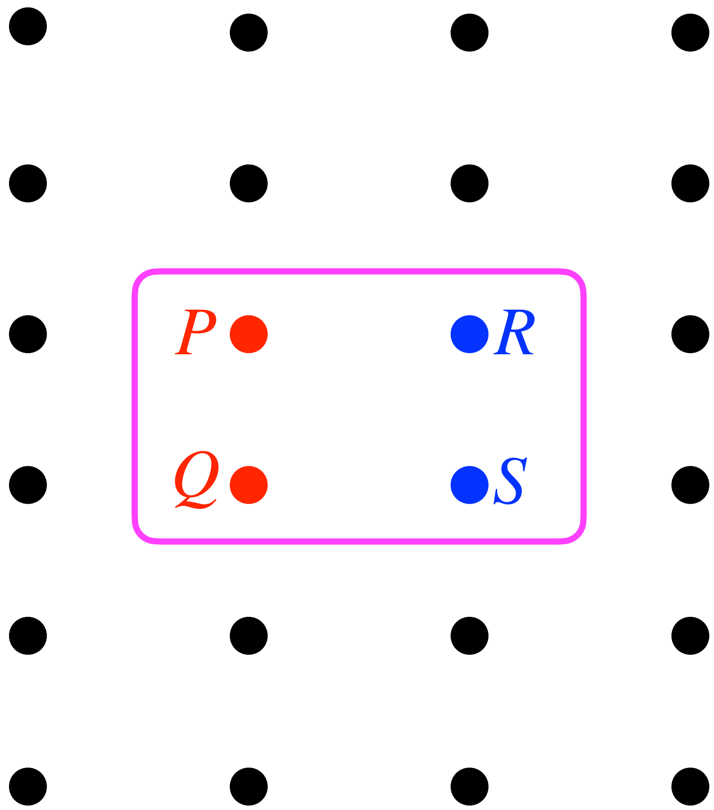
Quantum entanglement of a fragment with its environment

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



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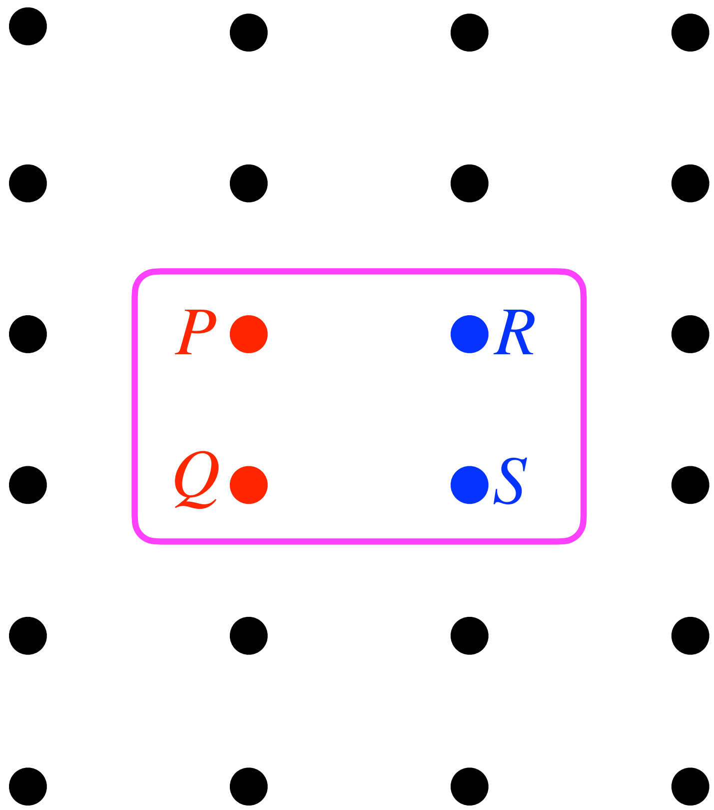


Open quantum subsystem

Quantum entanglement of a fragment with its environment

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

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

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

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:

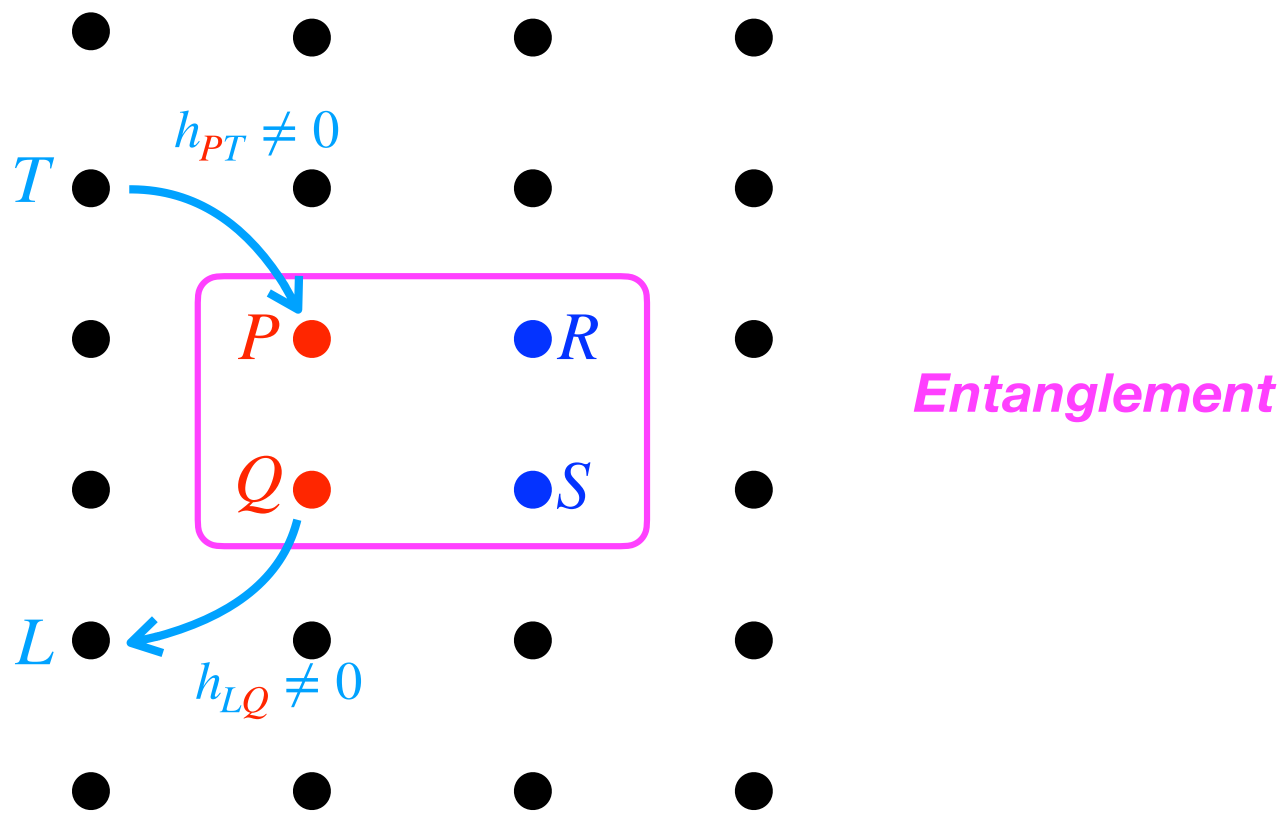
$$\hat{H} | \Psi_0 \rangle = E_0 | \Psi_0 \rangle$$

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

$$\hat{H} \equiv \sum_{PQ} h_{PQ}\,\hat{c}^{\dagger}_{P}\hat{c}_{Q} + \frac{1}{2}\sum_{PQRS} g_{PQRS}\,\hat{c}^{\dagger}_{P}\hat{c}^{\dagger}_{Q}\hat{c}_{S}\hat{c}_{R}$$

Summation running
over the **full lattice!**



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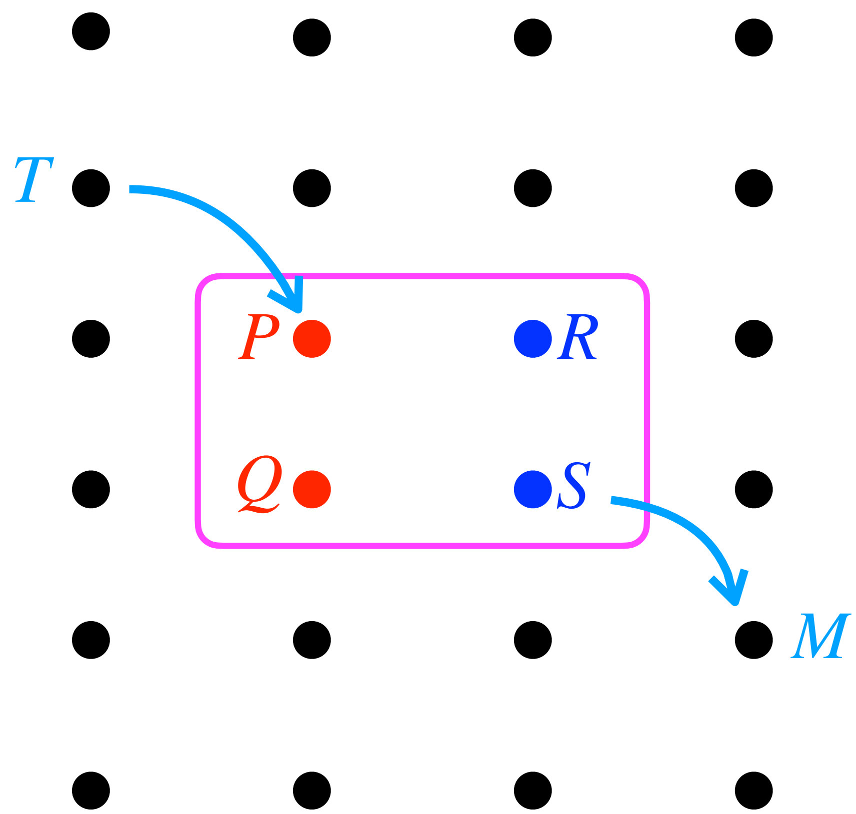


$$g_{PMTS} \neq 0$$

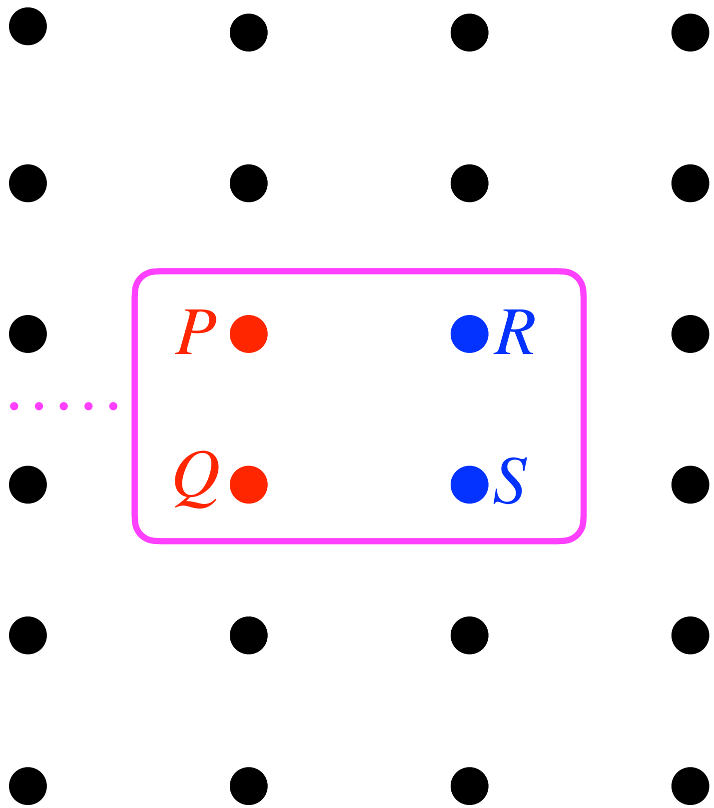
Entanglement

Quantum entanglement of a fragment with its environment

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

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

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



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

G. Knizia and G. K.-L. Chan, Phys. Rev. Lett. ***109****, 186404 (2012).*
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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

Gerald Knizia and Garnet Kin-Lic Chan

Department of Chemistry, Frick Laboratory, Princeton University, Princeton, New Jersey 08544, USA

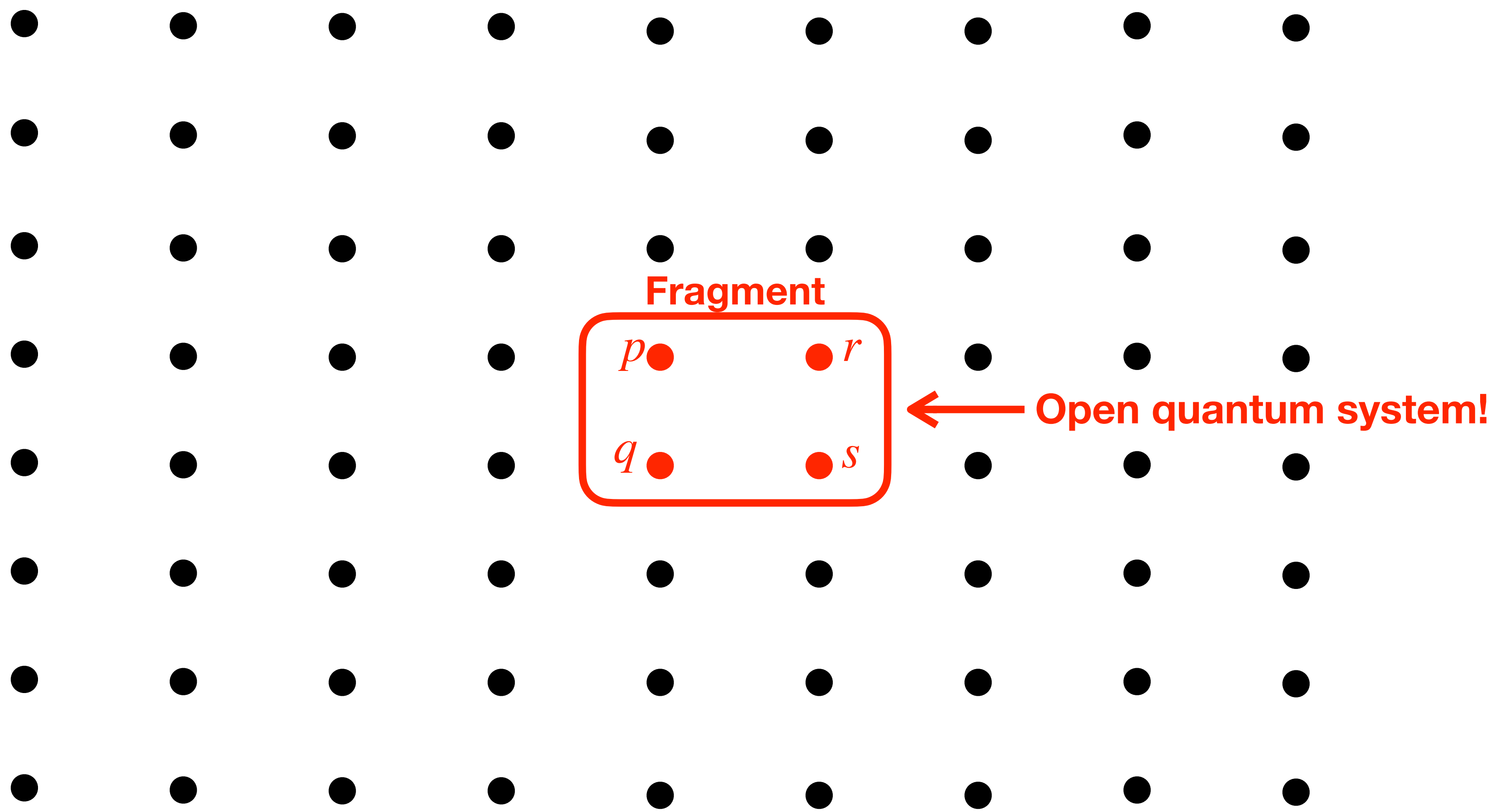
(Received 25 April 2012; published 2 November 2012)

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.

DOI: 10.1103/PhysRevLett.109.186404 PACS numbers: 71.10.Fd, 71.27.+a, 71.30.+h, 74.72.−h

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

So-called "lattice" representation



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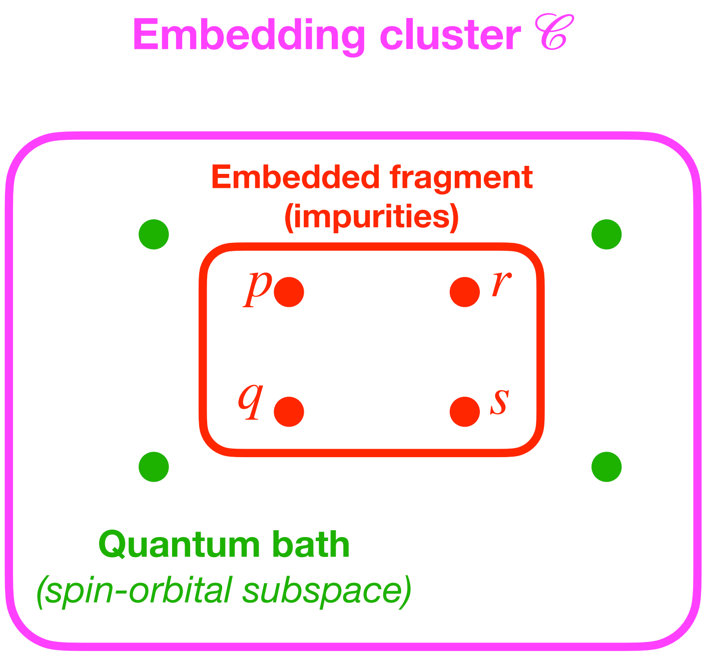
Clusterization procedure



Clusterization procedure

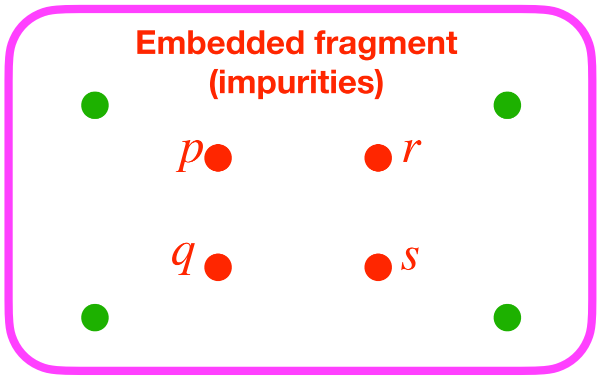
Reduction in size of the problem to be solved:

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

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

Embedding cluster $\mathscr{C}$

Quantum bath
$\equiv$ electronic reservoir



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

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

Clusterization procedure

Reduction in size of the problem to be solved:

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

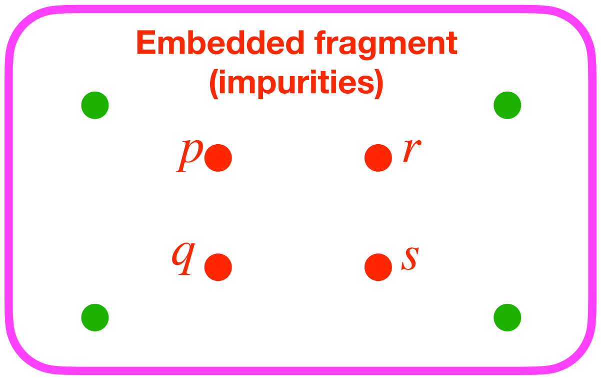
$$\langle \hat{c}^\dagger_p \hat{c}^\dagger_q \hat{c}_s \hat{c}_r \rangle_{full\ system} \approx \langle \hat{c}^\dagger_p \hat{c}^\dagger_q \hat{c}_s \hat{c}_r \rangle_{\Psi^{\mathscr{C}}}$$

How many bath orbitals?

Quantum bath

$\equiv$ electronic reservoir

Embedding cluster $\mathscr{C}$



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

G. Knizia and G. K.-L. Chan, Phys. Rev. Lett. ***109****, 186404 (2012).*

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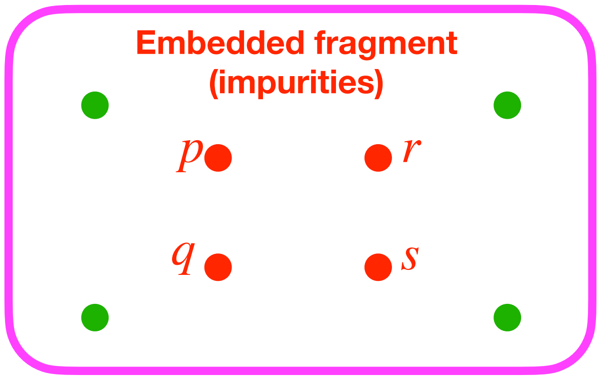
How many bath orbitals?

↓

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

Reduction in size of the problem to be solved:

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

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

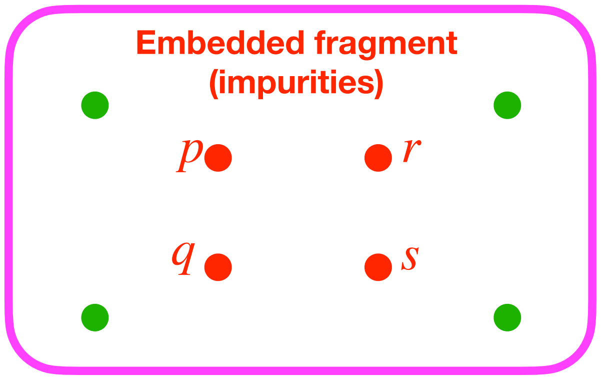
4 orbitals here: Why and how?

↓

Quantum bath

≡ electronic reservoir

Embedding cluster $\mathscr{C}$



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

How many?

↓

Few-electron

correlated wave function

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Clusterization procedure

Reduction in size of the problem to be solved:

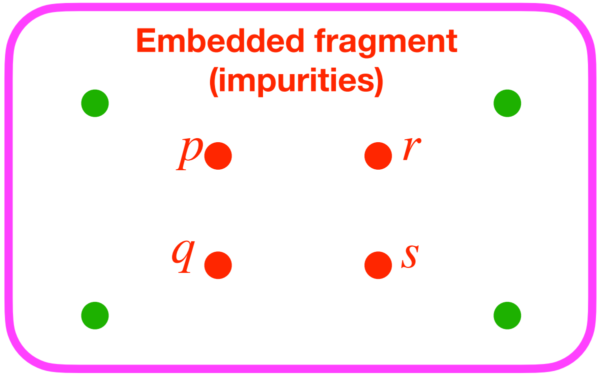
$$\langle \hat{c}_p^\dagger \hat{c}_q \rangle_{full\ system} \approx \langle \hat{c}_p^\dagger \hat{c}_q \rangle_{\Psi^{\mathscr{C}}}$$

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

4 orbitals here:
Why and how?

Quantum bath
≡ electronic reservoir

Embedding cluster $\mathscr{C}$



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

How many?

Few-electron correlated wave function

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

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).
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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

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

Original lattice representation

Embedding representation

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

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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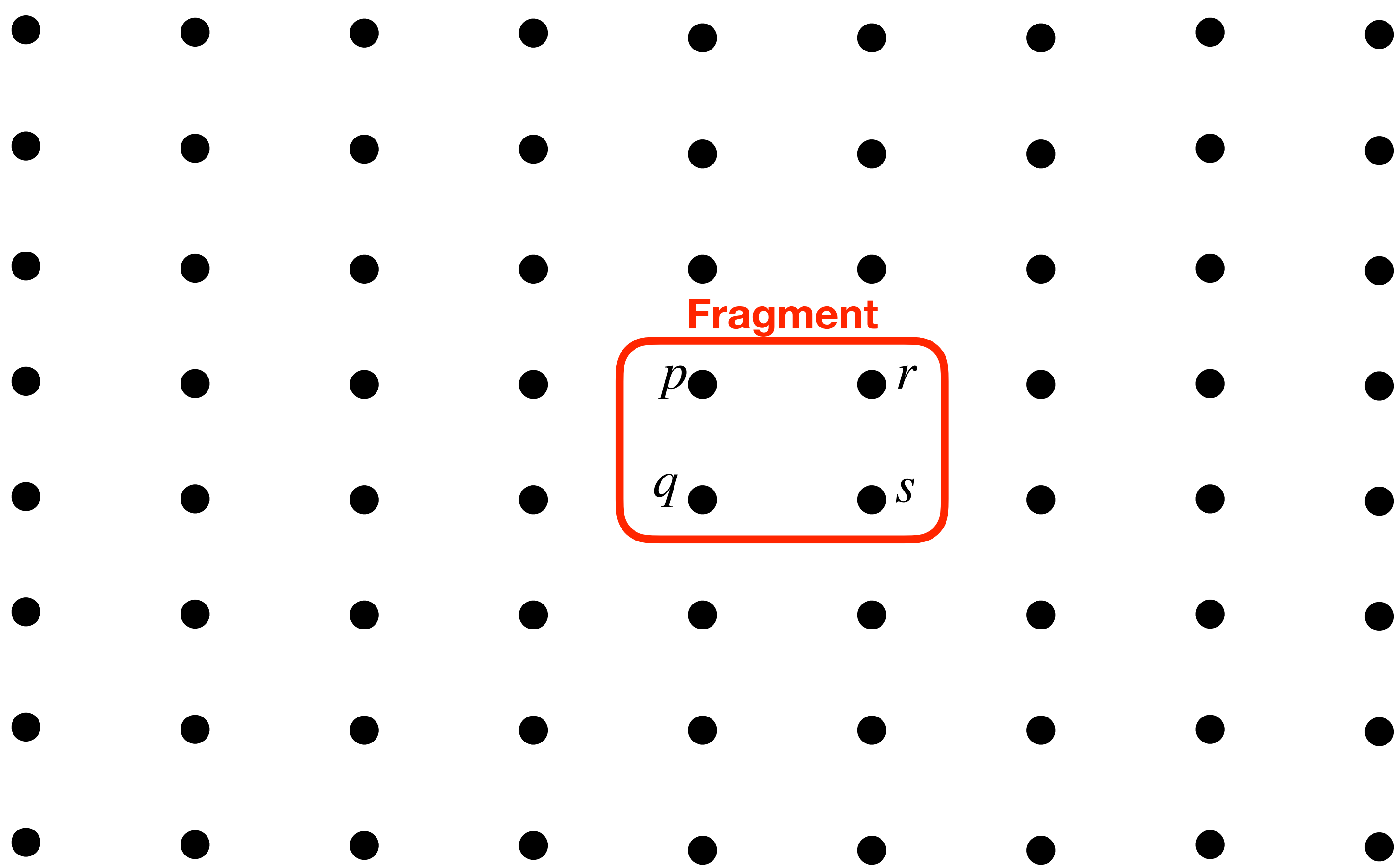
Clusterization through a unitary one-electron transformation

So-called "lattice representation"



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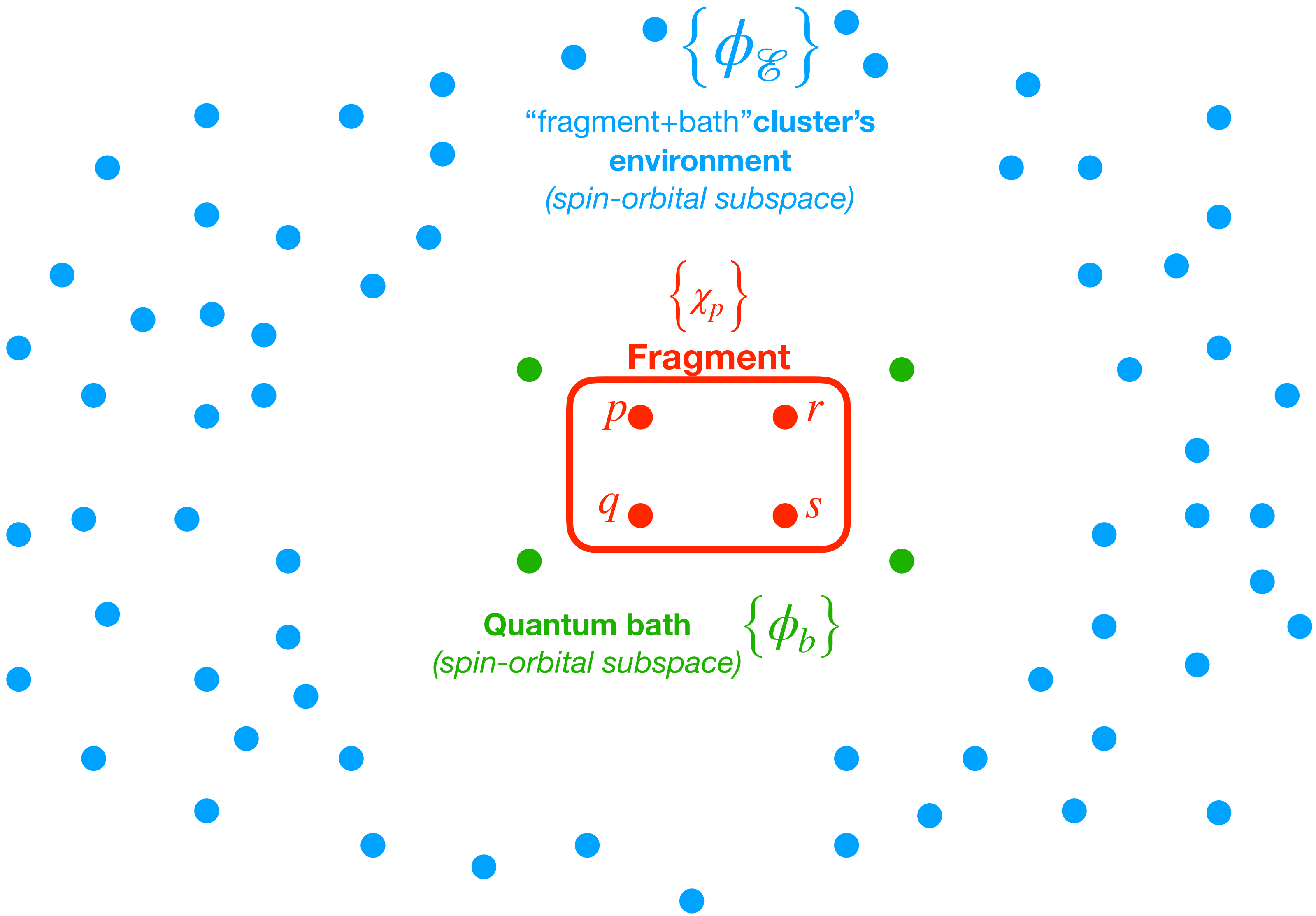
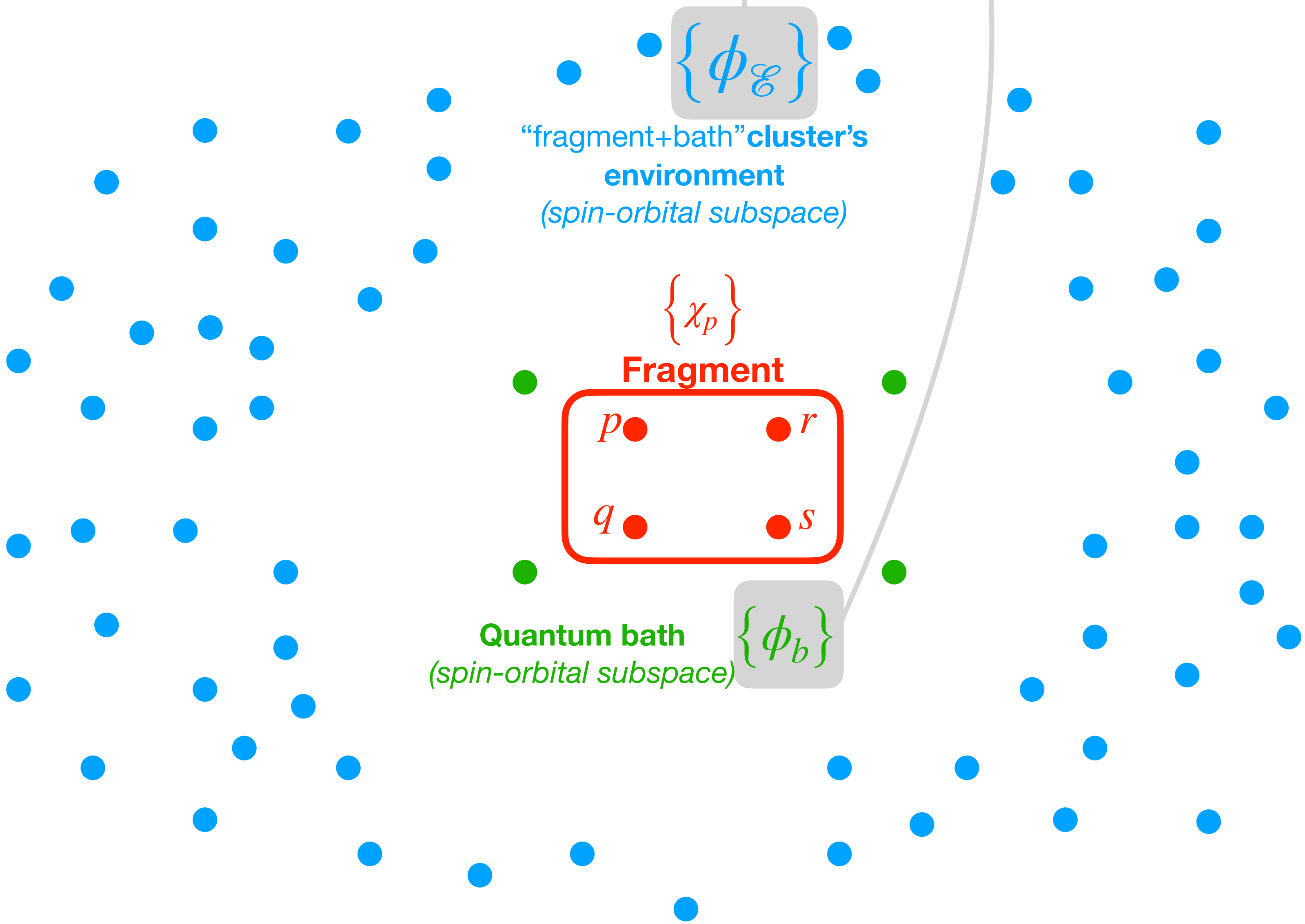
Clusterization through a unitary one-electron transformation



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

Clusterization through a unitary one-electron transformation

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



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

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

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

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

Embedding representation

Lattice representation

Unitary transformed density matrix

"**fragment**+**bath**"
embedding cluster

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

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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!)

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

Unitary transformed density matrix

"fragment+bath"
embedding cluster

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

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

Density matrix in the original lattice representation (known!)

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Unitary transformed density matrix

"fragment+bath"
embedding cluster

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

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

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** $\gamma \equiv \langle \hat{c}_p^\dagger \hat{c}_q \rangle$

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

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The bath is a functional of the density matrix

*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

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

Normalised eigenvector

Eigenvalue

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

Orthonormalisation of the bath orbitals

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

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

Overlap matrix

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

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

Unitary transformed density matrix

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

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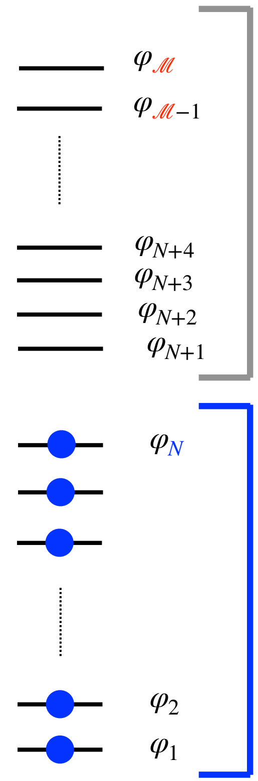
What if the full-system density matrix is idempotent?

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

Molecular orbital representation!

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



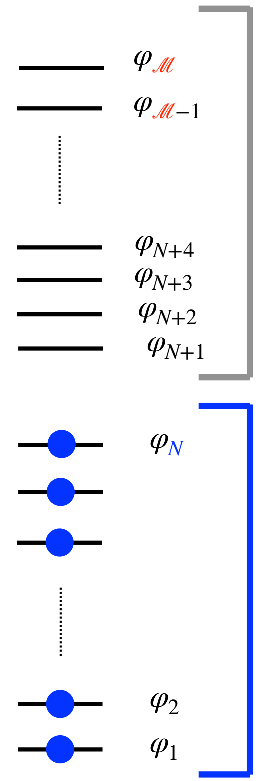
Mean-field (HF) or Kohn-Sham DFT

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

What if the full-system density matrix is idempotent?

$$\bar{\gamma} \equiv \boxed{\begin{matrix} 1 & & & & & & & \\ & 1 & & & & 0 & & \\ & & 1 & & & & & \\ & & & \ddots & & & & \\ & & & & 1 & & & \\ & 0 & & & & 0 & & \\ & & & & & & \ddots & \\ & & & & & & & 0 \end{matrix}}$$

$\longleftarrow$ **Molecular orbital representation!**



Mean-field (HF) or Kohn-Sham DFT

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

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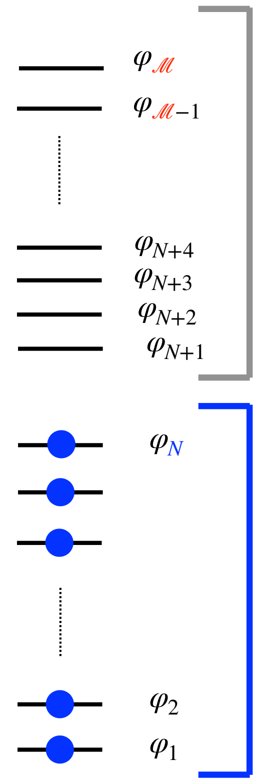
What if the full-system density matrix is *idempotent*?

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

← **Molecular orbital representation!**



Mean-field (HF)
or Kohn-Sham DFT

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Unitary transformed idempotent density matrix

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

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

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

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

Unitary transformed idempotent density matrix

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

$$\|$$

$$\tilde{\gamma}_{\mathscr{E}b}\tilde{\gamma}_{bf}$$ ⟵ **Invertible!**

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

Unitary transformed idempotent density matrix

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

$$\| $$

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

Invertible!

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Unitary transformed density matrix

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

Mean-field or
non-interacting
full-size calculation

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Unitary transformed idempotent density matrix

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

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Unitary transformed idempotent density matrix

Invertible!

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

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

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

The embedding cluster contains exactly L_f electrons!

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Unitary transformed density matrix

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

Dimension of the fragment

If $\gamma^2 = \gamma$

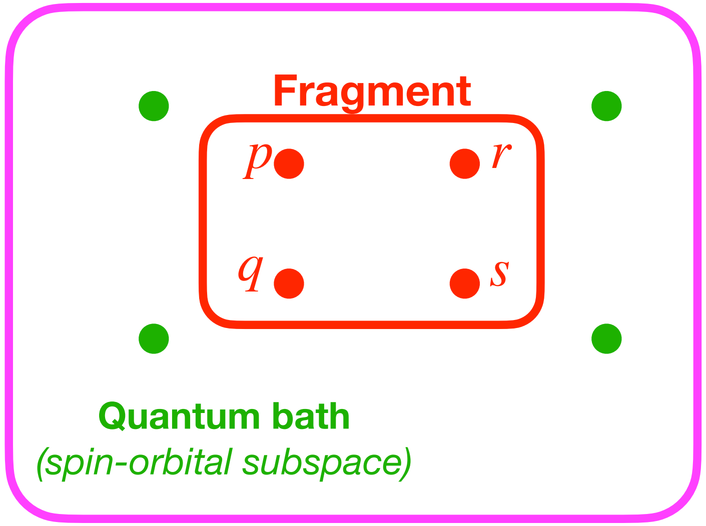
$$\tilde{\gamma} \equiv \begin{array}{cc} \begin{array}{ccc} \text{Frag.} & \text{Bath} & \text{Cluster env.} \end{array} & \\ \left[\begin{array}{cc|c} \gamma_{ff} & \tilde{\gamma}^{\dagger}_{bf} & 0 \\ \tilde{\gamma}_{bf} & \tilde{\gamma}_{bb} & 0 \\ \hline 0 \quad 0 & & \tilde{\gamma}_{\mathscr{E}\mathscr{E}} \end{array}\right] & \begin{array}{c} \text{Frag.} \\ \text{Bath} \\ \text{Cluster env.} \end{array} \end{array}$$

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

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



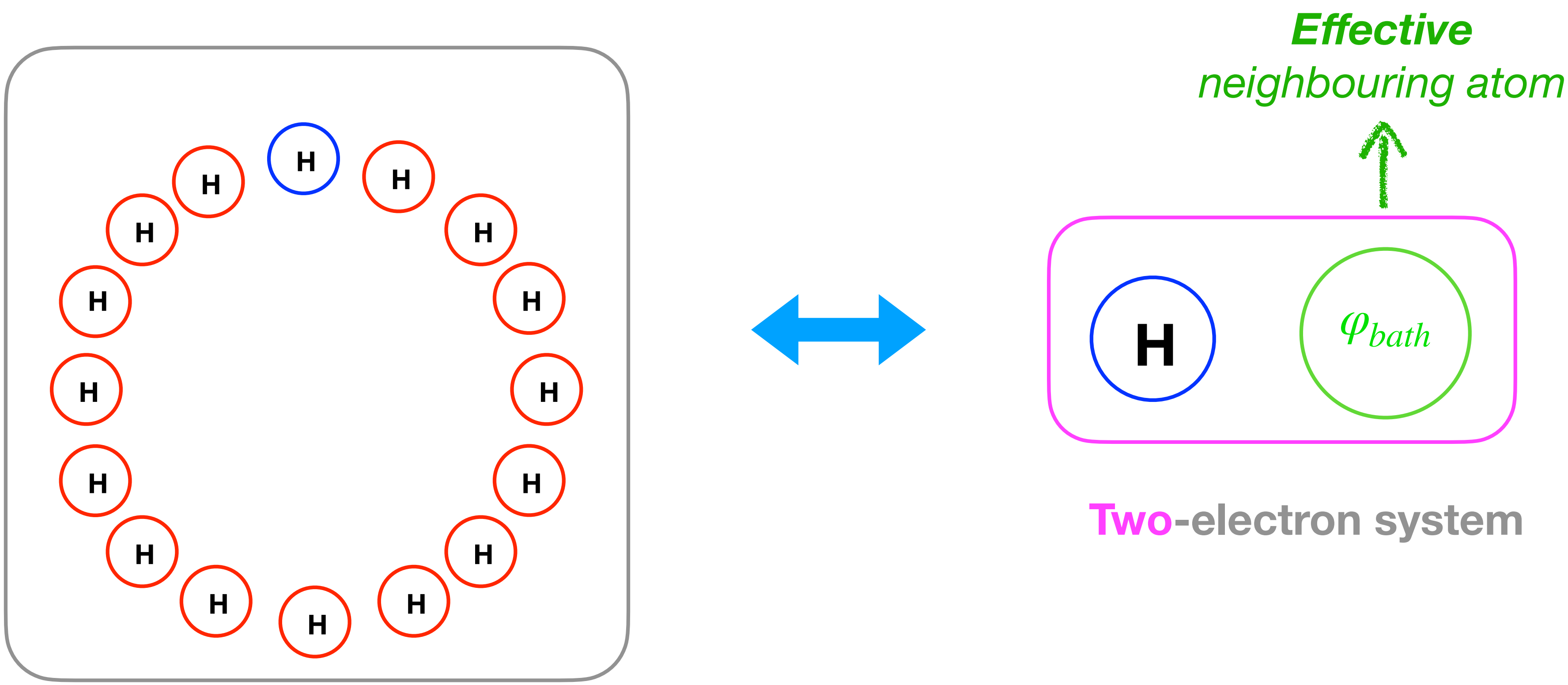
$\Psi^{\mathscr{C}}$

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

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

Illustrative example

Rings of hydrogen atoms (Hubbard model)

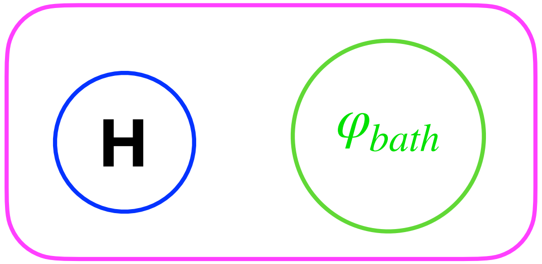


N-electron system

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

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

Approximate embedding of interacting Hamiltonians



One-electron Hamiltonian of the cluster

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

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

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

Approximate embedding of interacting Hamiltonians

One-electron Hamiltonian of the cluster

Two-electron repulsion on the impurity

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

Exact non-interacting
embedding

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Approximate embedding of interacting Hamiltonians

One-electron Hamiltonian of the cluster

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

Exact non-interacting
embedding

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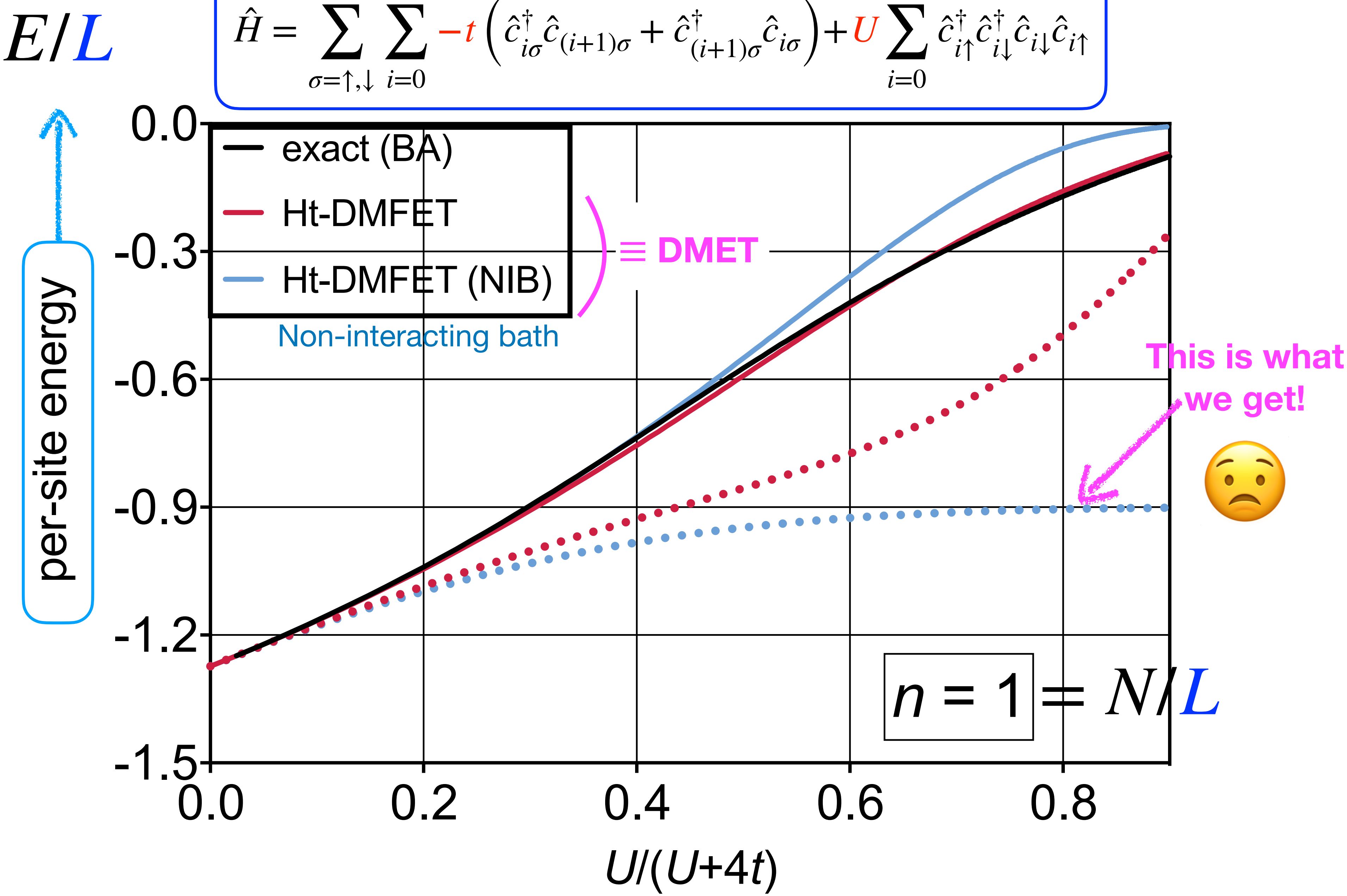
S. Sekaran, M. Saubanère, and E. Fromager, Computation **2022***, 10, 45.*

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

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



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

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

Exact non-interacting
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Approximate embedding of interacting Hamiltonians

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

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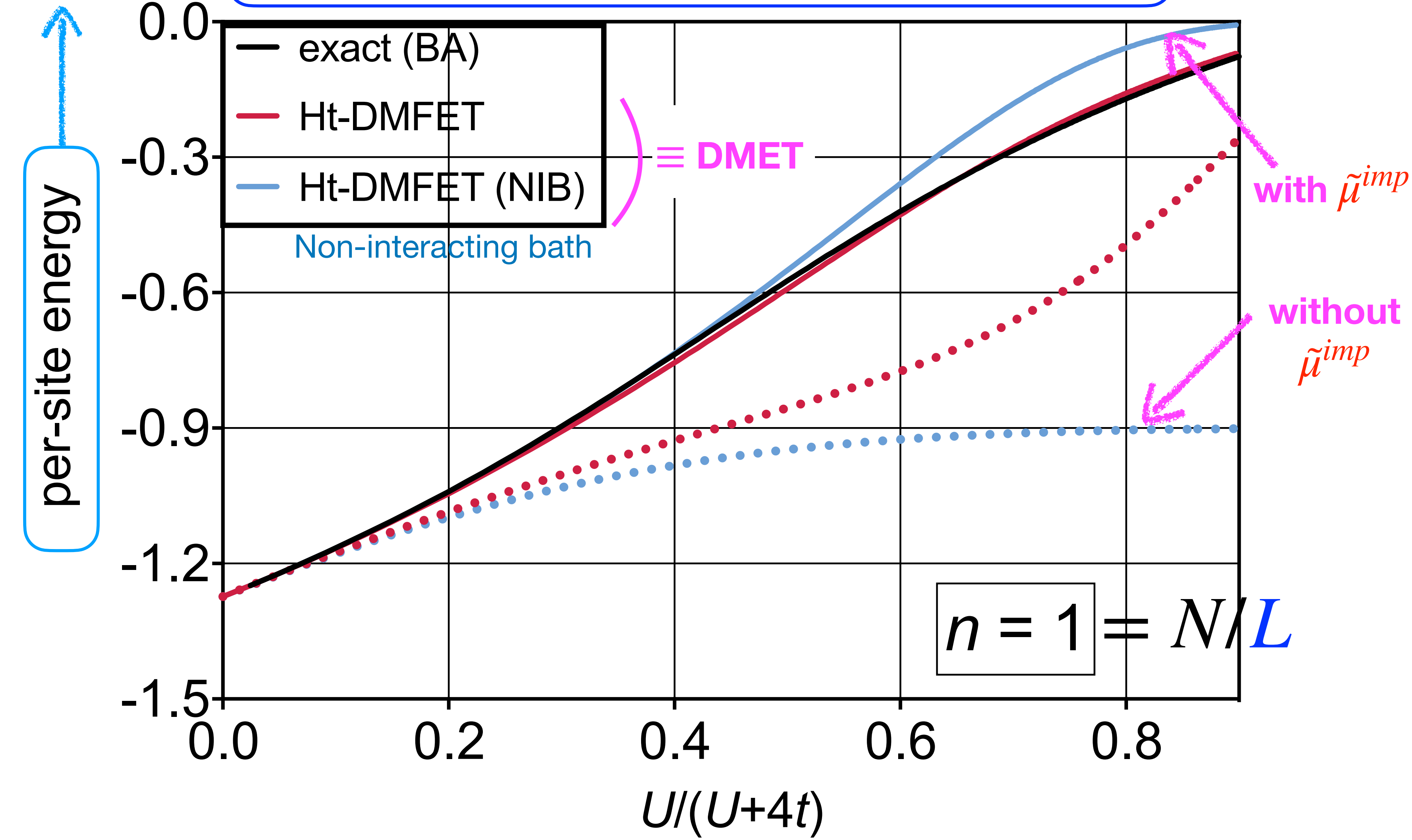
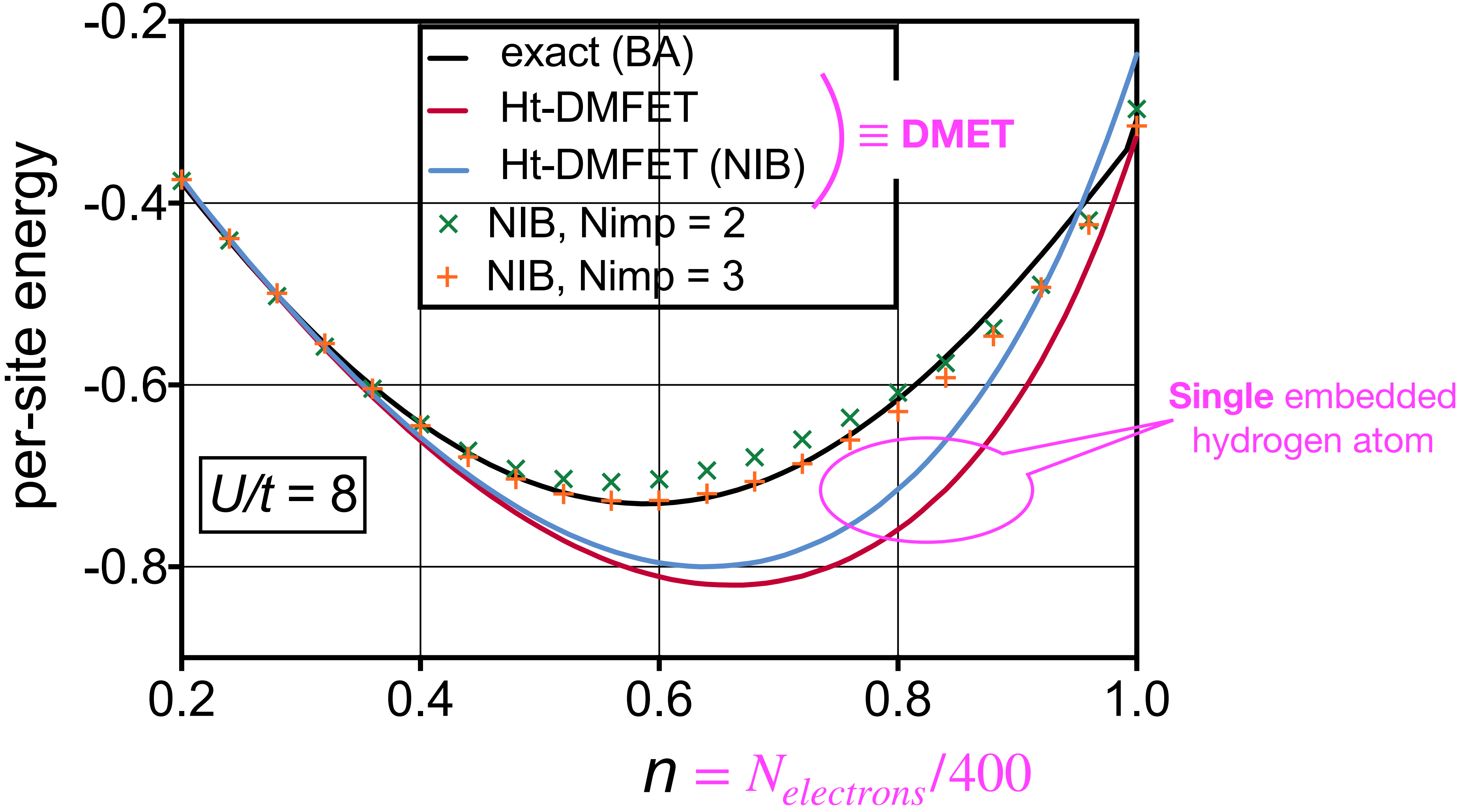


*S. Sekaran, M. Tsuchiizu, M. Saubanère, and E. Fromager, Phys. Rev. B **104**, 035121 (2021).*

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



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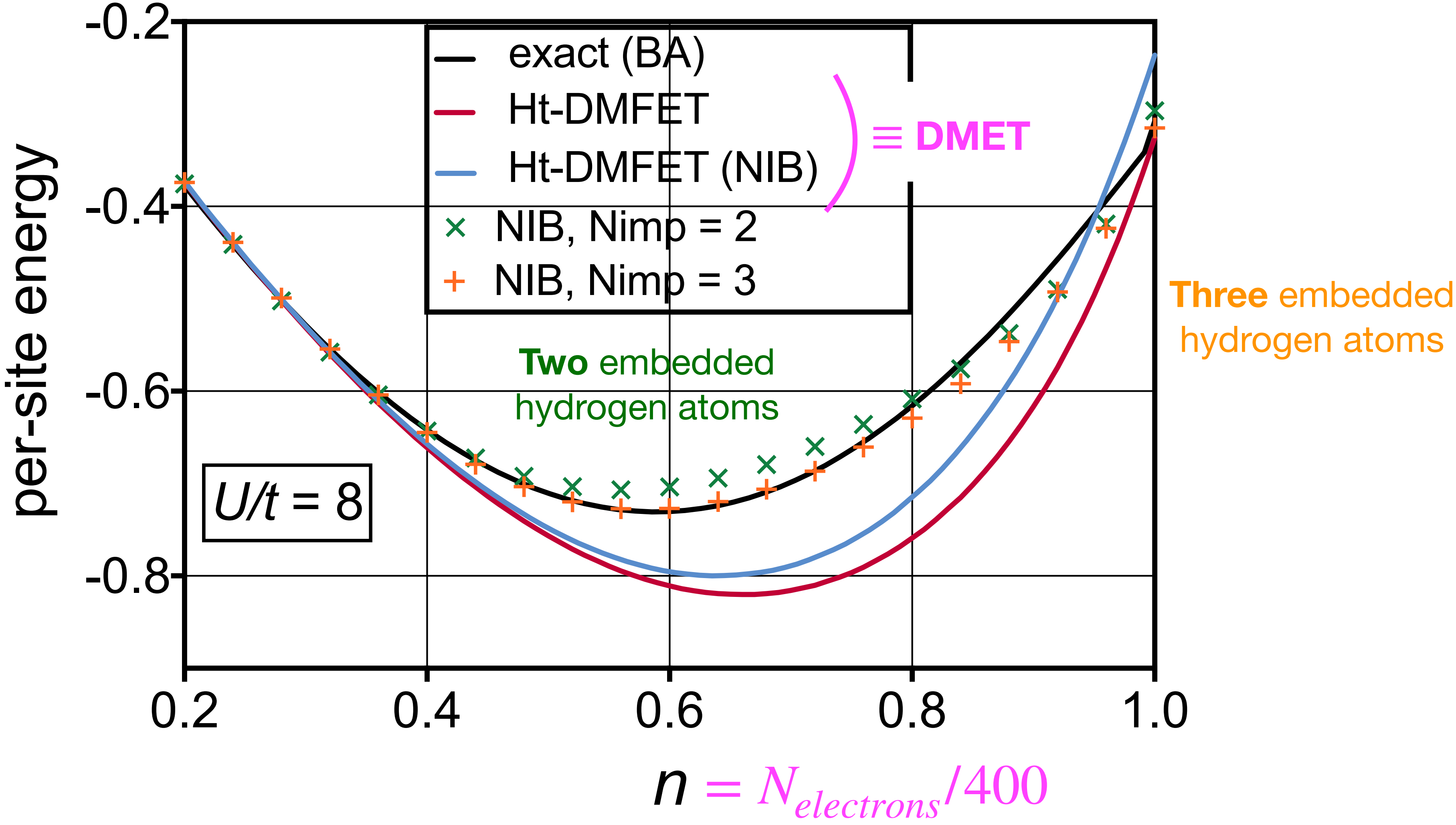

*S. Sekaran, M. Tsuchiizu, M. Saubanère, and E. Fromager, Phys. Rev. B **104**, 035121 (2021).*

Self-consistent embedding inspired by DFT

(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

$\equiv$ 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

$\equiv$ uniform external potential

Uniform density profile (twice the filling):

$\equiv N(\mu)$: 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

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

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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

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

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

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**

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

Unknown Kohn—Sham chemical potential

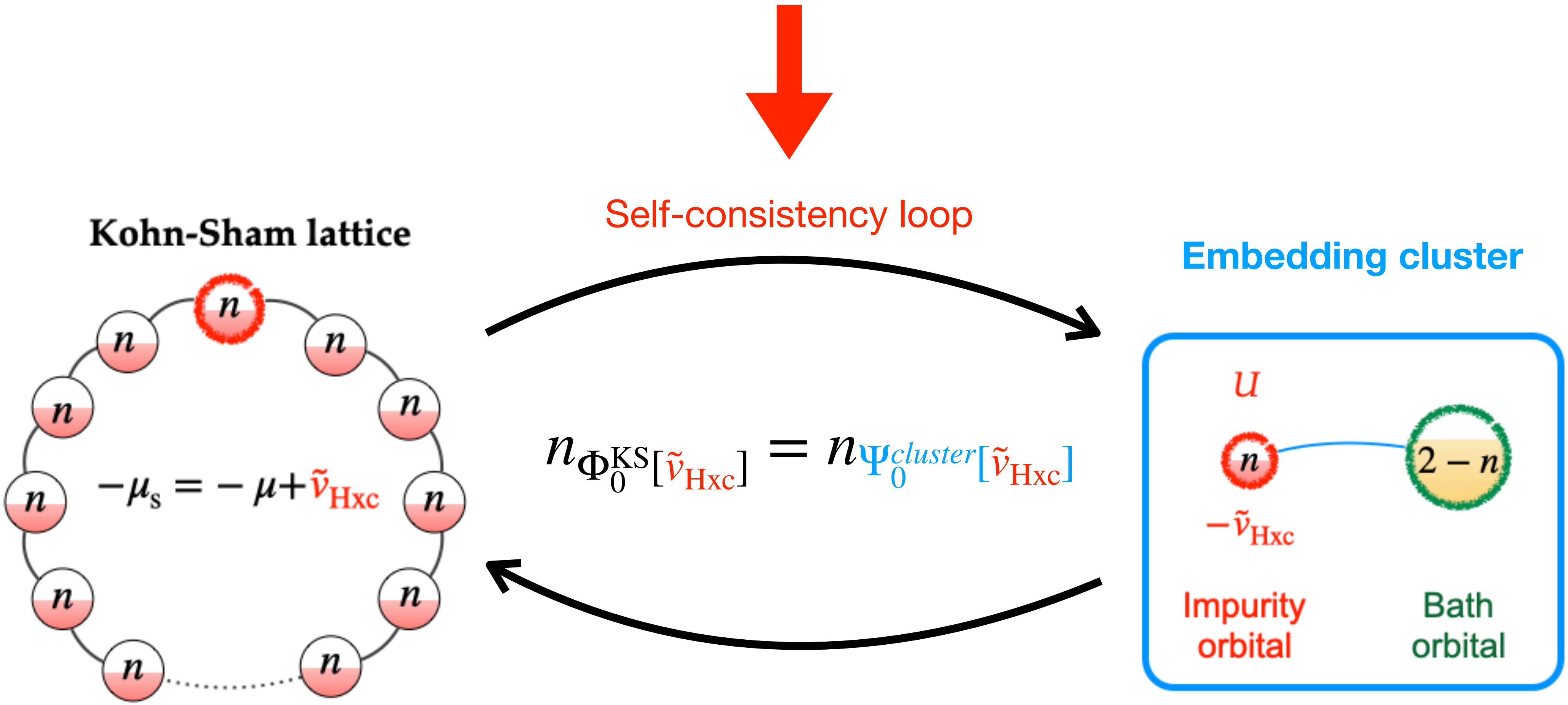
$$-\mu^{\mathrm{KS}} = -\mu + v_{\mathrm{Hxc}} \longleftarrow n^{\mathrm{KS}} = n(\mu) = ?$$

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

Impurity-interacting Hamiltonian of the two-electron embedding cluster

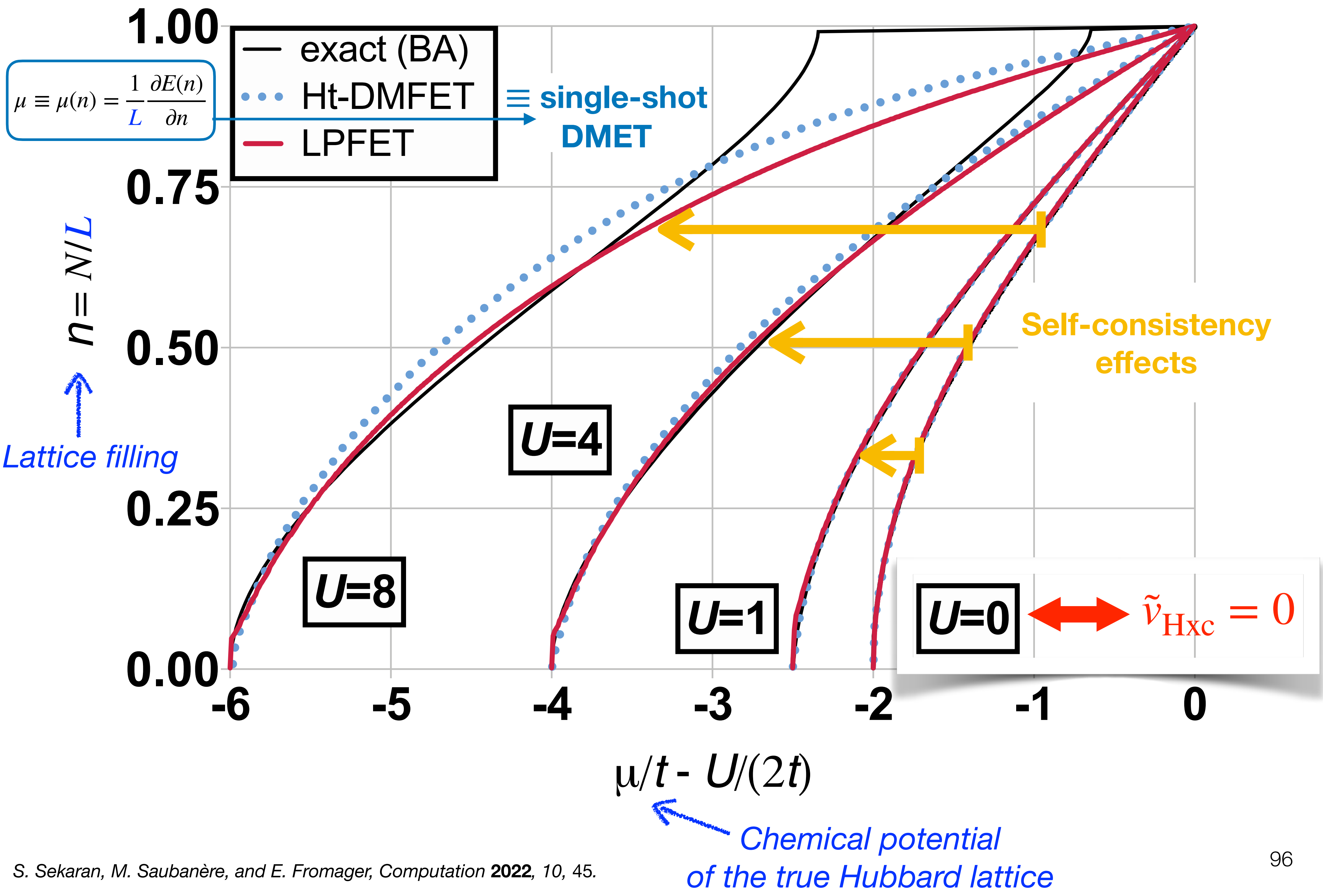
Local potential-functional embedding theory (LPFET)

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



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

Local potential-functional embedding theory (LPFET)



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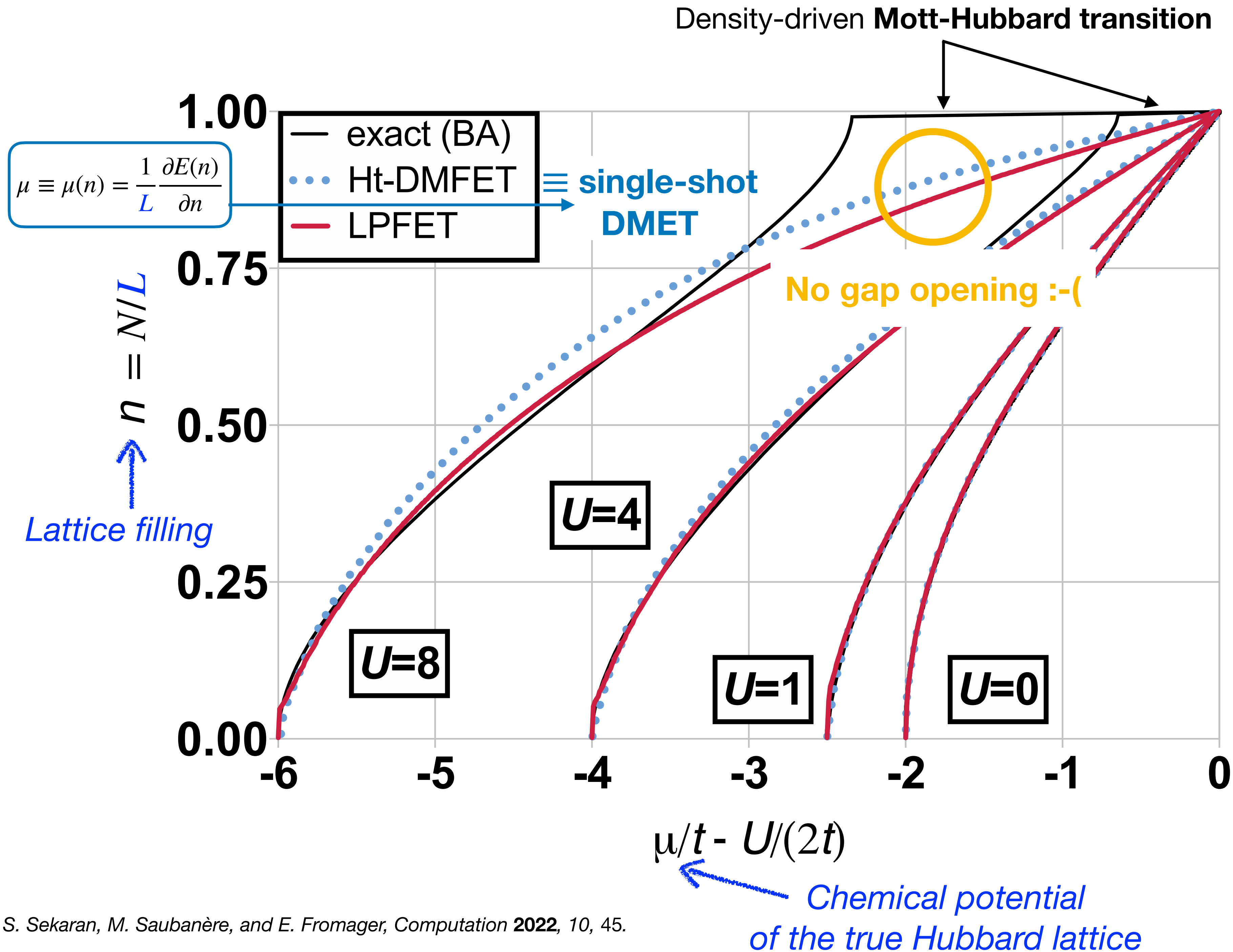
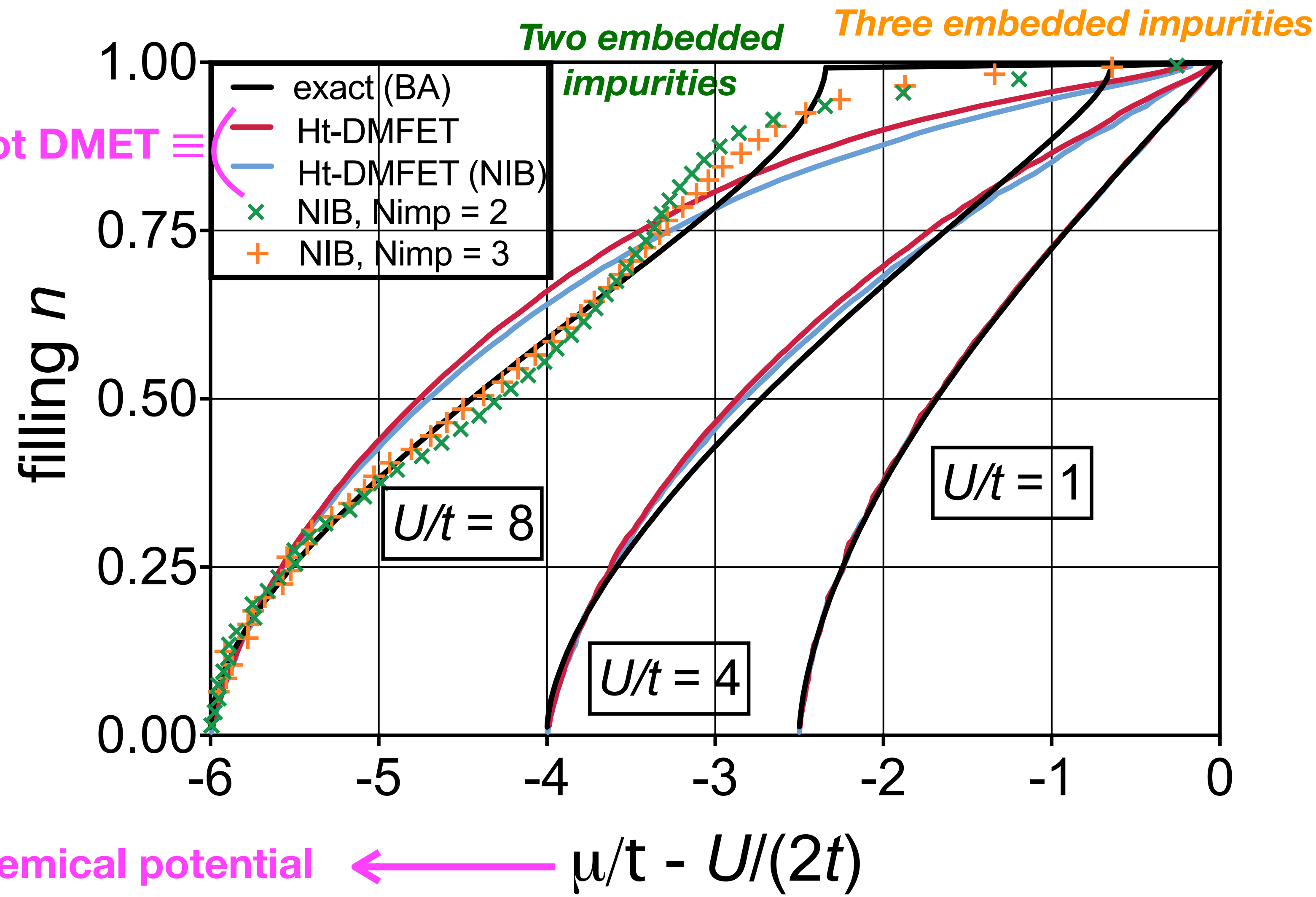


S. Sekaran, M. Saubanère, and E. Fromager, Computation **2022**, 10, 45.

Mott-Hubbard density-driven transition and multiple 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 D(M)ET

computation

MDPI

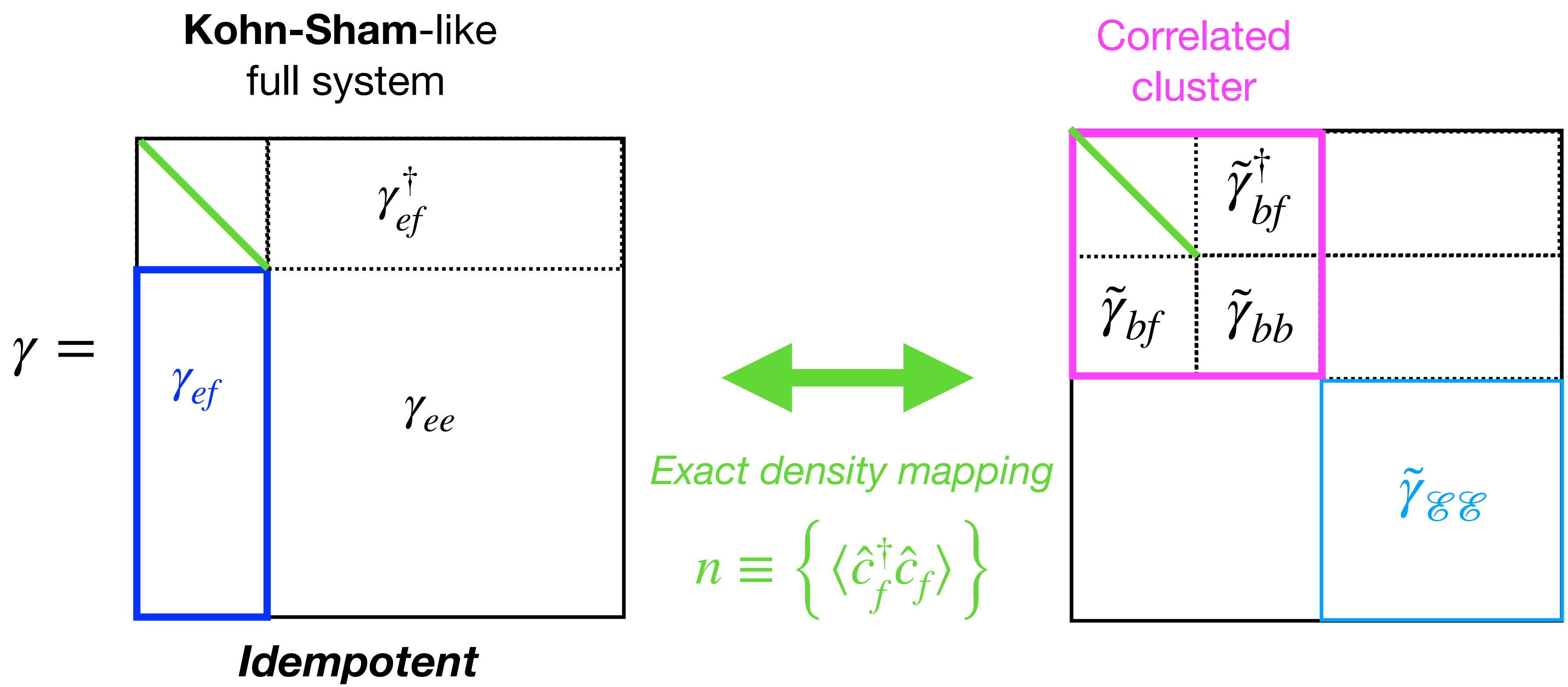
check for updates

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



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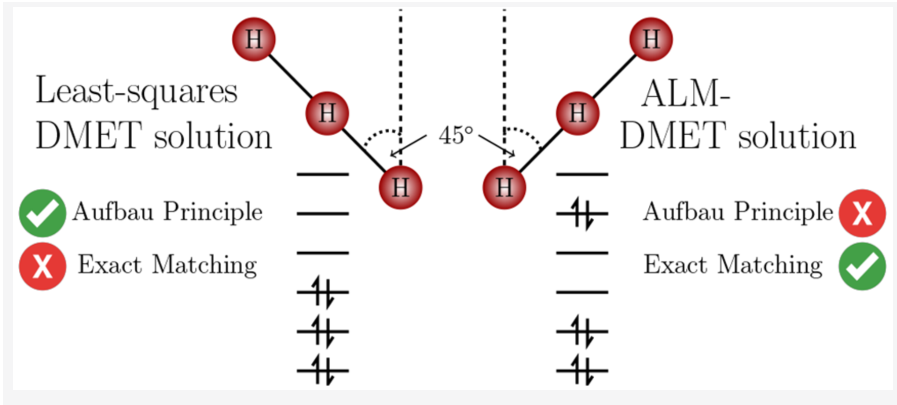
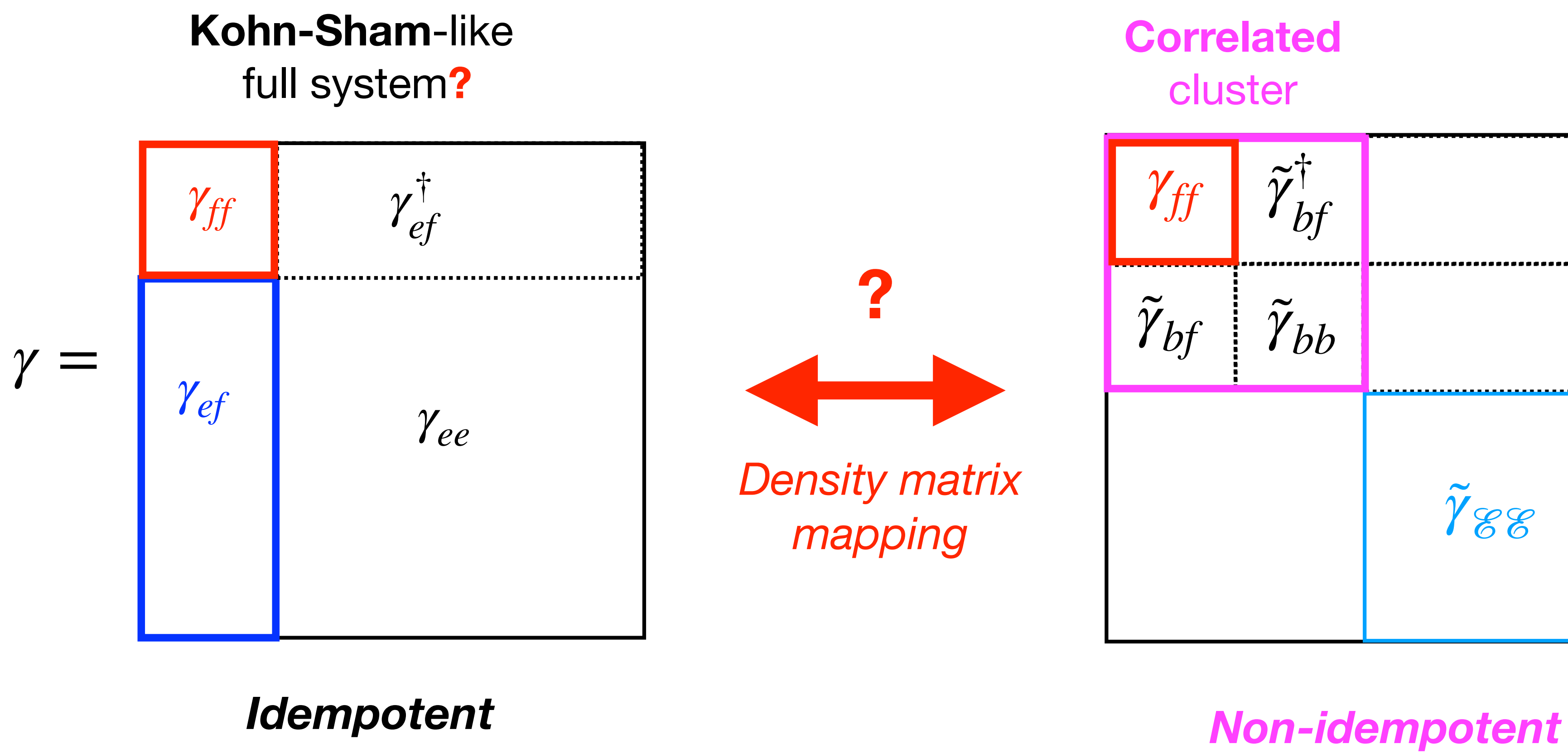
U. Mordovina, T. E. Reinhard, I. Theophilou, H. Appel, and A. Rubio, J. Chem. Theory Comput. ***15****, 5209 (2019).*

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





JCTC Journal of Chemical Theory and Computation

pubs.acs.org/JCTC

Article

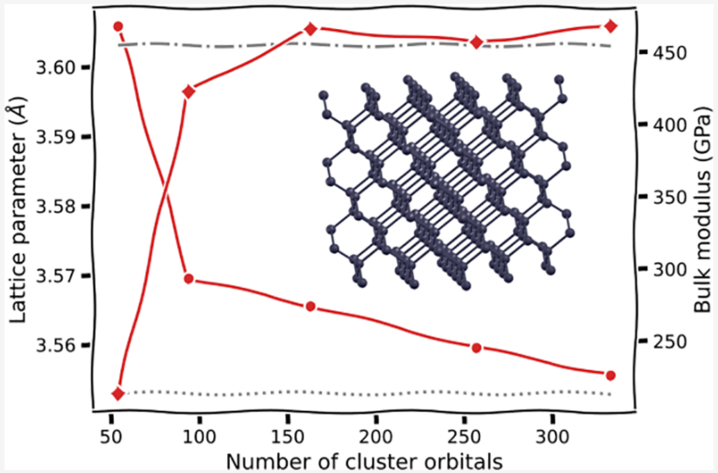
Effective Reconstruction of Expectation Values from Ab Initio Quantum Embedding

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

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

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.

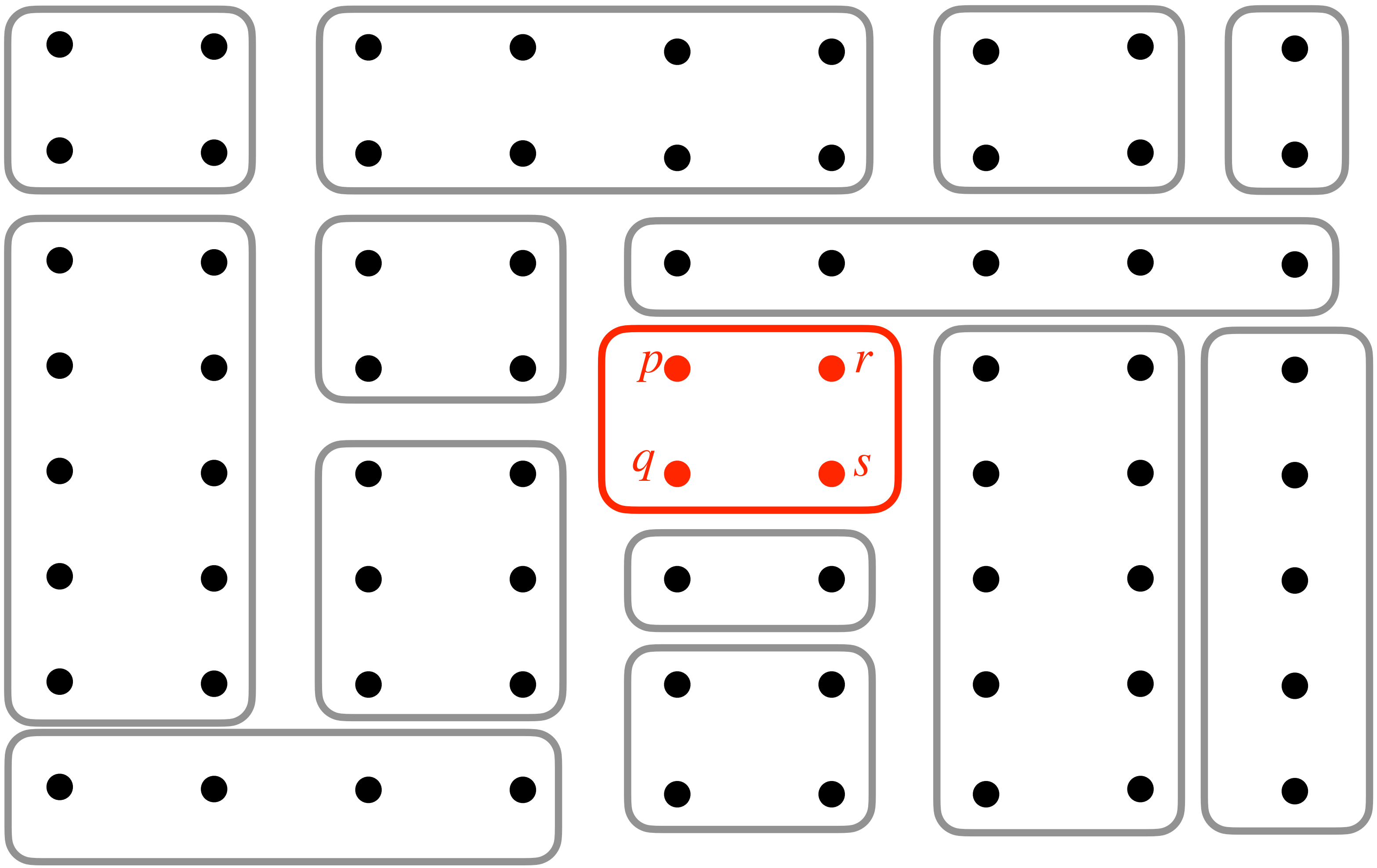


Local evaluation of the energy (in a localised spin-orbital basis)

So-called "lattice representation"

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

Fragmentation



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

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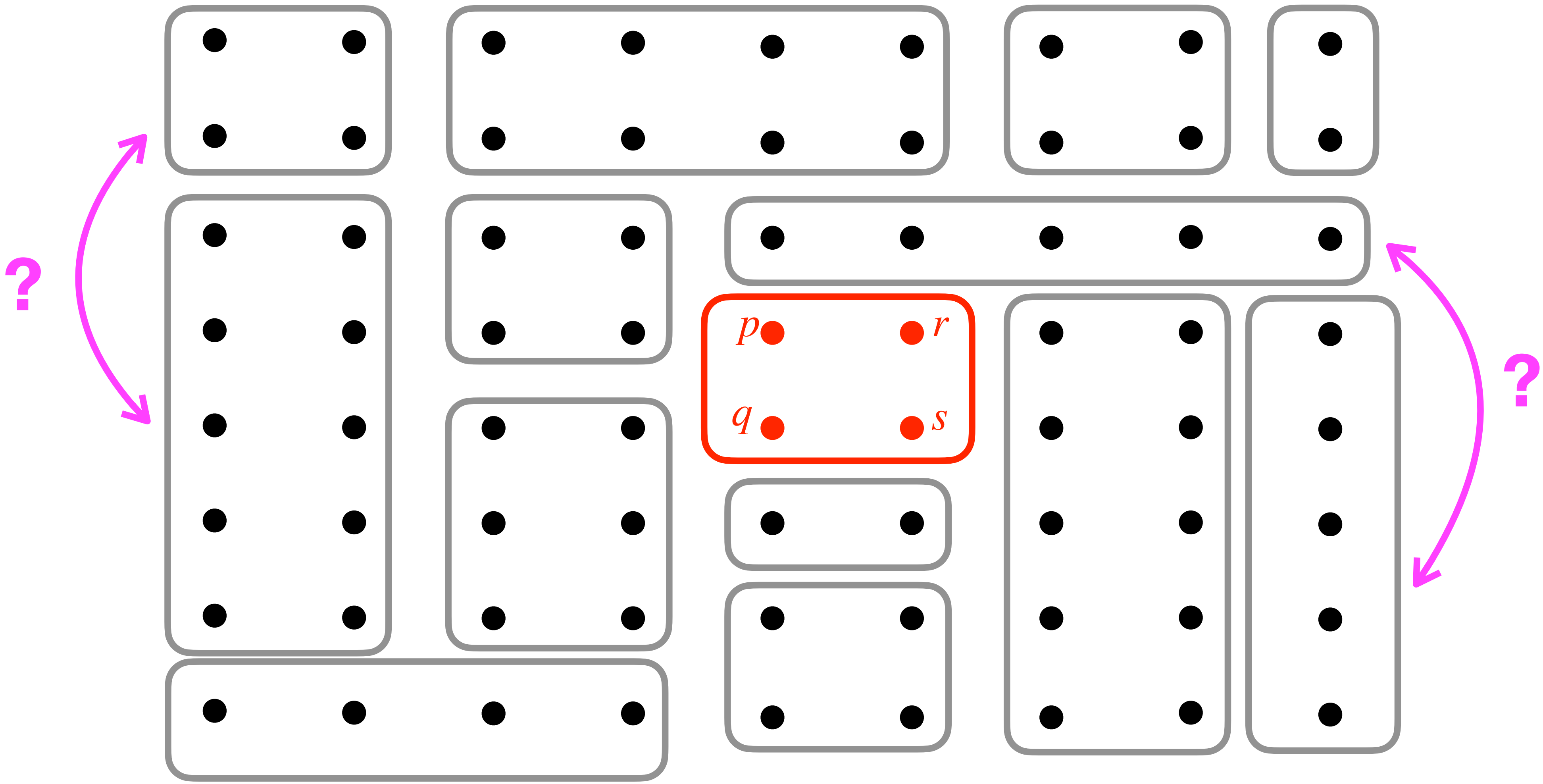
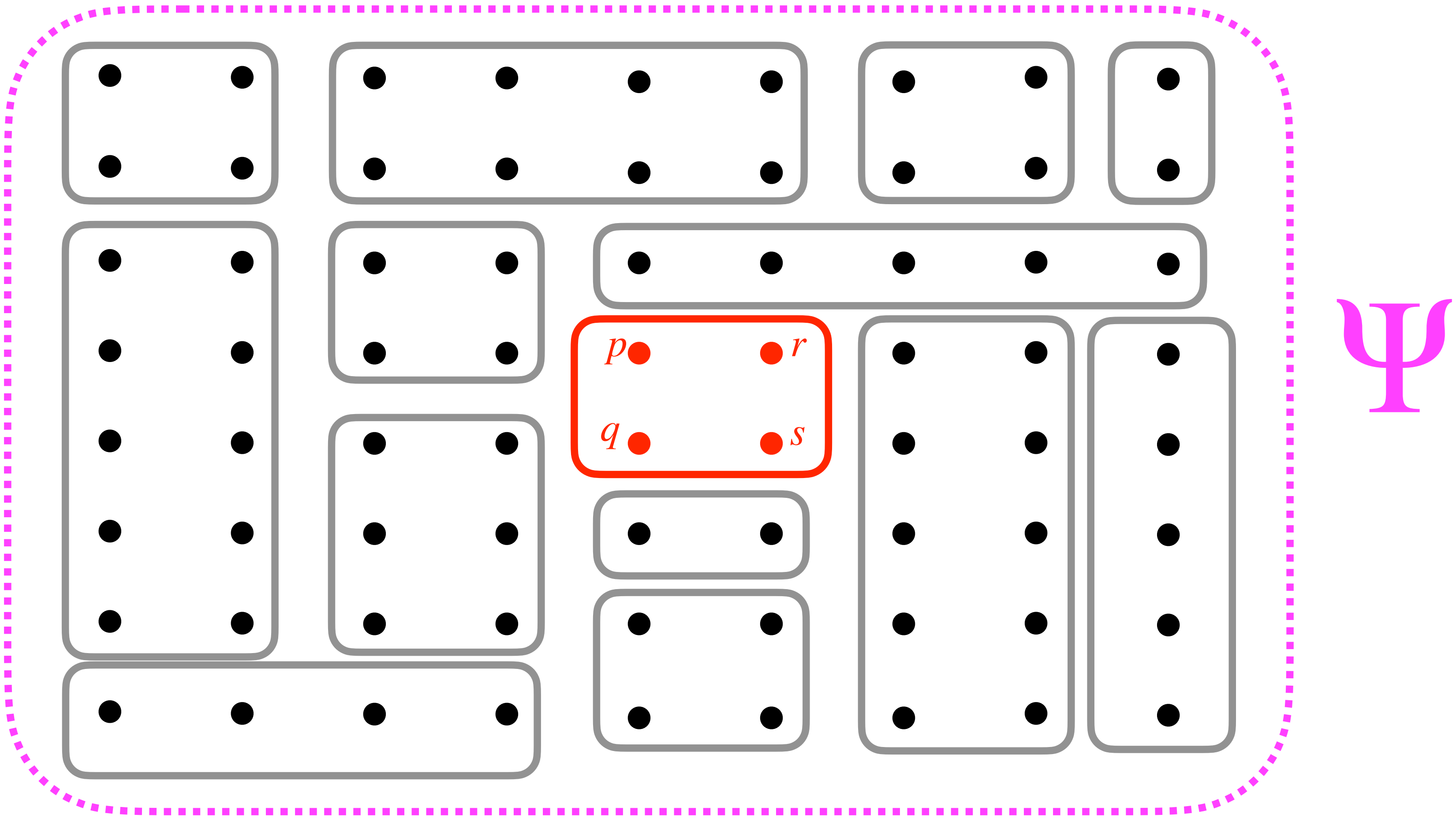


N-representability problem

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

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



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

$$\gamma = \sum_{\nu} \mathtt{w}_{\nu}\, \gamma_{\nu} \neq \gamma^2$$

$$\gamma_{\nu}^2 = \gamma_{\nu}$$

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

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Published Online: 23 September 2024

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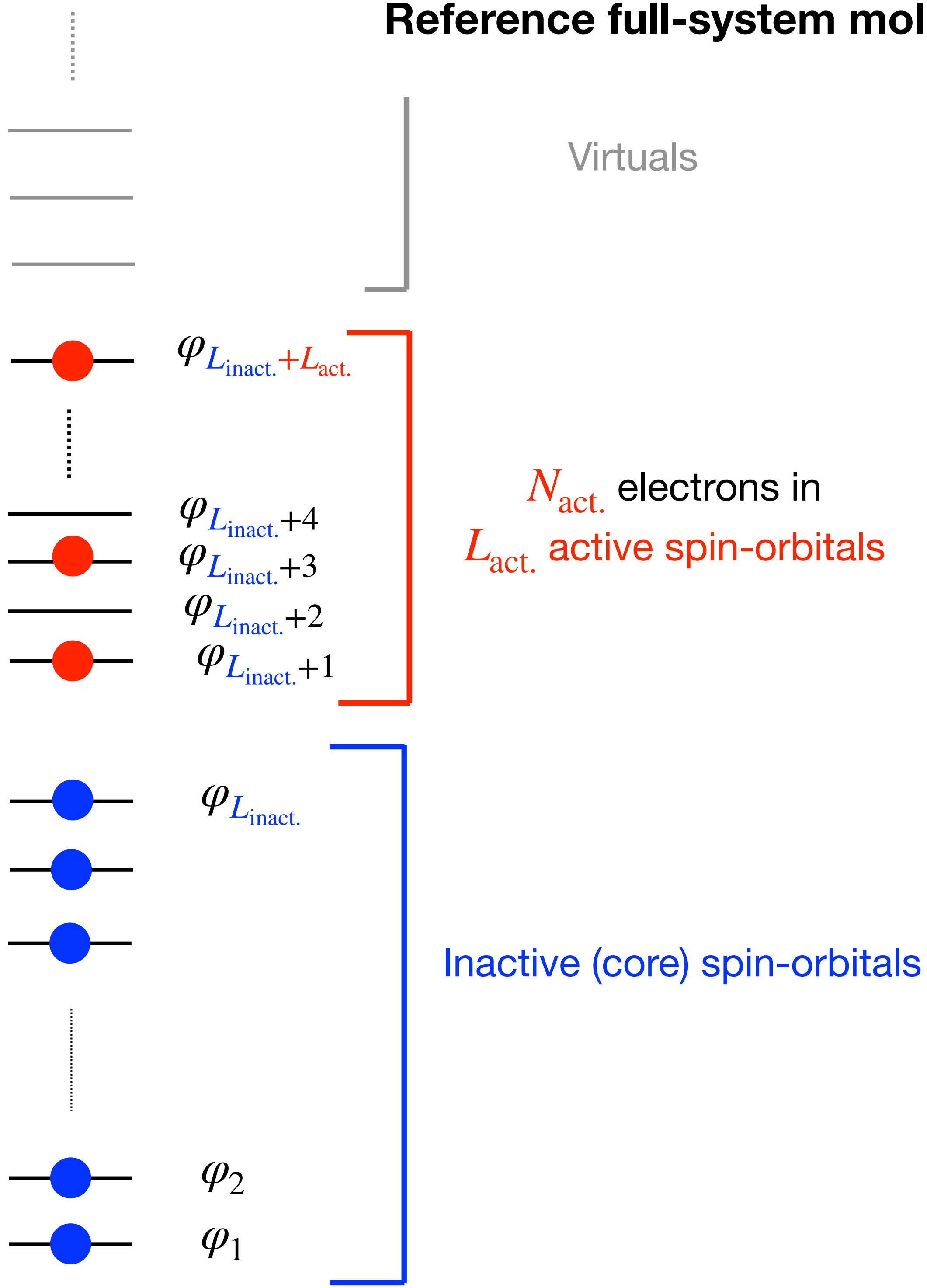
It is possible to design successive (Householder) unitary transformations

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

But …

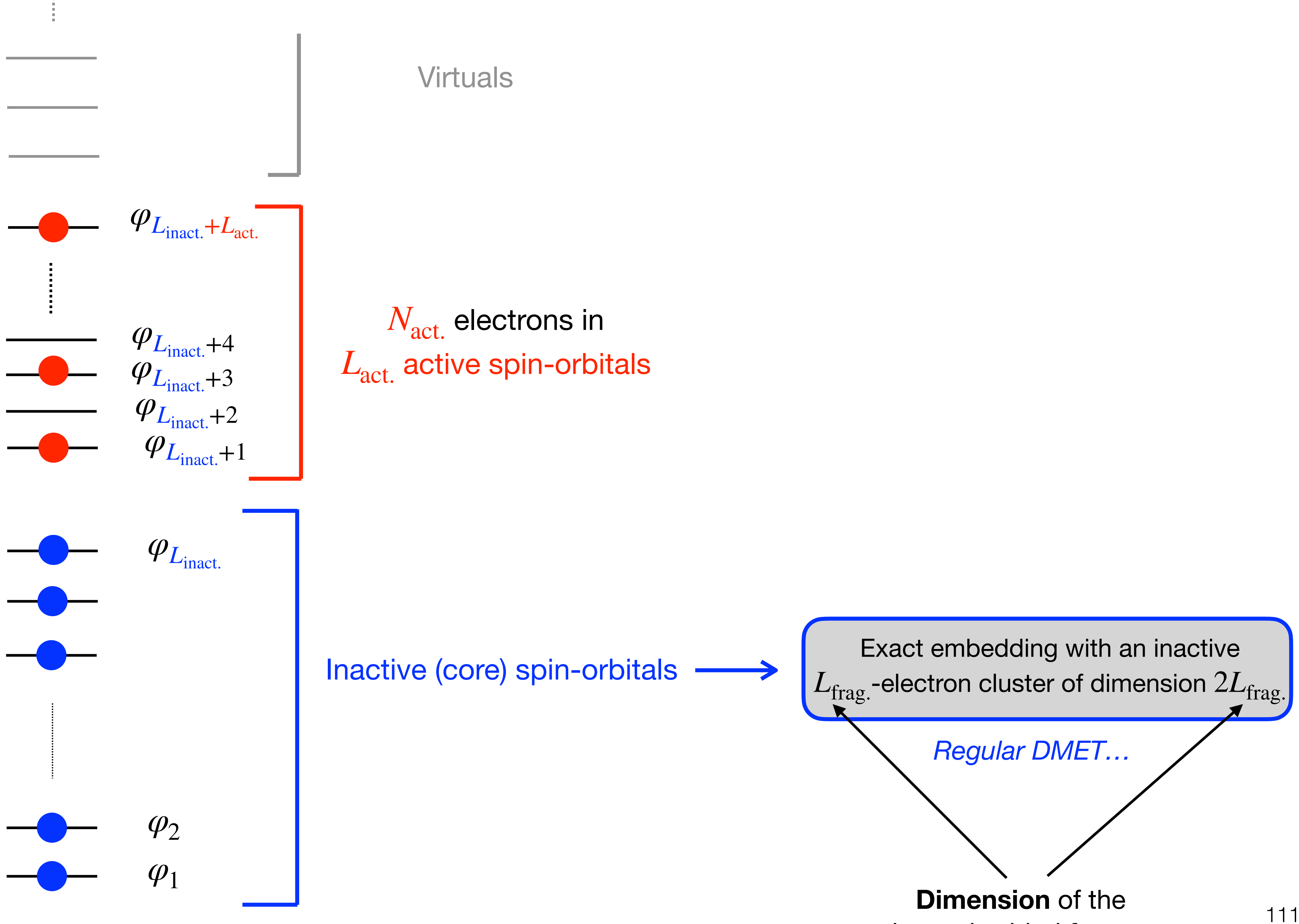
… the **bath is larger** and the cluster contains **more electrons**.

Reference full-system molecular orbital representation



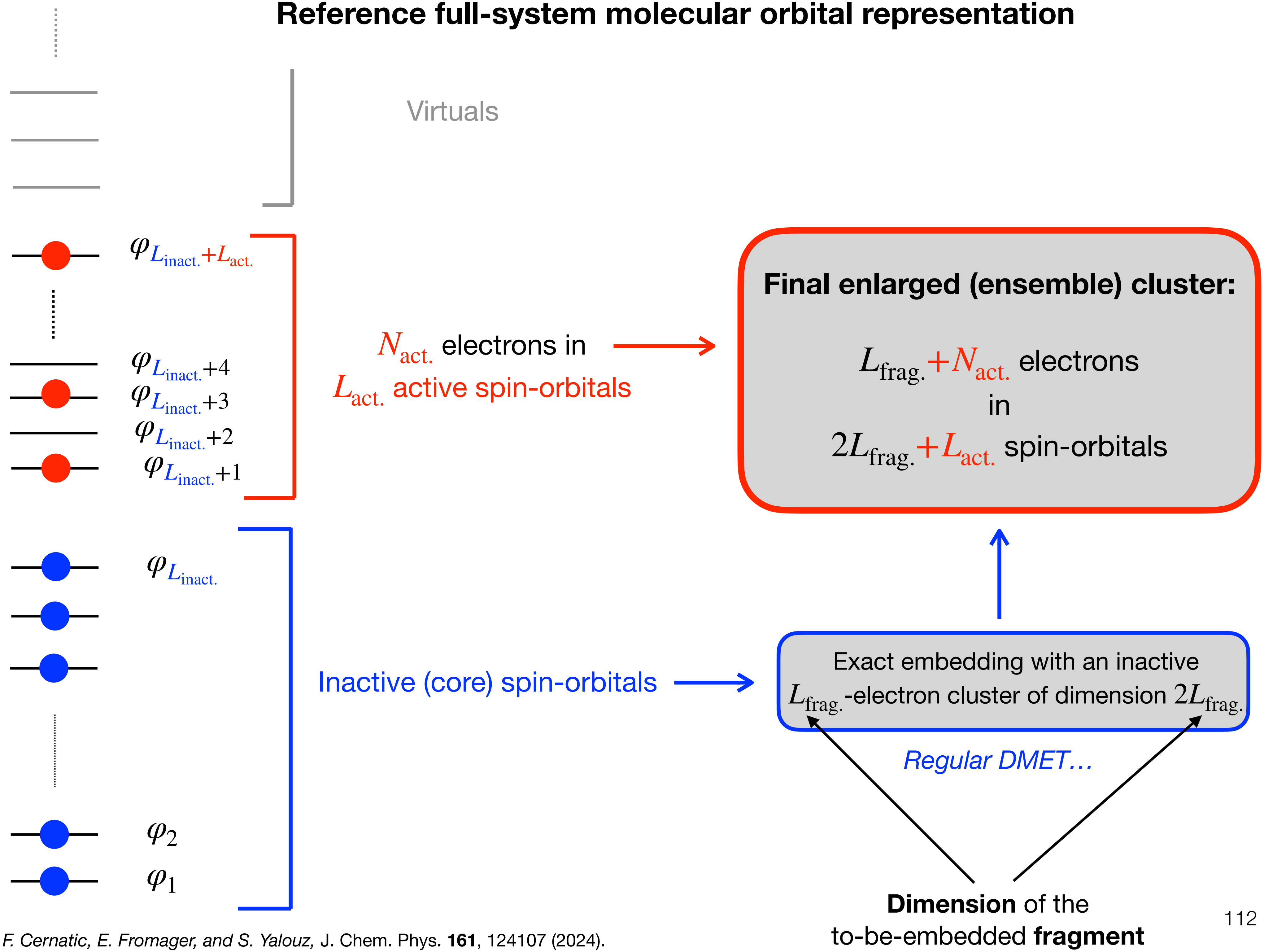
F. Cernatic, E. Fromager, and S. Yalouz, J. Chem. Phys. **161**, 124107 (2024).

Reference full-system molecular orbital representation



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

Reference full-system molecular orbital representation



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

Ensemble DMET

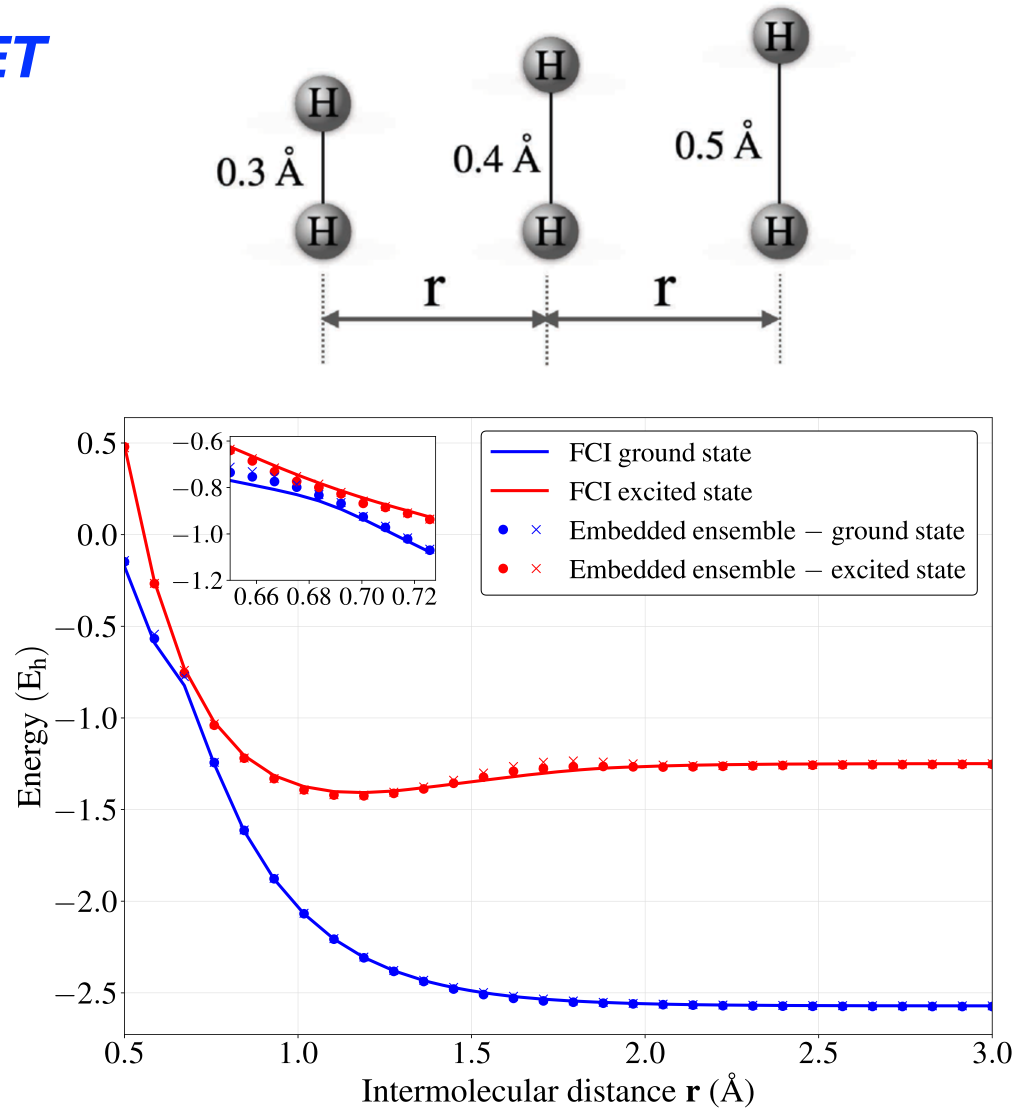


FIG. 5. Top: a schematic picture of the system of hydrogen atoms by Tran *et al.*[24] **Bottom**: dissociation curves of the FCI ground and first excited singlet states (blue and red lines, respectively), and the embedding results for the ground and first excited state (blue and red markers, respectively) 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).