Introduction to density matrix embedding theory

Emmanuel Fromager

Laboratoire de Chimie Quantique, Institut de Chimie de Strasbourg,
Université de Strasbourg, Strasbourg, France

ISTPC 2024, Aussois, Savoie, France **26/06/2024**

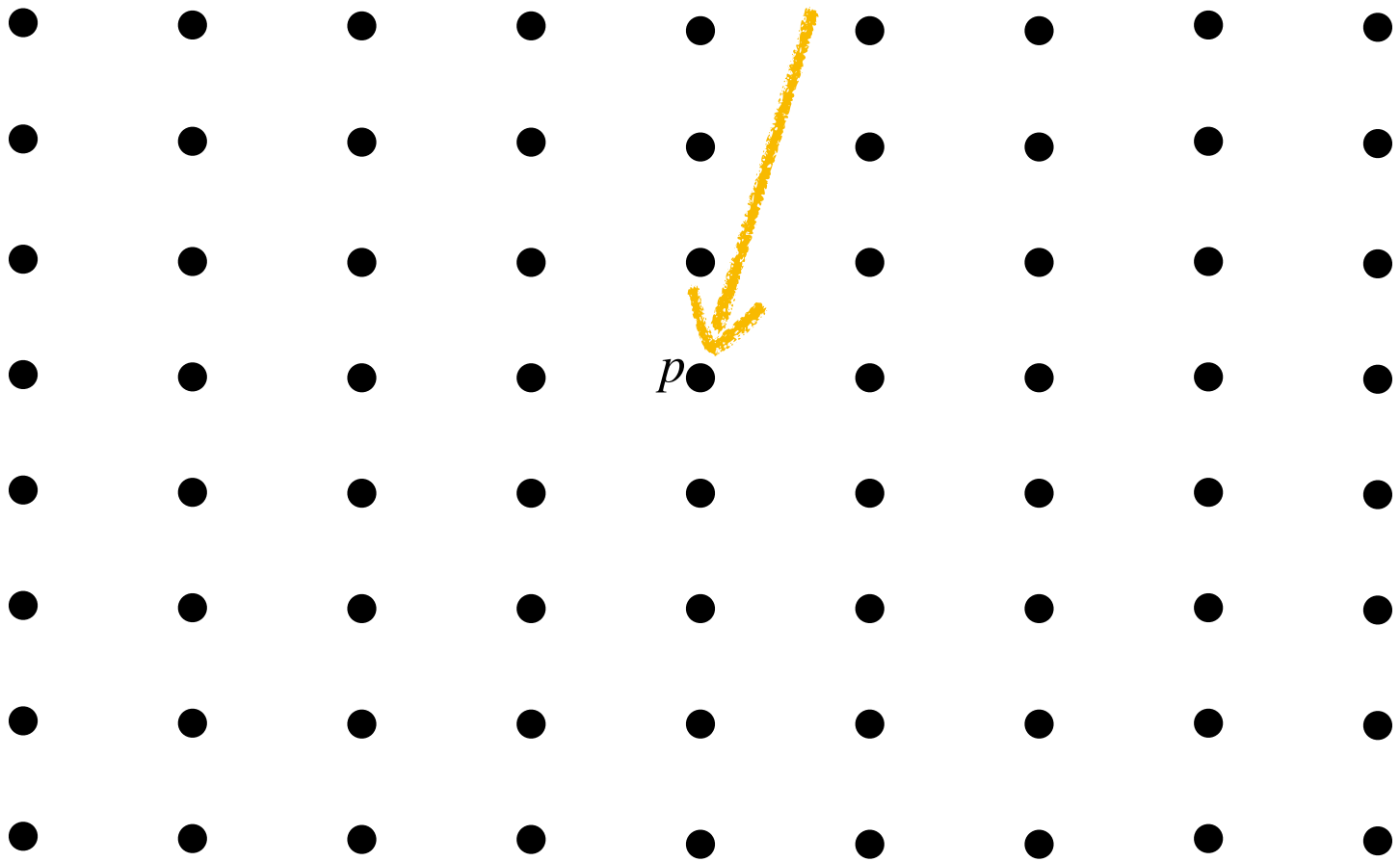
On the local treatment of (strong) electron correlation

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

So-called "lattice representation"

$\chi_p(\mathbf{r})$

Atomic or localized molecular orbital

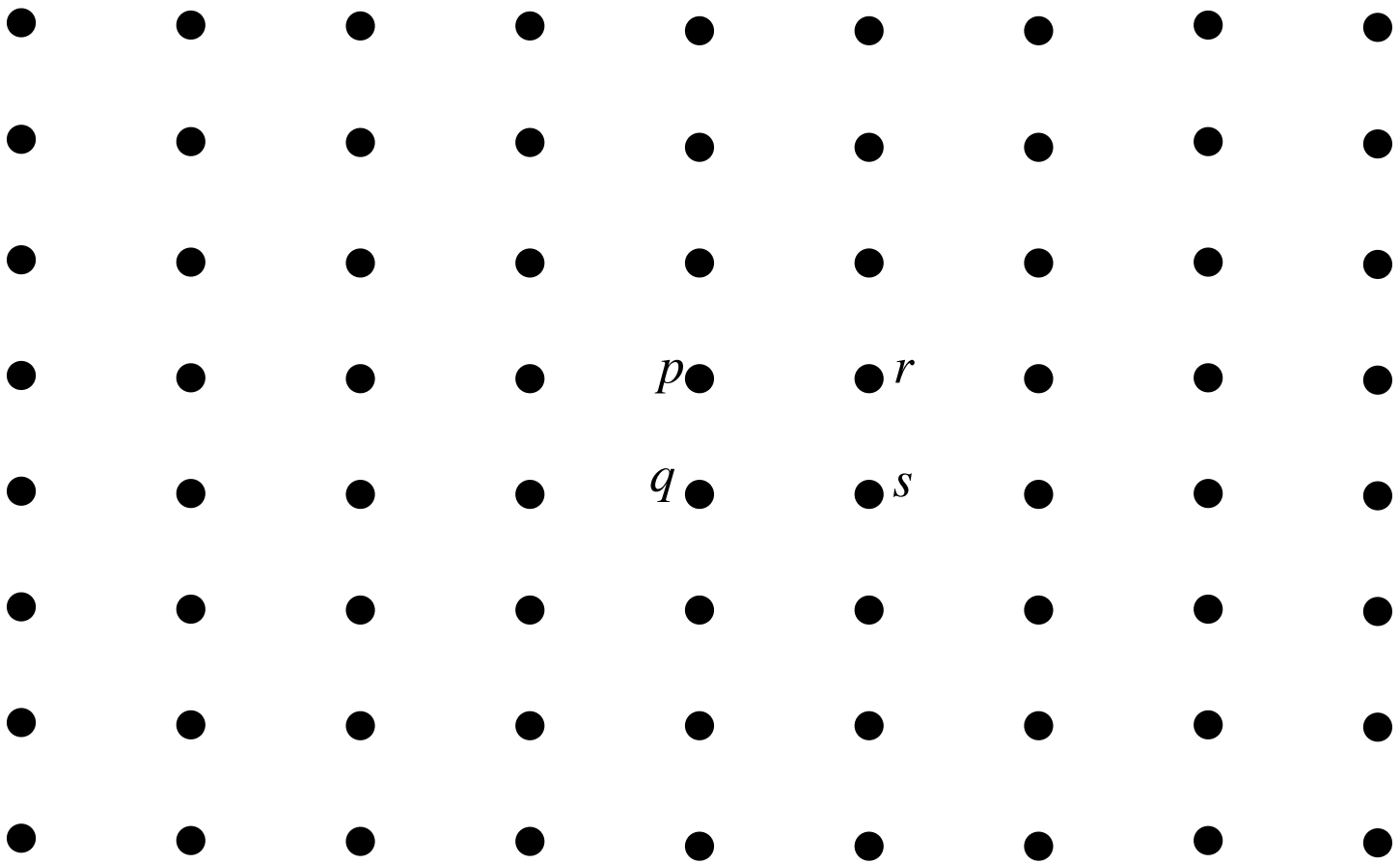


G. Knizia and G. K.-L. Chan, Phys. Rev. Lett. ***109****, 186404 (2012).*
S. Wouters, C. A. Jiménez-Hoyos, Q. Sun, and G. K.-L. Chan, J. Chem. Theory Comput. 12, 2706 (2016).

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

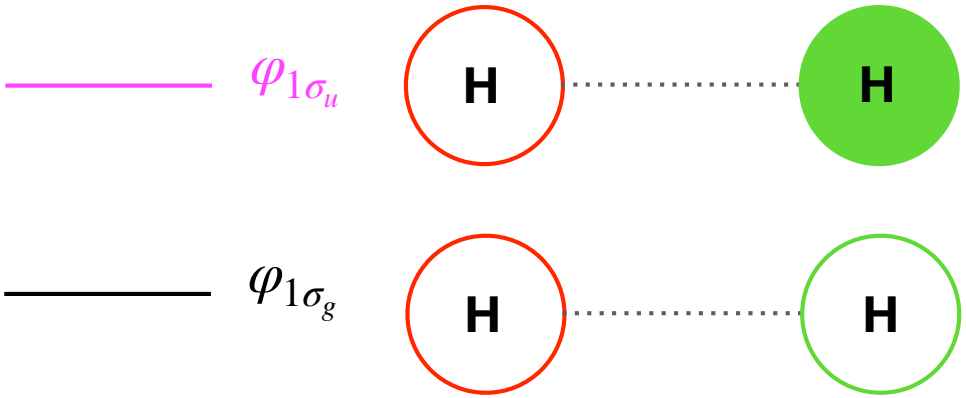
So-called "lattice representation"

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



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).

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



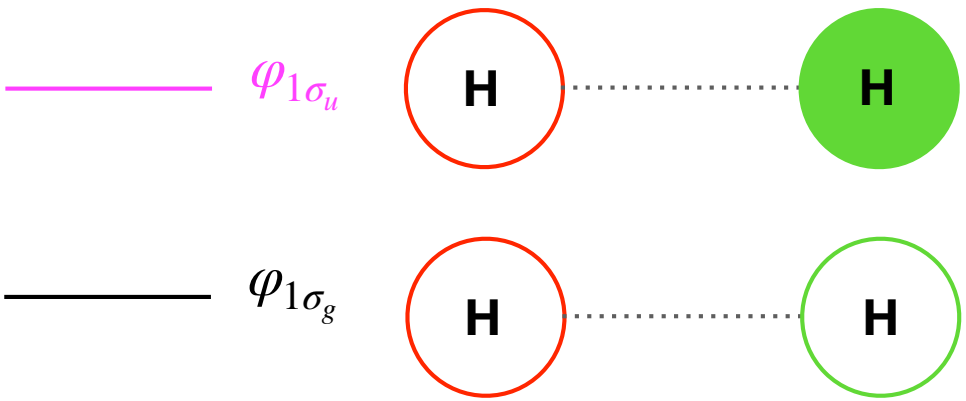
Anti-bonding orbital

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

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

Bonding orbital

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



Anti-bonding orbital

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

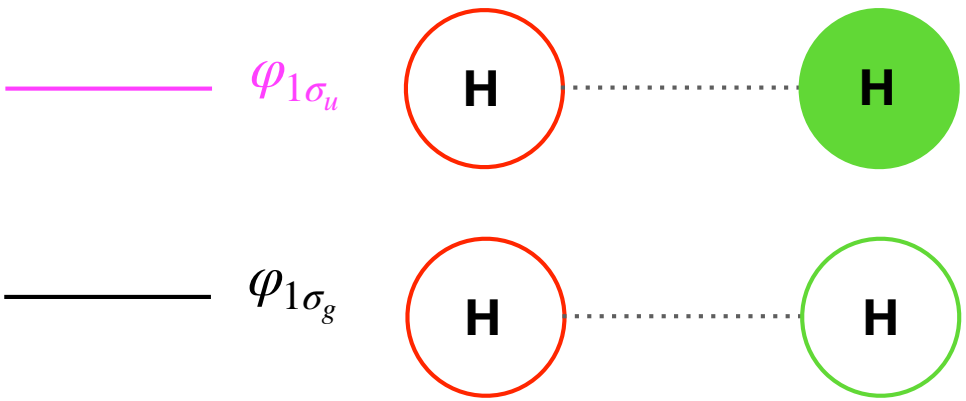
$$\varphi_{1\sigma_g}(\mathbf{r}) = \frac{1}{\sqrt{2}}\left(\chi_{s_A}(\mathbf{r}) + \chi_{s_B}(\mathbf{r})\right)$$

Bonding orbital

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

← **Delocalised picture (Chemistry)**

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



Anti-bonding orbital

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

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

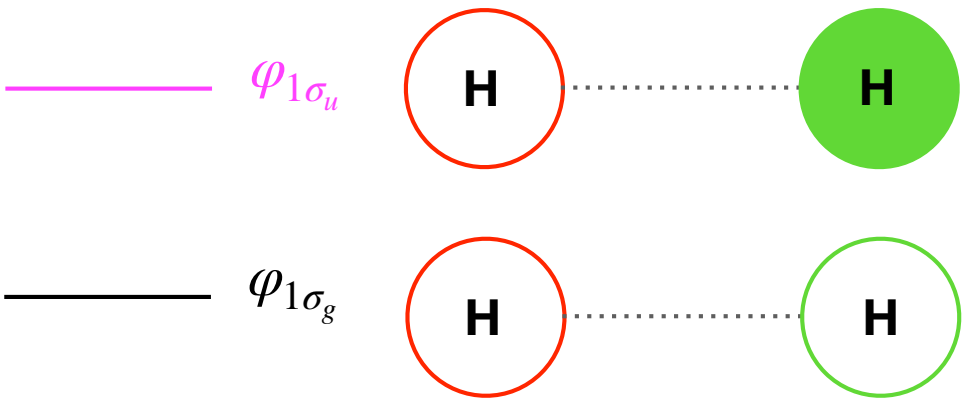
Bonding orbital

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

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

H ..... H H ..... H

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

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

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

H ..... H H ..... H

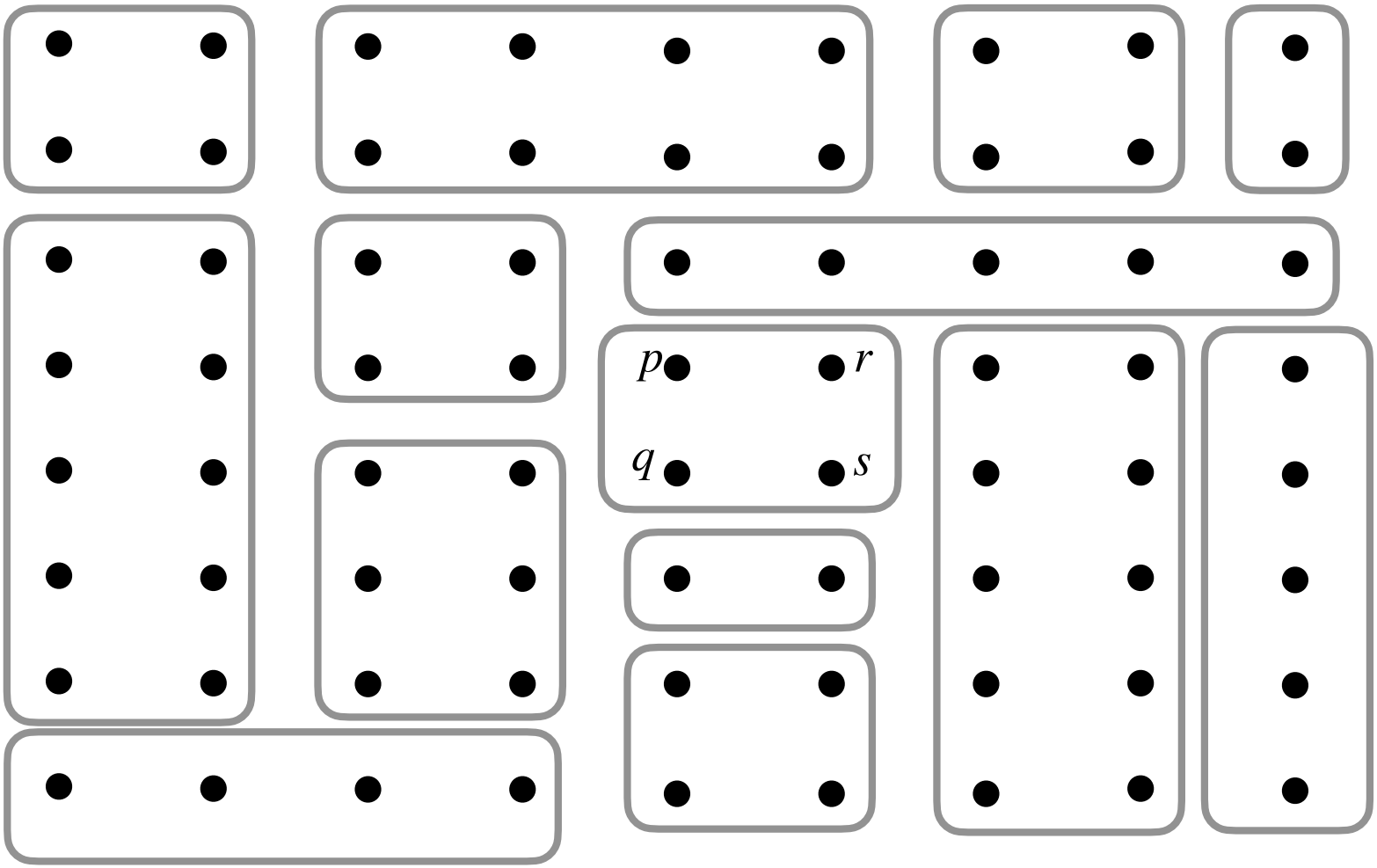
Consequence of the electronic repulsion on each atom!

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

Fragmentation

for treating strong local electron correlations

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

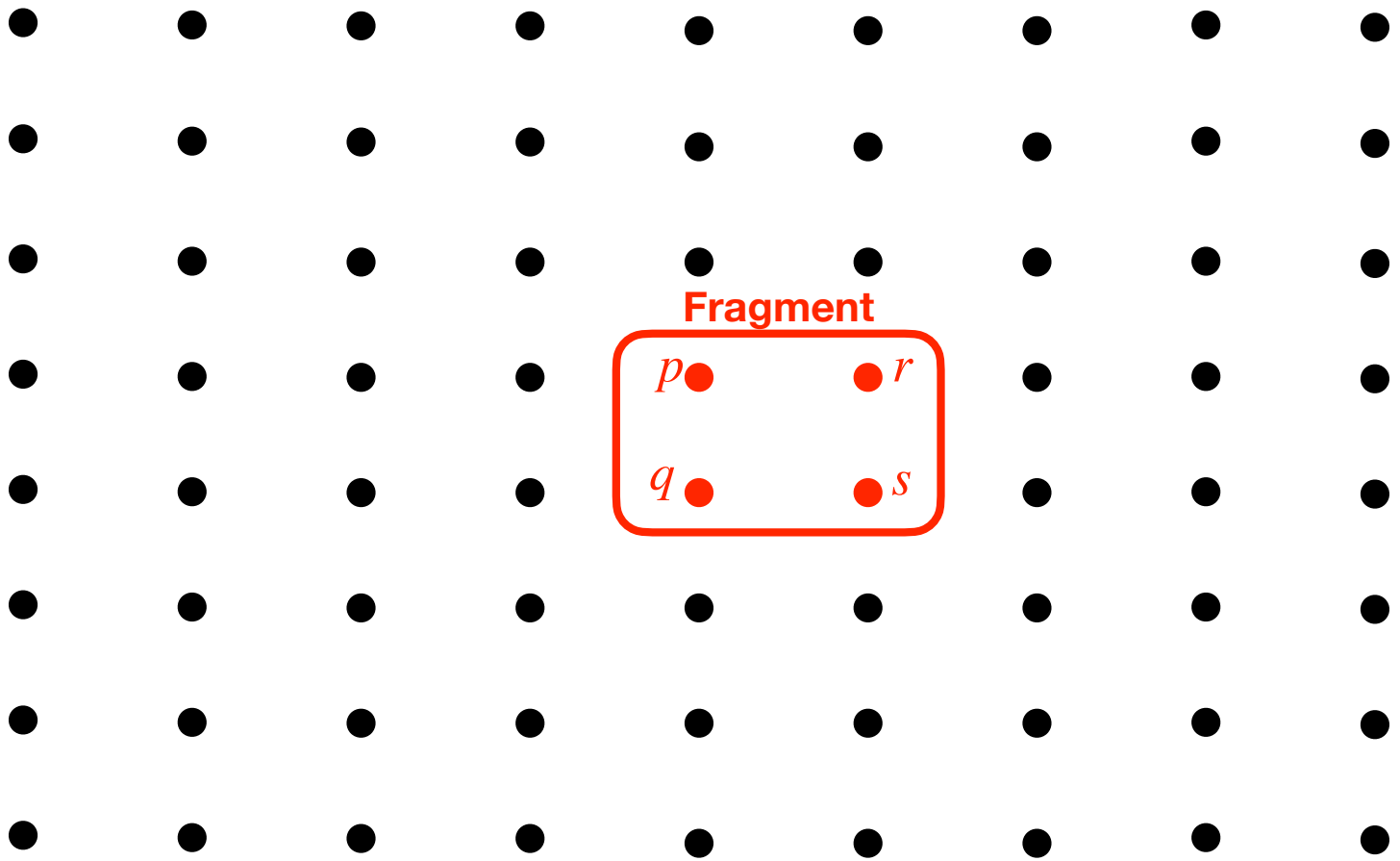


G. Knizia and G. K.-L. Chan, Phys. Rev. Lett. ***109****, 186404 (2012).*
S. Wouters, C. A. Jiménez-Hoyos, Q. Sun, and G. K.-L. Chan, J. Chem. Theory Comput. 12, 2706 (2016).

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

So-called "lattice representation"

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

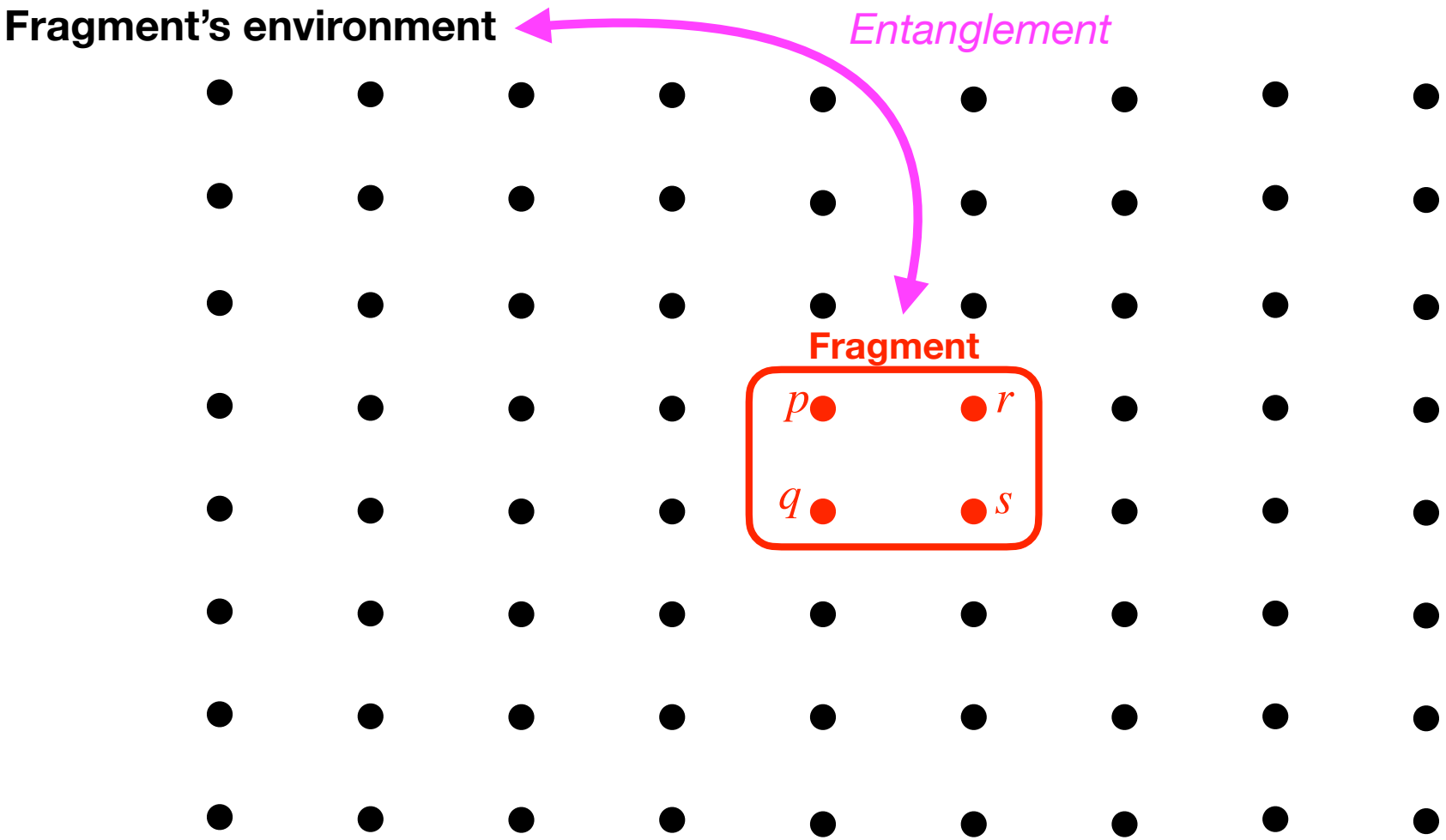


G. Knizia and G. K.-L. Chan, Phys. Rev. Lett. ***109****, 186404 (2012).*
S. Wouters, C. A. Jiménez-Hoyos, Q. Sun, and G. K.-L. Chan, J. Chem. Theory Comput. 12, 2706 (2016).

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

So-called "lattice representation"

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

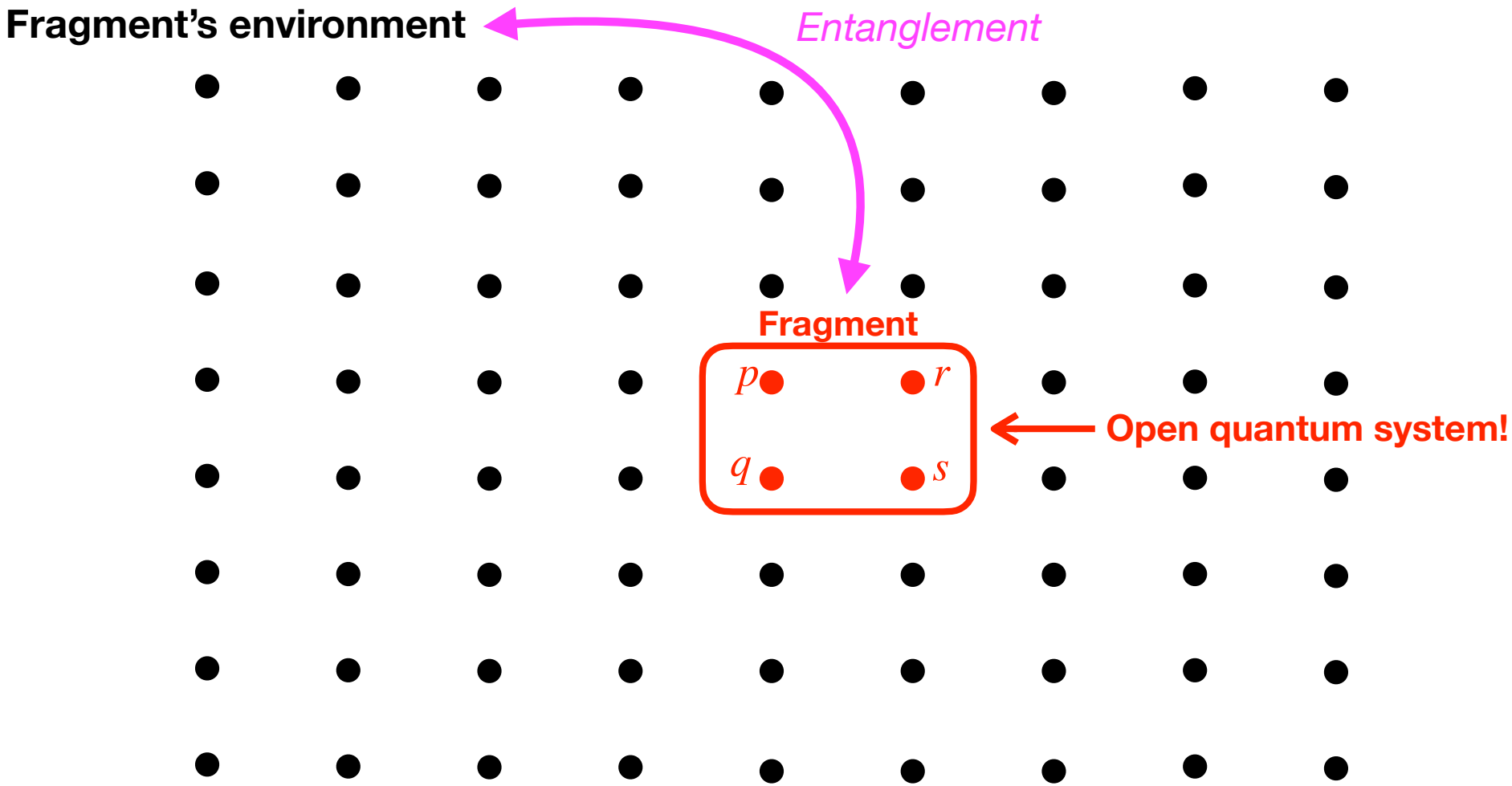


G. Knizia and G. K.-L. Chan, Phys. Rev. Lett. ***109****, 186404 (2012).*
S. Wouters, C. A. Jiménez-Hoyos, Q. Sun, and G. K.-L. Chan, J. Chem. Theory Comput. 12, 2706 (2016).

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

So-called "lattice representation"

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



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).

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

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

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

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

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

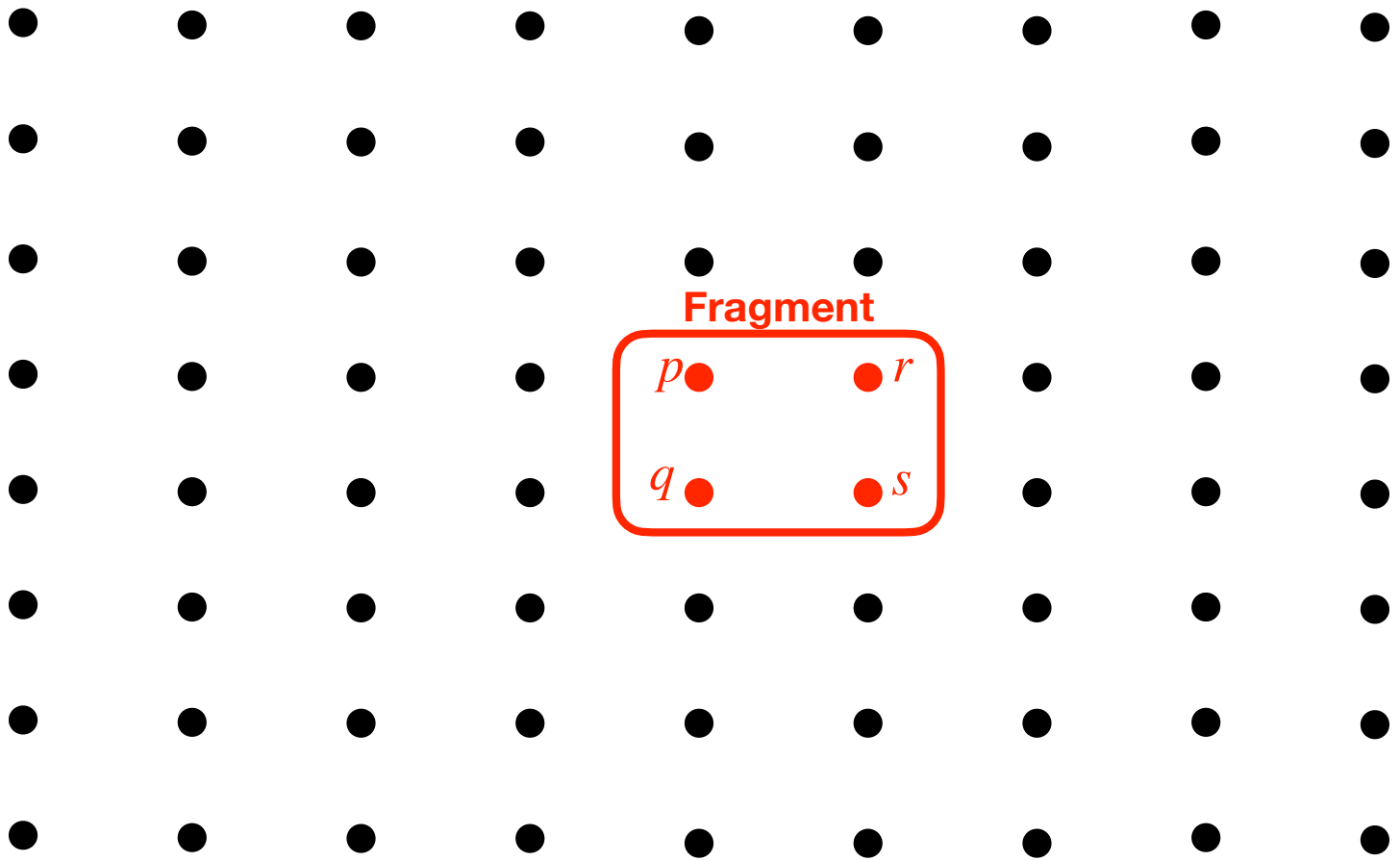
Philosophy of ***density matrix embedding theory*** *(DMET)*

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).

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

So-called "lattice representation"

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



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).

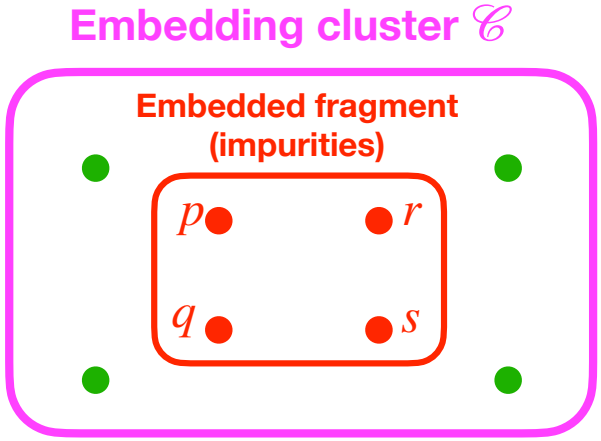
What are we aiming at?

Reduction in size of the problem to be solved:

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

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

Quantum bath
≡ electronic reservoir



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

G. Knizia and G. K.-L. Chan, Phys. Rev. Lett. ***109****, 186404 (2012).*
S. Wouters, C. A. Jiménez-Hoyos, Q. Sun, and G. K.-L. Chan, J. Chem. Theory Comput. 12, 2706 (2016).
S. Sekaran, M. Tsuchiizu, M. Saubanère, and E. Fromager, Phys. Rev. B **104**, 035121 (2021).
S. Sekaran, O. Bindech, and E. Fromager, J. Chem. Phys. **159**, 034107 (2023).

What are we aiming at?

Reduction in size of the problem to be solved:

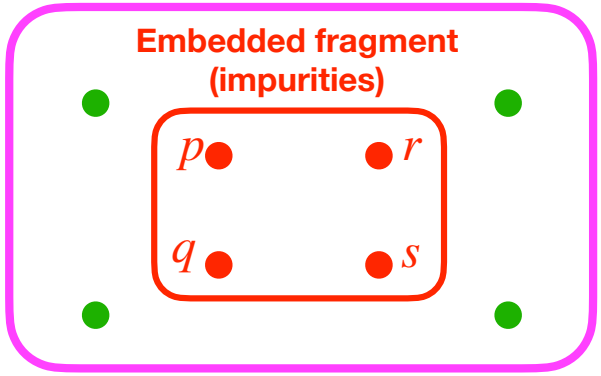
$$\langle \hat{c}_p^\dagger \hat{c}_q \rangle_{full\ system} \approx \langle \hat{c}_p^\dagger \hat{c}_q \rangle_{\Psi^{\mathscr{C}}}$$

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

4 orbitals here: Why and how?

Quantum bath
≡ electronic reservoir

Embedding cluster $\mathscr{C}$



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

G. Knizia and G. K.-L. Chan, Phys. Rev. Lett. ***109****, 186404 (2012).*
S. Wouters, C. A. Jiménez-Hoyos, Q. Sun, and G. K.-L. Chan, J. Chem. Theory Comput. 12, 2706 (2016).
S. Sekaran, M. Tsuchiizu, M. Saubanère, and E. Fromager, Phys. Rev. B **104**, 035121 (2021).
S. Sekaran, O. Bindech, and E. Fromager, J. Chem. Phys. **159**, 034107 (2023).

What are we aiming at?

Reduction in size of the problem to be solved:

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

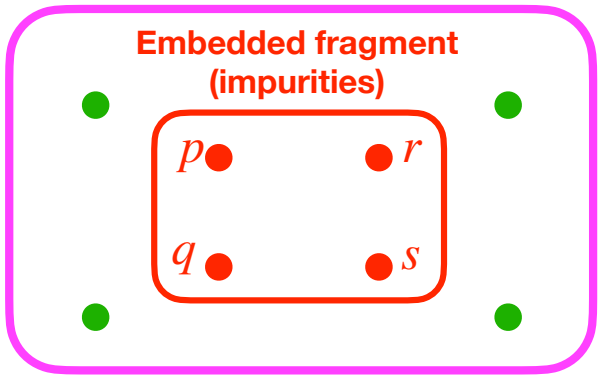
$$\langle \hat{c}_p^\dagger \hat{c}_q^\dagger \hat{c}_s \hat{c}_r \rangle_{full\ system} \approx \langle \hat{c}_p^\dagger \hat{c}_q^\dagger \hat{c}_s \hat{c}_r \rangle_{\Psi^{\mathscr{C}}}$$

4 orbitals here: Why and how?

↓

Quantum bath
≡ electronic reservoir

Embedding cluster $\mathscr{C}$



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

How many?

↓

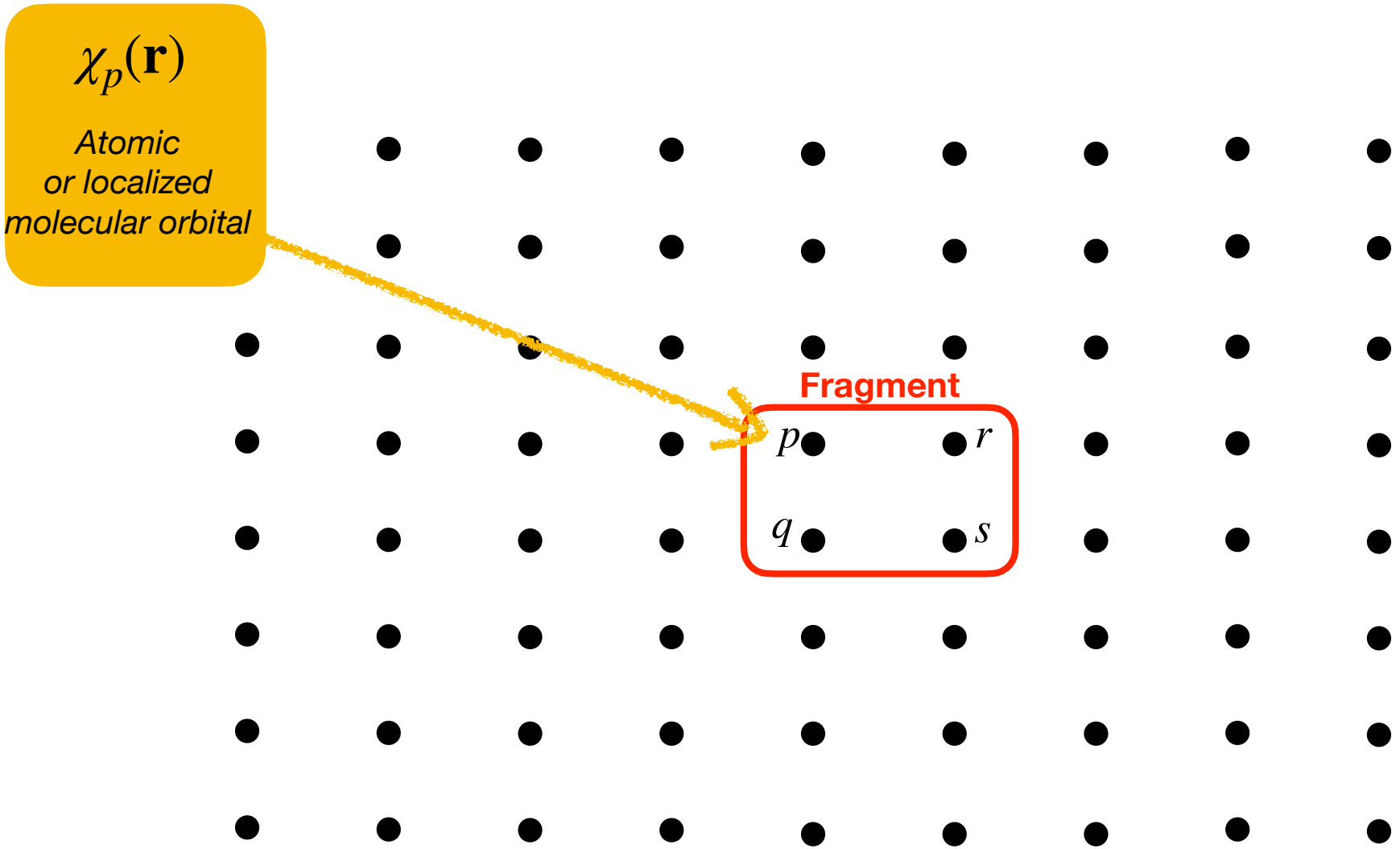
Few-electron
correlated wave function

G. Knizia and G. K.-L. Chan, Phys. Rev. Lett. ***109****, 186404 (2012).*
S. Wouters, C. A. Jiménez-Hoyos, Q. Sun, and G. K.-L. Chan, J. Chem. Theory Comput. 12, 2706 (2016).
S. Sekaran, M. Tsuchiizu, M. Saubanère, and E. Fromager, Phys. Rev. B **104**, 035121 (2021).
S. Sekaran, O. Bindech, and E. Fromager, J. Chem. Phys. **159**, 034107 (2023).

Mathematical construction of the quantum bath in DMET

Clusterization through a unitary one-electron transformation

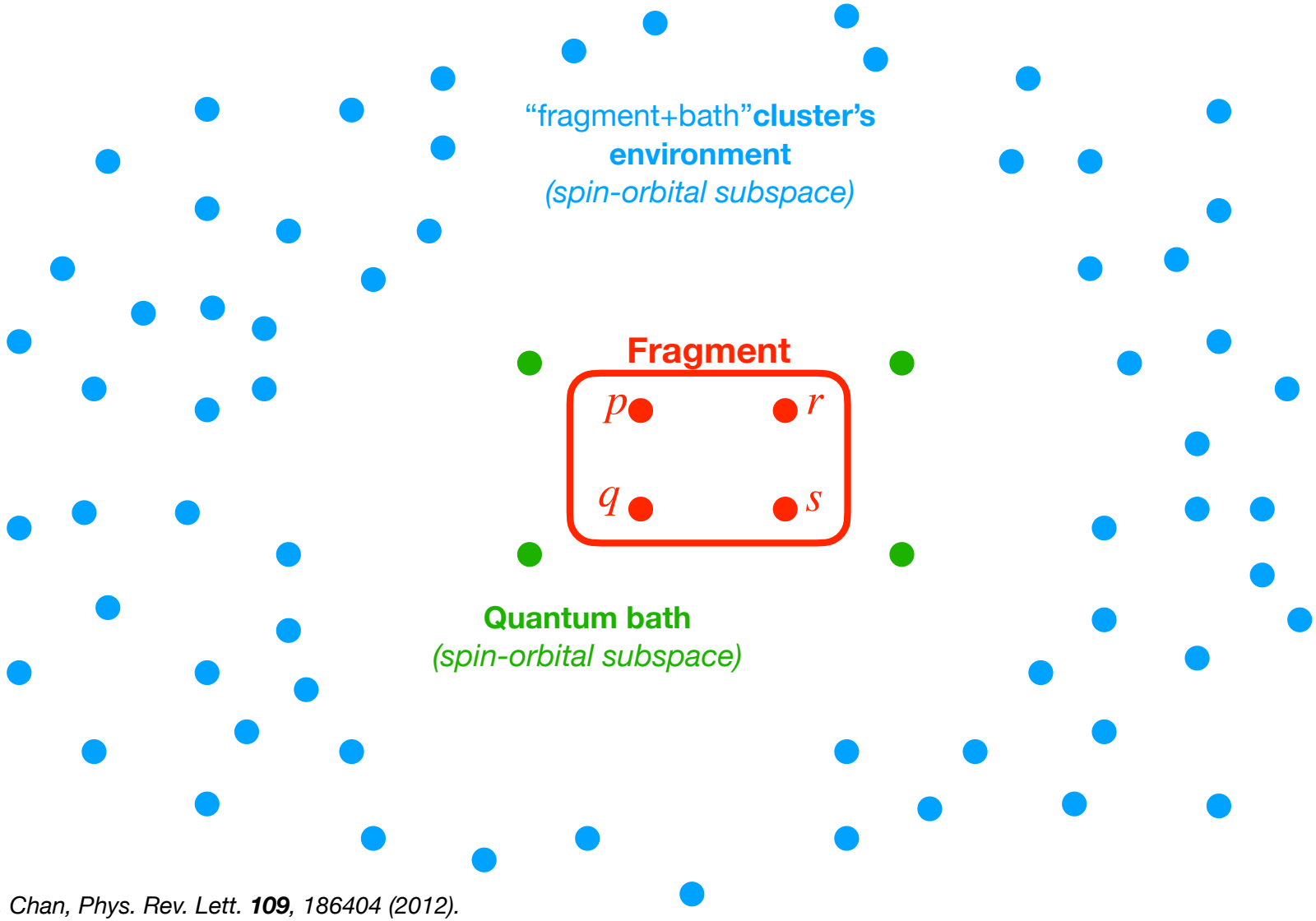
So-called "lattice representation"



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).

Clusterization through a unitary one-electron transformation

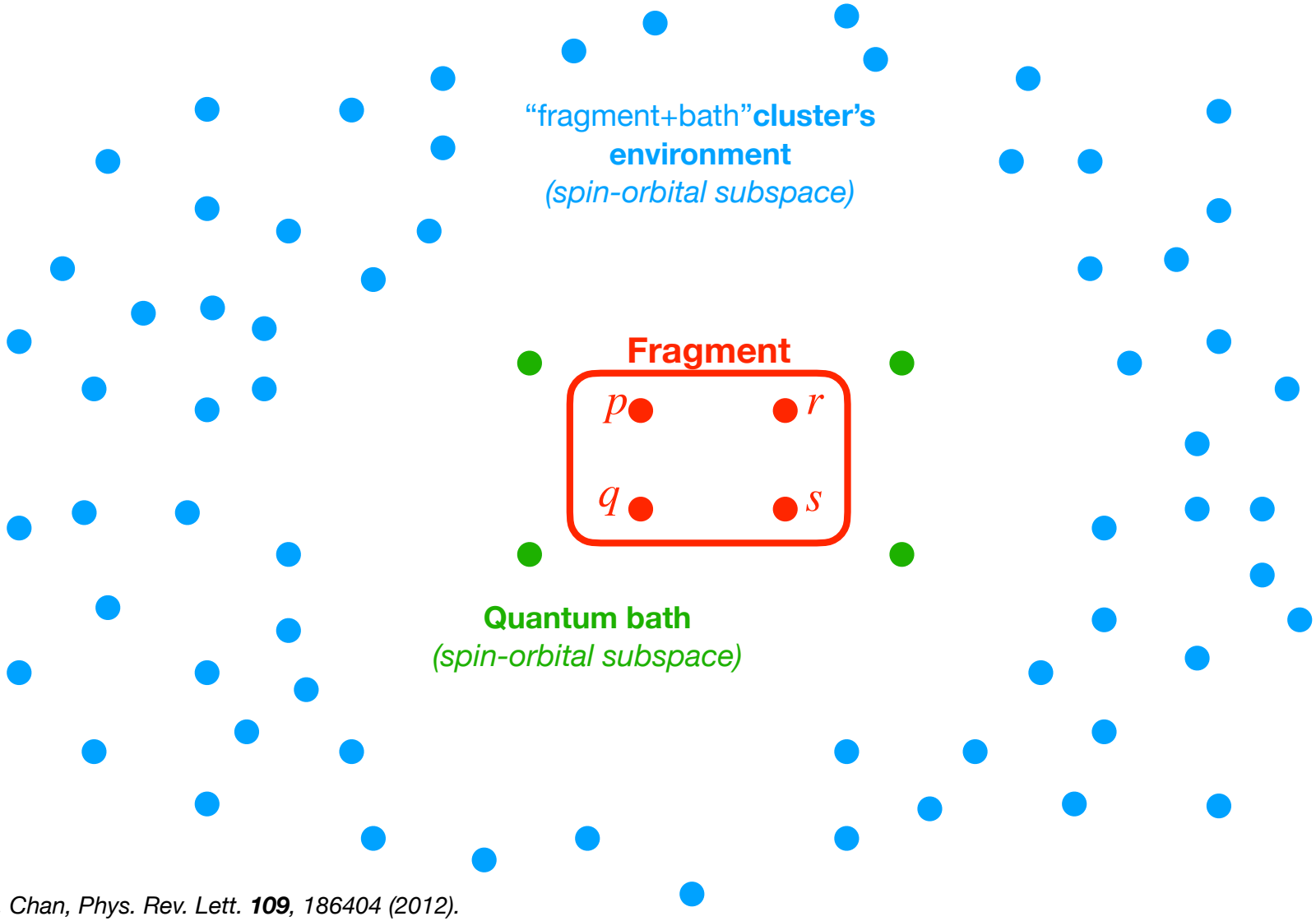
$$|\chi_q\rangle \rightarrow \sum_p^{lattice} \mathcal{U}^*_{pq} |\chi_p\rangle \quad \Leftrightarrow \quad \langle\chi_q| \rightarrow \sum_p^{lattice} \mathcal{U}_{pq} \langle\chi_p|$$



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).

Clusterization through a unitary one-electron transformation

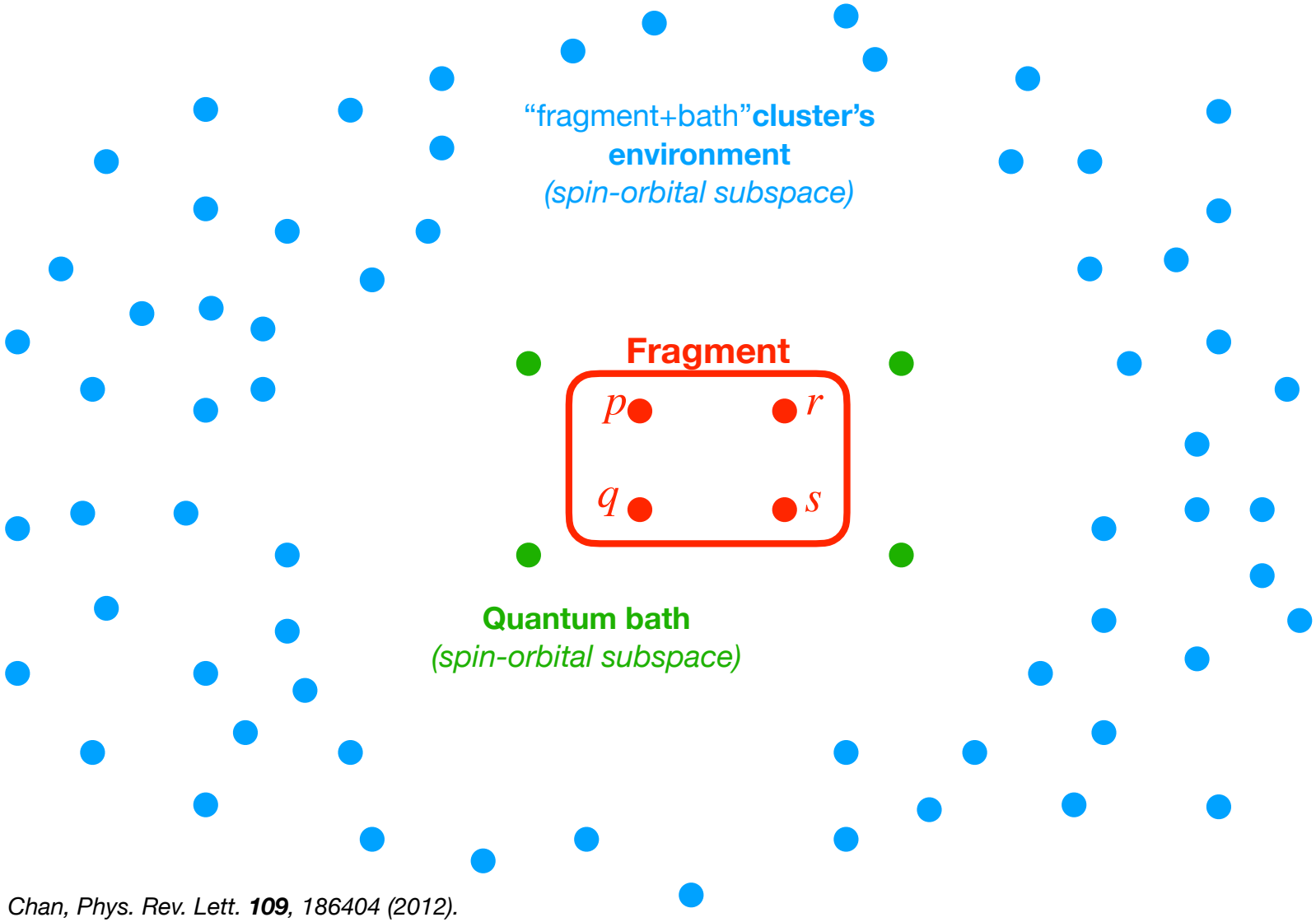
$$\langle \chi_q | \rightarrow \sum_p^{lattice} \mathcal{U}_{pq} \langle \chi_p | \quad \Leftrightarrow \quad \hat{c}_q \rightarrow \sum_p^{lattice} \mathcal{U}_{pq} \hat{c}_p \overset{notation}{=} \hat{d}_q$$



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).

$$\hat{c}_q \rightarrow \sum_{p}^{lattice} \mathcal{U}_{pq} \hat{c}_p \overset{notation}{=} \hat{d}_q$$

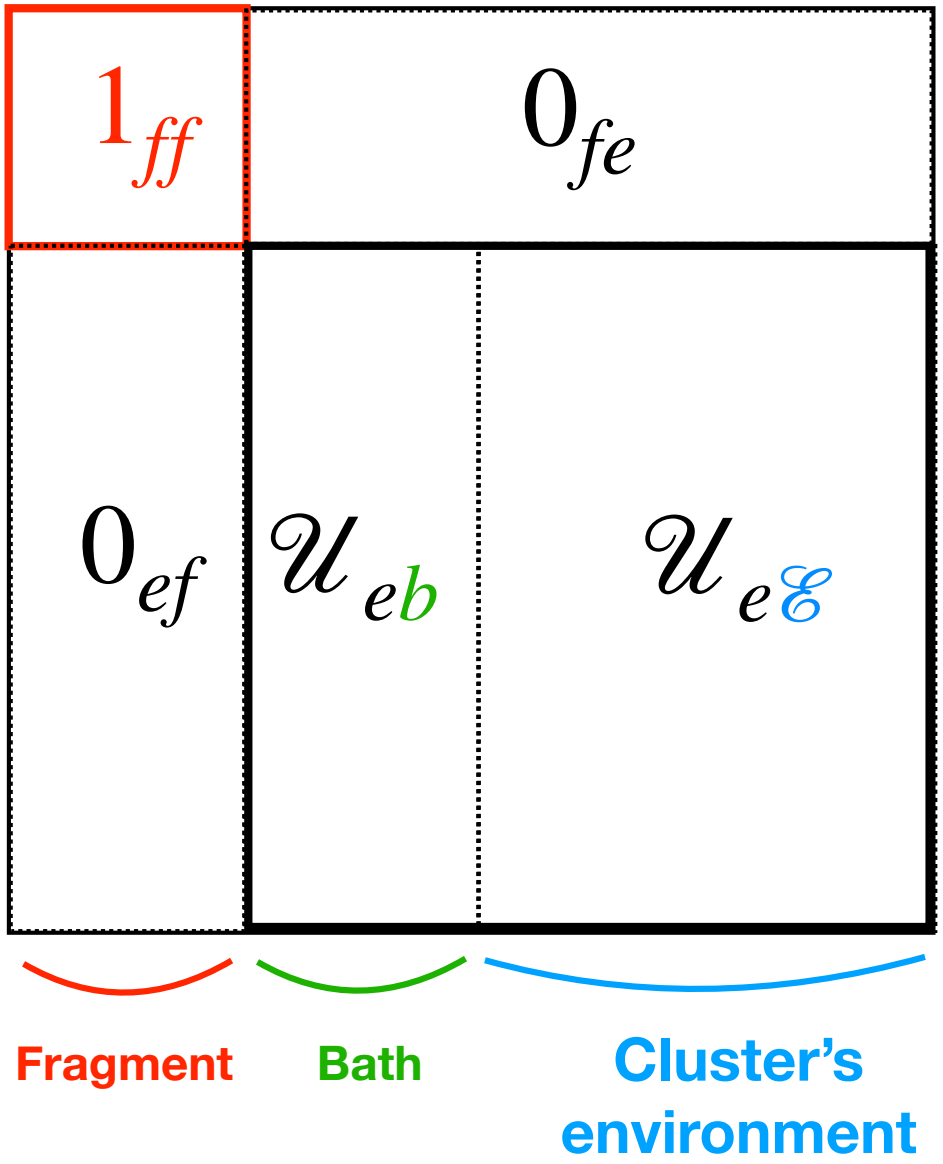
???



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).

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

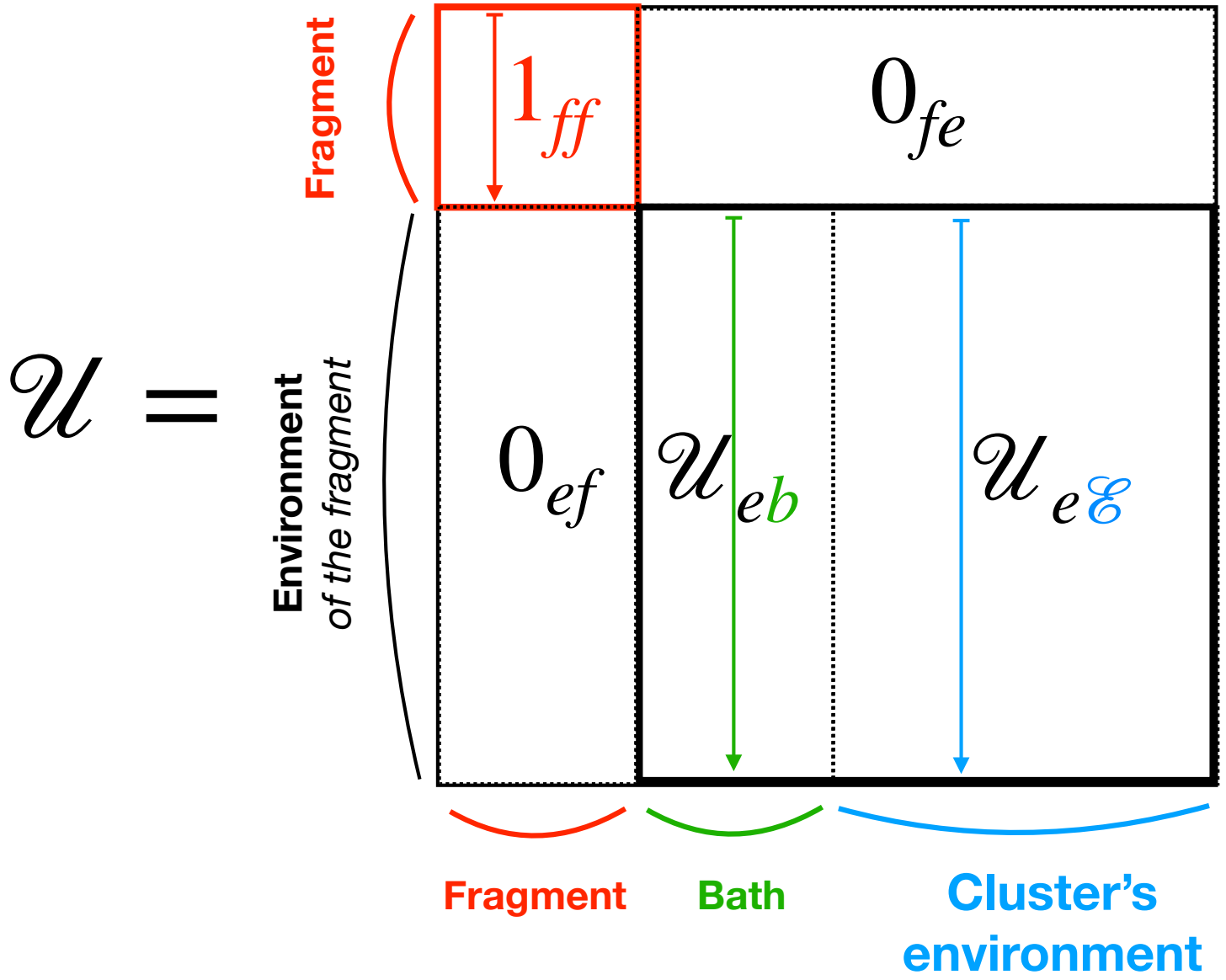
$$\mathcal{U} =$$



$$\hat{d}_q = \sum_{p}^{lattice} \mathcal{U}_{pq} \hat{c}_p$$

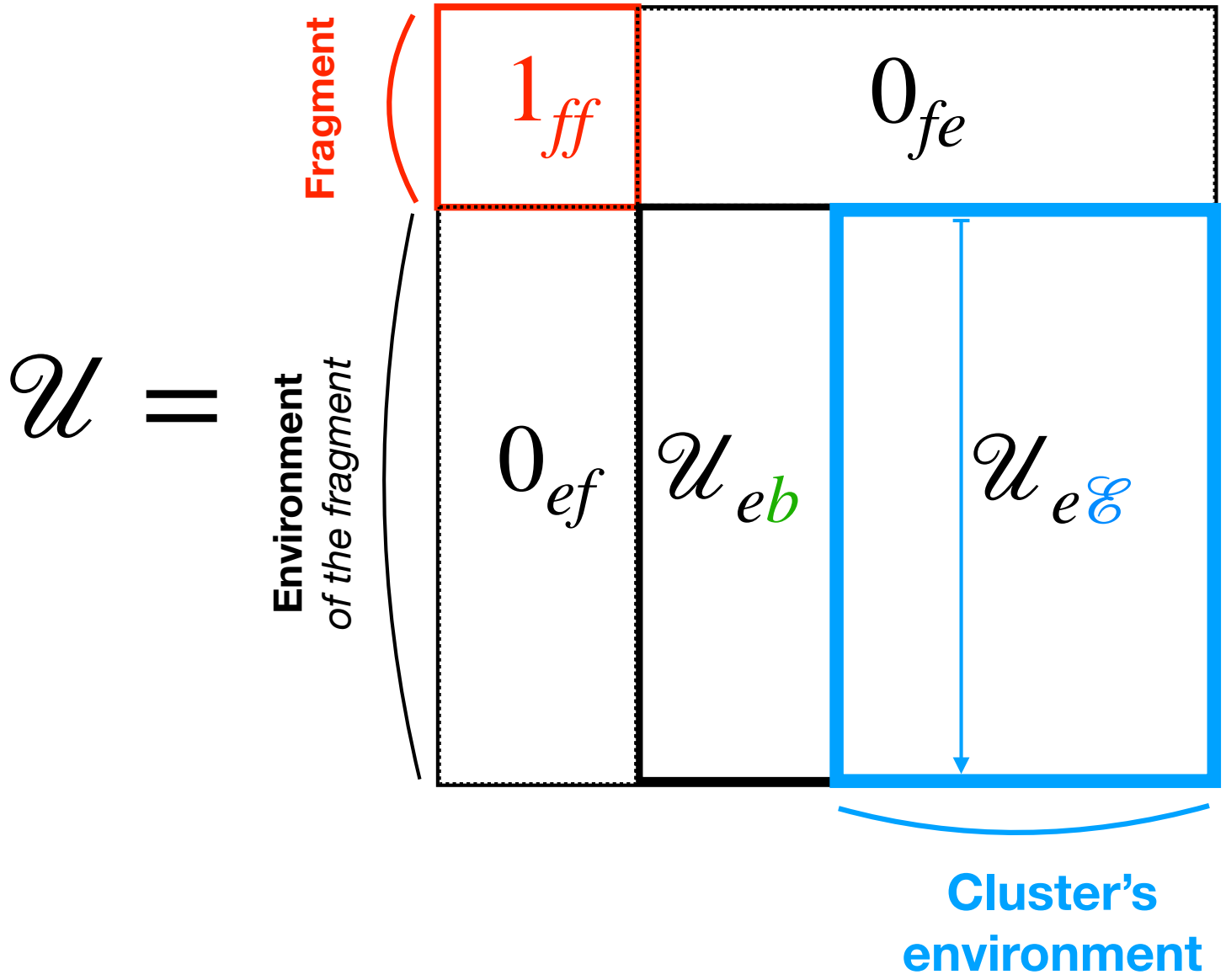
S. Sekaran, O. Bindech, and E. Fromager, J. Chem. Phys. **159**, 034107 (2023).

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



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

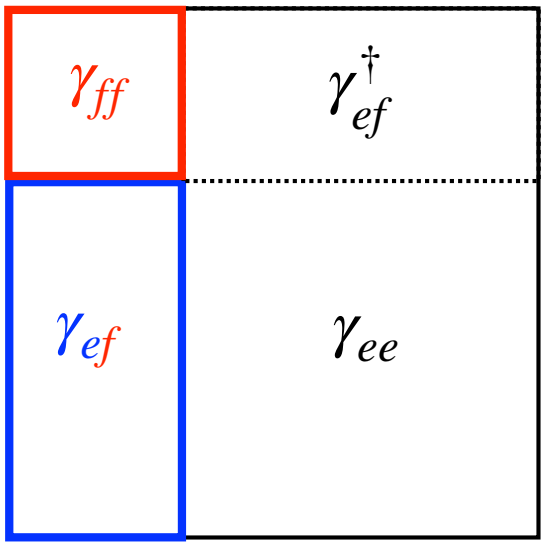
Quantum bath seen as a functional of the density matrix (1RDM)



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

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

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



← **Lattice representation!**

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

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

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

Env.-fragment block

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

Cluster's environment

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

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

Will be justified later on…

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

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

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

Env.-fragment block

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

Cluster's environment

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

Orthogonality constraint

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

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

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

Env.-fragment block

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

Cluster's environment

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

Orthogonality constraint

Spin-orbital subspace →

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

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

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

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

Env.-fragment block

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

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

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

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

Env.-fragment block

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

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

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

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

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

Env.-fragment block

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

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

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

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

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

Env.-fragment block

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

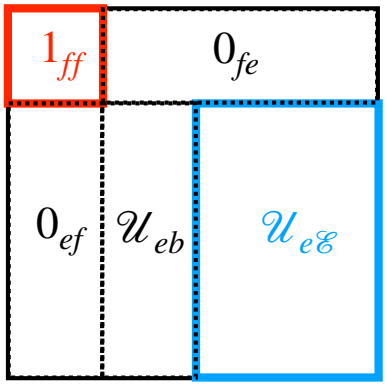
Cluster's environment

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

Orthogonality constraint

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

Unitary transformed density matrix



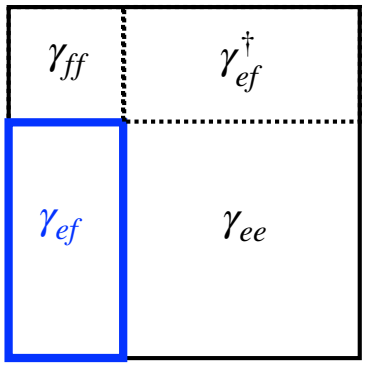
$$\left\{\langle \hat{d}_p^\dagger \hat{d}_q \rangle\right\} \equiv \tilde{\gamma} = \mathcal{U}^\dagger \gamma \mathcal{U} \equiv$$

New *embedding representation*

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

$$\left\{\langle \hat{c}_p^\dagger \hat{c}_q \rangle\right\} \equiv$$

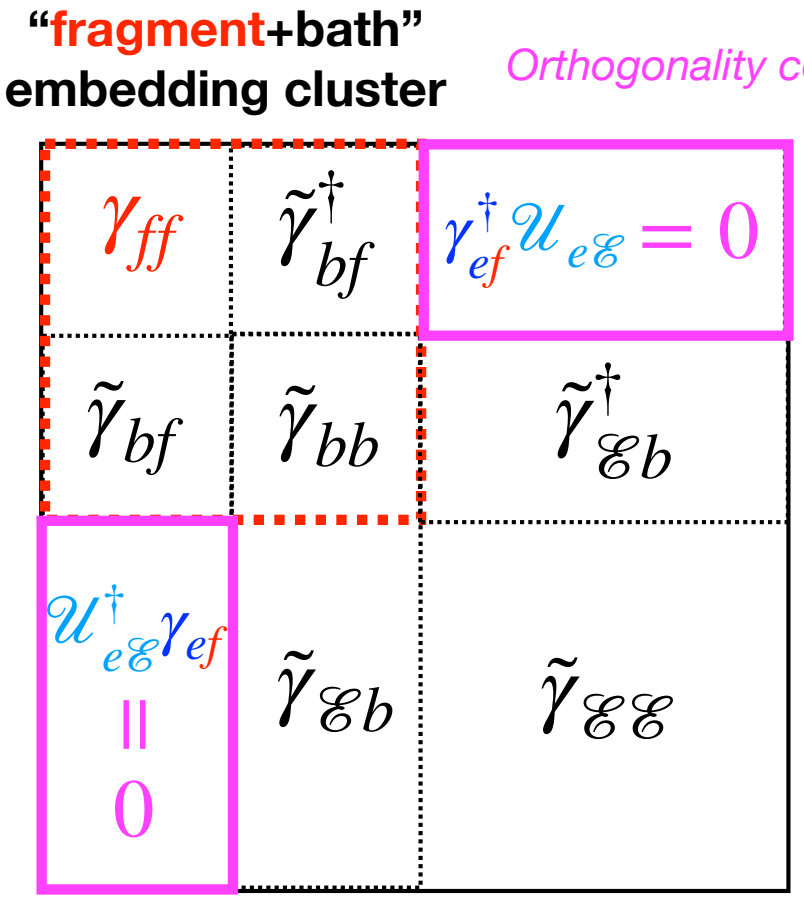
Original *lattice representation*



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

Unitary transformed density matrix

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

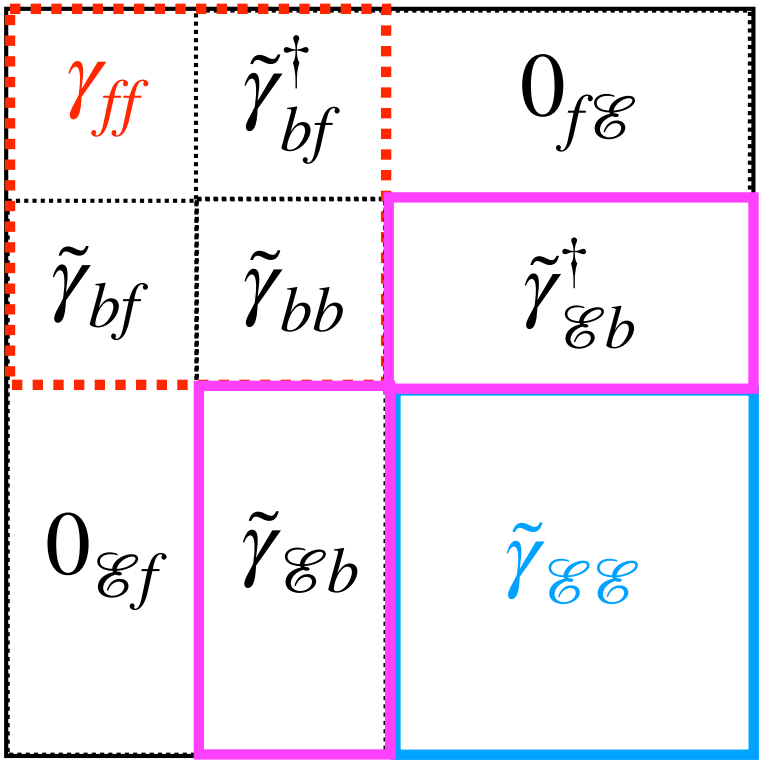


S. Sekaran, O. Bindech, and E. Fromager, J. Chem. Phys. **159**, 034107 (2023).

Unitary transformed density matrix

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

"fragment+bath" embedding cluster



Cluster's environment

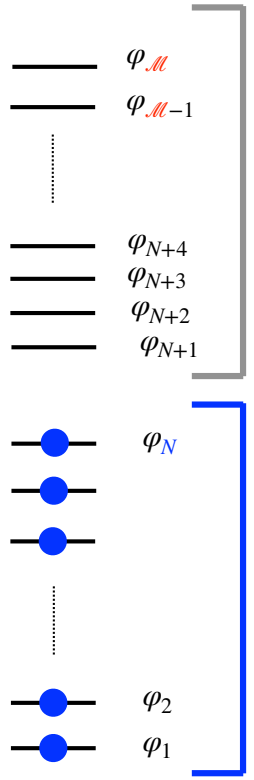
Entanglement

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

What if the full-system density matrix is idempotent?

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

Molecular orbital representation!



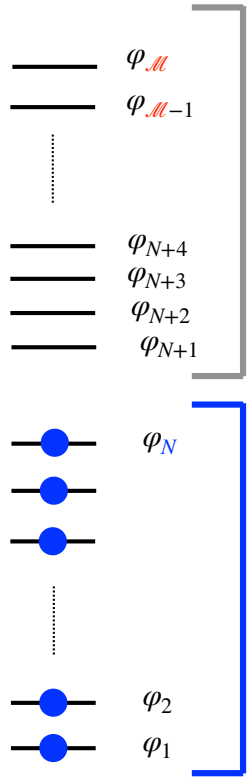
Mean-field (HF)
or Kohn-Sham DFT

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

What if the full-system density matrix is idempotent?

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

← **Molecular orbital representation!**



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

Mean-field (HF) or Kohn-Sham DFT

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

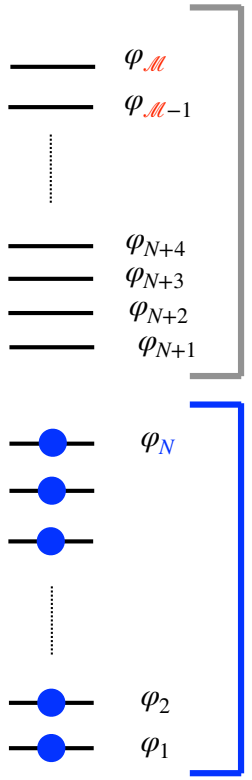
What if the full-system density matrix is idempotent?

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

$$\| $$

$$\gamma^2$$

Molecular orbital representation!

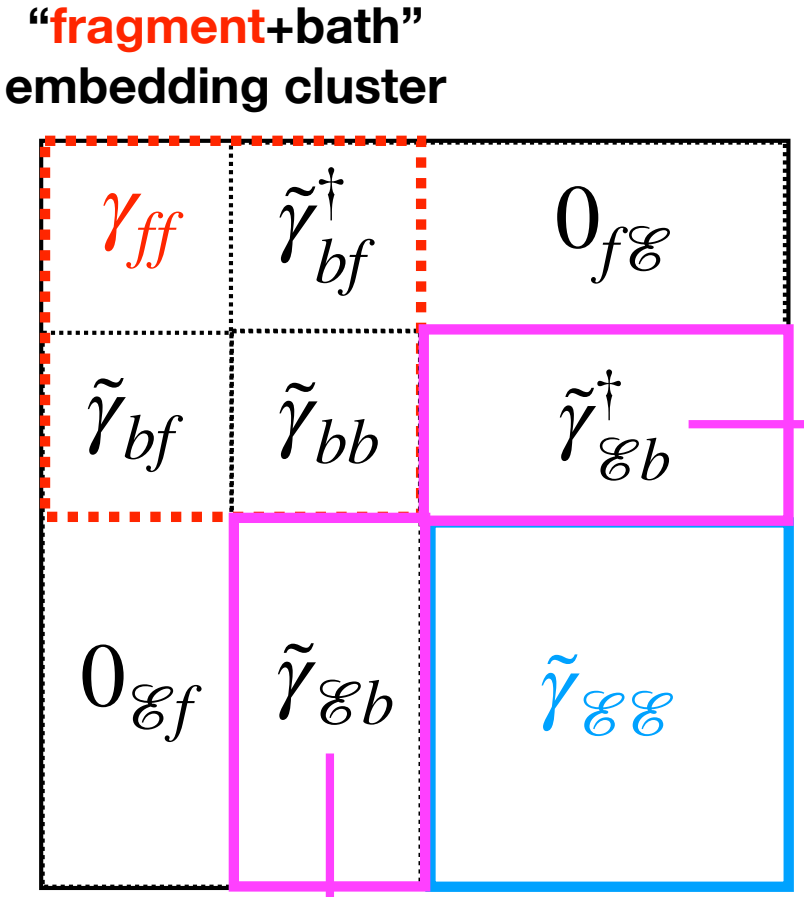


Mean-field (HF)
or Kohn-Sham DFT

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

Unitary transformed density matrix

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



if $\gamma^2 = \gamma$ then

idempotency

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

Unitary transformed density matrix

Disconnected embedding cluster ✅

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

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

Cluster's environment

idempotency

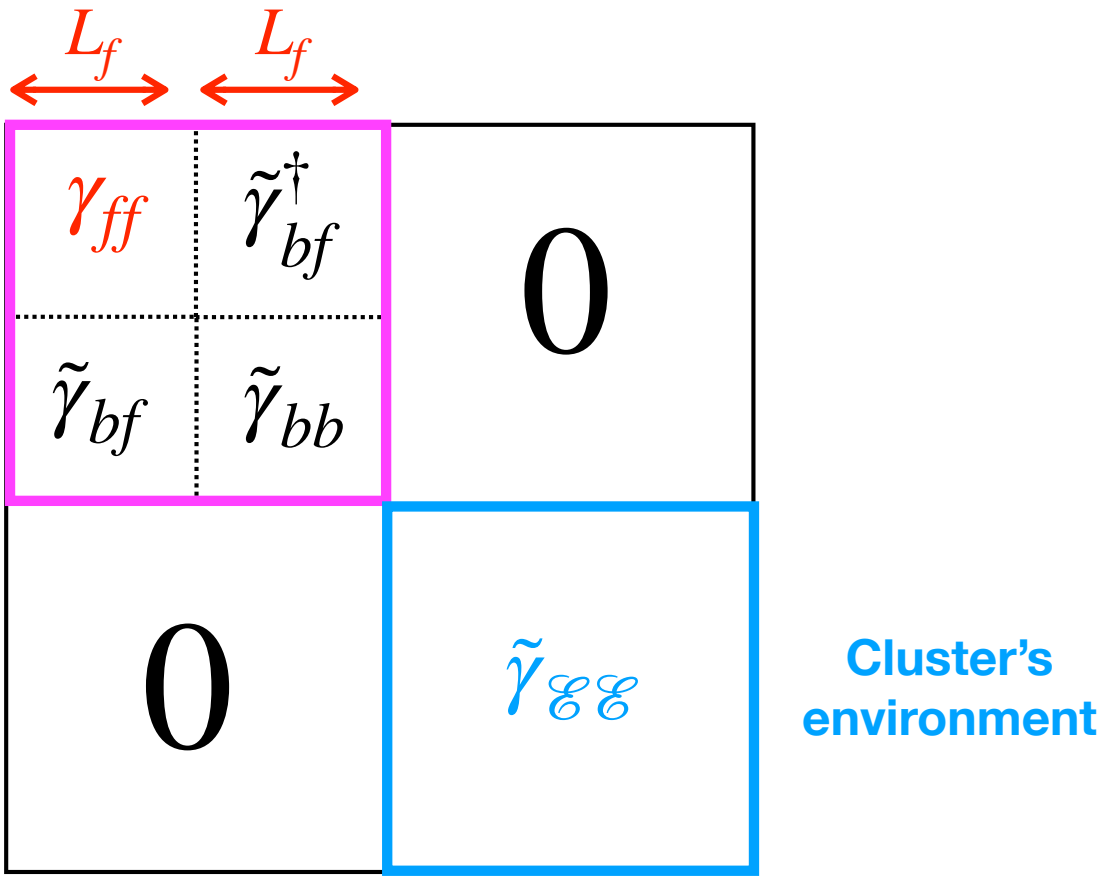
S. Sekaran, O. Bindech, and E. Fromager, J. Chem. Phys. **159**, 034107 (2023).

Unitary transformed density matrix

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

$\gamma^2 = \gamma$

idempotency



Cluster's environment

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

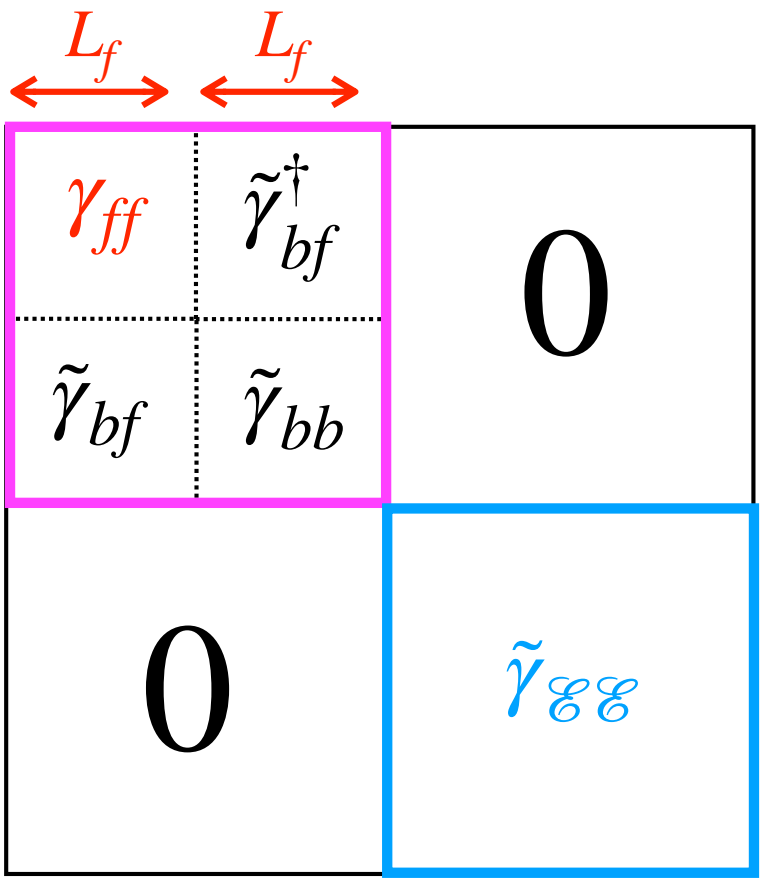
Unitary transformed density matrix

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

$\gamma^2 = \gamma$

idempotency

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



Cluster's environment

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

Unitary transformed density matrix

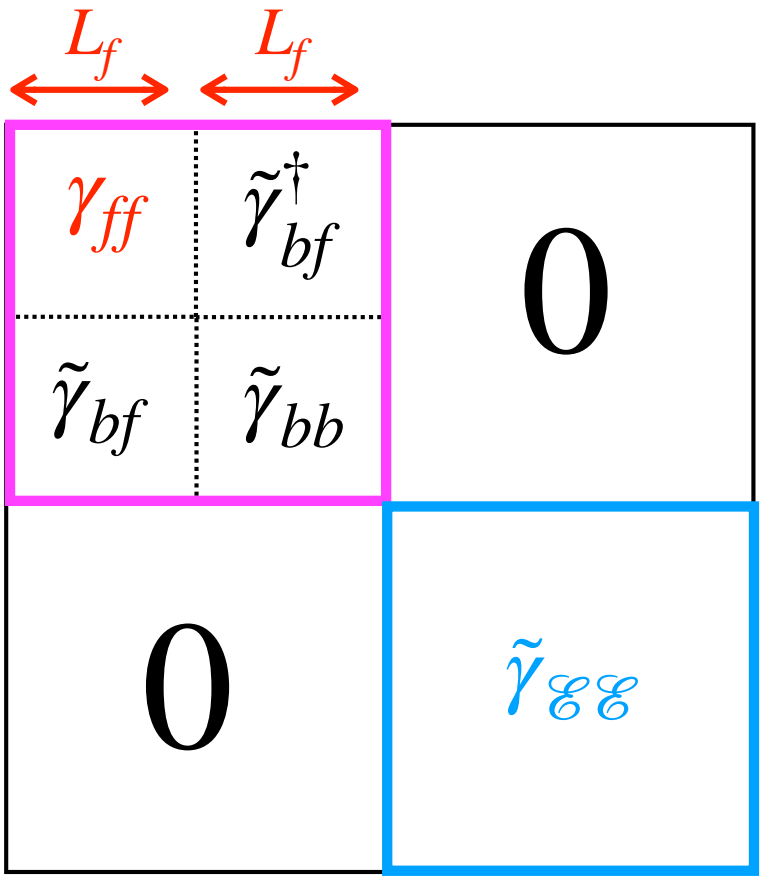
$$\gamma_{ff} + \tilde{\gamma}_{bf}^{-1}\tilde{\gamma}_{bb}\tilde{\gamma}_{bf} = 1_{ff}$$

$\gamma^2 = \gamma$

idempotency

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

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



Cluster's environment

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

Starting a DMET calculation…

Density matrix of the **full system**

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

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

Starting a DMET calculation…

Density matrix of the **full system**

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

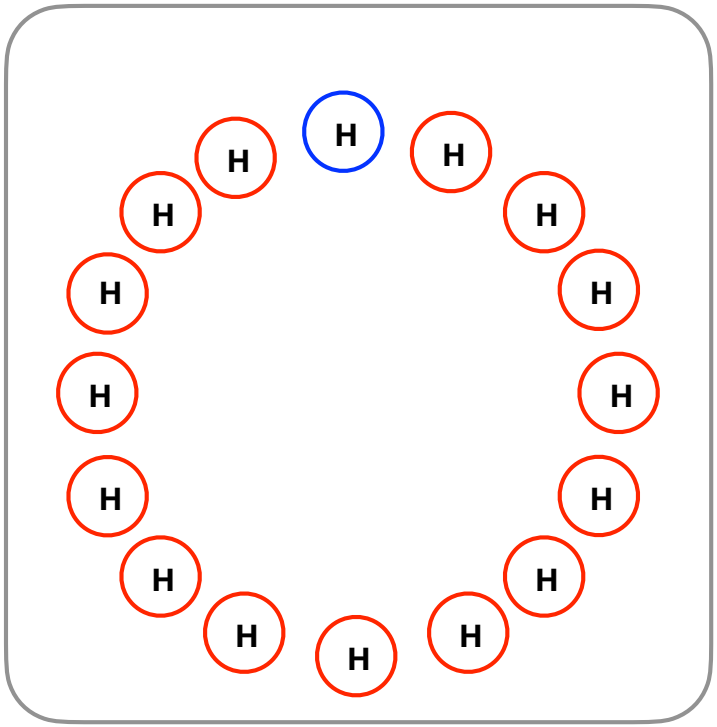
Mean-field evaluation in practice

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

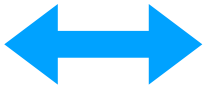
S. Wouters, C. A. Jiménez-Hoyos, Q. Sun, and G. K.-L. Chan, J. Chem. Theory Comput. 12, 2706 (2016).

Illustrative example

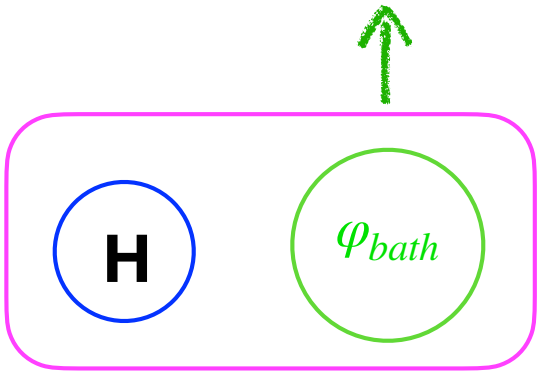
Rings of hydrogen atoms (Hubbard model)



N-electron system



Effective
neighbouring atom



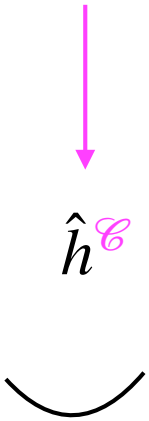
Two-electron system

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

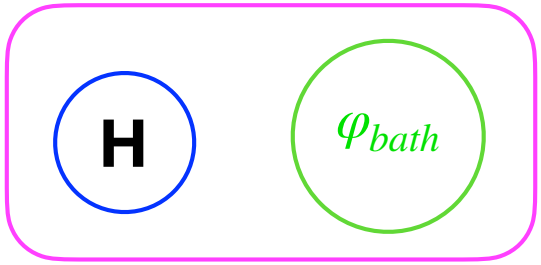
G. Knizia and G. K.-L. Chan, Phys. Rev. Lett. ***109****, 186404 (2012).*
S. Sekaran, M. Tsuchiizu, M. Saubanère, and E. Fromager, Phys. Rev. B ***104****, 035121 (2021).*
S. Sekaran, M. Saubanère, and E. Fromager, Computation **2022***, 10,* 45.

Approximate embedding of interacting Hamiltonians

One-electron Hamiltonian of the cluster



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



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

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

Approximate embedding of interacting Hamiltonians

One-electron Hamiltonian of the cluster

Two-electron repulsion on the impurity

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

Exact non-interacting embedding

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

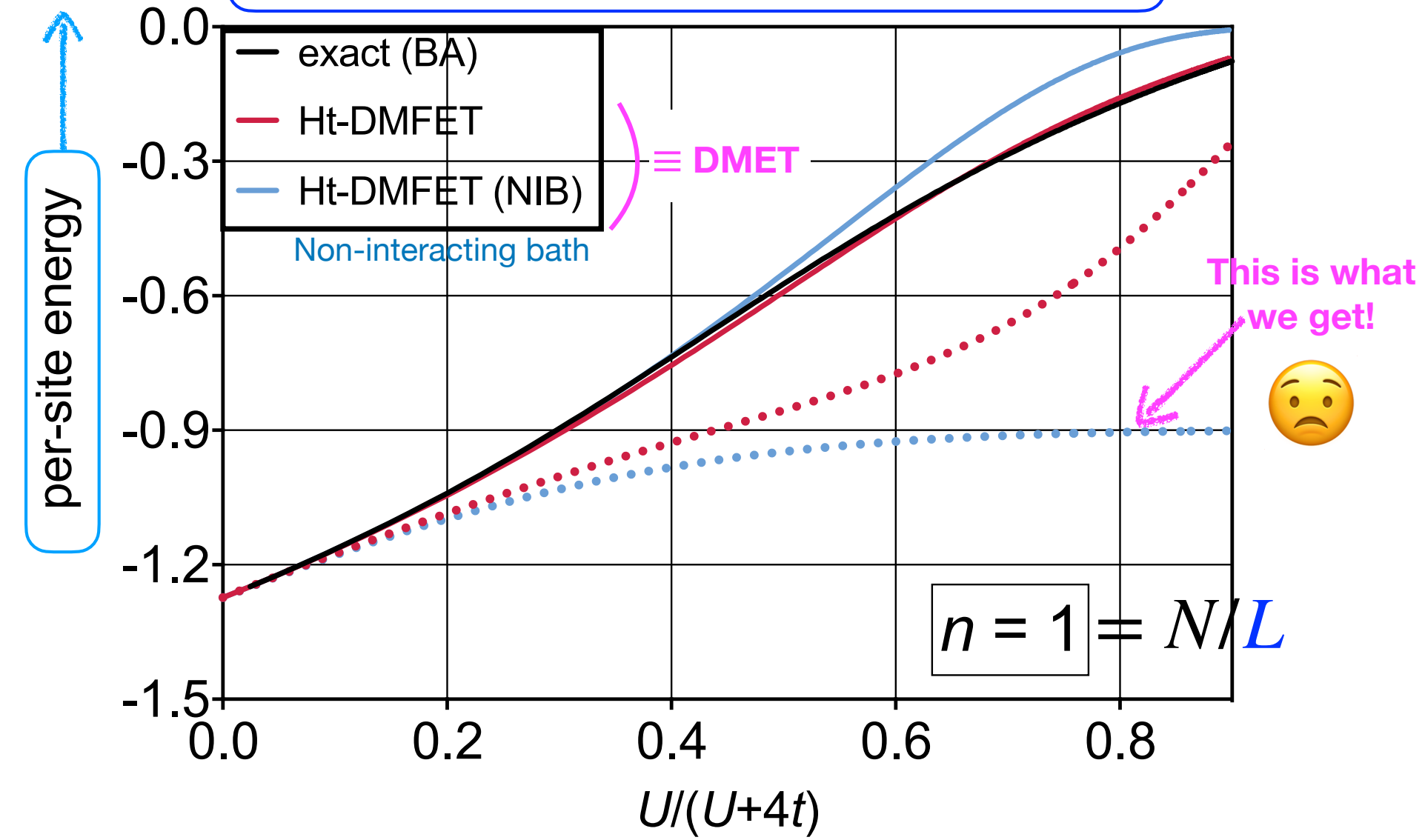
$$\hat{h}^{\mathscr{C}} \xrightarrow{single\ impurity} \hat{h}^{\mathscr{C}} + \overbrace{\langle pp\,|\,pp\rangle}^{U} \hat{c}^{\dagger}_{p\uparrow}\hat{c}^{\dagger}_{p\downarrow}\hat{c}_{p\downarrow}\hat{c}_{p\uparrow}$$

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.

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

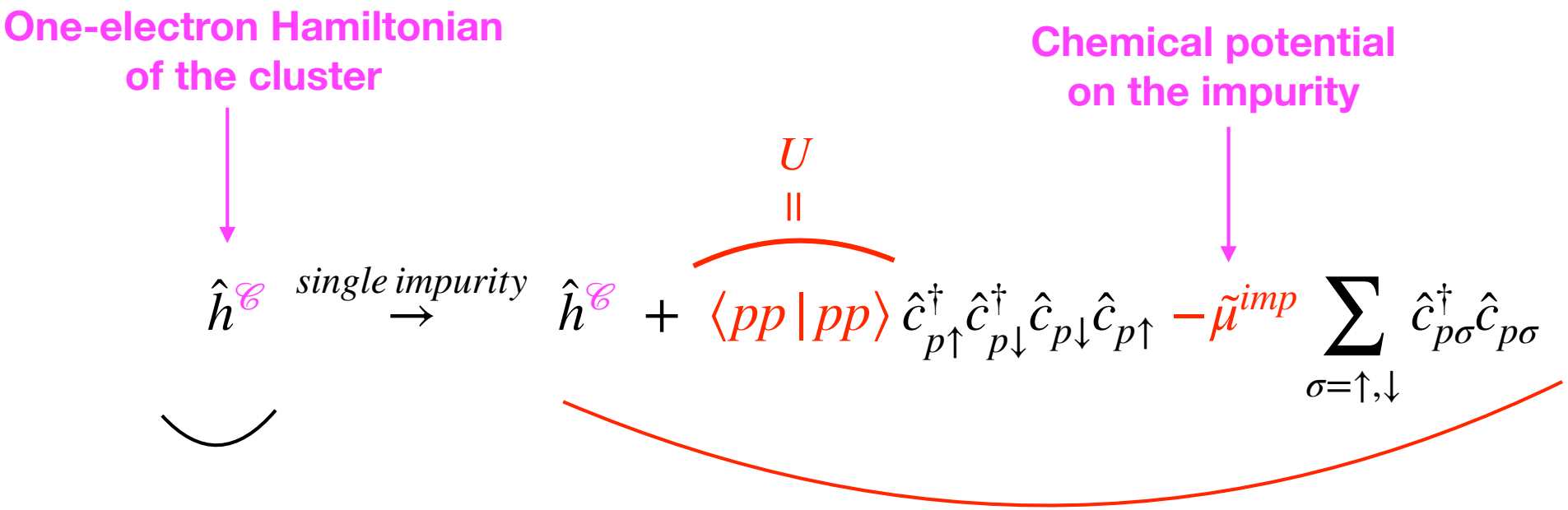
Chemical potential on the impurity

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

Exact non-interacting embedding

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

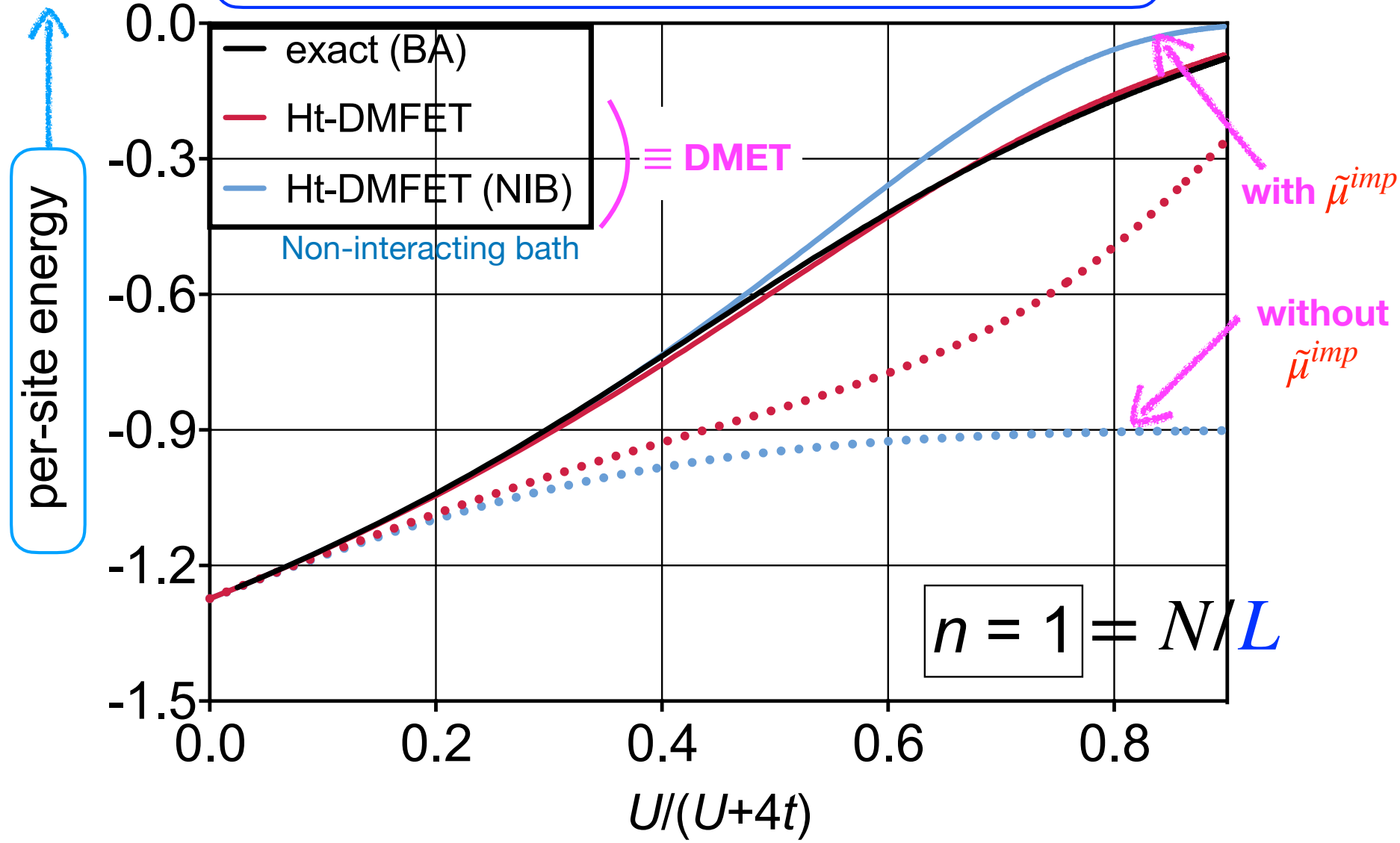


S. Wouters, C. A. Jiménez-Hoyos, Q. Sun, and G. K.-L. Chan, J. Chem. Theory Comput. ***12****, 2706 (2016).*
S. Sekaran, M. Tsuchiizu, M. Saubanère, and E. Fromager, Phys. Rev. B ***104****, 035121 (2021).*
S. Sekaran, M. Saubanère, and E. Fromager, Computation **2022***, 10,* 45.

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

$$E/L$$

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



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

Self-consistency in DMET

(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):

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

$\equiv N(\mu)$: Total number of electrons

Total number of sites

Self-consistency through a connection with density functional theory

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

True interacting Hamiltonian $(U \neq 0)$

Fixed chemical potential

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

Self-consistency through a connection with density functional theory

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

True interacting Hamiltonian $(U \neq 0)$

Fixed chemical potential

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

Self-consistency through a connection with density functional theory

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

True interacting Hamiltonian $(U \neq 0)$

Fixed chemical potential

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

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

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

Unknown Kohn—Sham chemical potential

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

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

Self-consistency through a connection with density functional theory

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

True interacting Hamiltonian $(U \neq 0)$

Fixed chemical potential

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

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

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

Unknown Kohn—Sham chemical potential

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

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

Self-consistency through a connection with density functional theory

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

True interacting Hamiltonian $(U \neq 0)$

Fixed chemical potential

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

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

"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

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

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

Impurity-interacting Hamiltonian of the two-electron embedding cluster

Self-consistency through a connection with density functional theory

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

True interacting Hamiltonian $(U \neq 0)$

Fixed chemical potential

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

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

"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

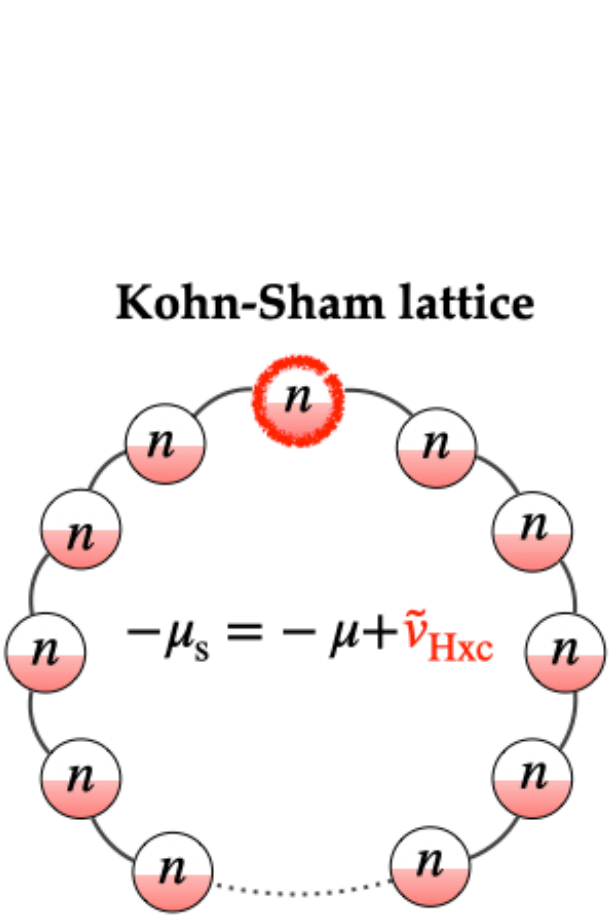
$$-\mu^{\mathrm{KS}} = -\mu + v_{\mathrm{Hxc}} \qquad n^{\mathrm{KS}} = n(\mu) = ?$$

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

Impurity-interacting Hamiltonian of the two-electron embedding cluster

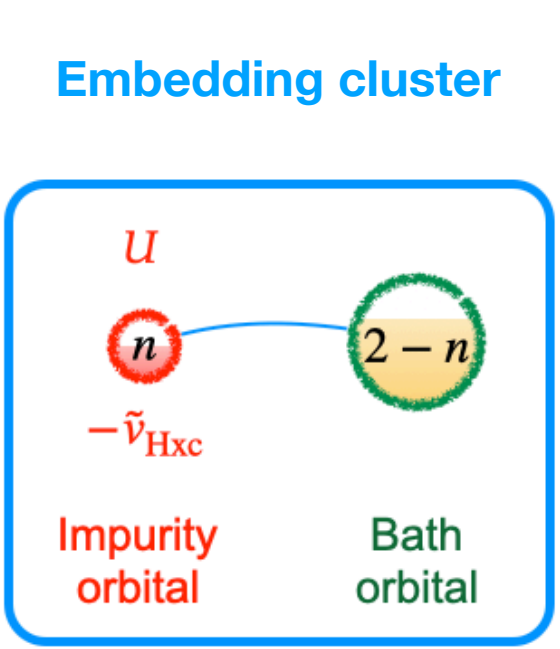
Local potential-functional embedding theory (LPFET)

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



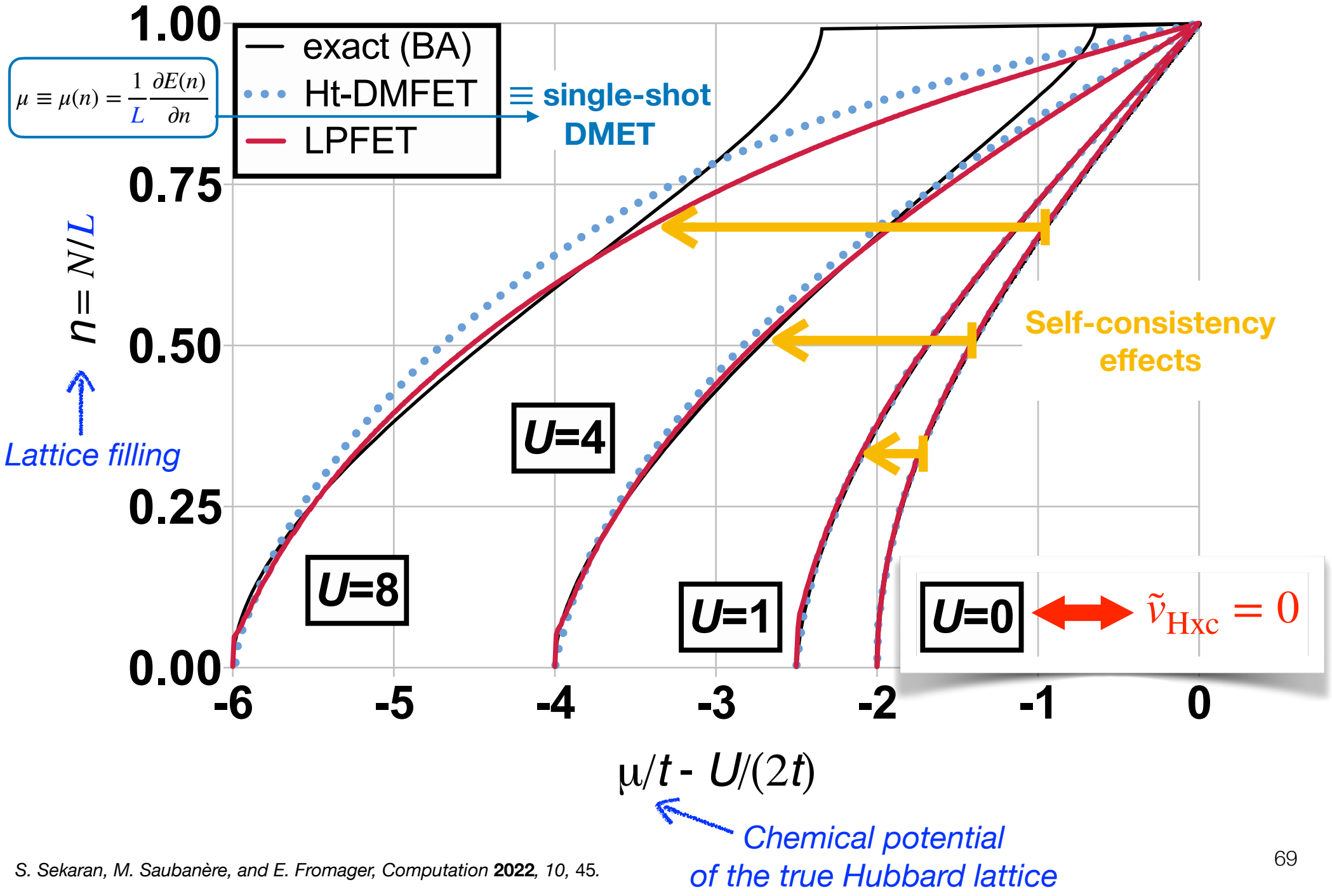
Self-consistency loop

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



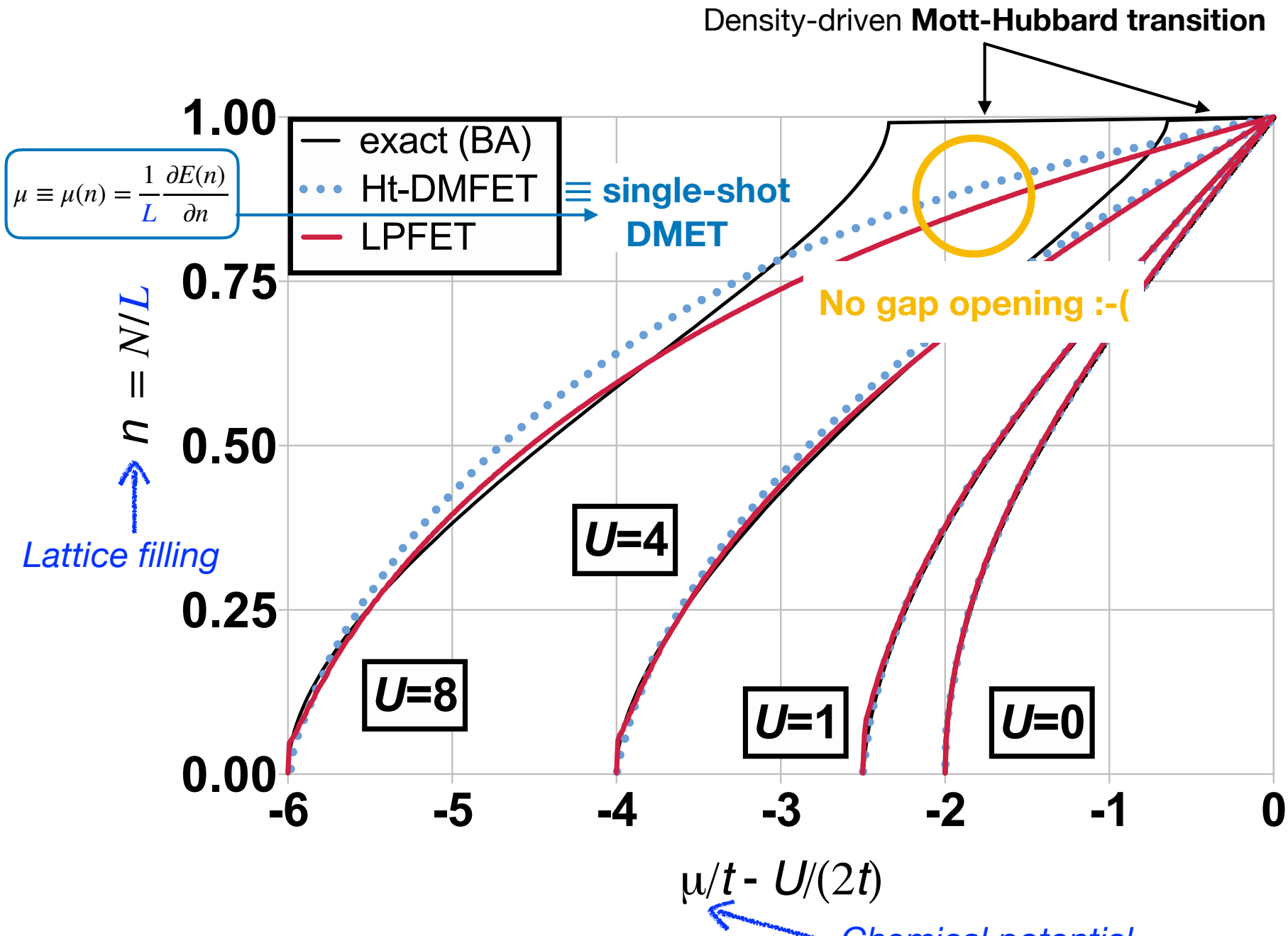
S. Sekaran, M. Saubanère, and E. Fromager, Computation **2022**, *10*, 45.

Local potential-functional embedding theory (LPFET)



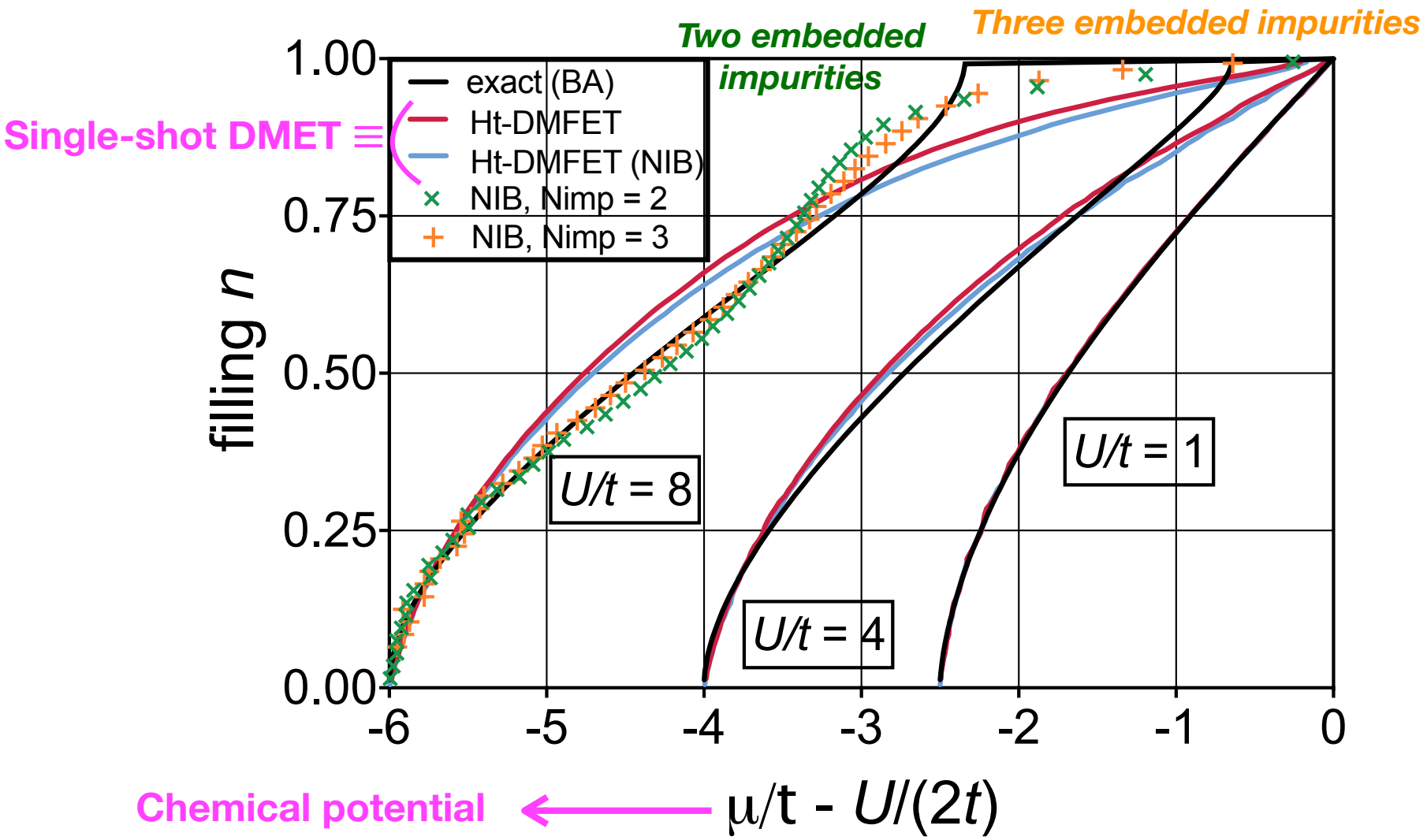
S. Sekaran, M. Saubanère, and E. Fromager, Computation **2022**, *10*, 45.

Local potential-functional embedding theory (LPFET)



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

Mott-Hubbard density-driven transition and multiple impurities



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

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

Density-functional exactification of DMET (for Hubbard)

computation

MDPI

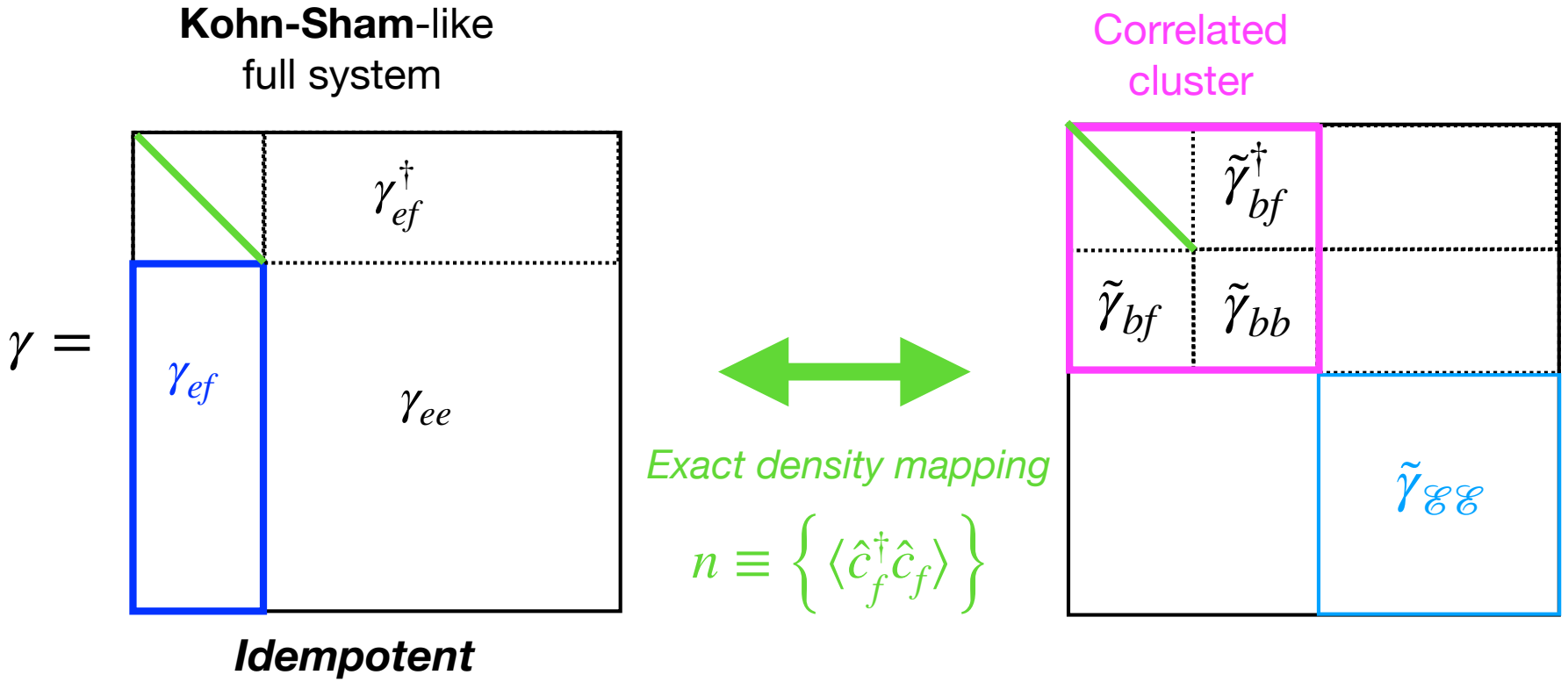
check for updates

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

Article

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

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

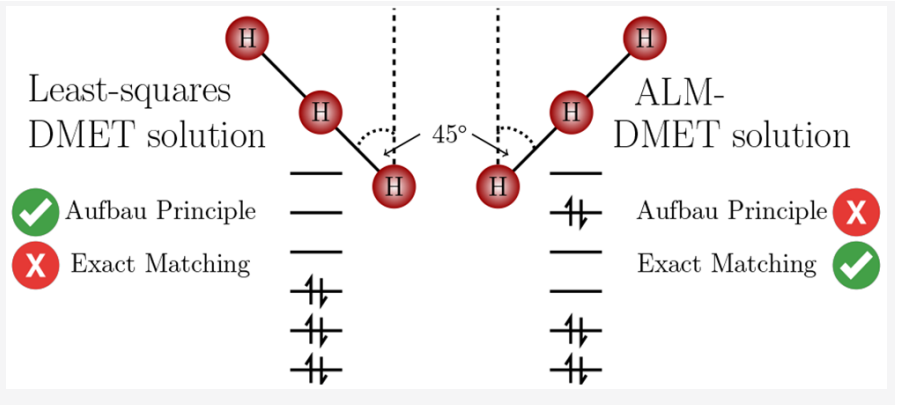


W. Bulik, G. E. Scuseria, and J. Dukelsky, Phys. Rev. B ***89****, 035140 (2014).*
U. Mordovina, T. E. Reinhard, I. Theophilou, H. Appel, and A. Rubio, J. Chem. Theory Comput. ***15****, 5209 (2019).*

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

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

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



Kohn-Sham-like
full system?

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

Idempotent

?

Density matrix mapping

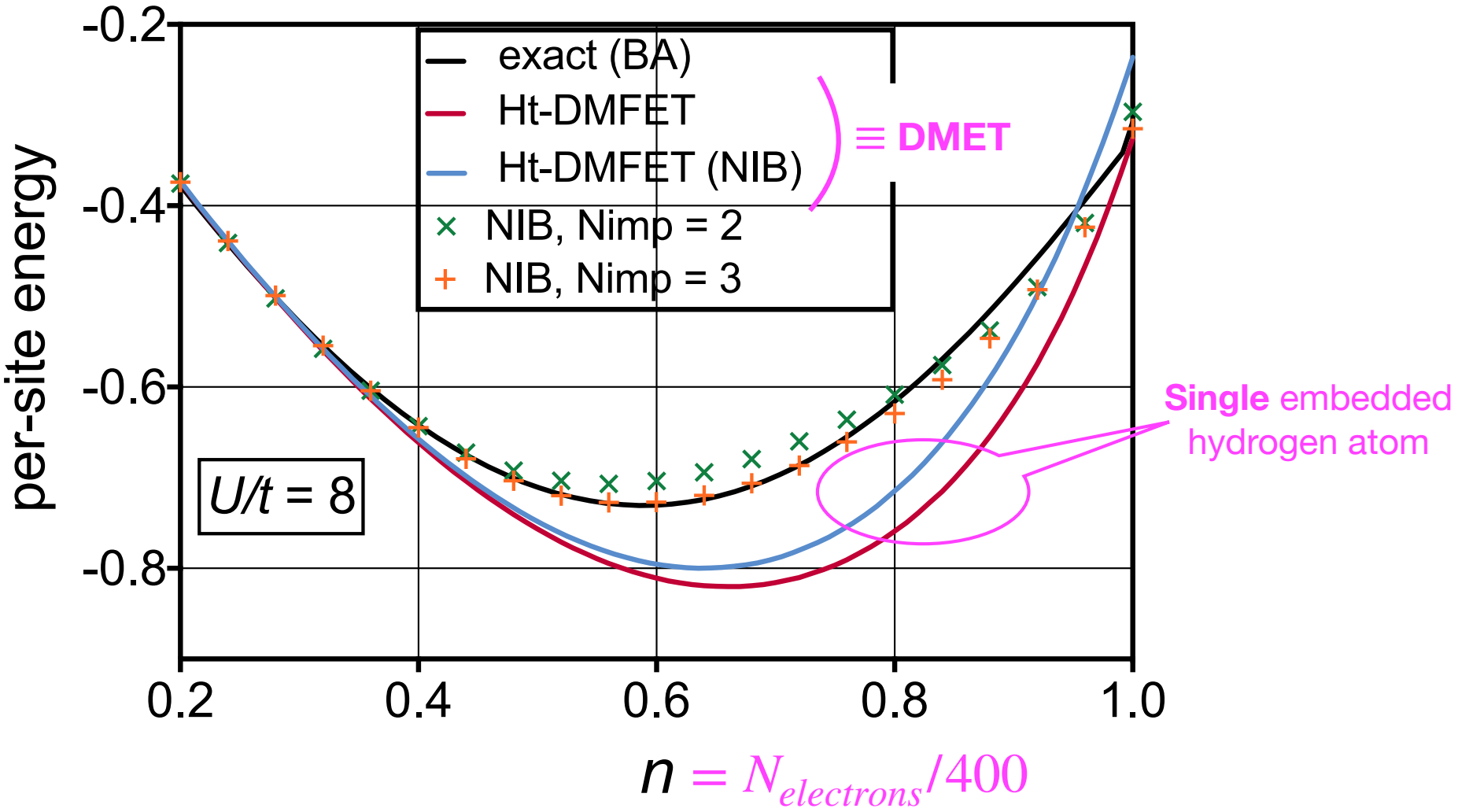
Correlated
cluster

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

Non-idempotent

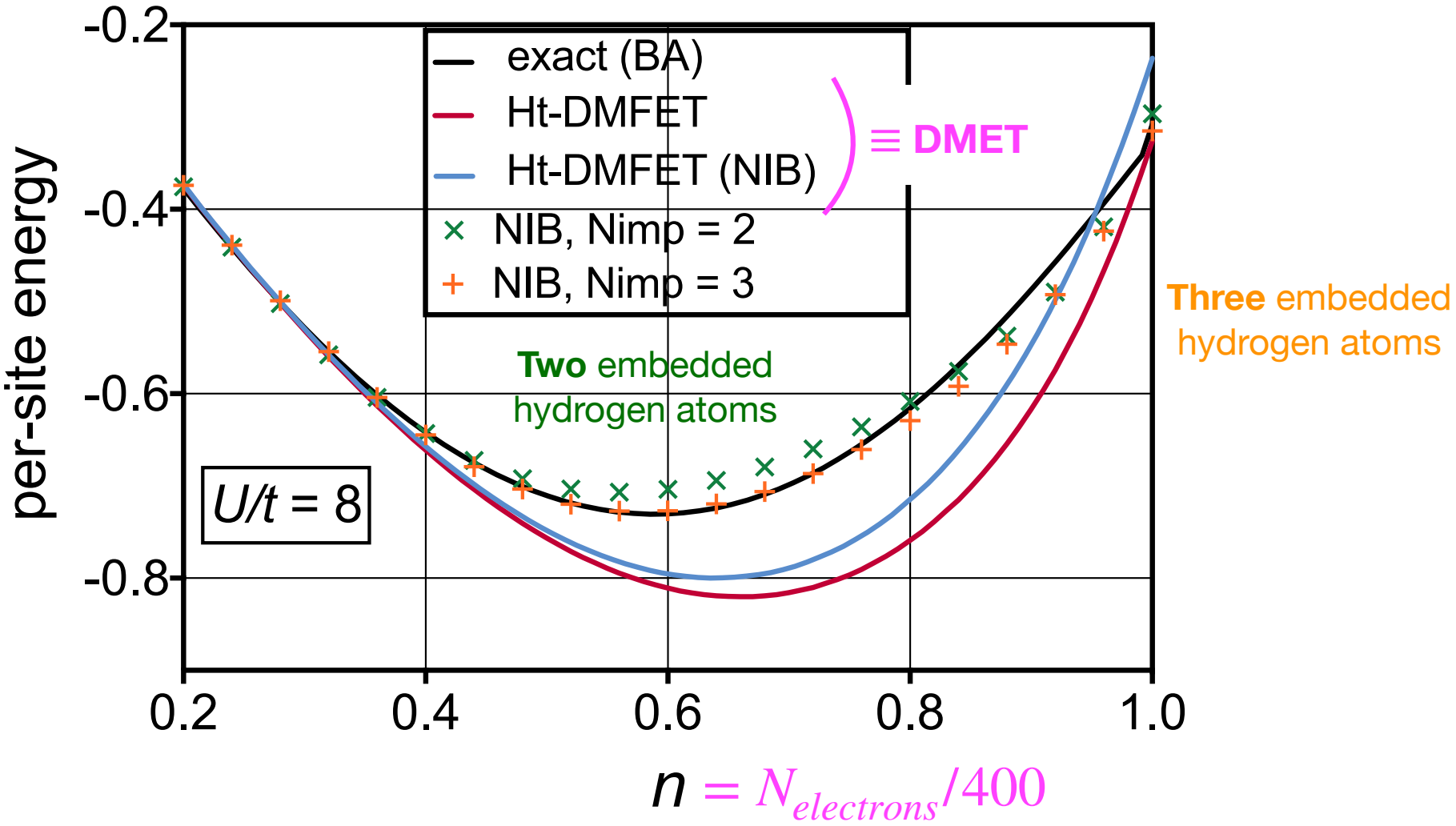
Complements

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



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

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

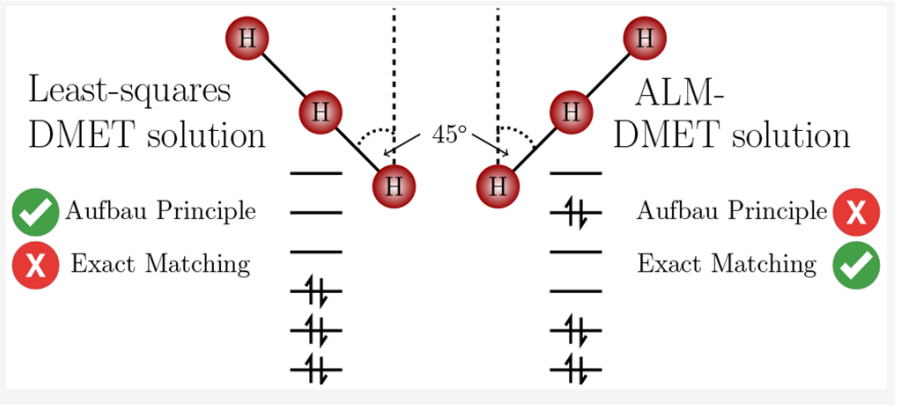


*S. Sekaran, M. Tsuchiizu, M. Saubanère, and E. Fromager, Phys. Rev. B **104**, 035121 (2021).*

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

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

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



Kohn-Sham-like
full system?

$\gamma =$

γ_{ff} $\gamma_{ef}^{\dagger}$

γ_{ef} γ_{ee}

Idempotent

?

Density matrix mapping

Correlated
cluster

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

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

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

Non-idempotent

Non-Hermitian quantum mechanics?

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

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

Another approach to
one-electron reduced density matrix functional theory…

Non-Hermitian quantum mechanics?

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

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

Non-Hermitian quantum mechanics?

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

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

Using an enlarged bath *(ghost orbitals)*?

N. Lanatà, Phys. Rev. B 108, 235112 (2023).
C. Mejuto-Zaera, Faraday Discuss., 2024, DOI: 10.1039/D4FD00053F

Quantum embedding for molecules using auxiliary particles – The ghost Gutzwiller Ansatz†

Carlos Mejuto-Zaera*[a]

Faraday Discussions

Accepted Manuscript

DOI: 10.1039/D4FD00053F

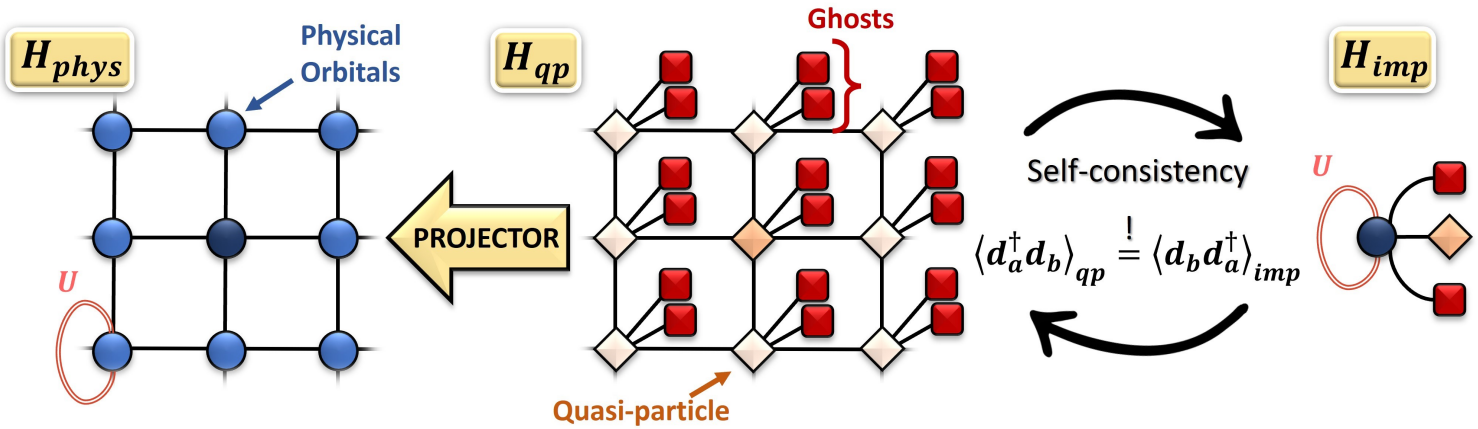


Fig. 1 Schematic representation of the Gutzwiller and ghost Gutzwiller Ansatz. Gutzwiller corresponds to the limit with no ghost orbitals. Local interactions are marked with the symbol U. See text for details.

JCTC Journal of Chemical Theory and Computation

pubs.acs.org/JCTC Article

Effective Reconstruction of Expectation Values from Ab Initio Quantum Embedding

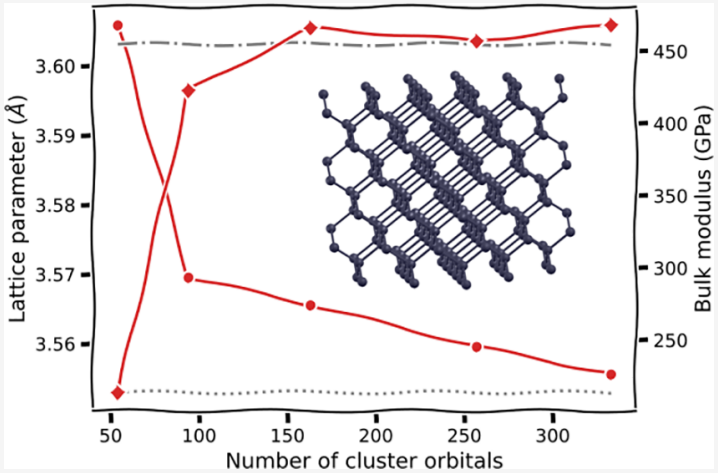
Max Nusspickel, Basil Ibrahim, and George H. Booth*

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

Read Online

ACCESS | Metrics & More | Article Recommendations | Supporting Information

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

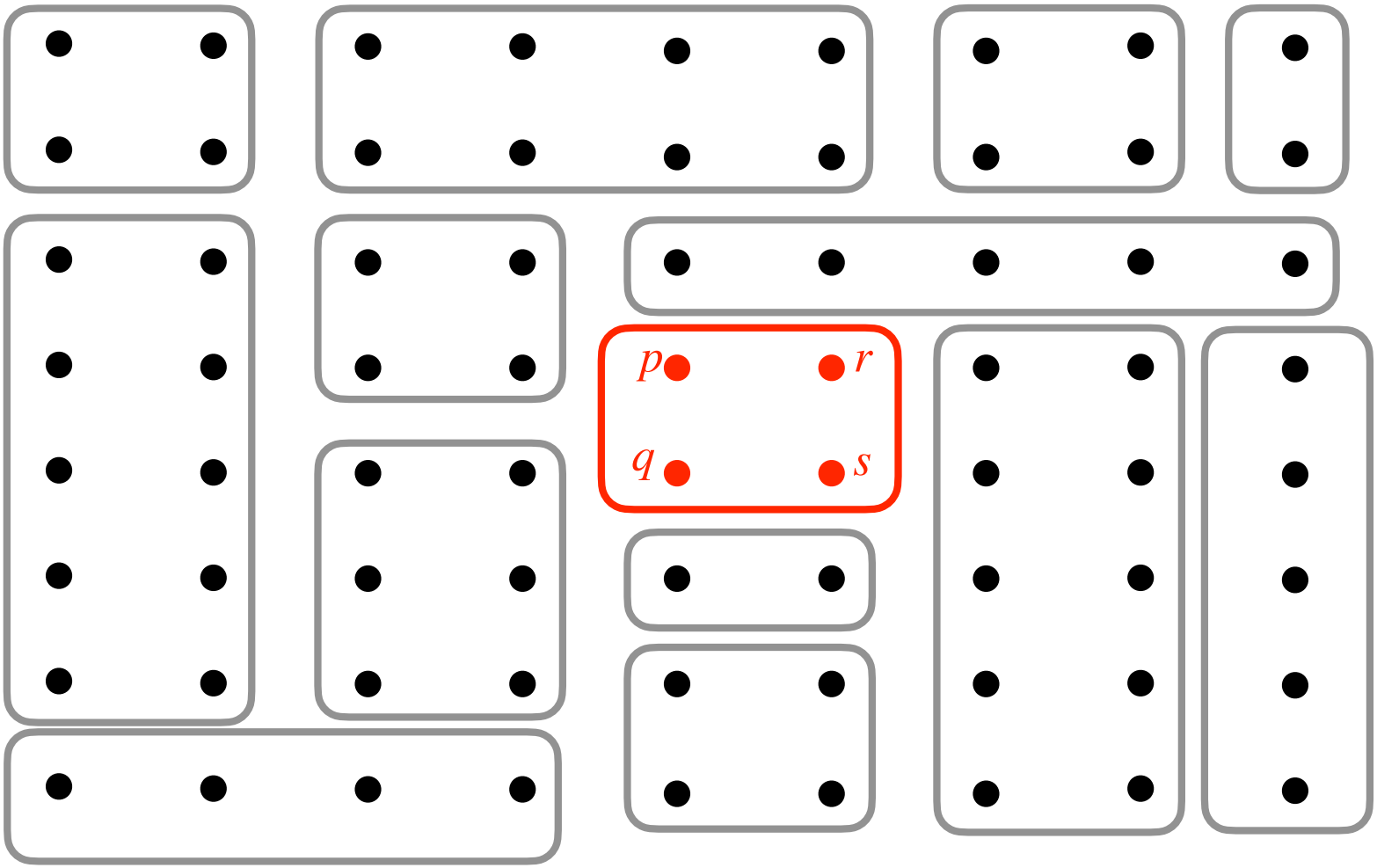


Local evaluation of the energy (in a localised spin-orbital basis)

So-called "lattice representation"

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

Fragmentation

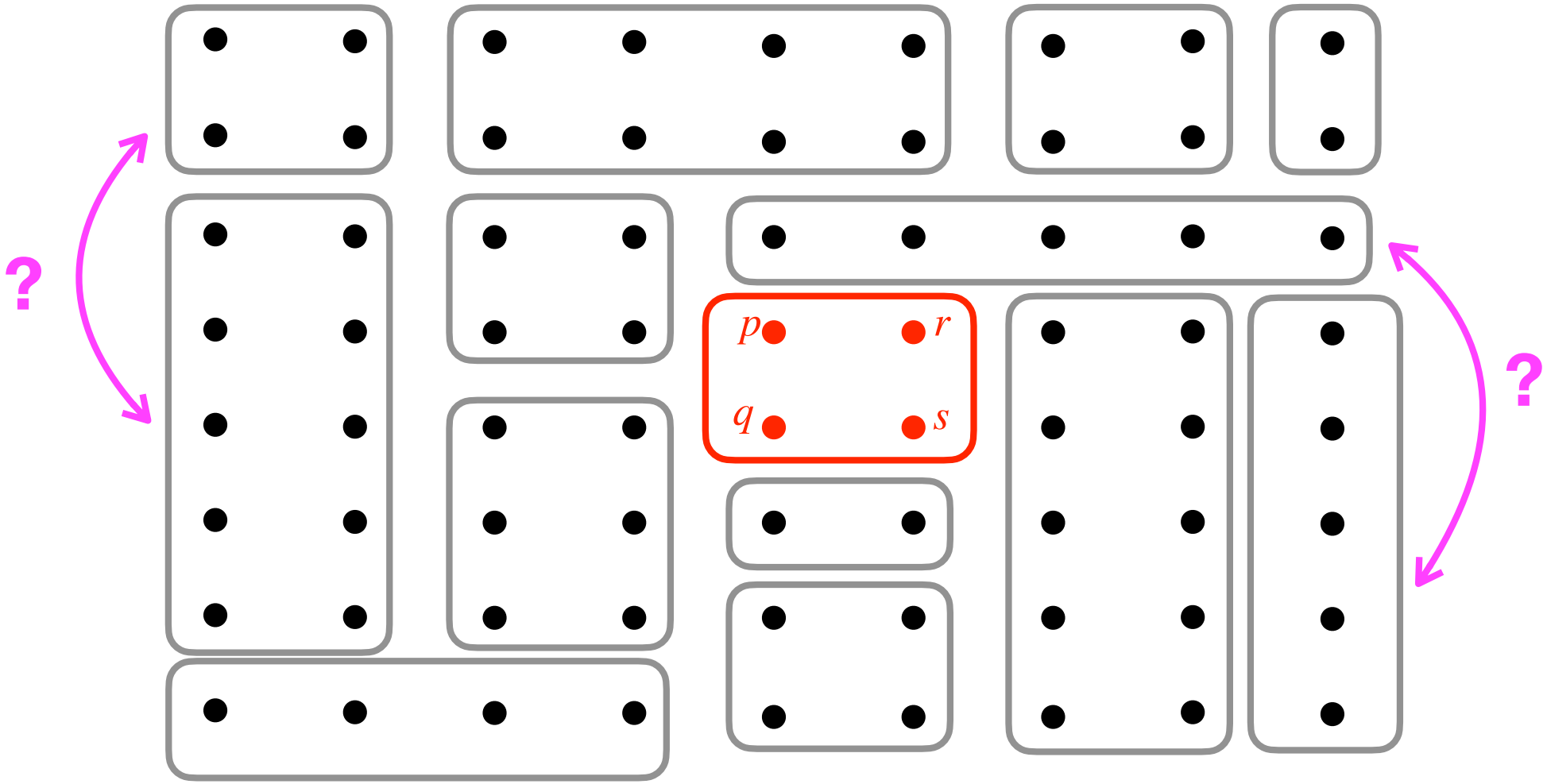


G. Knizia and G. K.-L. Chan, Phys. Rev. Lett. ***109****, 186404 (2012).*
S. Wouters, C. A. Jiménez-Hoyos, Q. Sun, and G. K.-L. Chan, J. Chem. Theory Comput. 12, 2706 (2016).

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

One-electron density matrix (1RDM)

Two-electron density matrix (2RDM)



N-representability problem

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

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