Towards an in-principle-exact density matrix functional embedding theory

Saad Yalouz and Emmanuel Fromager

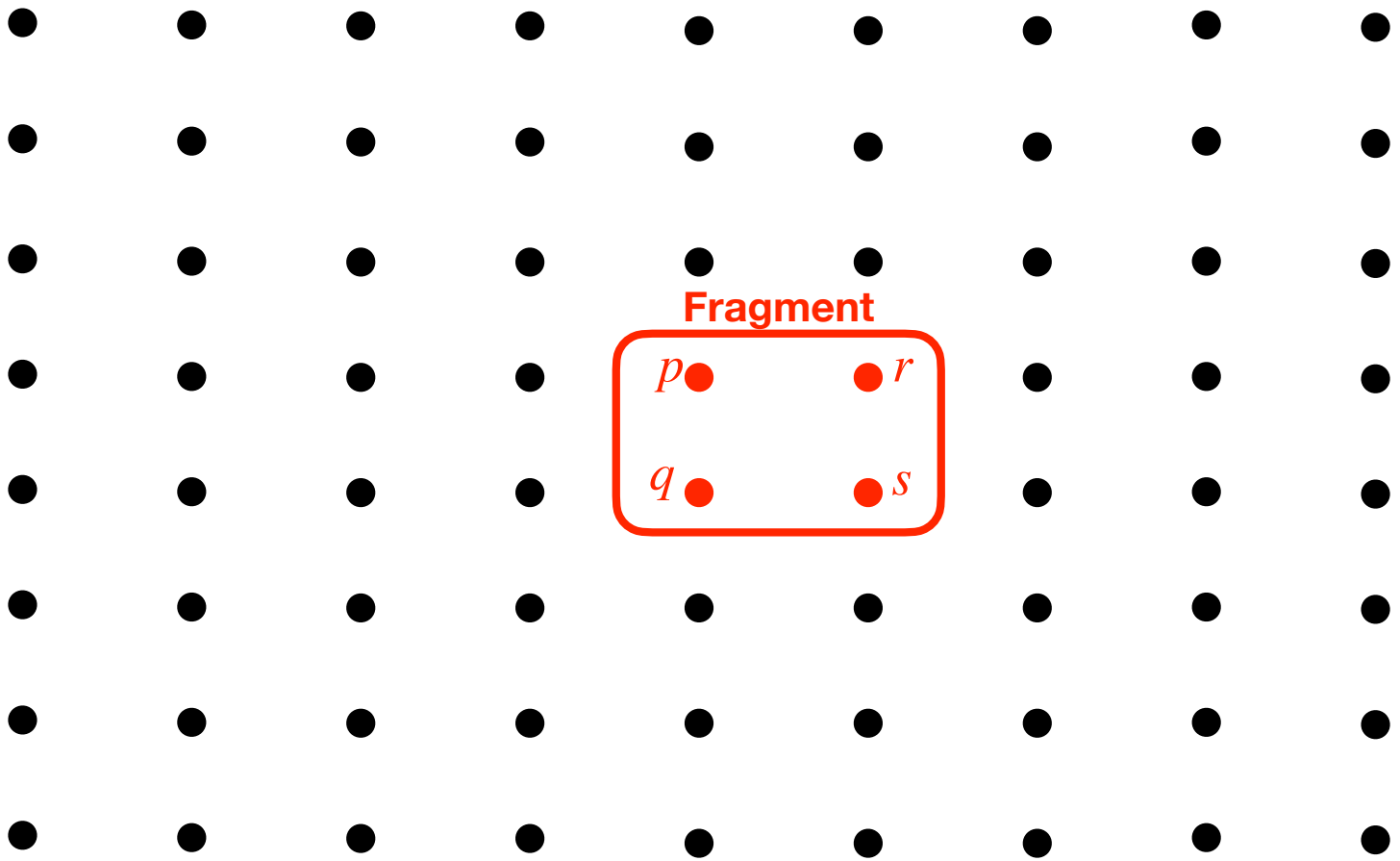
Laboratoire de Chimie Quantique, Institut de Chimie de Strasbourg,
Université de Strasbourg, Strasbourg, France

International workshop on RDMFT, ECT*, Trento, Italy **05/10/2022**

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

So-called "lattice representation"

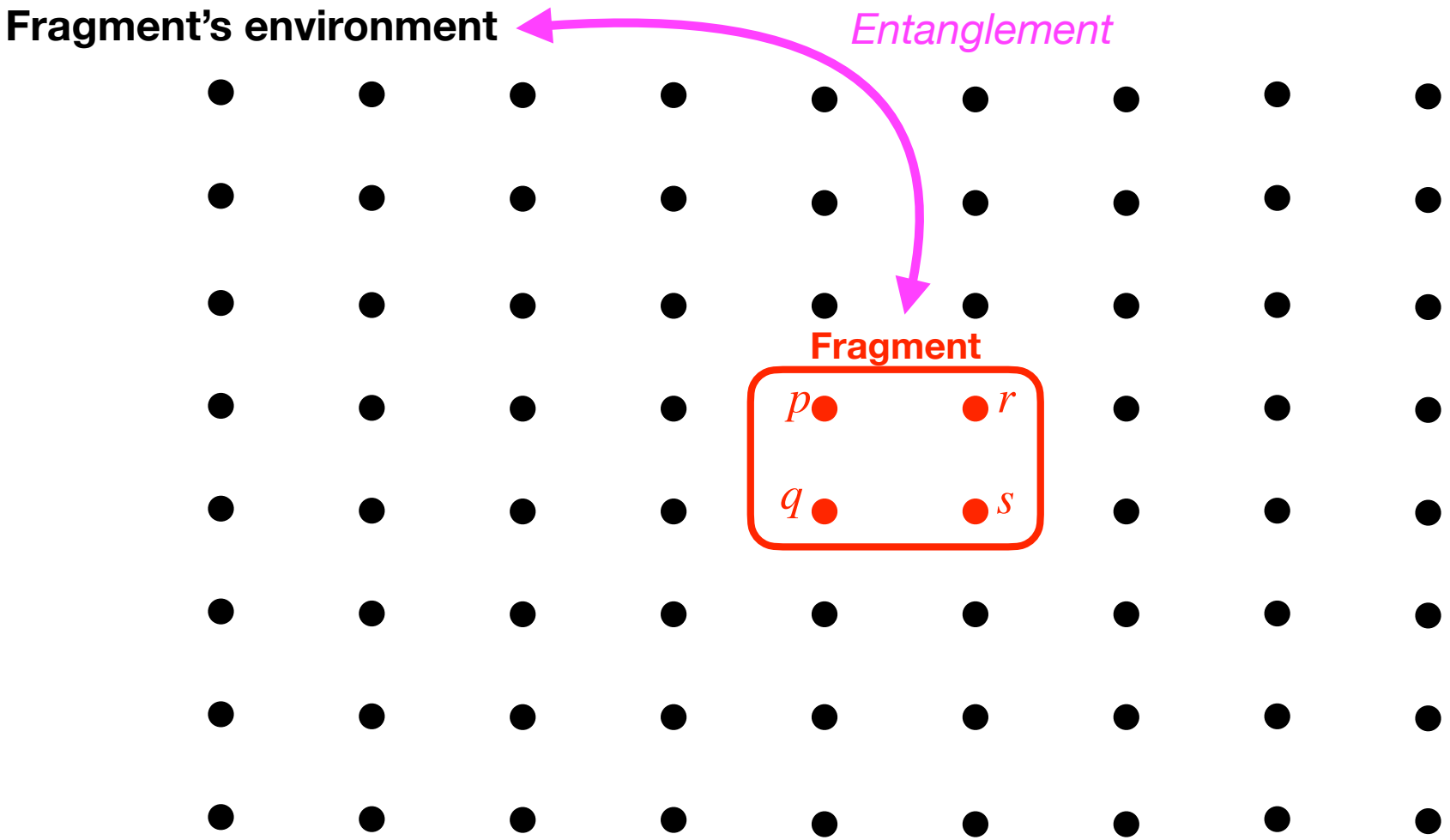
$$\langle \hat{H} \rangle = \sum_{pq} h_{pq} \underbrace{\langle \hat{c}_p^\dagger \hat{c}_q \rangle}_{\text{One-electron density matrix}} + \frac{1}{2} \sum_{pqrs} \langle pq \,|\, rs \rangle \underbrace{\langle \hat{c}_p^\dagger \hat{c}_q^\dagger \hat{c}_s \hat{c}_r \rangle}_{\text{Two-electron density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



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

So-called "lattice representation"

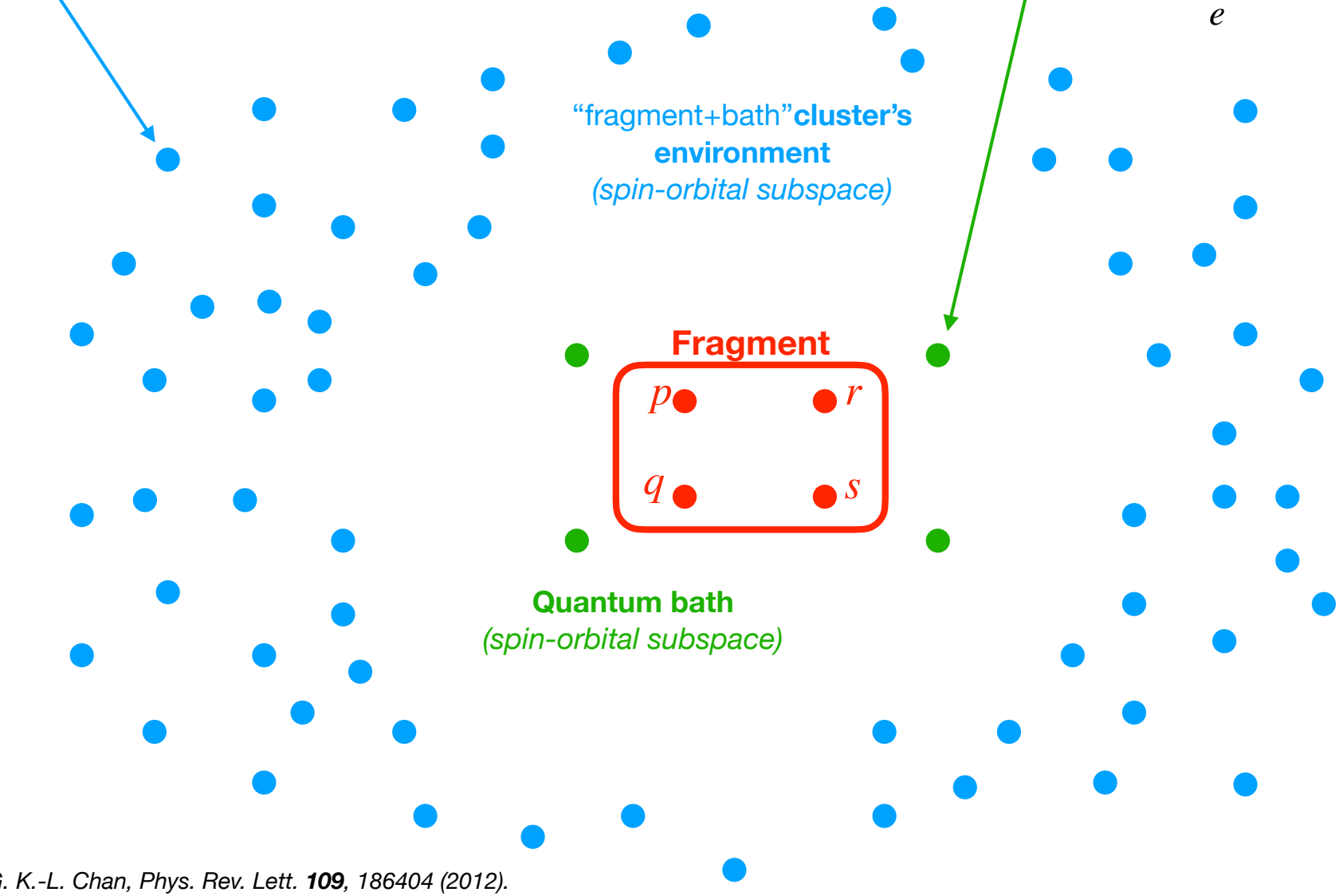
$$\langle \hat{H} \rangle = \sum_{pq} h_{pq} \langle \hat{c}_p^\dagger \hat{c}_q \rangle + \frac{1}{2} \sum_{pqrs} \langle pq \,|\, rs \rangle \langle \hat{c}_p^\dagger \hat{c}_q^\dagger \hat{c}_s \hat{c}_r \rangle$$



Clusterization through a unitary one-electron transformation

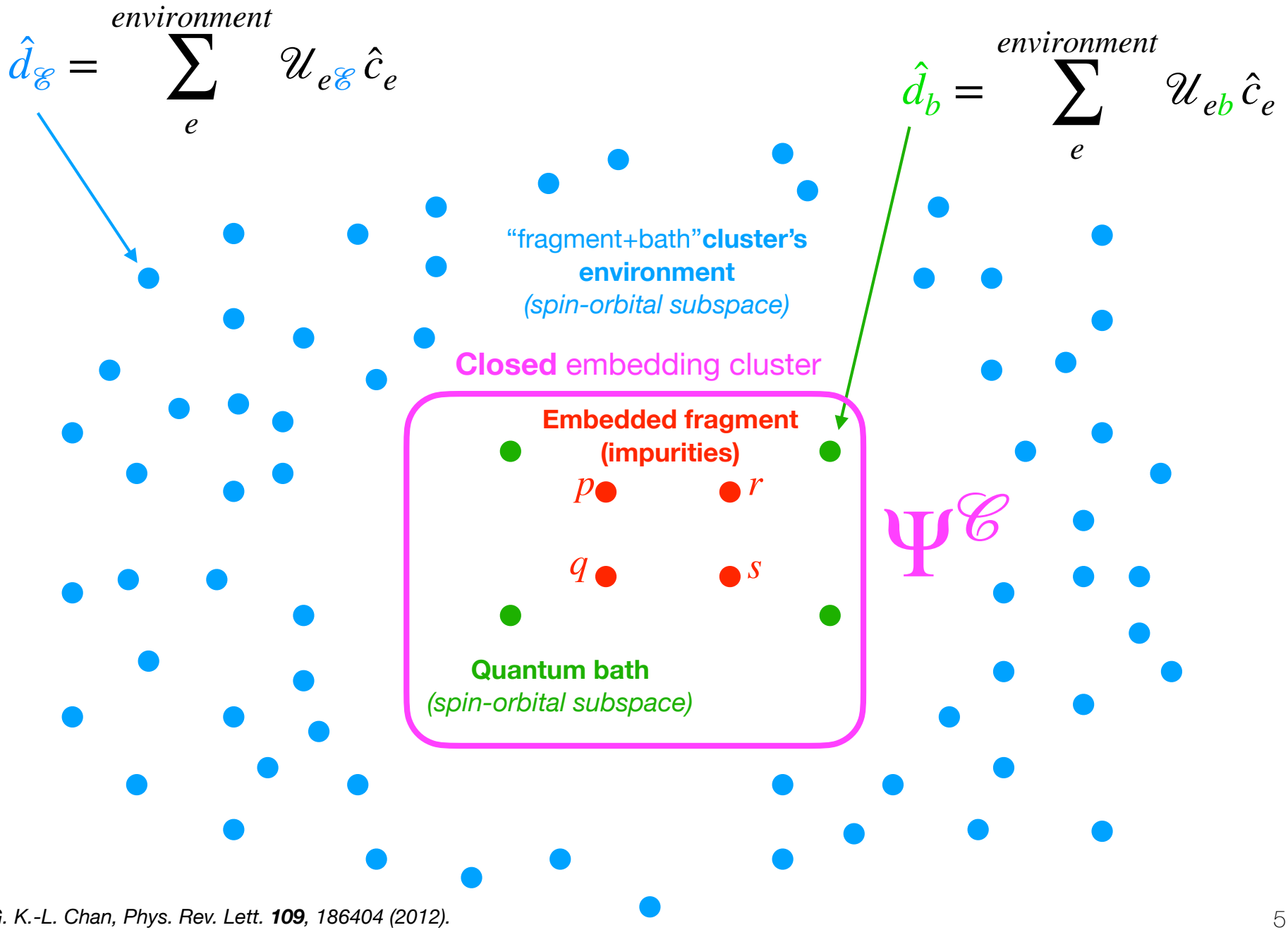
$$\hat{d}_{\mathscr{E}} = \sum_{e}^{environment} \mathcal{U}_{e\mathscr{E}}\,\hat{c}_e$$

$$\hat{d}_{b} = \sum_{e}^{environment} \mathcal{U}_{eb}\,\hat{c}_e$$



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).

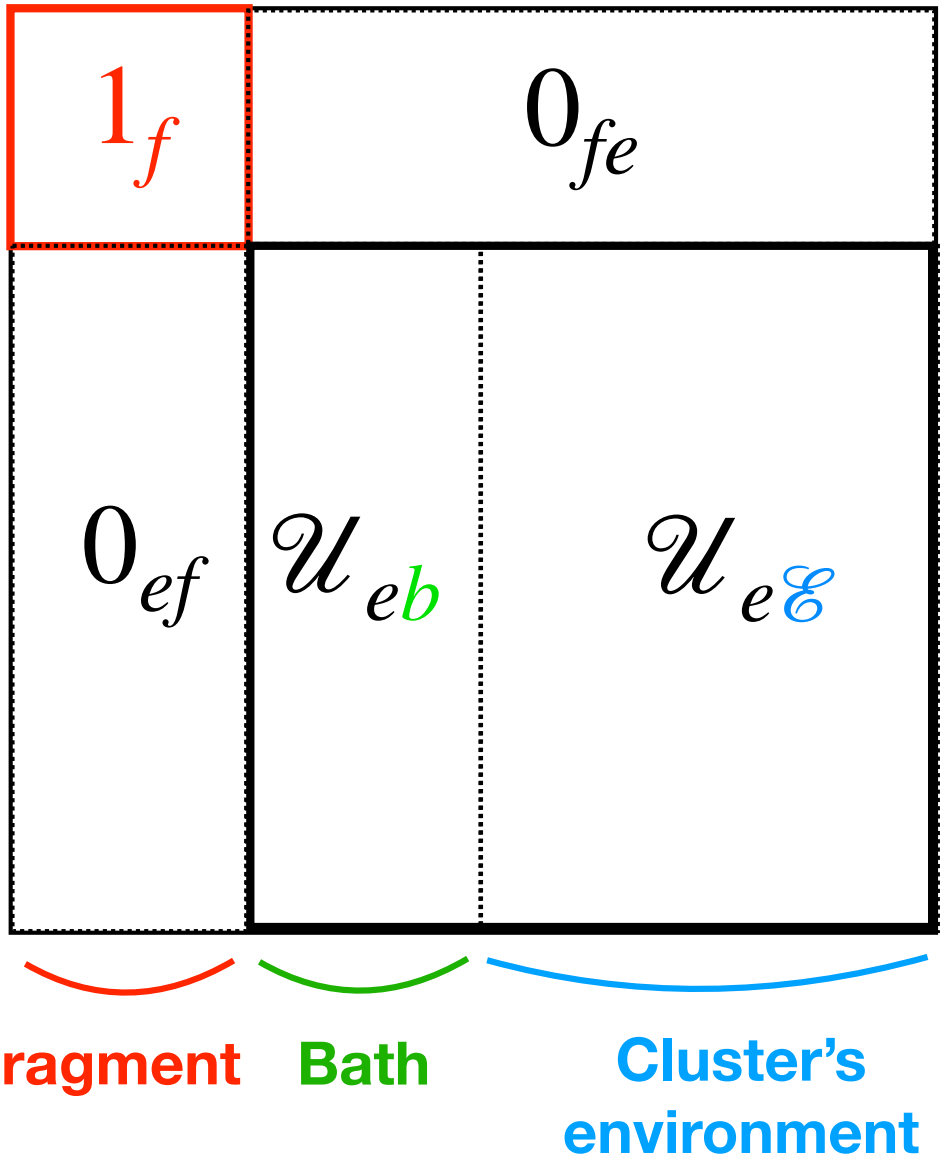
Density matrix embedding theory (DMET)



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).

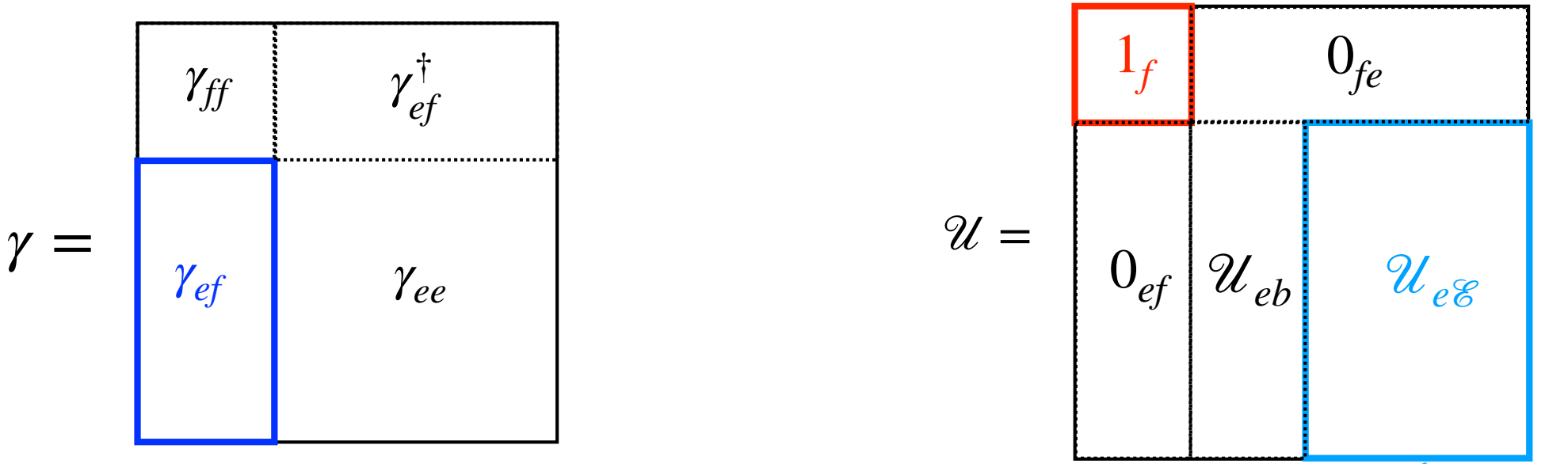
Clusterization through a unitary one-electron transformation

$$\mathcal{U} \equiv \mathcal{U}[\gamma] =$$



S. Sekaran, O. Bindech, and E. Fromager, to be submitted *(2022).*

Clusterization through a unitary one-electron transformation



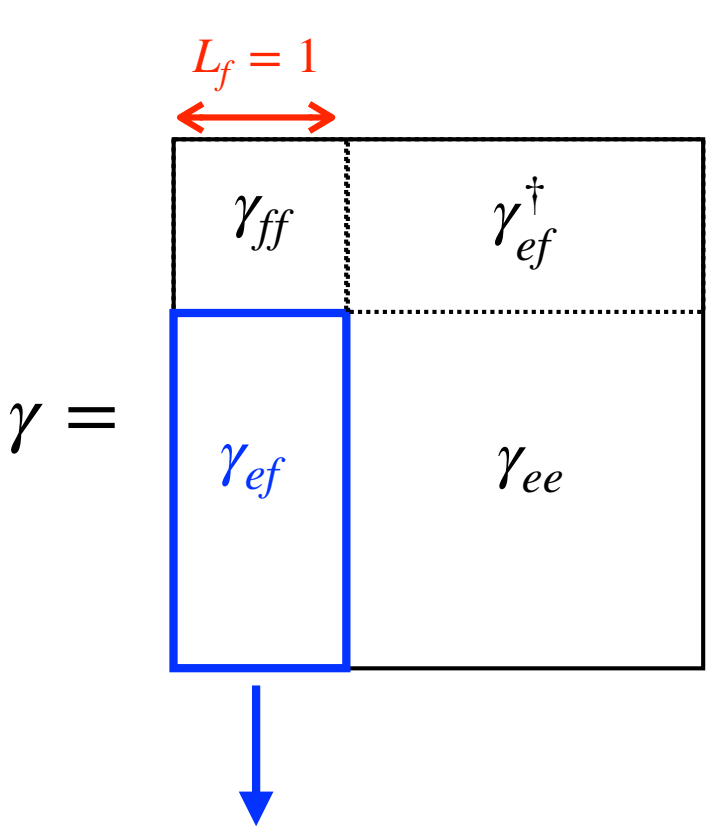
Environment of the embedding cluster
(usually neglected)

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

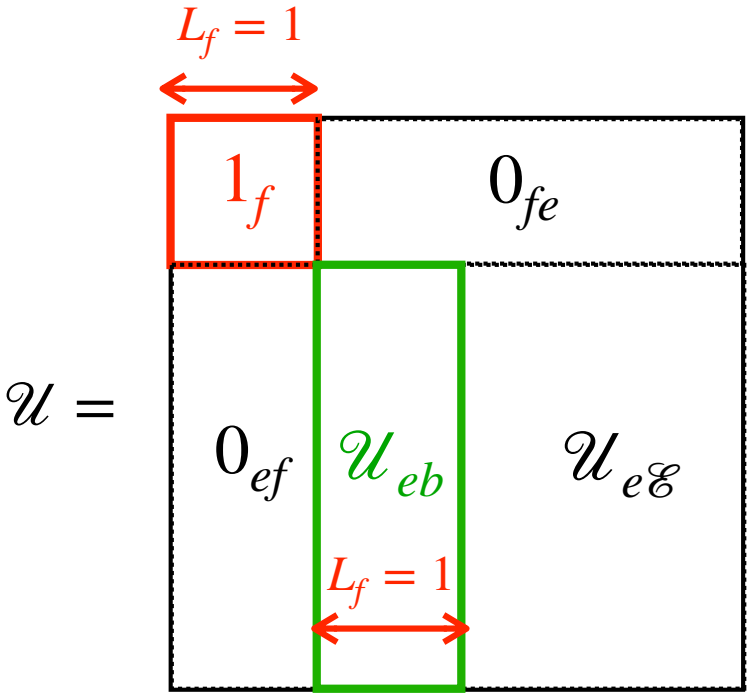
Orthogonality constraint

S. Sekaran, O. Bindech, and E. Fromager, to be submitted *(2022).*

Single-impurity case



Column vector



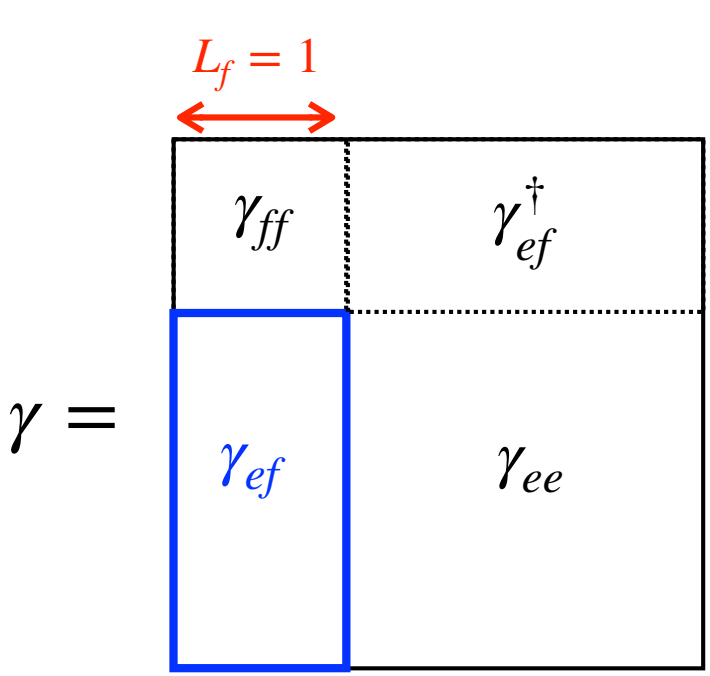
Quantum bath

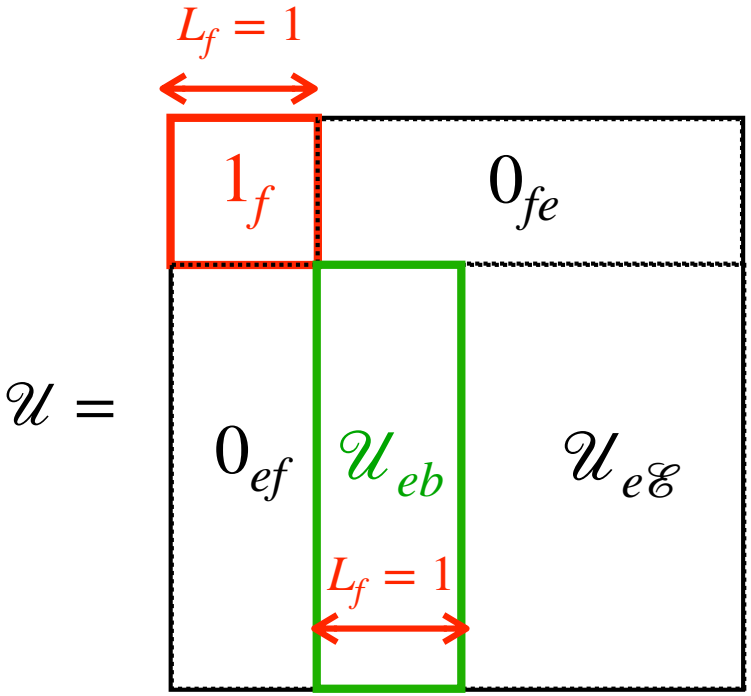
$$\mathcal{U}_{eb} = \frac{\gamma_{ef}}{\sqrt{\gamma_{ef}^\dagger \gamma_{ef}}}$$

Column vector

S. Sekaran, O. Bindech, and E. Fromager, to be submitted *(2022).*

Single-impurity case





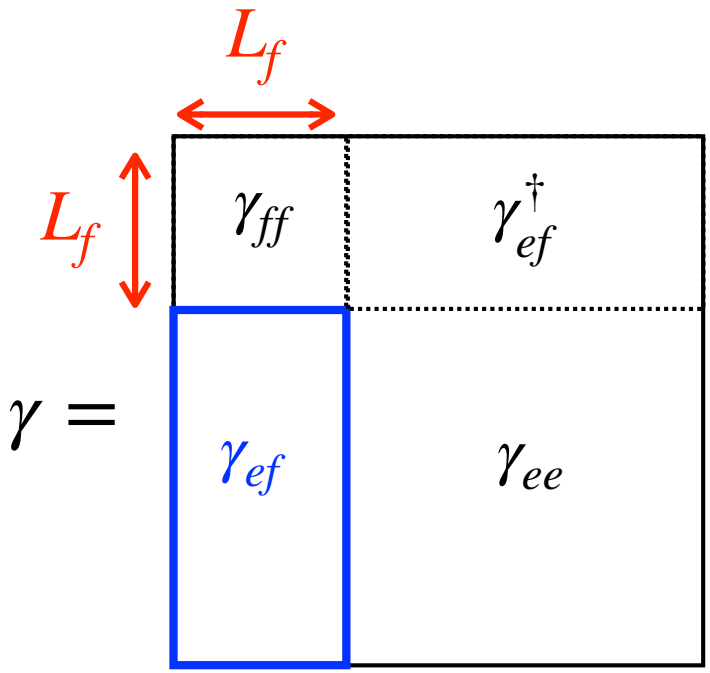
$$\varphi_{bath}(\mathbf{x}) \sim \sum_{e}^{environment} \gamma_{ef}^{*}\, \varphi_{e}(\mathbf{x})$$

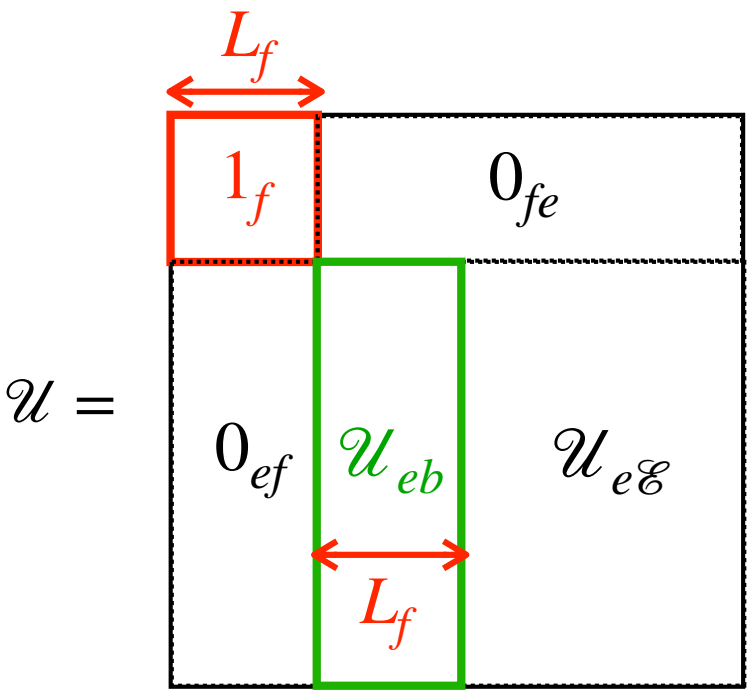
$$\mathcal{U}_{eb} = \frac{\gamma_{ef}}{\sqrt{\gamma_{ef}^{\dagger}\gamma_{ef}}}$$

Column vector

S. Sekaran, O. Bindech, and E. Fromager, to be submitted *(2022).*

Clusterization through a unitary one-electron transformation





Equivalent constructions of the L_f orthonormal **bath** spin-orbitals

Singular value decomposition[1] *of* γ_{ef} **or** ***Block Householder transformation***[2,3,4]

S. Sekaran, O. Bindech, and E. Fromager, to be submitted *(2022).*

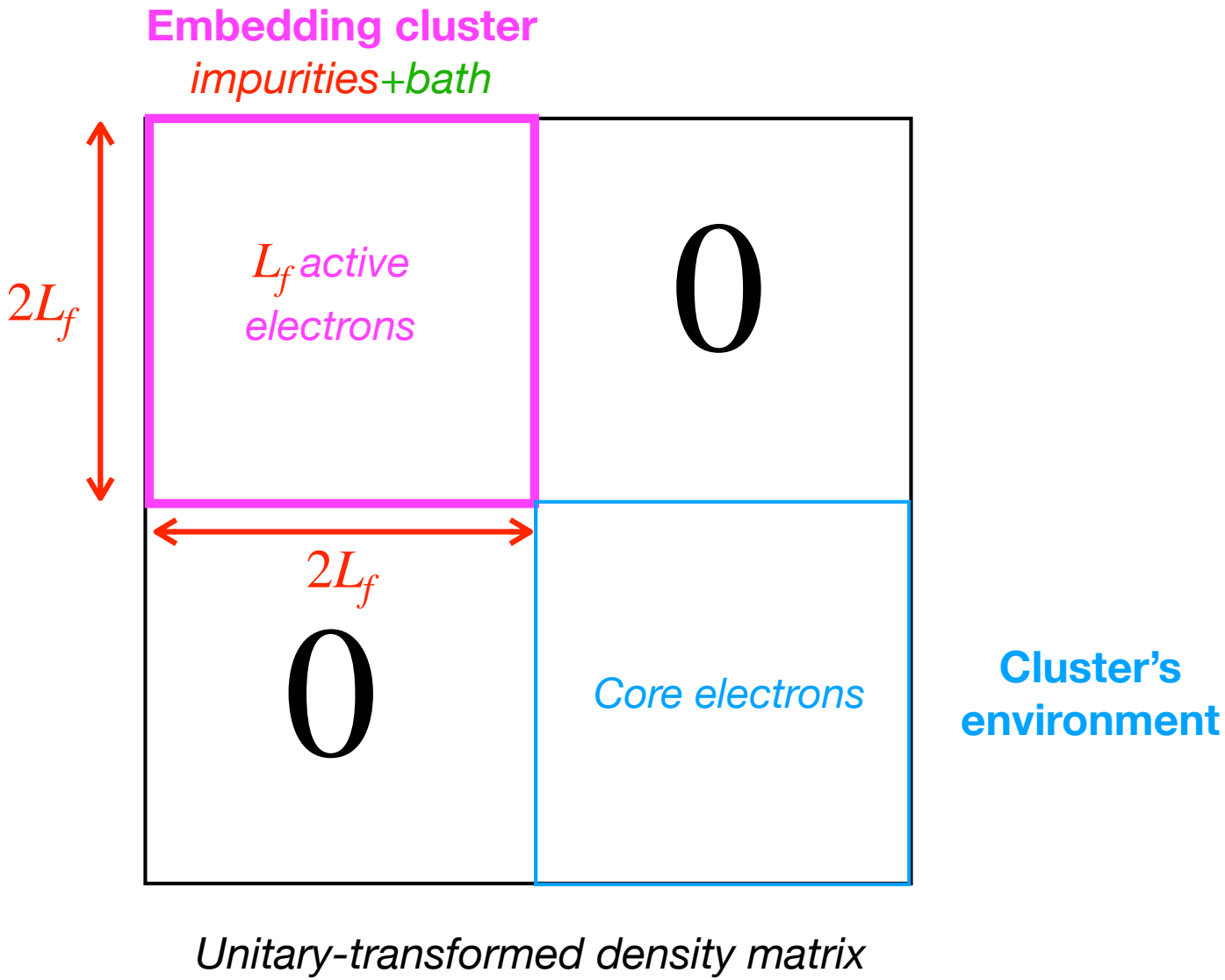
[1] *B.-X. Zheng, PhD thesis,* **arXiv:1803.10259** (2018).

[2] *F. Rotella and I. Zambettakis, Appl. Math. Lett.* ***12****, 29 (1999).*

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

[4] *S. Yalouz, S. Sekaran, and M. Saubanère,* **arXiv:2209.10302** *(2022).*

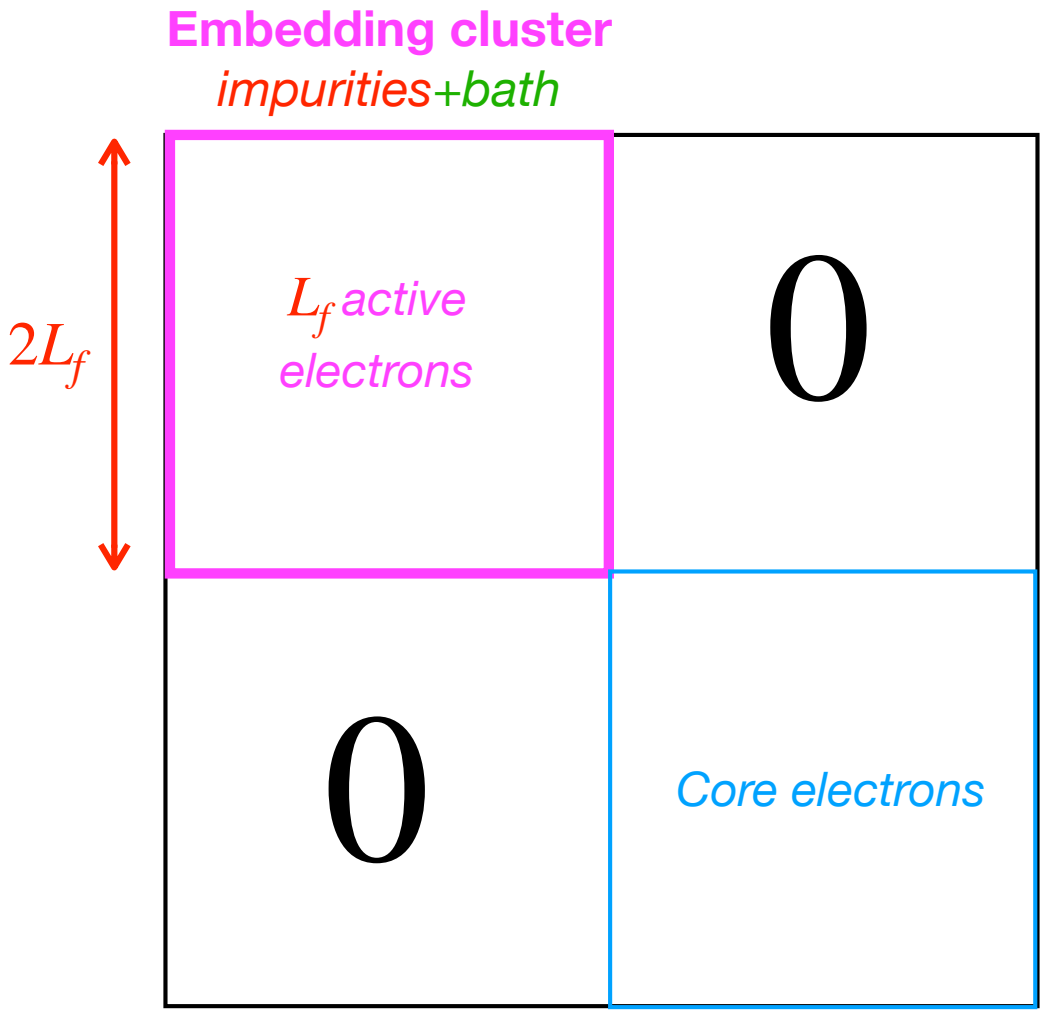
Embedding based on idempotent density matrices



Unitary-transformed density matrix

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.

Embedding based on idempotent density matrices



Unitary-transformed density matrix

*The embedding is **exact** for non-interacting (or mean-field) electrons!*

Cluster's environment

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.

Non-interacting bath embedding of a single interacting impurity

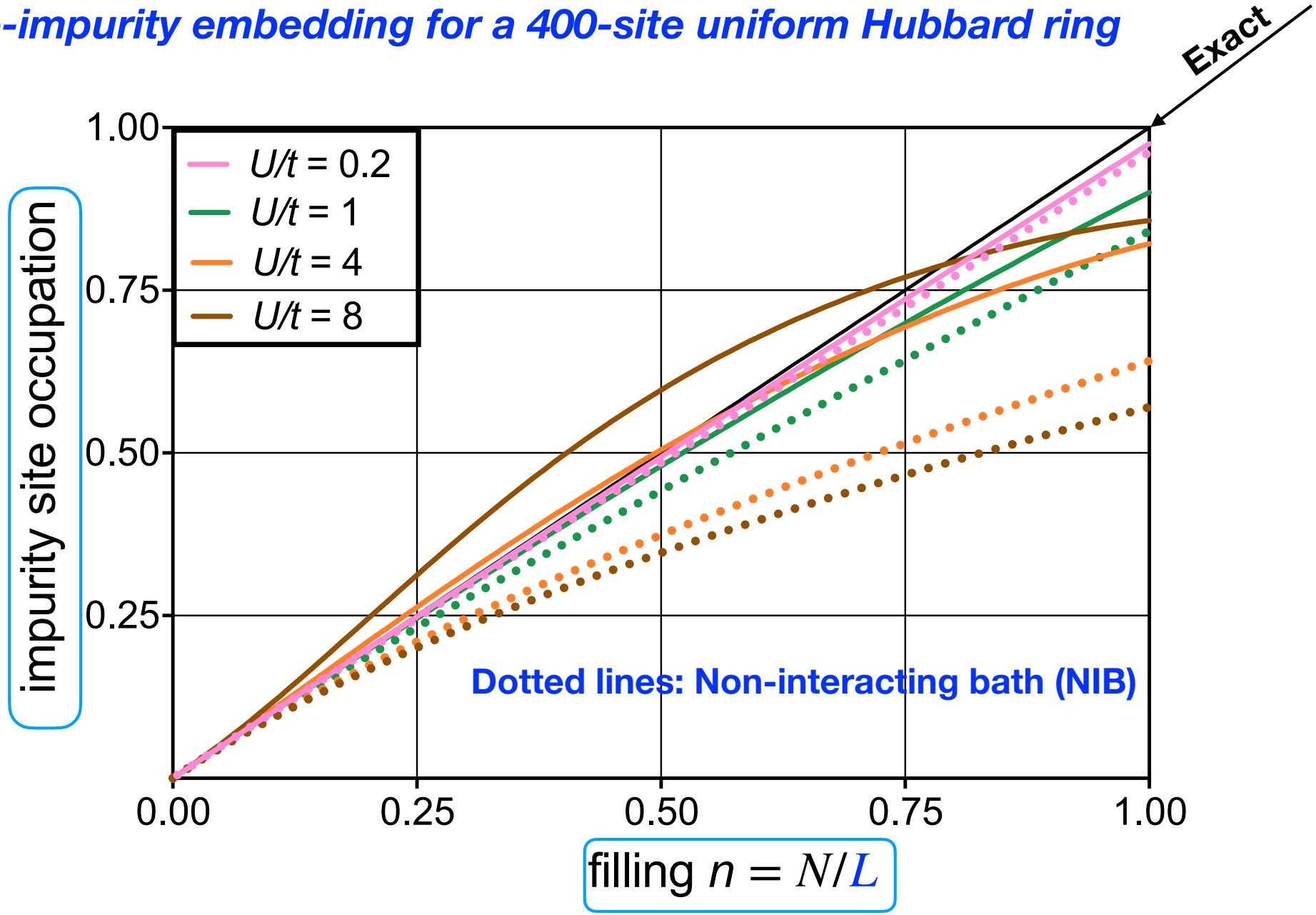
$$\hat{h}^{\mathscr{C}} \xrightarrow{single\ impurity} \hat{h}^{\mathscr{C}} + \langle pp\,|\,pp\rangle\, \hat{c}^{\dagger}_{p\uparrow}\hat{c}^{\dagger}_{p\downarrow}\hat{c}_{p\downarrow}\hat{c}_{p\uparrow}$$

Exact non-interacting
embedding

Approximate interacting
embedding

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

Single-impurity embedding for a 400-site uniform Hubbard ring



$L = 400$ sites

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

Non-interacting bath embedding of a single impurity

Chemical potential on the impurity

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

Exact non-interacting embedding

Approximate interacting embedding

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

Density-functional exactification of single-impurity DMET *(for Hubbard)*

$$v_{\mathrm{Hxc}}(n) = \tilde{\mu}^{\mathrm{imp}}(n) + \ldots$$

The "low-level" full-size non-interacting system of DMET is becoming the ***Kohn-Sham system!***

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

Density-functional exactification of single-impurity DMET *(for Hubbard)*

Functional-free DFT!

$$v_{\mathrm{Hxc}}(n) = \tilde{\mu}^{\mathrm{imp}}(n) + \ldots$$

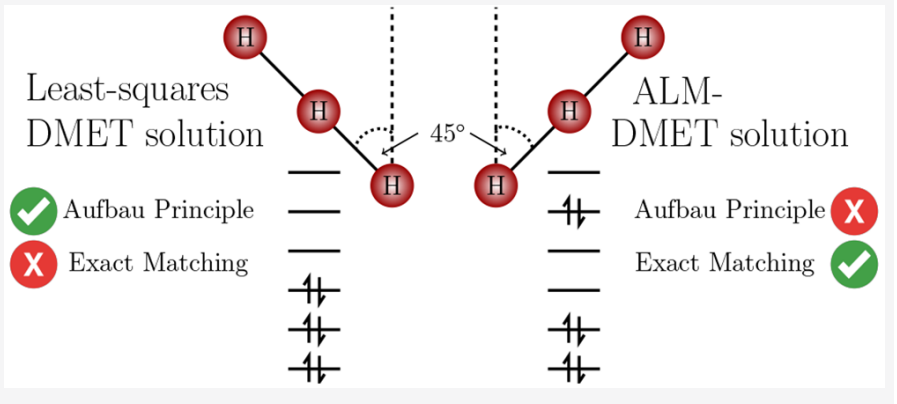
The "low-level" full-size non-interacting system of DMET is becoming the ***Kohn-Sham system!***

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

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



Non-interacting full system

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

Idempotent

?

Correlated cluster

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

Non-idempotent

Density matrix of non-interacting (or mean-field) systems

$$\hat{h} = \sum_{p \neq q} t_{pq} \hat{c}_p^\dagger \hat{c}_q + \sum_p v_p \hat{c}_p^\dagger \hat{c}_p$$

Density matrix of non-interacting (or mean-field) systems

$$\hat{h} = \sum_{p \neq q} t_{pq} \hat{c}_p^\dagger \hat{c}_q + \sum_p v_p \hat{c}_p^\dagger \hat{c}_p$$

Diagonalization

$$\hat{h} = \sum_k \varepsilon_k \hat{a}_k^\dagger \hat{a}_k$$

$$\begin{pmatrix} 1 & & & & \\ & 1 & & & \\ & & 1 & & \\ & & & 0 & \\ & & & & 0 \end{pmatrix} = \left\{ \left\langle \hat{a}_k^\dagger \hat{a}_{k'} \right\rangle_{\hat{h}} \right\}$$

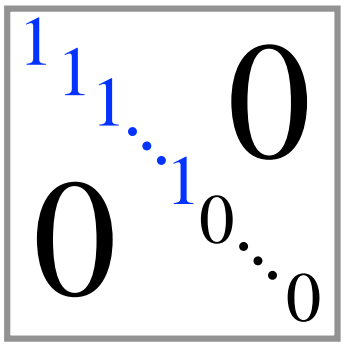
Delocalised molecular orbital representation

Density matrix of non-interacting (or mean-field) systems

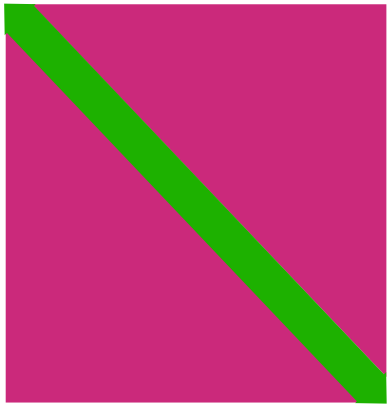
$$\hat{h} = \sum_{p \neq q} t_{pq} \hat{c}_p^\dagger \hat{c}_q + \sum_p v_p \hat{c}_p^\dagger \hat{c}_p$$

Diagonalization

$$\hat{h} = \sum_k \varepsilon_k \hat{a}_k^\dagger \hat{a}_k$$



$$= \left\{ \left\langle \hat{a}_k^\dagger \hat{a}_{k'} \right\rangle_{\hat{h}} \right\}$$



$$= \left\{ \left\langle \hat{c}_p^\dagger \hat{c}_q \right\rangle_{\hat{h}} \right\}$$

Delocalised molecular orbital representation

Localised molecular orbital representation

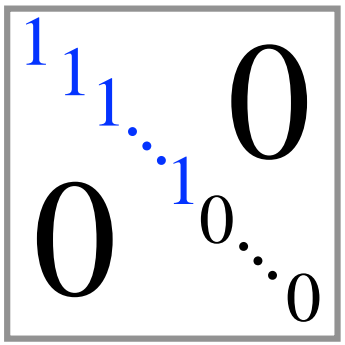
Density matrix of non-interacting (or mean-field) systems

$$\hat{h} = \sum_{p \neq q} t_{pq} \hat{c}_p^\dagger \hat{c}_q + \sum_p v_p \hat{c}_p^\dagger \hat{c}_p$$

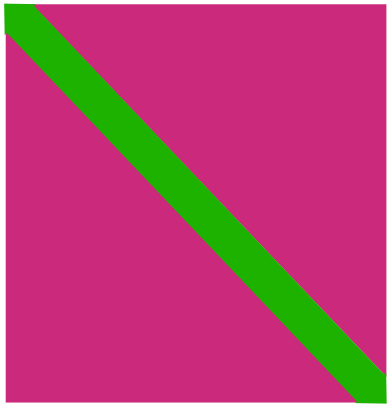
Diagonalization

$$\hat{h} = \sum_k \varepsilon_k \hat{a}_k^\dagger \hat{a}_k$$

*Key (**idempotent**) ingredient in the quantum embedding*



$$= \left\{ \left\langle \hat{a}_k^\dagger \hat{a}_{k'} \right\rangle_{\hat{h}} \right\}$$



$$= \left\{ \left\langle \hat{c}_p^\dagger \hat{c}_q \right\rangle_{\hat{h}} \right\}$$

Delocalised molecular orbital representation

Localised molecular orbital representation

Density matrix of non-interacting (or mean-field) non-hermitian systems

$$\hat{h} = \sum_{p \neq q} t_{pq} \hat{c}_p^\dagger \hat{c}_q + \sum_p v_p \hat{c}_p^\dagger \hat{c}_p + \sum_{p>q} \sigma_{pq} \left(\hat{c}_p^\dagger \hat{c}_q - \hat{c}_q^\dagger \hat{c}_p \right)$$

Diagonalization

$$\hat{h} = \sum_k \varepsilon_k \hat{\bar{a}}_k \hat{a}_k$$

Density matrix of non-interacting (or mean-field) non-hermitian systems

$$\hat{h} = \sum_{p \neq q} t_{pq} \hat{c}_p^\dagger \hat{c}_q + \sum_p v_p \hat{c}_p^\dagger \hat{c}_p + \sum_{p>q} \sigma_{pq} \left(\hat{c}_p^\dagger \hat{c}_q - \hat{c}_q^\dagger \hat{c}_p \right)$$

Diagonalization

$$\hat{h} = \sum_k \varepsilon_k \hat{\bar{a}}_k \hat{a}_k$$

We assume that energies remain **real**

Density matrix of non-interacting (or mean-field) non-hermitian systems

$$\hat{h} = \sum_{p \neq q} t_{pq} \hat{c}_p^\dagger \hat{c}_q + \sum_p v_p \hat{c}_p^\dagger \hat{c}_p + \sum_{p>q} \sigma_{pq} \left(\hat{c}_p^\dagger \hat{c}_q - \hat{c}_q^\dagger \hat{c}_p \right)$$

Diagonalization

$$\hat{h} = \sum_k \varepsilon_k \hat{\bar{a}}_k \hat{a}_k$$

$$\left[\hat{\bar{a}}_k, \hat{a}_{k'} \right]_+ = \delta_{kk'}$$

Bi-orthonormal solutions

Density matrix of non-interacting (or mean-field) non-hermitian systems

$$\hat{h} = \sum_{p \neq q} t_{pq} \hat{c}_p^\dagger \hat{c}_q + \sum_p v_p \hat{c}_p^\dagger \hat{c}_p + \sum_{p>q} \sigma_{pq} \left(\hat{c}_p^\dagger \hat{c}_q - \hat{c}_q^\dagger \hat{c}_p \right)$$

Diagonalization

$$\hat{h} = \sum_k \varepsilon_k \hat{\bar{a}}_k \hat{a}_k$$

$$\left[\hat{\bar{a}}_k, \hat{a}_{k'} \right]_+ = \delta_{kk'}$$

Bi-orthonormal solutions

Left solutions

$$\hat{h}^\dagger |\Phi^L\rangle = \left(\sum_k^{occ.} \varepsilon_k \right) |\Phi^L\rangle$$

$$|\Phi^L\rangle = \prod_k^{occ.} \hat{a}_k^\dagger |\text{vac}\rangle$$

Right solutions

$$\hat{h} |\Phi^R\rangle = \left(\sum_k^{occ.} \varepsilon_k \right) |\Phi^R\rangle$$

$$|\Phi^R\rangle = \prod_k^{occ.} \hat{\bar{a}}_k |\text{vac}\rangle$$

Density matrix of non-interacting (or mean-field) non-hermitian systems

$$\hat{h} = \sum_{p \neq q} t_{pq} \hat{c}_p^\dagger \hat{c}_q + \sum_p v_p \hat{c}_p^\dagger \hat{c}_p + \sum_{p>q} \sigma_{pq} \left(\hat{c}_p^\dagger \hat{c}_q - \hat{c}_q^\dagger \hat{c}_p \right)$$

Diagonalization

$$\hat{h} = \sum_k \varepsilon_k \hat{\bar{a}}_k \hat{a}_k$$

$$\begin{pmatrix} 1 & & & & \\ & 1 & & & \\ & & 1 & & \\ & & & 0 & \\ & & & & 0 \end{pmatrix} = \left\{ \left\langle \hat{\bar{a}}_k \hat{a}_{k'} \right\rangle_{\hat{h}} = \left\langle \Phi^L \middle| \hat{\bar{a}}_k \hat{a}_{k'} \middle| \Phi^R \right\rangle \right\}$$

Delocalised molecular orbital representation

Density matrix of non-interacting (or mean-field) non-hermitian systems

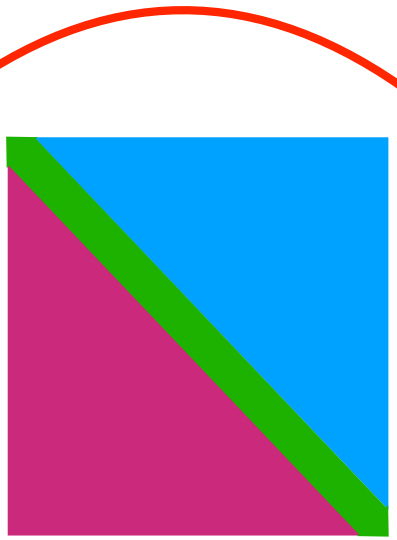
$$\hat{h} = \sum_{p \neq q} t_{pq} \hat{c}_p^\dagger \hat{c}_q + \sum_p v_p \hat{c}_p^\dagger \hat{c}_p + \sum_{p>q} \sigma_{pq} \left(\hat{c}_p^\dagger \hat{c}_q - \hat{c}_q^\dagger \hat{c}_p \right)$$

Diagonalization

$$\hat{h} = \sum_k \varepsilon_k \hat{\bar{a}}_k \hat{a}_k$$

Idempotent
(bi-orthonormally speaking)

$$\begin{pmatrix} 1 & & & & \\ & 1 & & & \\ & & 1 & & \\ & & & 0 & \\ & & & & 0 \end{pmatrix} = \left\{ \left\langle \hat{\bar{a}}_k \hat{a}_{k'} \right\rangle_{\hat{h}} \right\}$$

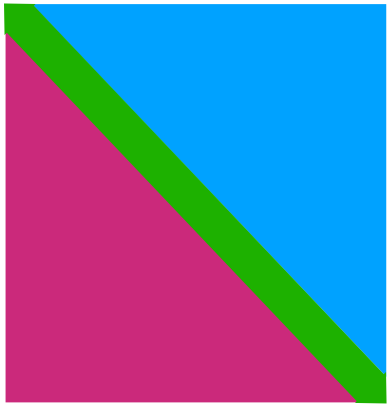


$$= \left\{ \left\langle \hat{c}_p^\dagger \hat{c}_q \right\rangle_{\hat{h}} \right\}$$

Delocalised molecular orbital representation

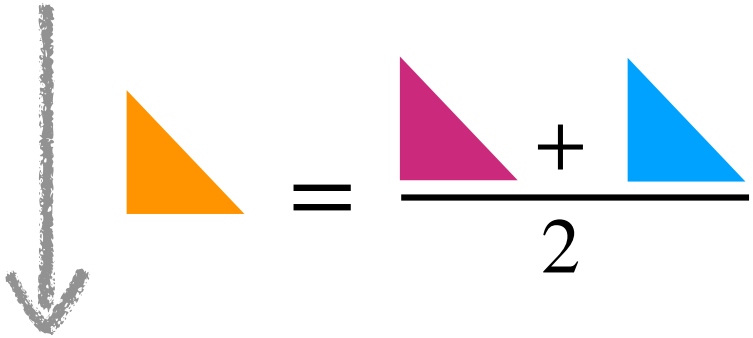
Localised molecular orbital representation

What about an indirect mapping of the 1RDM?

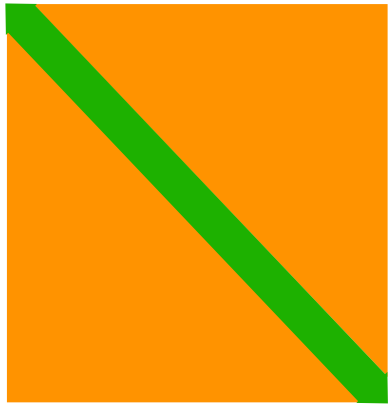


$$= \left\{ \bar{\gamma}_{pq} \right\}$$

Not physical



$$= \frac{+}{2}$$



$$= \left\{ \bar{\gamma}^{\text{ref}}_{pq} \underset{p \geq q}{=} \frac{1}{2} \left(\bar{\gamma}_{pq} + \bar{\gamma}_{qp} \right) \right\}$$

True 1RDM in non-interacting or mean-field cases

Kohn-Sham DFT

$$\delta\left\{\left\langle \Phi^{L}\middle|\hat{h}\middle|\Phi^{R}\right\rangle + E_{\mathrm{Hxc}}\left[\left\langle \Phi^{L}\middle|\hat{n}\middle|\Phi^{R}\right\rangle\right]\right\} = 0$$

$$\Downarrow$$

$$\Phi^{L} = \Phi^{R} = \Phi^{\mathrm{KS}}$$

Regular Kohn-Sham determinant

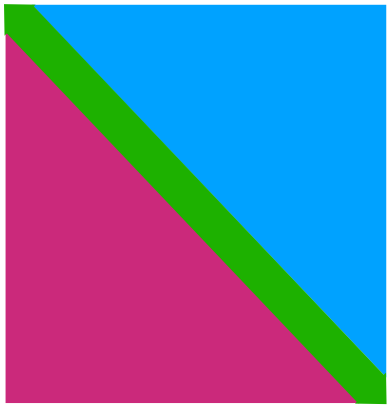
$$\Downarrow$$

$$\bar{\gamma} = \bar{\gamma}^{\mathrm{ref}} = \gamma^{\mathrm{KS}}$$

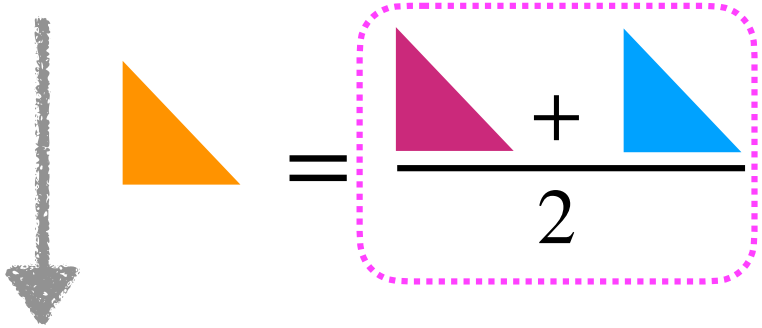
No explicit *density-matrix functional description of electron correlation*

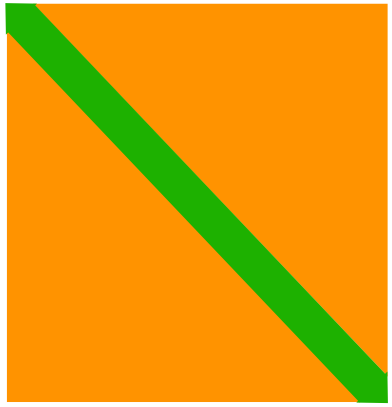
What about an indirect mapping of the 1RDM?

Not physical

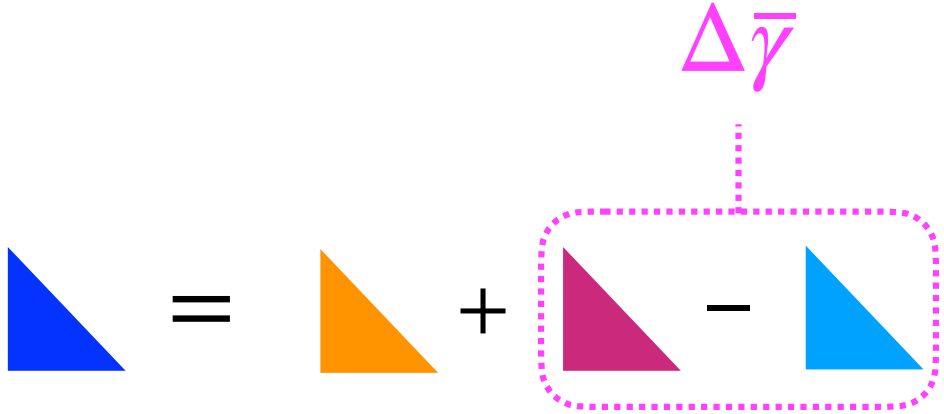


$$= \left\{ \bar{\gamma}_{pq} \right\}$$





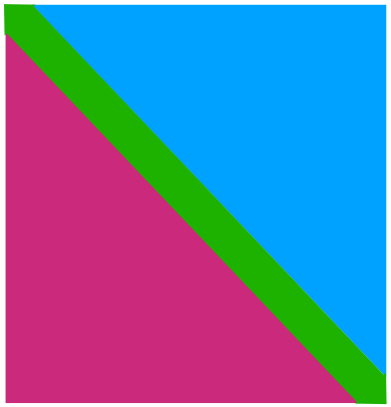
$$= \left\{ \bar{\gamma}^{\text{ref}}_{pq} \right\}$$



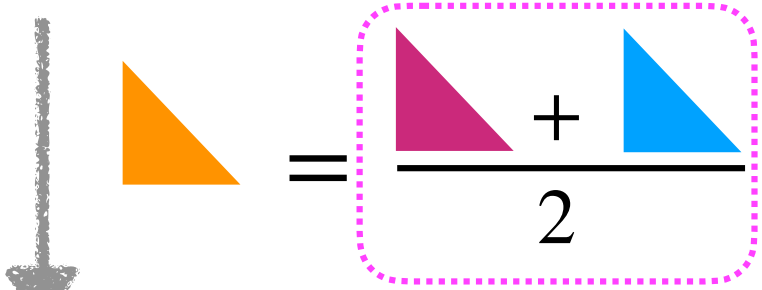
$$\left\{ \gamma_{pq} \underset{p \geq q}{=} \frac{1}{2} \left(3\bar{\gamma}_{pq} - \bar{\gamma}_{qp} \right) \right\}$$

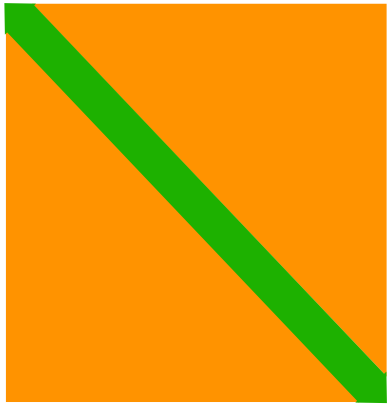
What about an indirect mapping of the 1RDM?

Not physical



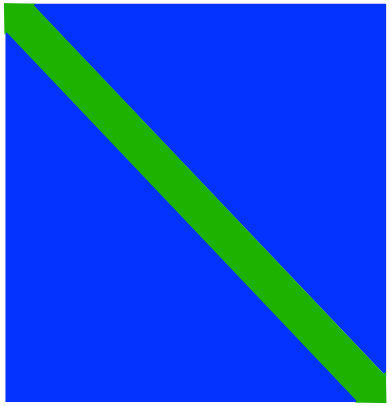
$$= \left\{ \bar{\gamma}_{pq} \right\}$$



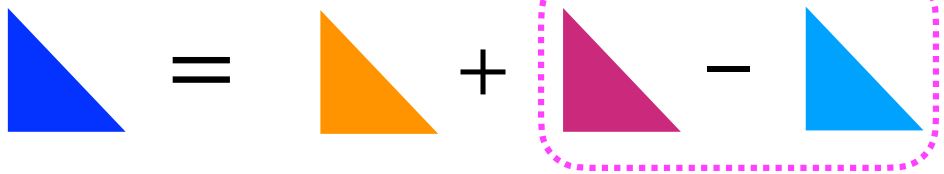


$$= \left\{ \bar{\gamma}^{\text{ref}}_{pq} \right\}$$

(more) physical



$$= \left\{ \gamma_{pq} \right\}$$



$$\Delta\bar{\gamma}$$

$$\left\{ \gamma_{pq} \underset{p \geq q}{=} \frac{1}{2}\left(3\bar{\gamma}_{pq} - \bar{\gamma}_{qp}\right) \right\}$$

Correlation in the 1RDM seen as a deviation from hermiticity

Looking for a variational principle…

$$\delta \left\{ h\left[\gamma^{\mathrm{ref}}\right] + E_{\mathrm{Hxc}}\left[n_{\gamma^{\mathrm{ref}}}\right] + \mathscr{W}_{\mathrm{c}}\left[n_{\gamma^{\mathrm{ref}}}, \Delta\bar{\gamma}\right] \right\} = 0$$

Will introduce non-hermiticity

Correlation in the 1RDM seen as a deviation from hermiticity

Looking for a variational principle…

$$\delta \left\{ h\left[\gamma^{\mathrm{ref}}\right] + E_{\mathrm{Hxc}}\left[n_{\gamma^{\mathrm{ref}}}\right] + \mathscr{W}_{\mathrm{c}}\left[n_{\gamma^{\mathrm{ref}}}, \Delta\bar{\gamma}\right] \right\} = 0$$

???

Will introduce non-hermiticity

Correlation in the 1RDM seen as a deviation from hermiticity

Looking for a variational principle…

$$\delta \left\{ h\left[\gamma^{\mathrm{ref}}\right] + E_{\mathrm{Hxc}}\left[n_{\gamma^{\mathrm{ref}}}\right] + \mathscr{W}_{\mathrm{c}}\left[n_{\gamma^{\mathrm{ref}}}, \Delta\bar{\gamma}\right] \right\} = 0$$

???

Can we map (indirectly) a correlated 1RDM onto a non-interacting and non-hermitian system?

Numerical experiment: Mapping through cost function minimisation

$$\min_{\{v_p\},\{\sigma_{pq}\}} \left\{ \sum_{p \geq q} \left(\gamma_{pq}^{FCI} - \frac{3}{2}\bar{\gamma}_{pq} + \frac{1}{2}\bar{\gamma}_{qp} \right)^2 \right\}$$

For this optimisation, we use scipy AND QuantNbody

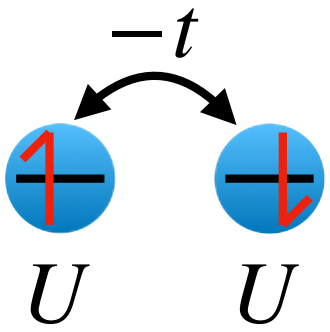
Saad Yalouz

|qnb⟩ **QuantNBody**

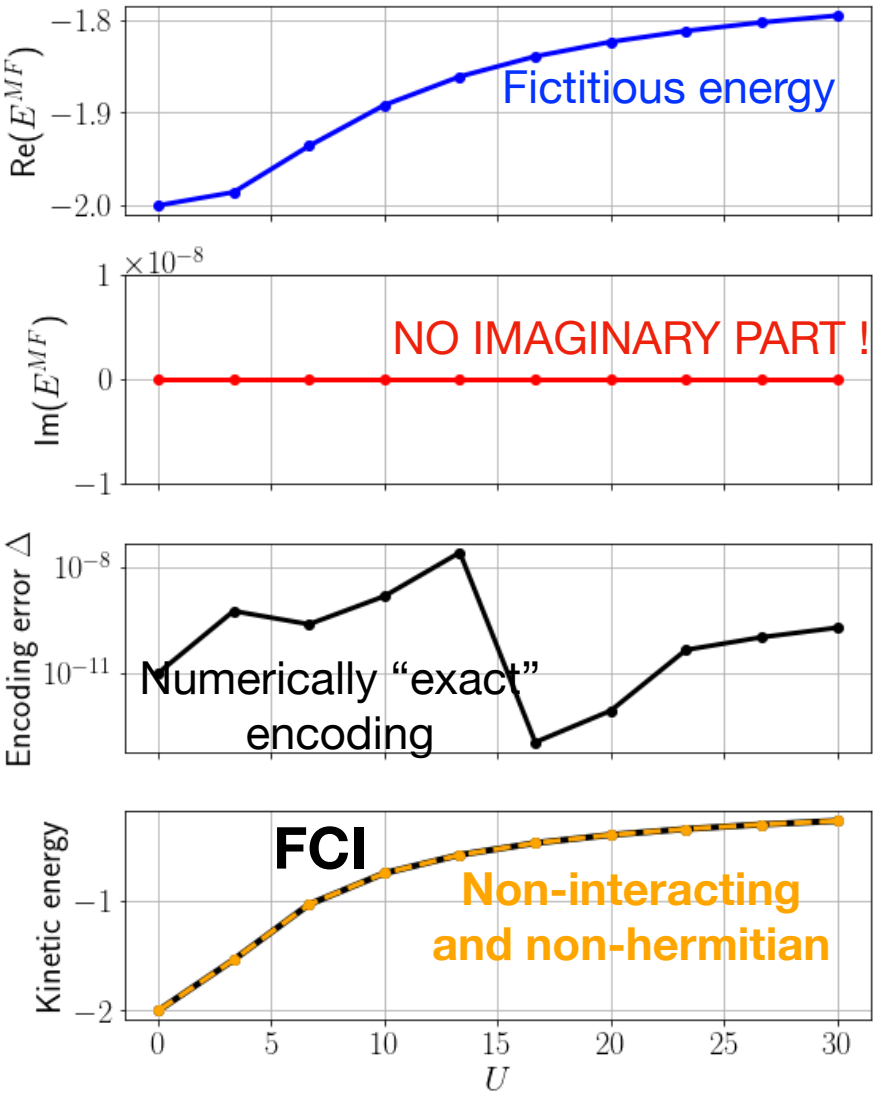
An open access python package for quantum chemistry/physics to manipulate many-body operators and wave functions

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

Preliminary results: Symmetric Hubbard dimer



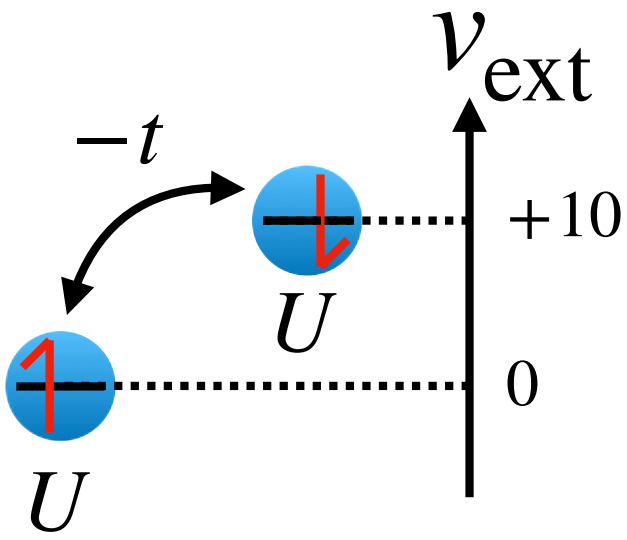
2 sites - 2 electrons



Kinetic (hopping) energy ⟶

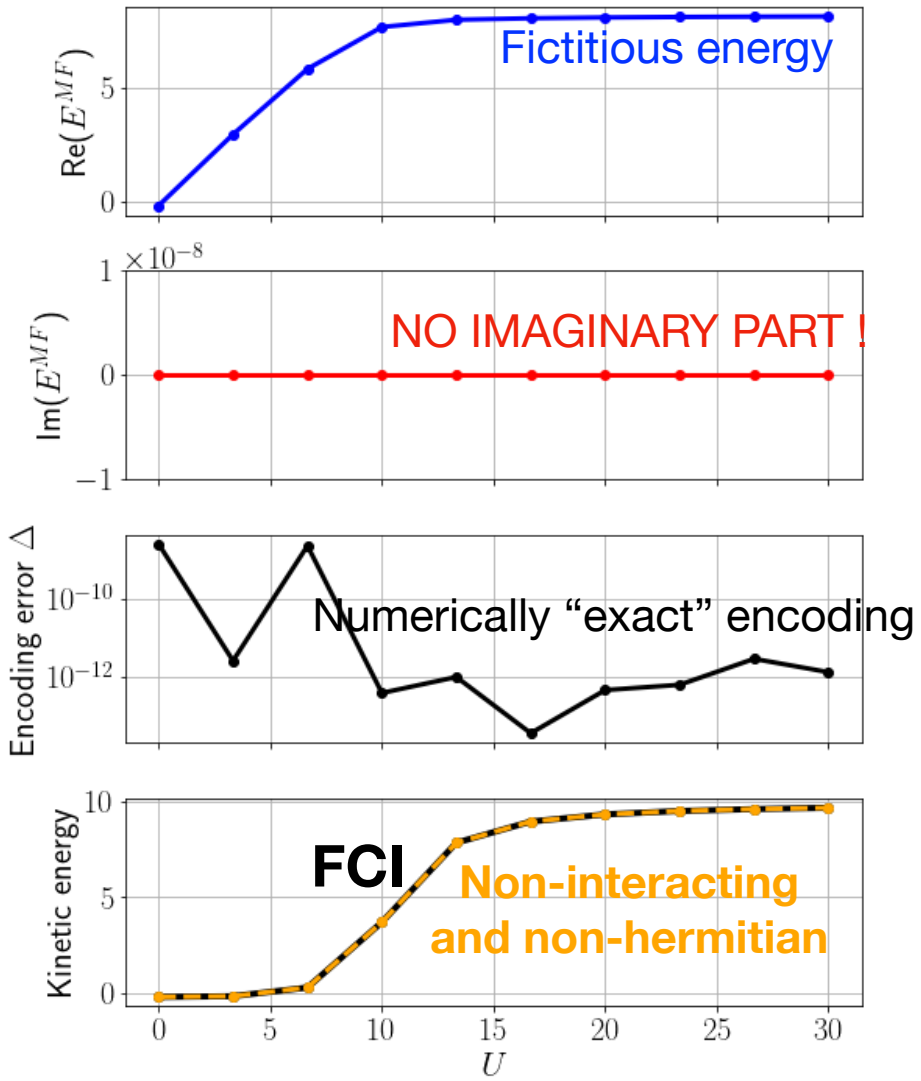
S. Yalouz and E. Fromager, in preparation (2022).

Preliminary results: Asymmetric Hubbard dimer



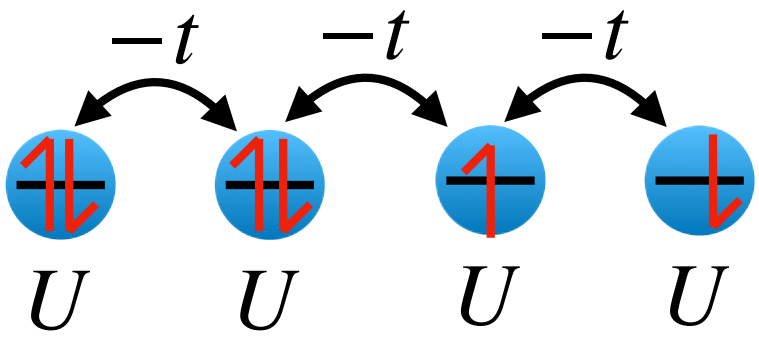
2 sites - 2 electrons

Kinetic (hopping) energy →



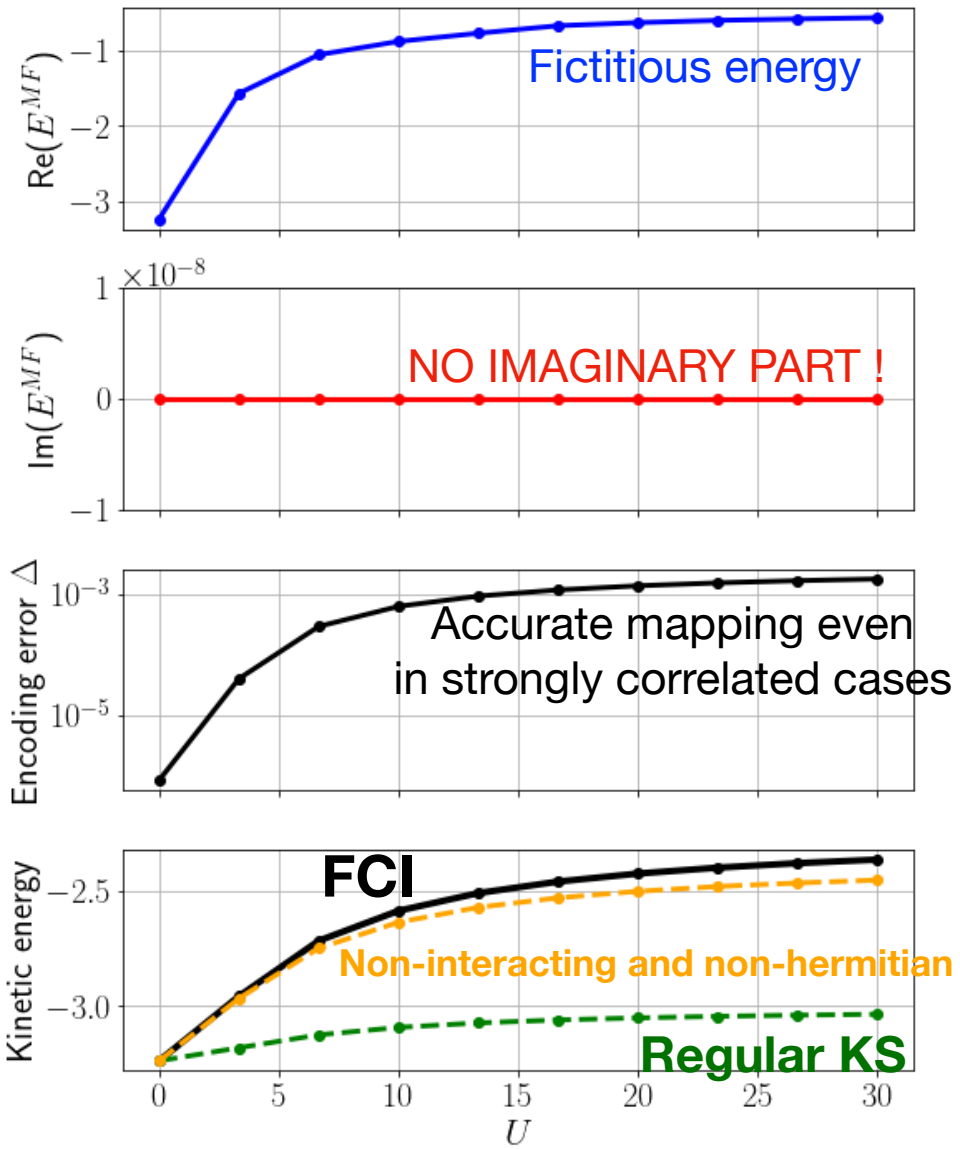
S. Yalouz and E. Fromager, in preparation (2022).

Preliminary results: Symmetric 4-site Hubbard chain



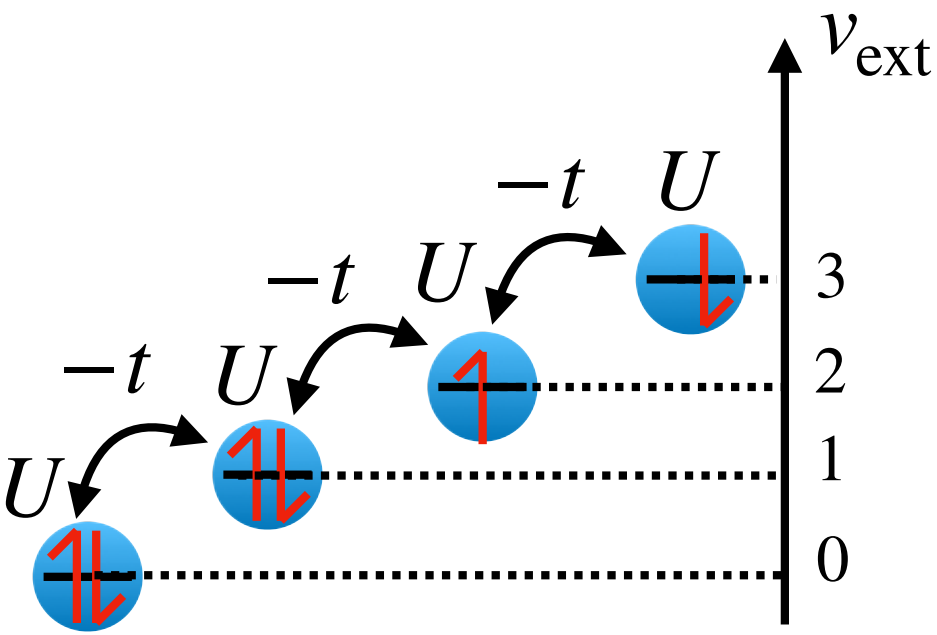
4 sites - 6 electrons

Kinetic (hopping) energy →

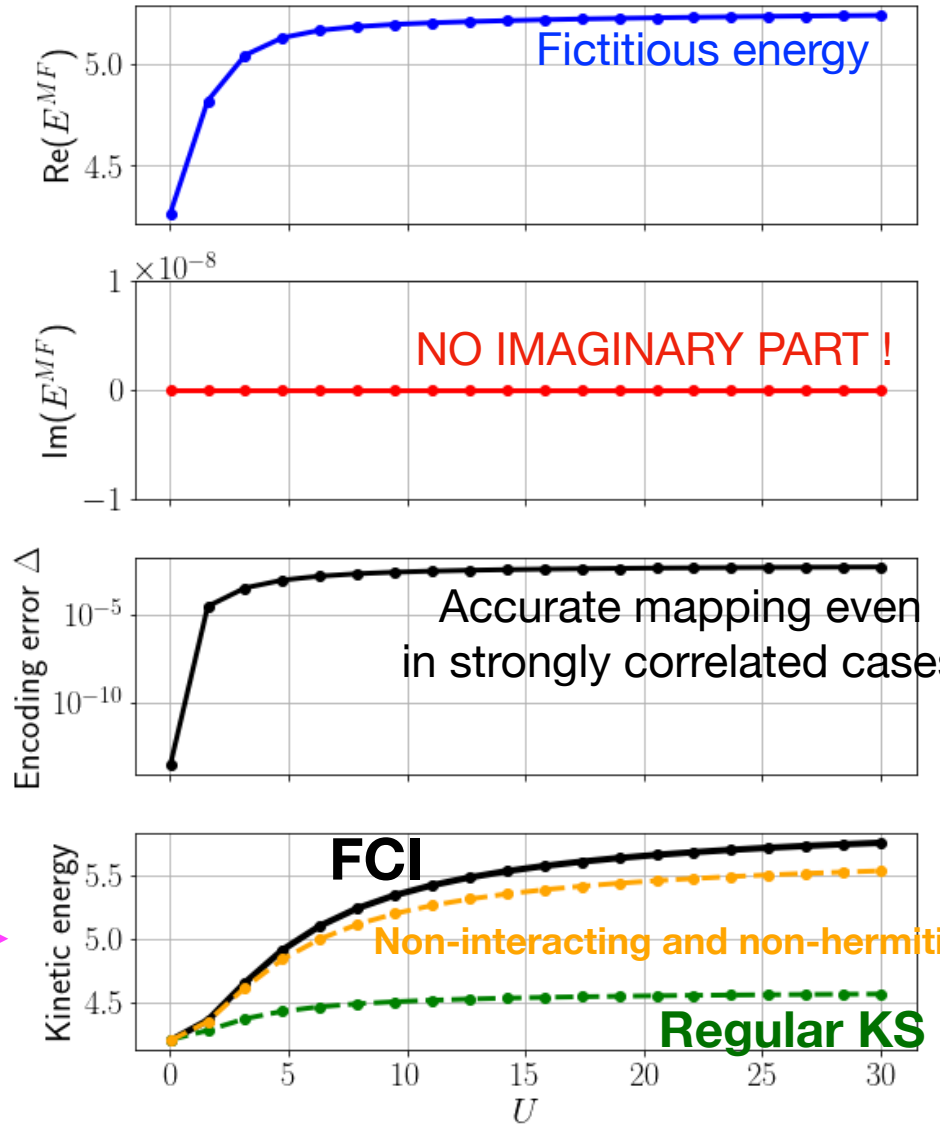


S. Yalouz and E. Fromager, in preparation (2022).

Preliminary results: Asymmetric 4-site Hubbard chain



4 sites - 6 electrons



Kinetic (hopping) energy →

S. Yalouz and E. Fromager, in preparation (2022).

Funding

“Lab of Excellence” project:
LabEx CSC (ANR-10-LABX-0026-CSC)

« Initiative d’Excellence » (IdEx) grant
University of Strasbourg

CoLab ANR project