Introduction to molecular electronic structure theory:

A quantum embedding approach to the electronic Schrödinger equation

Emmanuel Fromager

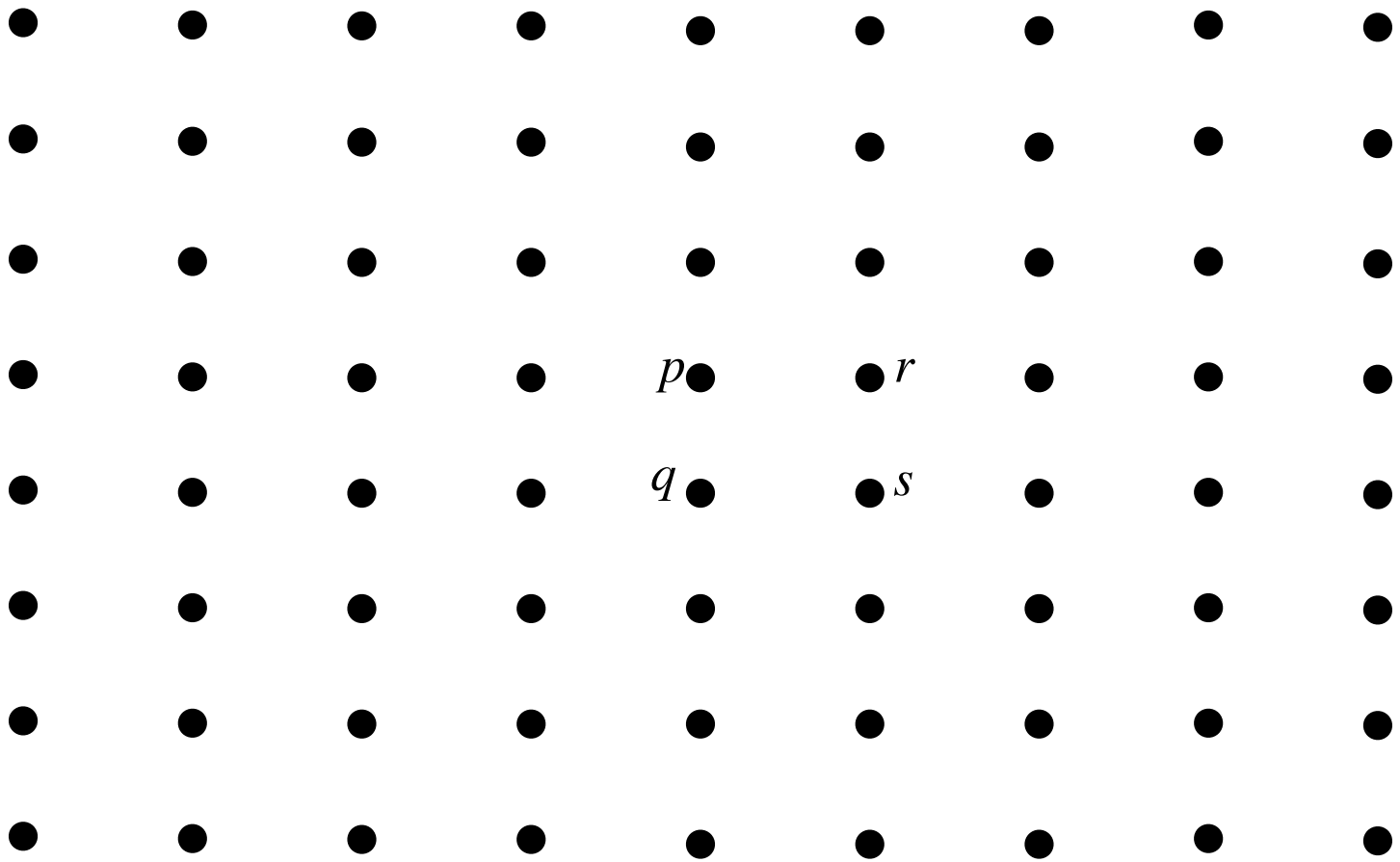
Laboratoire de Chimie Quantique, Institut de Chimie de Strasbourg,
Université de Strasbourg, Strasbourg, France.

Applying quantum mechanics to electrons

Electronic Schrödinger equation

$$\hat{H}\,|\,\Psi\rangle = E\,|\,\Psi\rangle$$

“Lattice” representation of a molecular or extended system



Schematic representation of a molecule or a solid

Electronic structure perspective of a molecule or a solid

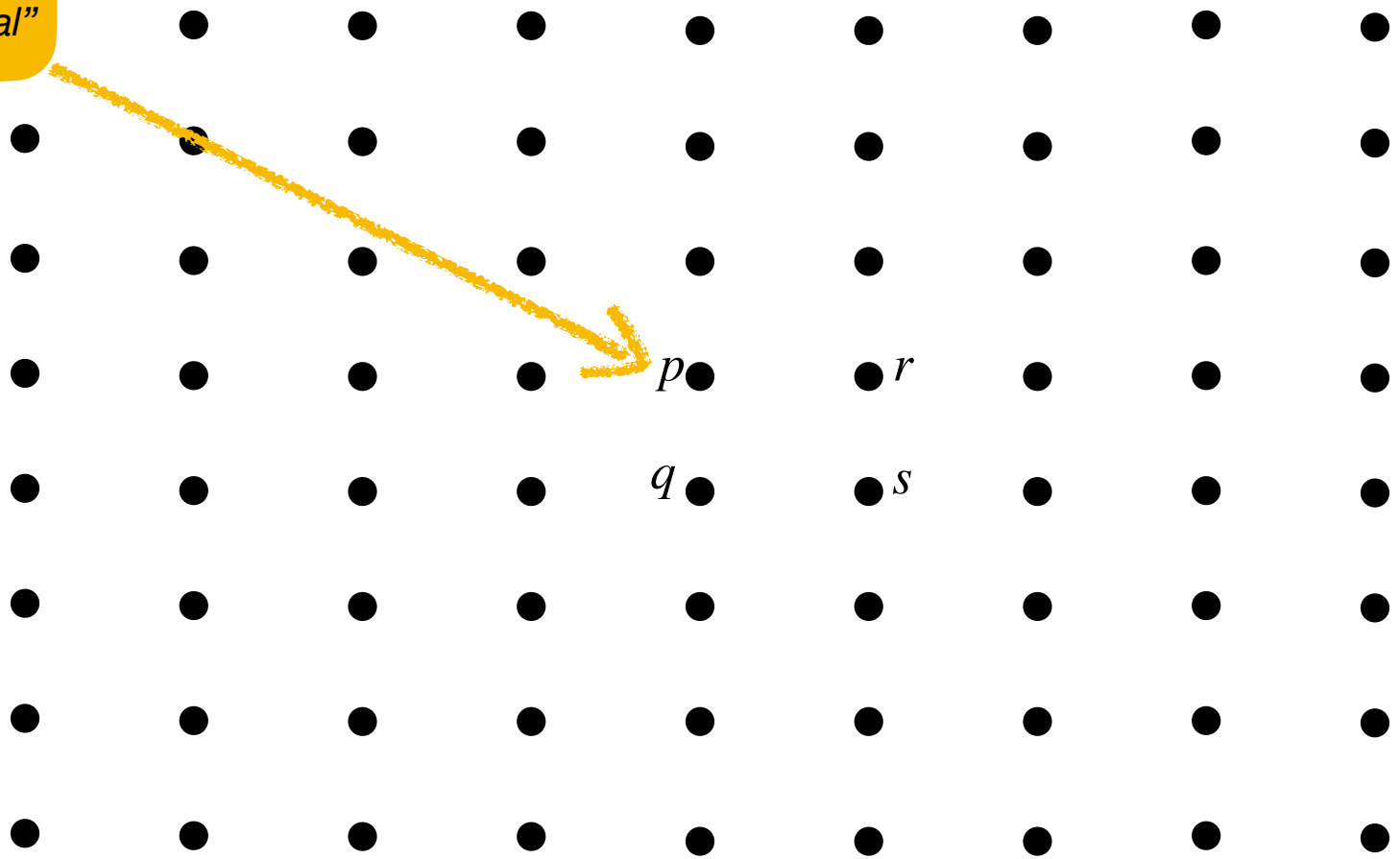
For example: $\chi_p(\mathbf{r}) \sim e^{-\alpha|\mathbf{r}-\mathbf{R}_p|^2}$

Position that a single electron could have

Position of the nucleus p

$\chi_p(\mathbf{r})$

*"**atomic** orbital"*



Schematic representation of a molecule or a solid

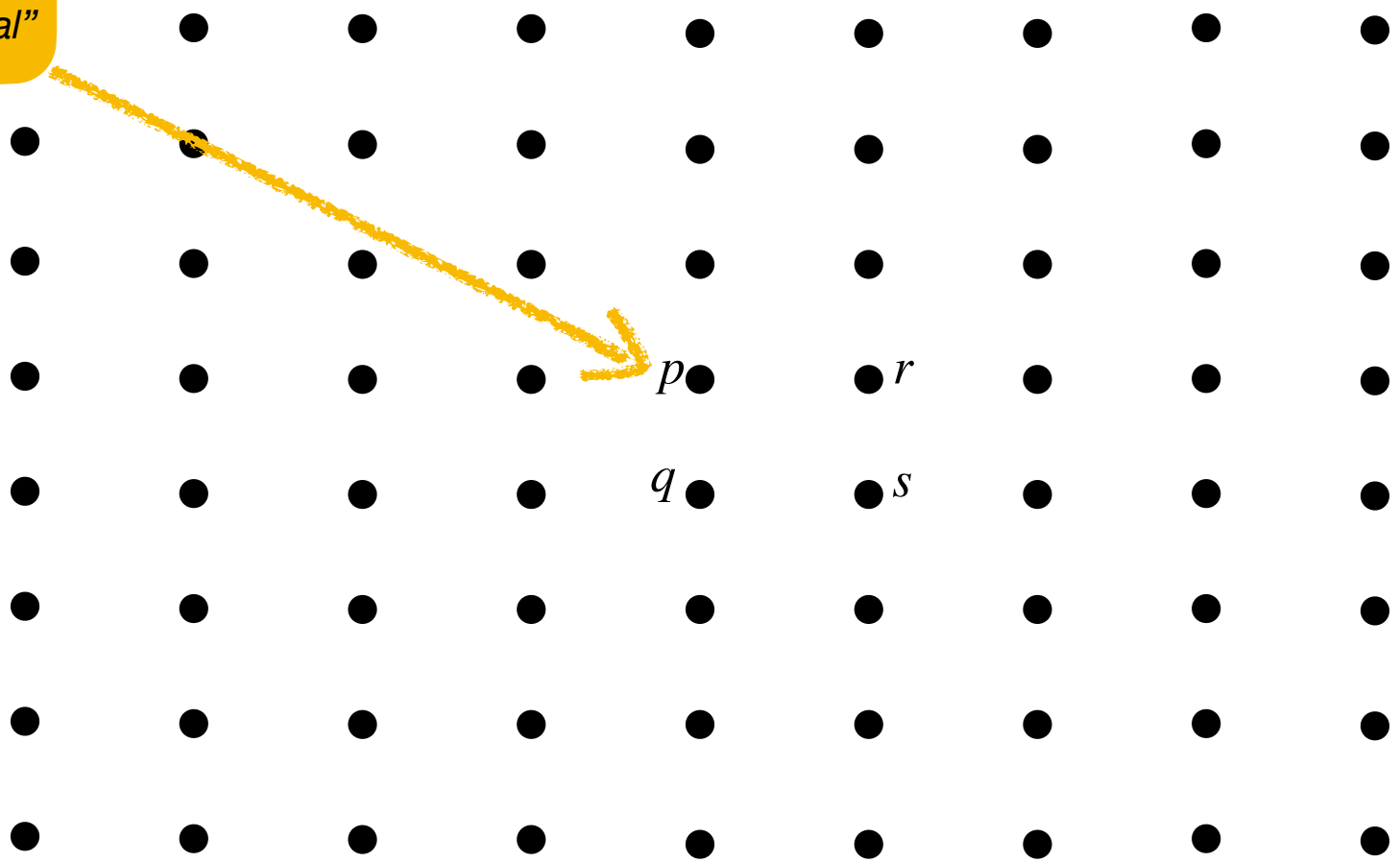
"Lattice" representation of a molecular or extended system

For example: $\chi_p(\mathbf{r}) \sim e^{-\alpha|\mathbf{r}-\mathbf{R}_p|^2}$

The density of probability (to find the electron) at position $\mathbf{r}$ is $|\chi_p(\mathbf{r})|^2$

$\chi_p(\mathbf{r})$

*"**atomic** orbital"*



Dirac notation of many-electron quantum states

One-electron **localised** state:

$$|\chi_p\rangle \equiv |0_1 \ldots 0_{p-1} 1_p 0_{p+1} \ldots 0_L\rangle$$

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Two-electron **localised** state:

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Many-electron **localised** state:

$$|\chi_1^{n_1} \chi_2^{n_2} \ldots \chi_{L-1}^{n_{L-1}} \chi_L^{n_L}\rangle \equiv |n_1 n_2 \ldots n_{L-1} n_L\rangle,\ n_i \in \{0,1\},\ 1 \leq i \leq L$$

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"Slater determinant"

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Many-electron **localised** state:

Pauli exclusion principle

$$|\chi_1^{n_1} \chi_2^{n_2} \ldots \chi_{L-1}^{n_{L-1}} \chi_L^{n_L}\rangle \equiv |n_1 n_2 \ldots n_{L-1} n_L\rangle, \; n_i \in \{0,1\}, \; 1 \leq i \leq L$$

"Slater determinant"

Dirac notation of many-electron quantum states

One-electron **localised** state:

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Many-electron **localised** state:

$$\underbrace{|\chi_1^{n_1} \chi_2^{n_2} \ldots \chi_{L-1}^{n_{L-1}} \chi_L^{n_L}\rangle}_{\text{“Slater determinant”}} \equiv |\underbrace{n_1 n_2 \ldots n_{L-1} n_L}_{\substack{\textbf{Disentangled} \\ \text{one-electron states}}}\rangle,\ n_i \in \{0,1\},\ 1 \le i \le L$$

Dirac notation of many-electron quantum states

The true quantum state $|\Psi\rangle$ of (interacting)
electrons cannot be described
by a single Slater determinant

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Mathematical description of electronic correlations:

Dirac notation of many-electron quantum states

The true quantum state $|\Psi\rangle$ of (interacting) electrons **cannot** be described by a single Slater determinant

It is what we call in quantum chemistry a **correlated** state

Mathematical description of electronic correlations:

$$|\Psi\rangle = \sum_{n_1=0}^{1} \sum_{n_2=0}^{1} \dots \sum_{n_L=0}^{1} C_{n_1 n_2 \dots n_{L-1} n_L} |n_1 n_2 \dots n_{L-1} n_L\rangle$$

$$\vec{\Psi} = \sum_i C_i \vec{e}_i$$

Dirac notation of many-electron quantum states

Probability of having n_i electrons occupying the orbital χ_i for $1 \leq i \leq L$:

$$\mathscr{P}(n_1 n_2 \ldots n_{L-1} n_L) = \left| C_{n_1 n_2 \ldots n_{L-1} n_L} \right|^2$$

$$|\Psi\rangle = \sum_{n_1=0}^{1} \sum_{n_2=0}^{1} \cdots \sum_{n_L=0}^{1} C_{n_1 n_2 \ldots n_{L-1} n_L} \, | n_1 n_2 \ldots n_{L-1} n_L \rangle$$

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$$\vec{\Psi} = \sum_i C_i \vec{e}_i \longrightarrow C_i = \vec{e}_i \,.\, \vec{\Psi}, \text{ if the basis is orthonormal } (\vec{e}_i \,.\, \vec{e}_j = \delta_{ij})$$

Dirac notation of many-electron quantum states

"Bra-ket" notation

$$\langle n_1 n_2 \ldots n_{L-1} n_L \,|\, \Psi \rangle$$

$$|\,\Psi\rangle = \sum_{n_1=0}^{1} \sum_{n_2=0}^{1} \cdots \sum_{n_L=0}^{1} C_{n_1 n_2 \ldots n_{L-1} n_L} \,|\, n_1 n_2 \ldots n_{L-1} n_L \rangle$$

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Dirac notation of many-electron quantum states

The space of electronic quantum states is a **Hilbert space**

"Bra-ket" notation

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How do we determine the coefficients $C_{n_1 n_2 \ldots n_{L-1} n_L}$?

We solve the Schrödinger equation!

Electronic Schrödinger equation

$$\hat{H}\,|\,\Psi\rangle = E\,|\,\Psi\rangle$$

Linear quantum operators

$$\hat{H}|\Psi\rangle = E|\Psi\rangle$$

$$|\Psi\rangle = \sum_{n_1=0}^{1}\sum_{n_2=0}^{1}\cdots\sum_{n_L=0}^{1} C_{n_1 n_2 \ldots n_{L-1} n_L}\,|n_1 n_2 \ldots n_{L-1} n_L\rangle$$

$$\vec{\Psi} = \sum_i C_i \vec{e}_i \longrightarrow \hat{H}(\vec{\Psi}) = \sum_i C_i \hat{H}(\vec{e}_i)$$

$$= \sum_i C_i \left(\sum_j [\hat{H}]_{ji} \vec{e}_j \right)$$

Matrix representation of $\hat{H}$

Linear quantum operators

$$\hat{H}|\Psi\rangle = E|\Psi\rangle$$

$$\hat{H}|\Psi\rangle = \sum_{n_1=0}^{1}\sum_{n_2=0}^{1}\cdots\sum_{n_L=0}^{1} C_{n_1 n_2 \ldots n_{L-1} n_L}\, \hat{H}|n_1 n_2 \ldots n_{L-1} n_L\rangle$$

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$$\hat{H}|\Psi\rangle = E|\Psi\rangle$$

?????

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"Second-quantized" expression of the electronic Hamiltonian operator

$$\hat{H} = \sum_{pq}^{\text{lattice}} \langle \chi_p | \hat{h} | \chi_q \rangle \hat{a}_p^\dagger \hat{a}_q + \frac{1}{2} \sum_{pqrs}^{\text{lattice}} \langle \chi_p \chi_q | \hat{w}_{\text{ee}} | \chi_r \chi_s \rangle \hat{a}_p^\dagger \hat{a}_q^\dagger \hat{a}_s \hat{a}_r$$

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$$\| $$

$$\int d\mathbf{x}\, \chi_p^*(\mathbf{x}) \left(-\frac{1}{2}\nabla_{\mathbf{r}}^2 + v_{\text{ne}}(\mathbf{r}) \right) \chi_q(\mathbf{x})$$

$$v_{\text{ne}}(\mathbf{r}) = -\sum_{A}^{\text{nuclei}} \frac{Z_A}{|\mathbf{r} - \mathbf{R}_A|}$$

"Nuclear potential"

"Second-quantized" expression of the electronic Hamiltonian operator

$$\hat{H} = \sum_{pq} \langle \chi_p | \hat{h} | \chi_q \rangle \hat{a}_p^\dagger \hat{a}_q + \frac{1}{2} \sum_{pqrs} \langle \chi_p \chi_q | \hat{w}_{\text{ee}} | \chi_r \chi_s \rangle \hat{a}_p^\dagger \hat{a}_q^\dagger \hat{a}_s \hat{a}_r$$

$$\| $$

$$\int d\mathbf{x} \int d\mathbf{x}' \, \chi_p^*(\mathbf{x}) \chi_q^*(\mathbf{x}') \frac{1}{|\mathbf{r} - \mathbf{r}'|} \chi_r(\mathbf{x}) \chi_s(\mathbf{x}')$$

Two-electron repulsion integral

"Second-quantized" expression of the electronic Hamiltonian operator

$$\hat{H}\,|\,n_1 n_2 \ldots n_{L-1} n_L\rangle \equiv \hat{H}\,|\,n_1 \ldots n_p \ldots n_q \ldots n_r \ldots n_s \ldots n_L\rangle = ?$$

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$\hat{a}_p$ "**Annihilation** operator"

$\hat{a}_p^\dagger$ "**Creation** operator"

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$$\hat{H}\,|\,n_1 n_2 \ldots n_{L-1} n_L\rangle \equiv \hat{H}\,|\,n_1 \ldots n_p \ldots n_q \ldots n_r \ldots n_s \ldots n_L\rangle = ?$$

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$\hat{a}_p$ "**Annihilation** operator"

$\hat{a}_p^\dagger$ "**Creation** operator"

$\hat{\mathcal{O}}^\dagger$ is the **adjoint** of $\hat{\mathcal{O}}$:

$$\forall \Psi, \Phi, \langle \Phi \,|\, \hat{\mathcal{O}} \,|\, \Psi \rangle = \langle \hat{\mathcal{O}}^\dagger \Phi \,|\, \Psi \rangle$$

Electronic Schrödinger equation ⇔ eigenvalue problem for $\hat{H}$

$$\hat{H}\,|\,\Psi\rangle = E\,|\,\Psi\rangle$$

The eigenvalues E of $\hat{H}$ are interpreted as the possible energy levels of the electronic system under study.

Electronic Schrödinger equation

$$\hat{H}\,|\,\Psi_I\rangle = E_I\,|\,\Psi_I\rangle$$

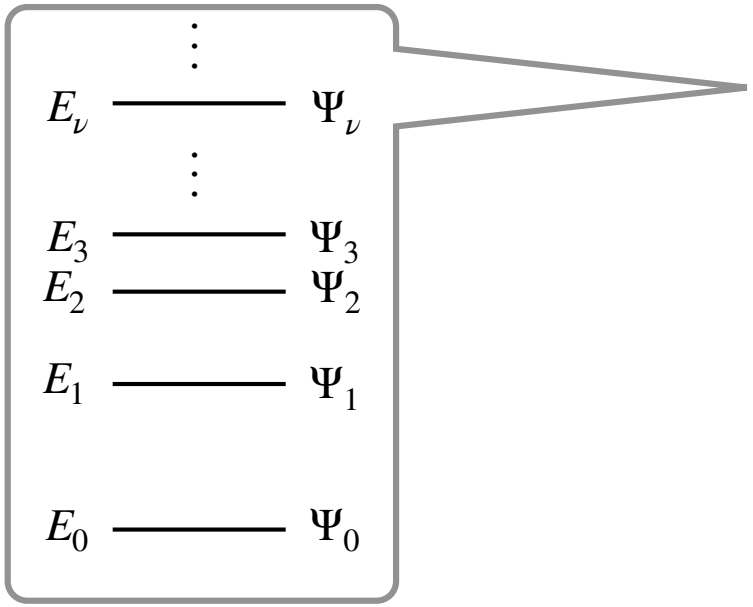
Electronic Schrödinger equation

$$\hat{H}\,|\,\Psi_I\rangle = E_I\,|\,\Psi_I\rangle$$

Ground $(I = 0)$ *and excited* $(I > 0)$
electronic energies

Electronic Schrödinger equation

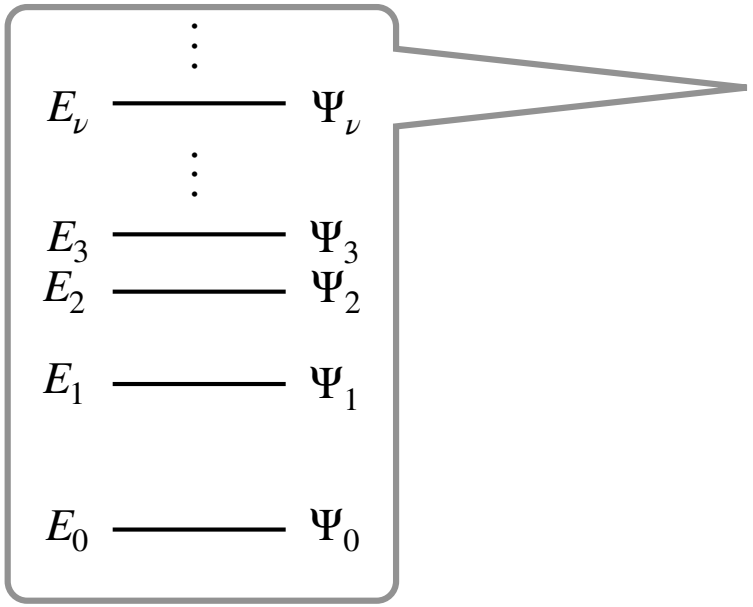
$$\hat{H}\,|\Psi_I\rangle = E_I\,|\Psi_I\rangle$$



Ground $(I = 0)$ *and excited* $(I > 0)$ *electronic energies*

Electronic Schrödinger equation

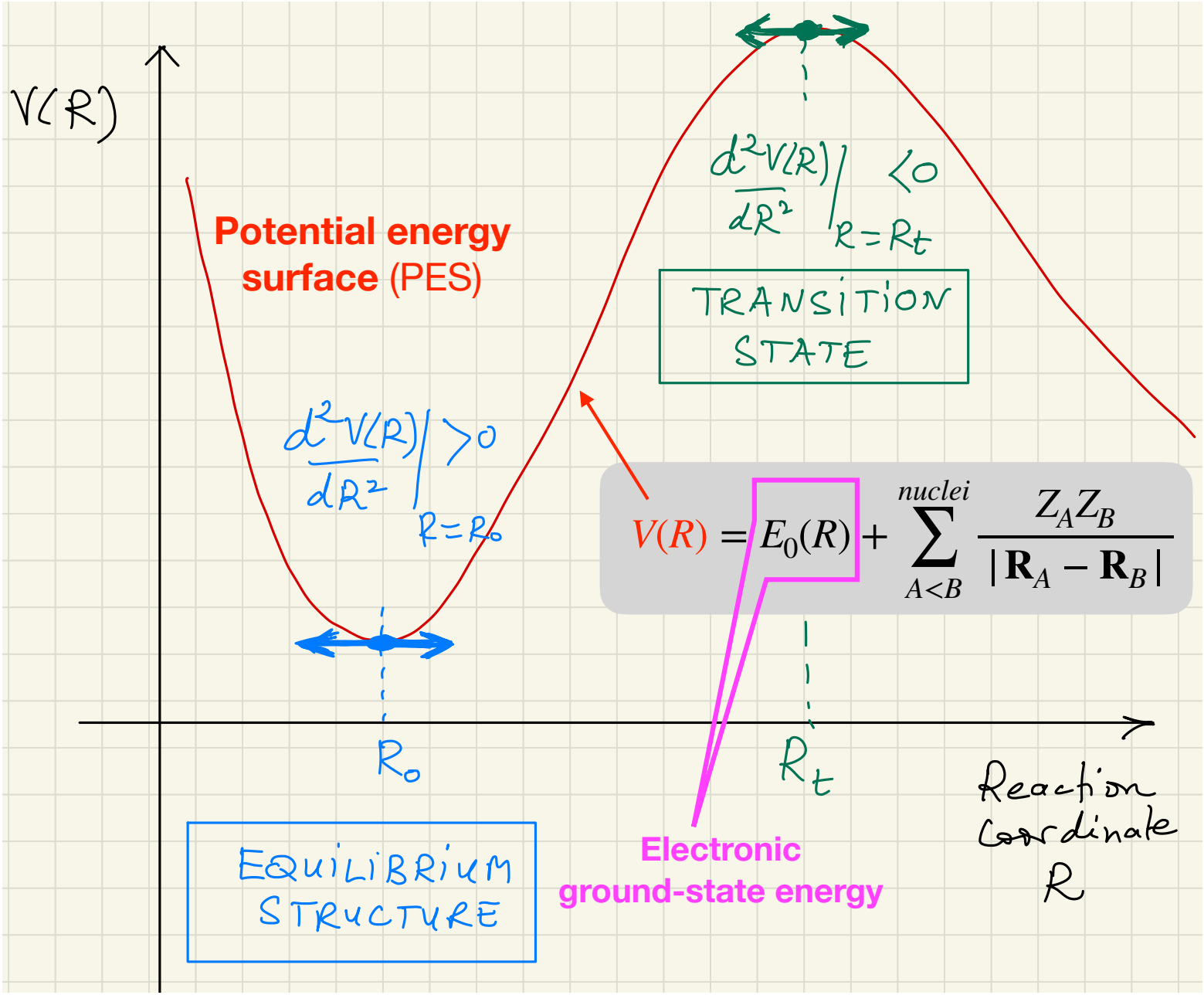
$$\hat{H}\,|\Psi_I\rangle = E_I\,|\Psi_I\rangle$$



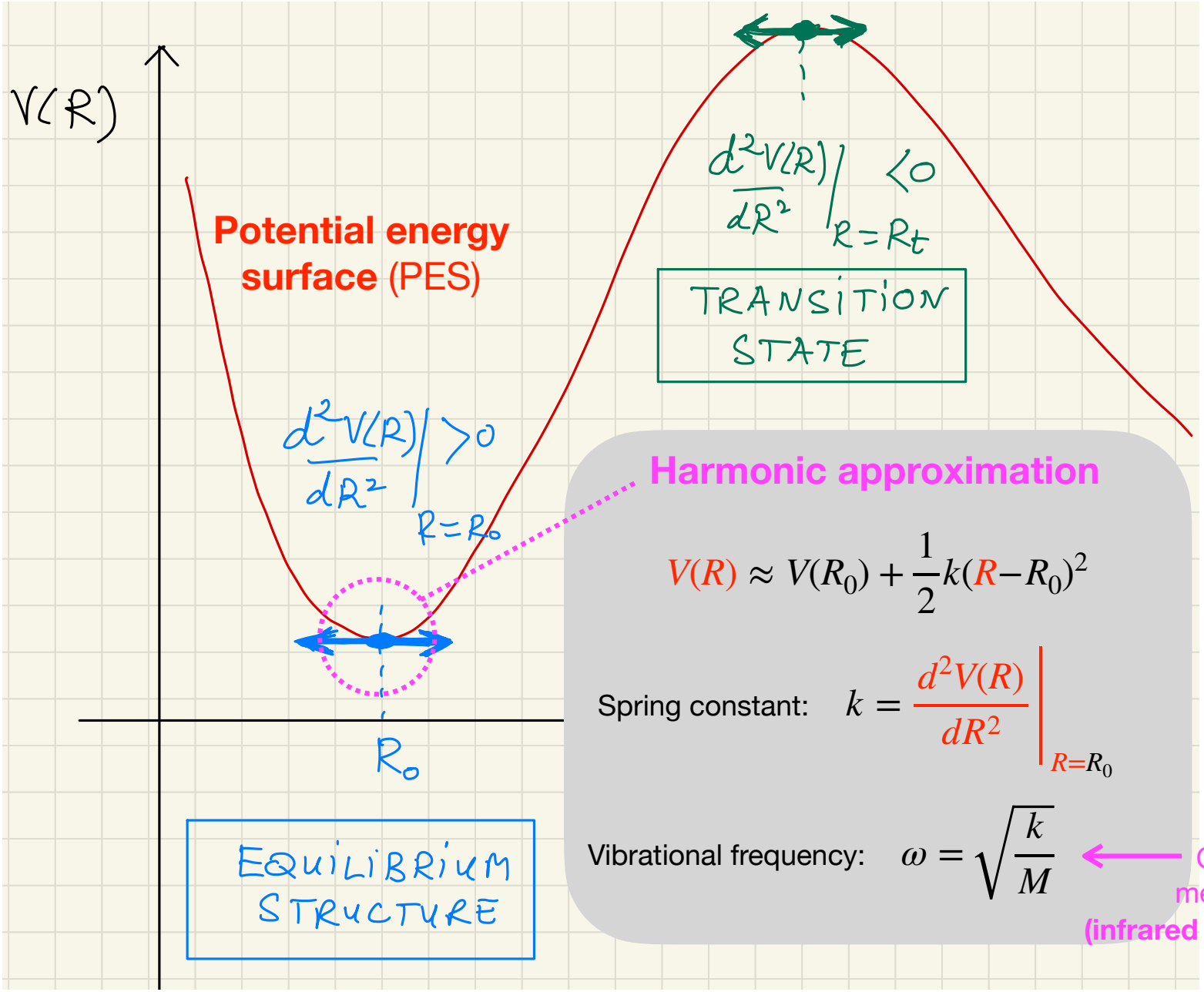
Ground $(I = 0)$ *and excited* $(I > 0)$ *electronic energies*

To be determined!

Computation of reaction paths in the ground electronic state



Vibrational molecular spectroscopy



Harmonic approximation

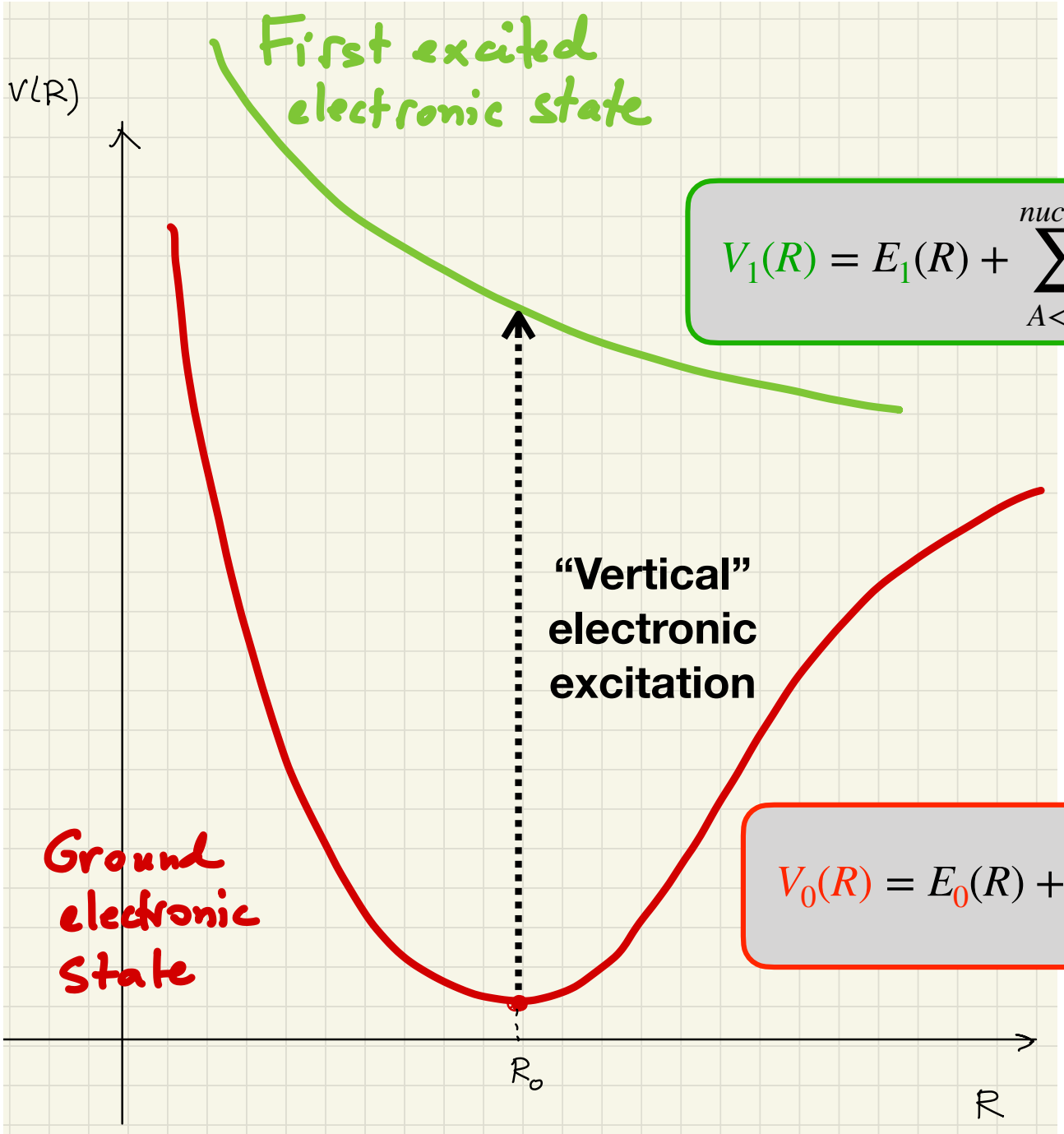
$$V(R) \approx V(R_0) + \frac{1}{2}k(R-R_0)^2$$

Spring constant: $$k = \left.\frac{d^2V(R)}{dR^2}\right|_{R=R_0}$$

Vibrational frequency: $$\omega = \sqrt{\frac{k}{M}}$$

← Can be measured! **(infrared spectroscopy)**

UV-visible electronic spectroscopy



$$V_1(R) = E_1(R) + \sum_{A<B}^{nuclei} \frac{Z_A Z_B}{|\mathbf{R}_A - \mathbf{R}_B|}$$

$$V_0(R) = E_0(R) + \sum_{A<B}^{nuclei} \frac{Z_A Z_B}{|\mathbf{R}_A - \mathbf{R}_B|}$$

Configuration interaction method

Full Configuration Interaction (FCI) method

$$\hat{H}\,|\,\Psi\rangle = E\,|\,\Psi\rangle$$

$$|\,\Psi\rangle \equiv |\,\Psi(\mathbf{C})\rangle = \sum_{\xi \geq 0}^{\text{all conf.}} C_\xi\,|\,\det_\xi\rangle$$

$$|\,n_1 n_2 \ldots n_{L-1} n_L\rangle$$

“Configuration”

Full Configuration Interaction (FCI) method

$$\hat{H}|\Psi\rangle = E|\Psi\rangle$$

$$|\Psi\rangle \equiv |\Psi(\mathbf{C})\rangle = \sum_{\xi \geq 0} C_\xi |\det_\xi\rangle$$

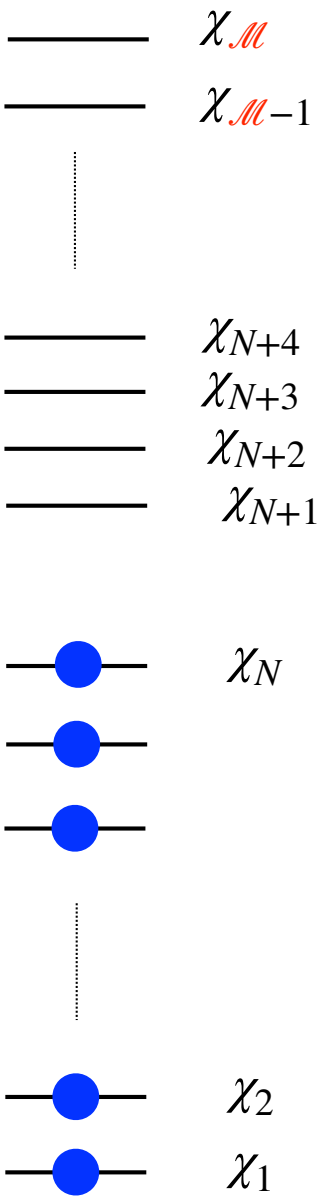
$$H_{\xi\xi'} = \langle \det_\xi | \hat{H} | \det_{\xi'} \rangle$$

$$\begin{bmatrix} H_{00} & H_{01} & \cdots & H_{0\xi'} & \cdots \\ H_{10} & \cdots & & & \\ \vdots & & & & \\ H_{\xi 0} & \cdots & & H_{\xi\xi'} & \cdots \\ \vdots & & & & \end{bmatrix} \begin{bmatrix} C_0 \\ C_1 \\ \vdots \\ C_\xi \\ \vdots \end{bmatrix} = E \begin{bmatrix} C_0 \\ C_1 \\ \vdots \\ C_\xi \\ \vdots \end{bmatrix}$$

Hamiltonian matrix diagonalization problem

How many Slater determinants in total

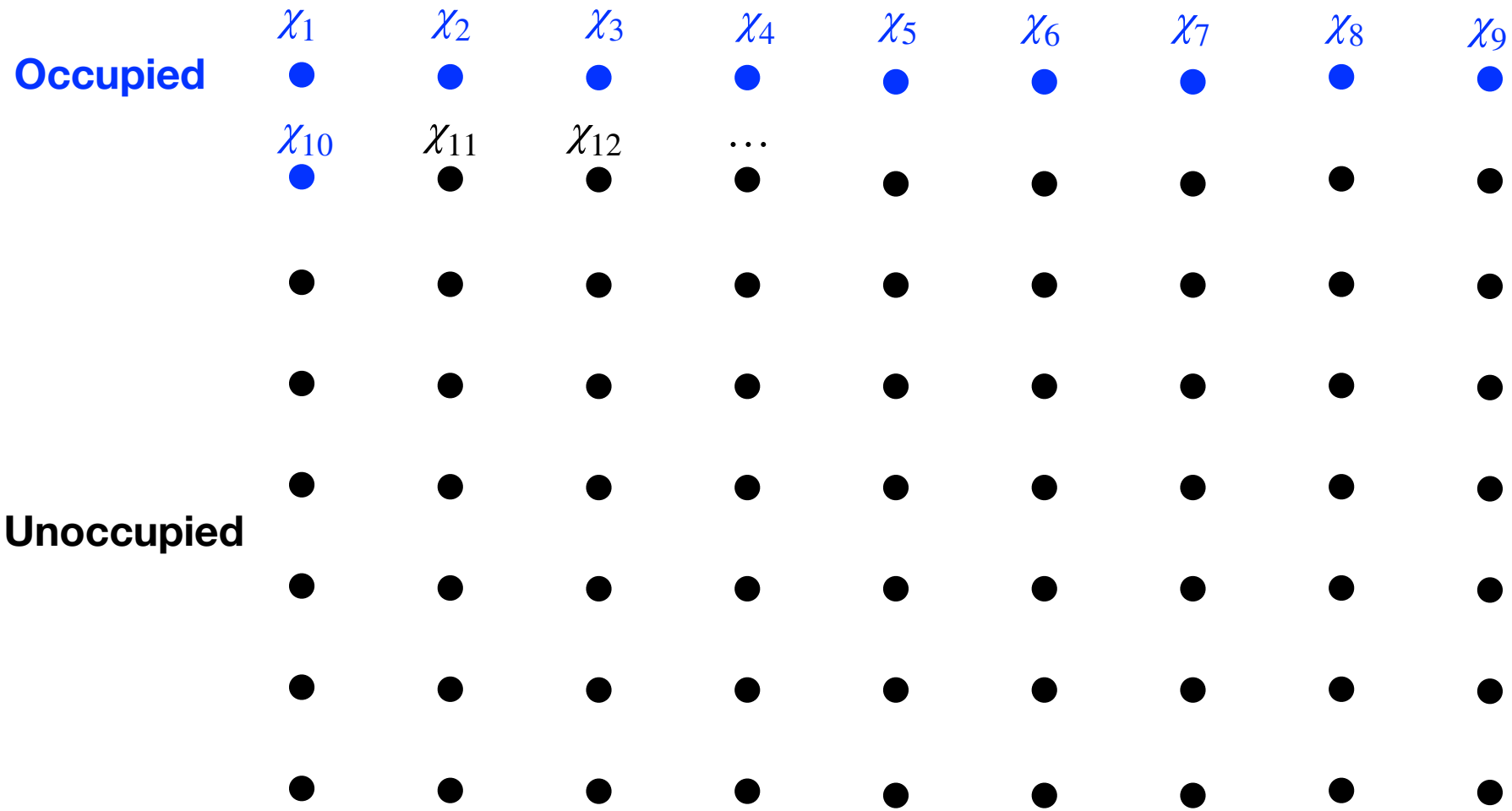
for a full CI (FCI) calculation?



Reference configuration

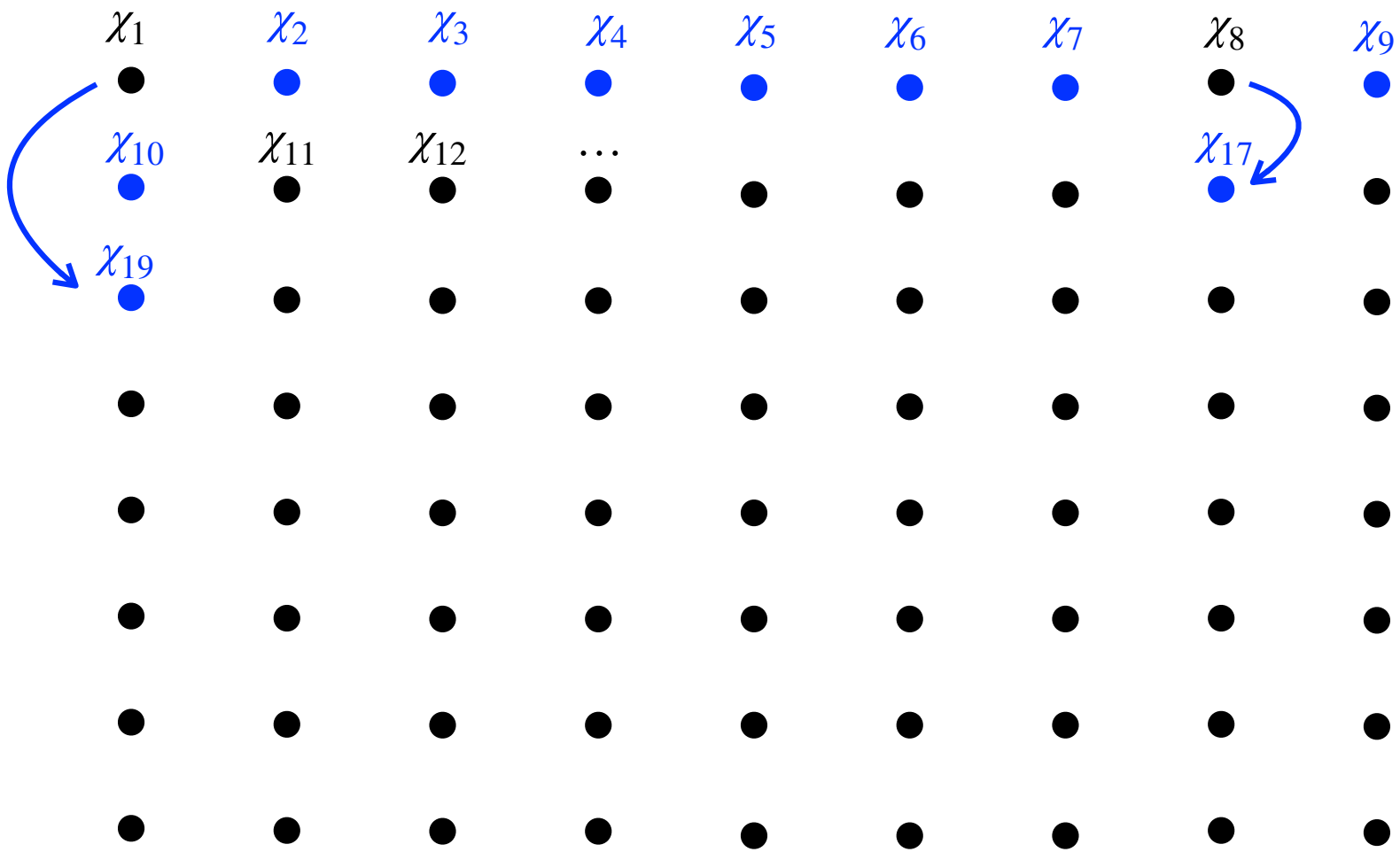
We have $\mathscr{M}$ (spin-) orbitals available for N electrons

Example of reference Slater determinant for 10 electrons



Schematic representation of a molecule or a solid

Example of (double) excitation to (previously) unoccupied orbitals



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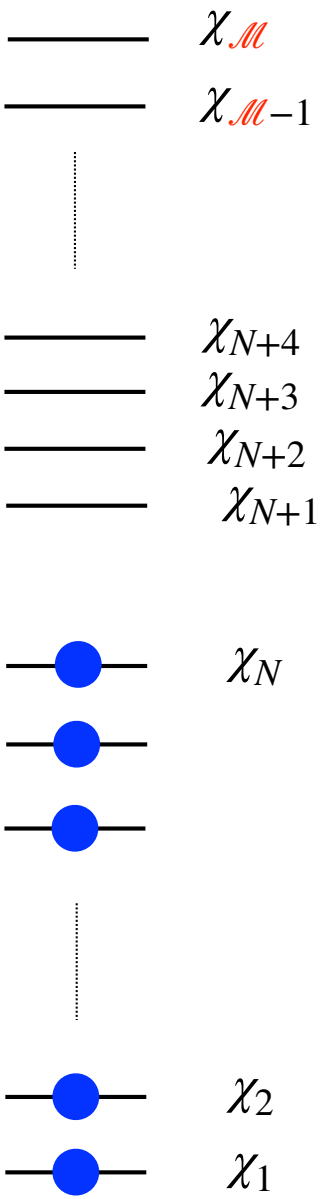
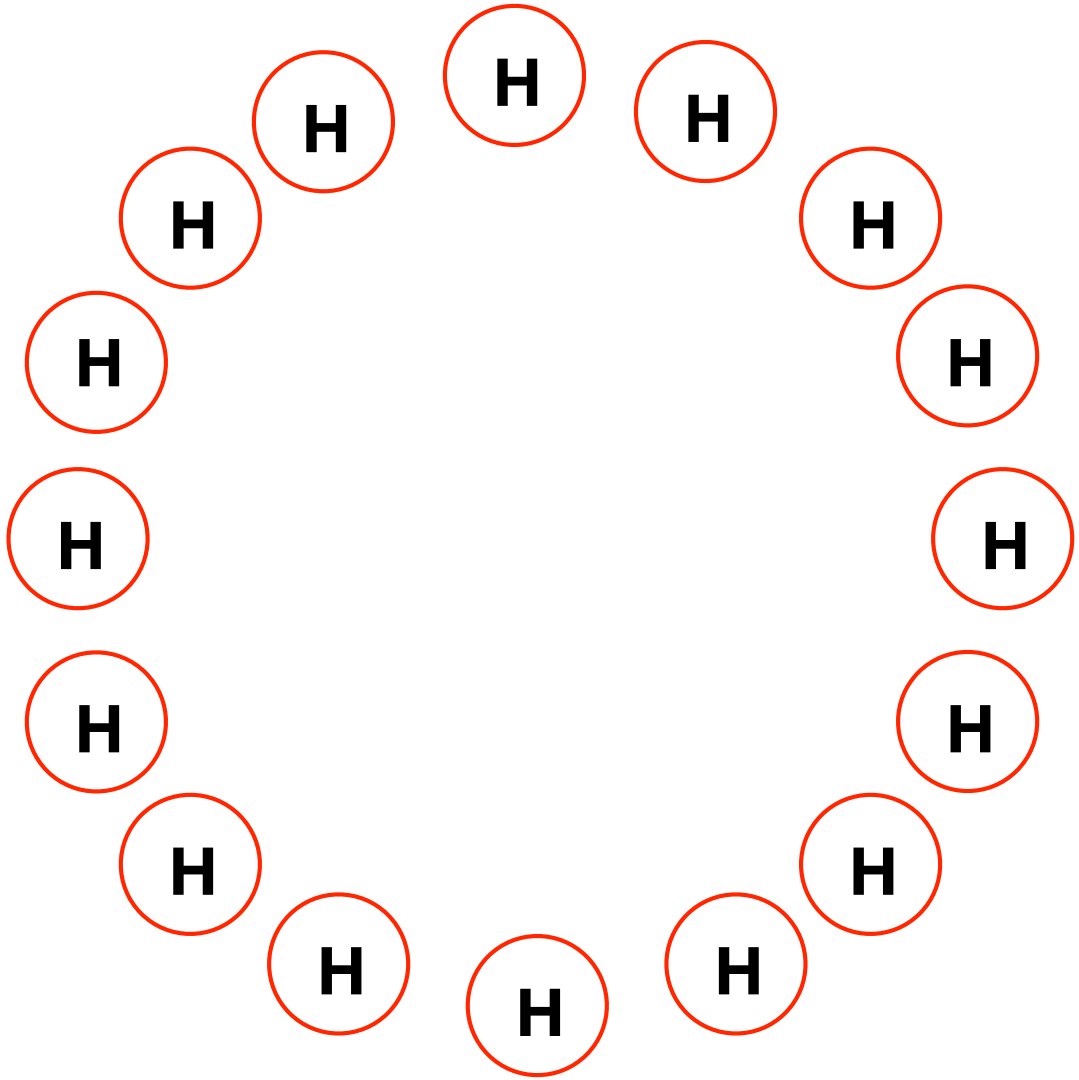


Reference configuration

We have $\mathscr{M}$ (spin-) orbitals available for N electrons

$$N_{\text{det.}} = \binom{\mathscr{M}}{N} = \frac{\mathscr{M}!}{N!(\mathscr{M}-N)!}$$

How many Slater determinants in total?



Ring of hydrogen atoms

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

Spin

How many Slater determinants in total?

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

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

How many Slater determinants in total?

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

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

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

Stirling formula for large N values

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

How many Slater determinants in total?

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

"Exponential wall"

How many Slater determinants in total?

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

How many Slater determinants in total?

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

A naive (important though) understanding of the "quantum advantage"

$$|\Psi_{\mathrm{FCI}}\rangle = \sum_{\xi} C_{\xi} |\det_{\xi}\rangle$$

- **Classical** encoding of all Slater determinants: $N_{\mathrm{det.}} \approx \dfrac{e^{2N \ln 2}}{\sqrt{\pi N}} \overset{N=50}{\approx} 10^{29}$

- The FCI wavefunction can in principle be encoded (in this example) with $\mathscr{M} = 2N$ **qubits**.

Exponential quantum advantage!

Quantum embedding approach to electron correlation

The non-interacting electronic problem is much easier to solve…

… and it can be used as a starting point for treating electron correlation locally!

From the interacting to the noninteracting electronic problem

$$\hat{H} = \sum_{pq} \langle \chi_p | \hat{h} | \chi_q \rangle \hat{a}_p^\dagger \hat{a}_q + \frac{1}{2} \sum_{pqrs} \langle \chi_p \chi_q | \hat{w}_{\mathrm{ee}} | \chi_r \chi_s \rangle \hat{a}_p^\dagger \hat{a}_q^\dagger \hat{a}_s \hat{a}_r$$

$$\hat{H}^{\mathrm{KS}} = \sum_{p \neq q} \langle \chi_p | \hat{h} | \chi_q \rangle \hat{a}_p^\dagger \hat{a}_q + \sum_{p} v_p^{\mathrm{KS}} \hat{a}_p^\dagger \hat{a}_p$$

"**Kohn-Sham** (KS) Hamiltonian"

W. Makhlouf, B. Senjean, and E. Fromager, *J. Chem. Theory Comput. 2025, 21, 20, 10293–10314,* Preprint: **arXiv:2507.19591**

Noninteracting electronic problem

$$\hat{H}^{\mathrm{KS}} \equiv \sum_{pq} h_{pq}^{\mathrm{KS}} \, \hat{a}_p^\dagger \hat{a}_q$$

Noninteracting electronic problem

$$\hat{H}^{\mathrm{KS}} \equiv \sum_{pq} h_{pq}^{\mathrm{KS}}\, \hat{a}_p^\dagger \hat{a}_q$$

$$h^{\mathrm{KS}} = u\ \mathrm{diag}\left\{\varepsilon_k^{\mathrm{KS}}\right\} u^\dagger$$

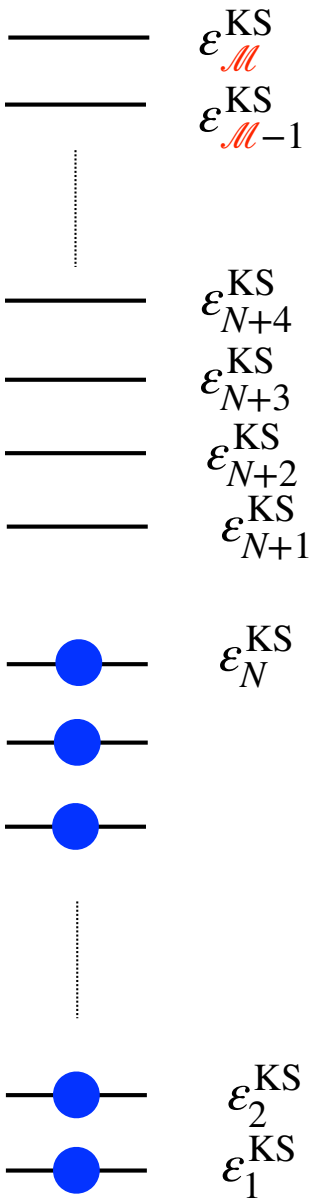
Diagonalization of h^{KS}:

$$h_{pq}^{\mathrm{KS}} = \sum_k u_{pk} u_{qk}^*\, \varepsilon_k^{\mathrm{KS}}$$

$$\hat{H}^{\mathrm{KS}} = \sum_k \varepsilon_k^{\mathrm{KS}} \underbrace{\left(\sum_p u_{pk} \hat{a}_p^\dagger \right)}_{\equiv\, \hat{a}_k^\dagger} \underbrace{\left(\sum_q u_{qk}^* \hat{a}_q \right)}_{\equiv\, \hat{a}_k}$$

W. Makhlouf, B. Senjean, and E. Fromager, *J. Chem. Theory Comput. 2025, 21, 20, 10293–10314,* Preprint: **arXiv:2507.19591**

"Molecular orbital energy diagram"



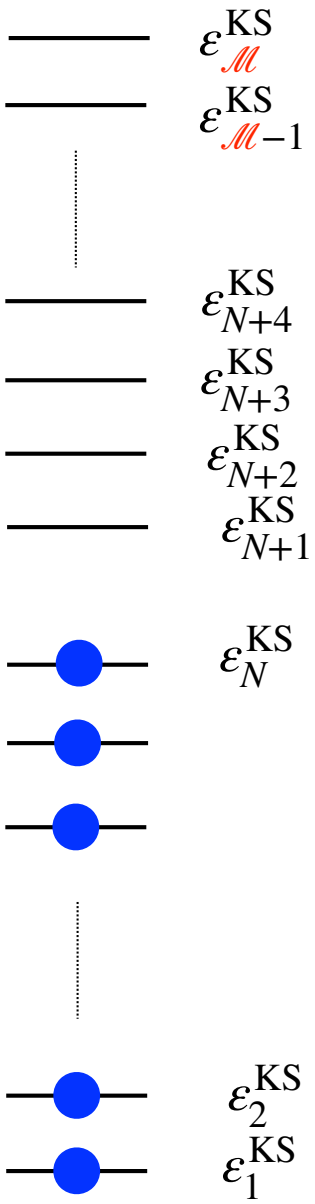
Ground-state molecular configuration

Noninteracting electronic problem

$$\hat{H}^{\mathrm{KS}} = \sum_{k} \varepsilon_k^{\mathrm{KS}} \, \hat{a}_k^{\dagger} \hat{a}_k$$

Unlike in the original lattice representation,
in this "molecular" representation,
an electron occupying the orbital k **remains on that orbital**

Noninteracting electronic problem



"Molecular orbital energy diagram"

$$\hat{H}^{\mathrm{KS}} = \sum_k \varepsilon_k^{\mathrm{KS}} \hat{a}_k^\dagger \hat{a}_k$$

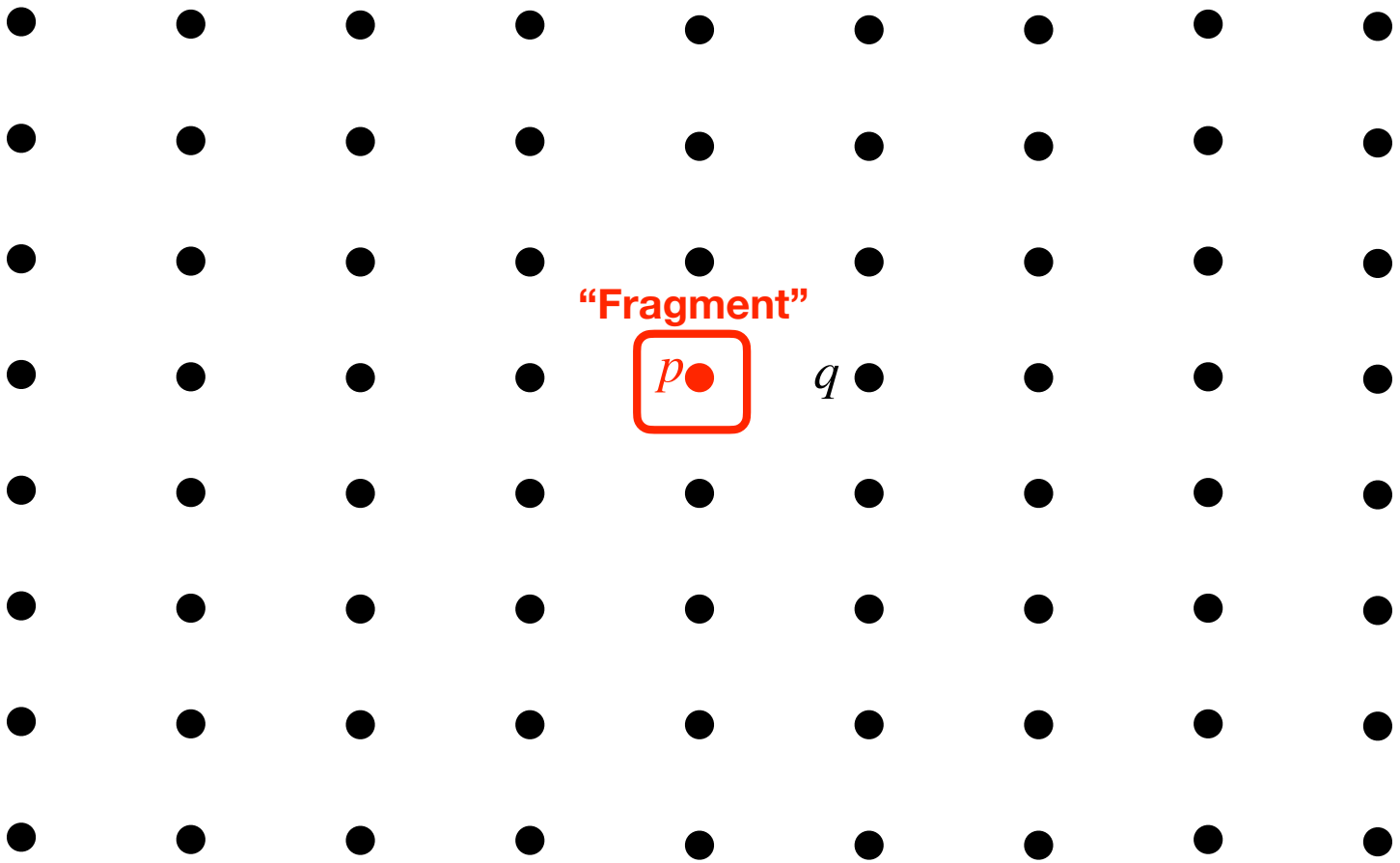
Unlike in the original lattice representation,
in this "molecular" representation,
an electron occupying the orbital k **remains on that orbital**

$$\hat{a}_k^\dagger \equiv \sum_p^{\text{lattice}} u_{pk} \hat{a}_p^\dagger$$

Molecular orbitals are
delocalized over the entire molecule

Calculation of local properties

Original "lattice" representation

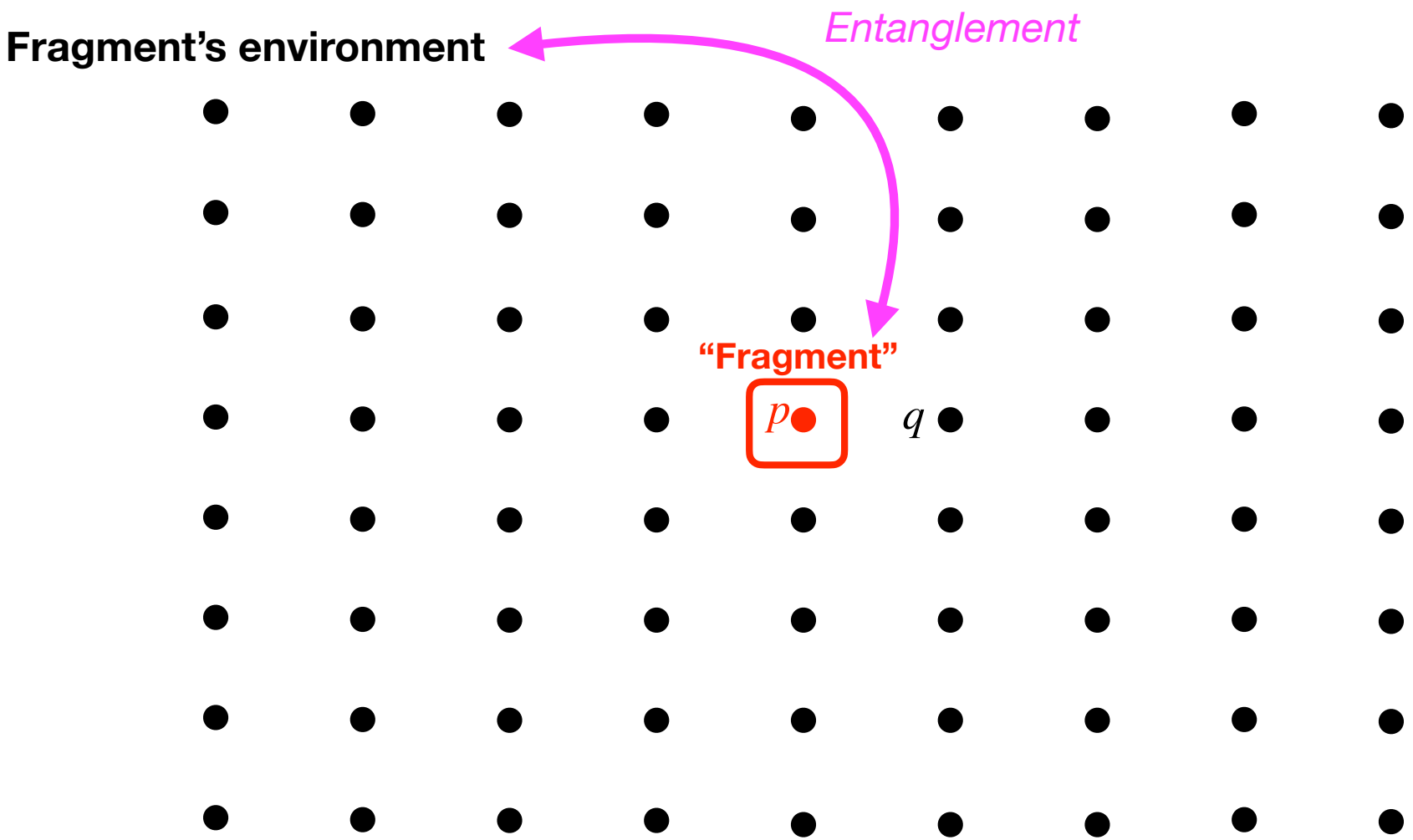


G. Knizia and G. K.-L. Chan, Phys. Rev. Lett. ***109****, 186404 (2012).*
S. Wouters, C. A. Jiménez-Hoyos, Q. Sun, and G. K.-L. Chan, J. Chem. Theory Comput. 12, 2706 (2016).

Calculation of local properties

Original "lattice" representation

$$\hat{H} = \sum_{pq}^{\text{lattice}} \langle \chi_p | \hat{h} | \chi_q \rangle \, \hat{a}_p^\dagger \hat{a}_q + \frac{1}{2} \sum_{pqrs}^{\text{lattice}} \langle \chi_p \chi_q | \hat{w}_{\text{ee}} | \chi_r \chi_s \rangle \, \hat{a}_p^\dagger \hat{a}_q^\dagger \hat{a}_s \hat{a}_r$$



G. Knizia and G. K.-L. Chan, Phys. Rev. Lett. ***109****, 186404 (2012).*
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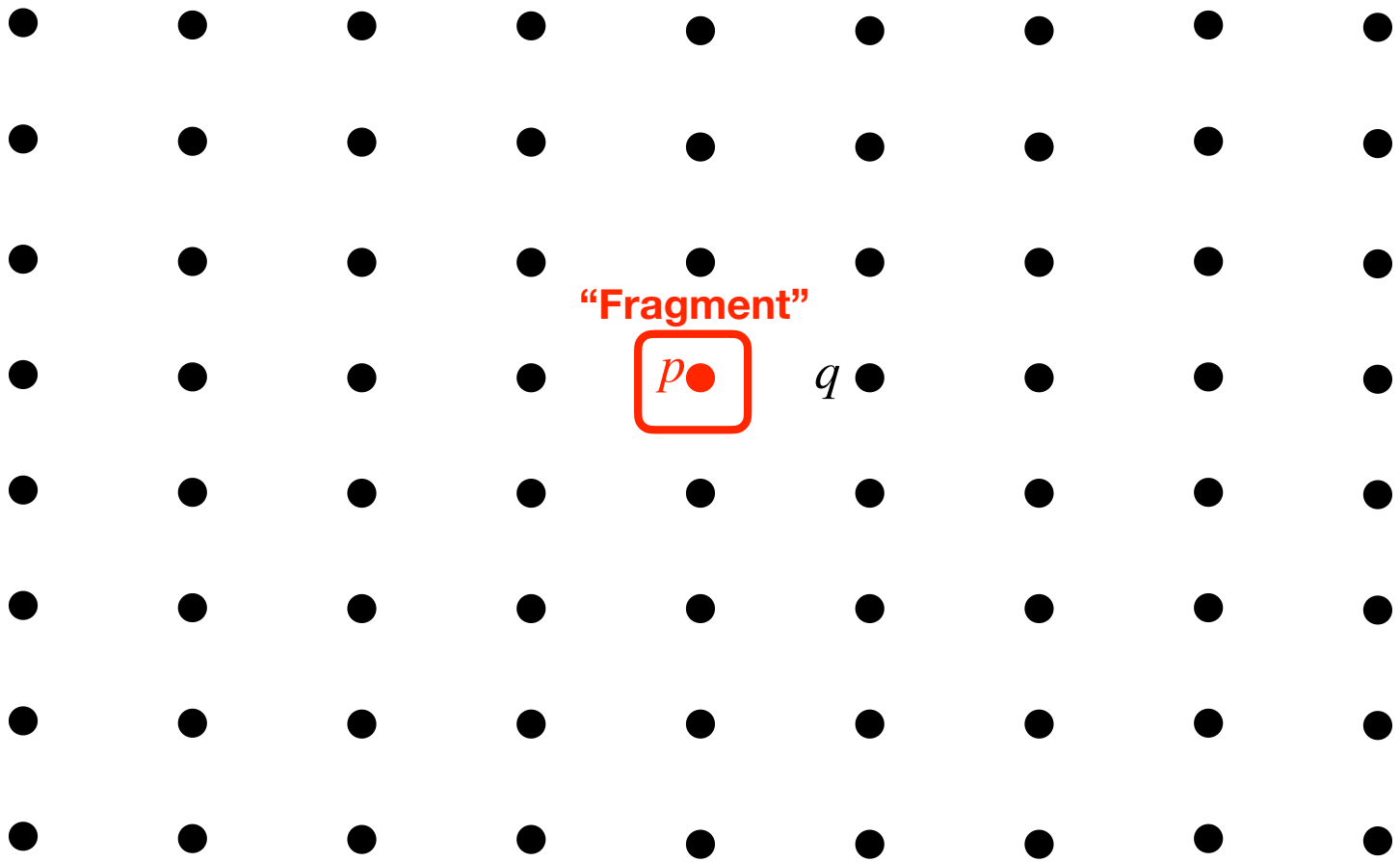
Quantum embedding of the *(single-orbital here)* ***fragment***

Original "lattice" representation



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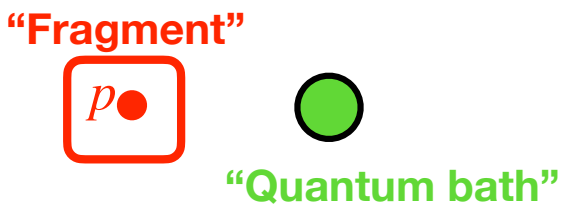

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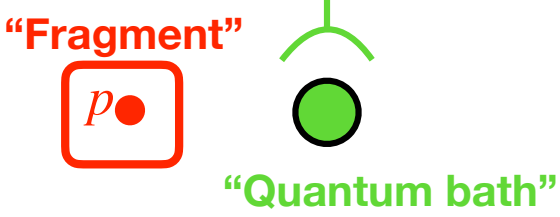
S. Wouters, C. A. Jiménez-Hoyos, Q. Sun, and G. K.-L. Chan, J. Chem. Theory Comput. 12, 2706 (2016).

Quantum embedding of the *(single-orbital here)* ***fragment***

$$\chi_q(\mathbf{r}) \rightarrow \varphi^{\text{bath}}(\mathbf{r}) = \sum_{q \neq p}^{\text{lattice}} \sum_{k=1,\ldots,N}^{\text{occupied}} \langle \varphi_k^{\text{KS}} | \chi_q \rangle \langle \chi_p | \varphi_k^{\text{KS}} \rangle \, \chi_q(\mathbf{r})$$



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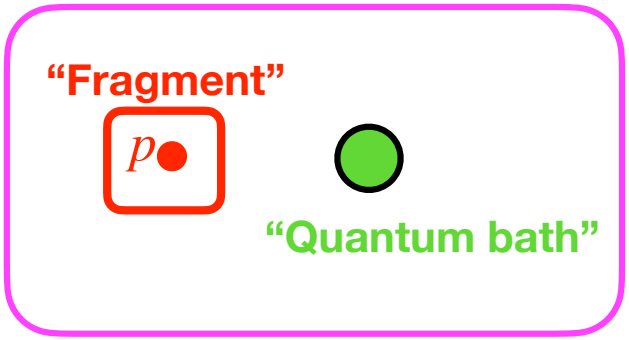
Quantum embedding of the *(single-orbital here)* ***fragment***

Two-electron embedding "cluster"…



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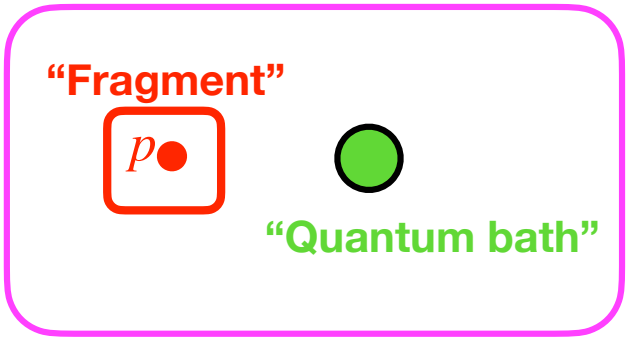
Quantum embedding of the *(single-orbital here)* ***fragment***

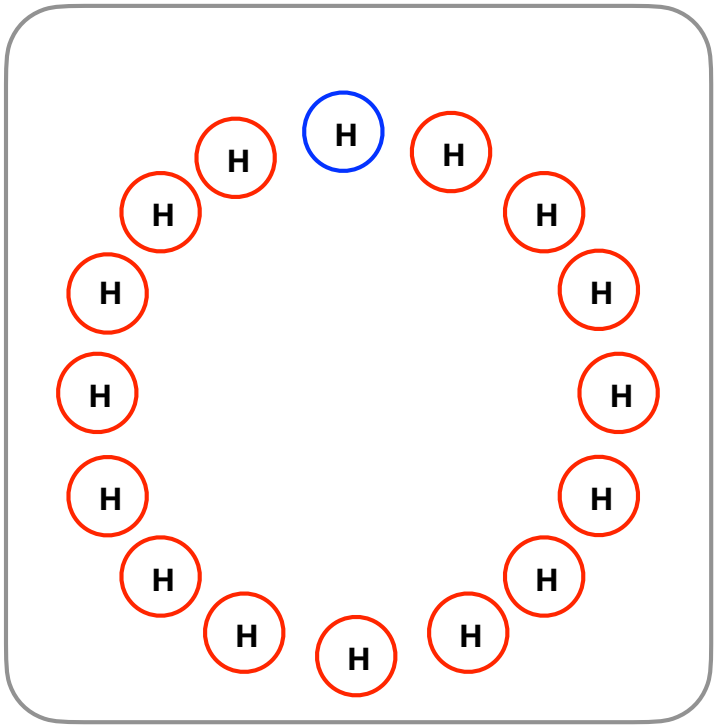
Two-electron
embedding "cluster"…



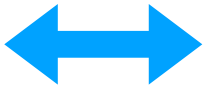
… for which the Schrödinger equation
can be **solved exactly!**

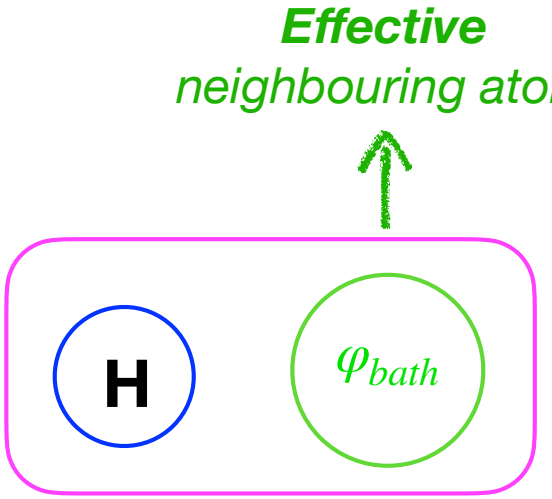
G. Knizia and G. K.-L. Chan, Phys. Rev. Lett. ***109****, 186404 (2012).*
S. Wouters, C. A. Jiménez-Hoyos, Q. Sun, and G. K.-L. Chan, J. Chem. Theory Comput. 12, 2706 (2016).

Rings of hydrogen atoms (Hubbard model)



N-electron system





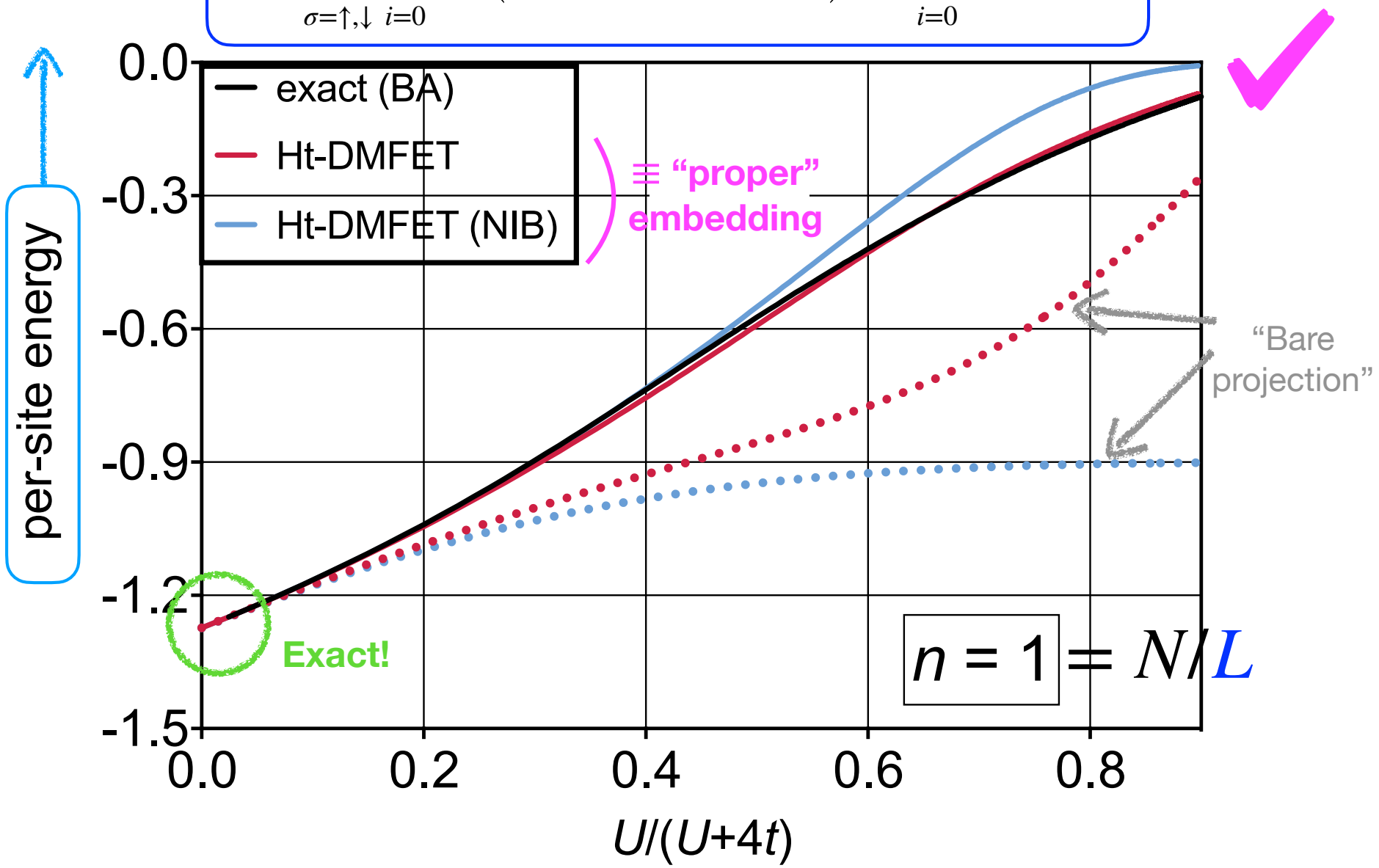
Two-electron system

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

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.

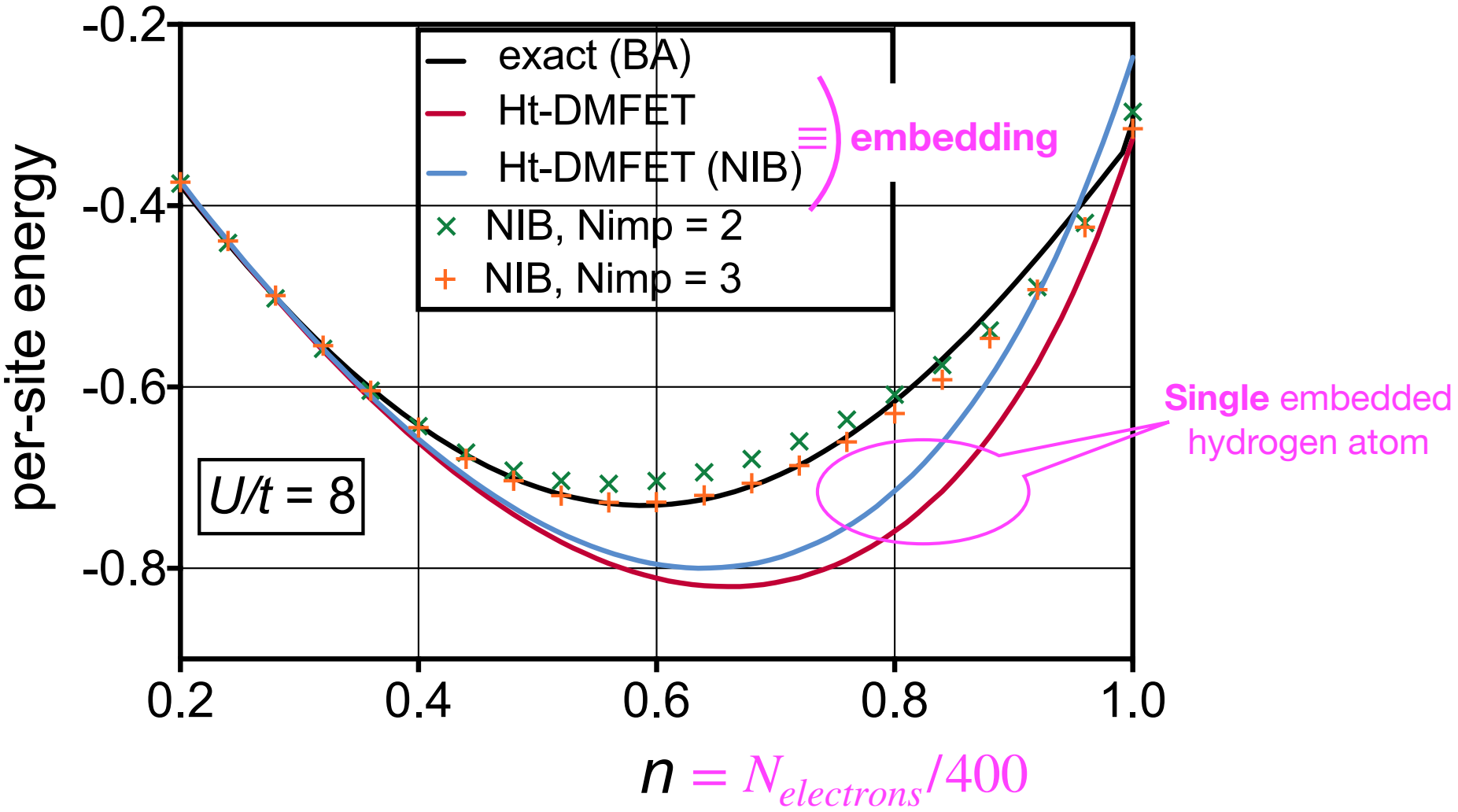
Half-filled uniform Hubbard ring with $L = 400$ atomic sites

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



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

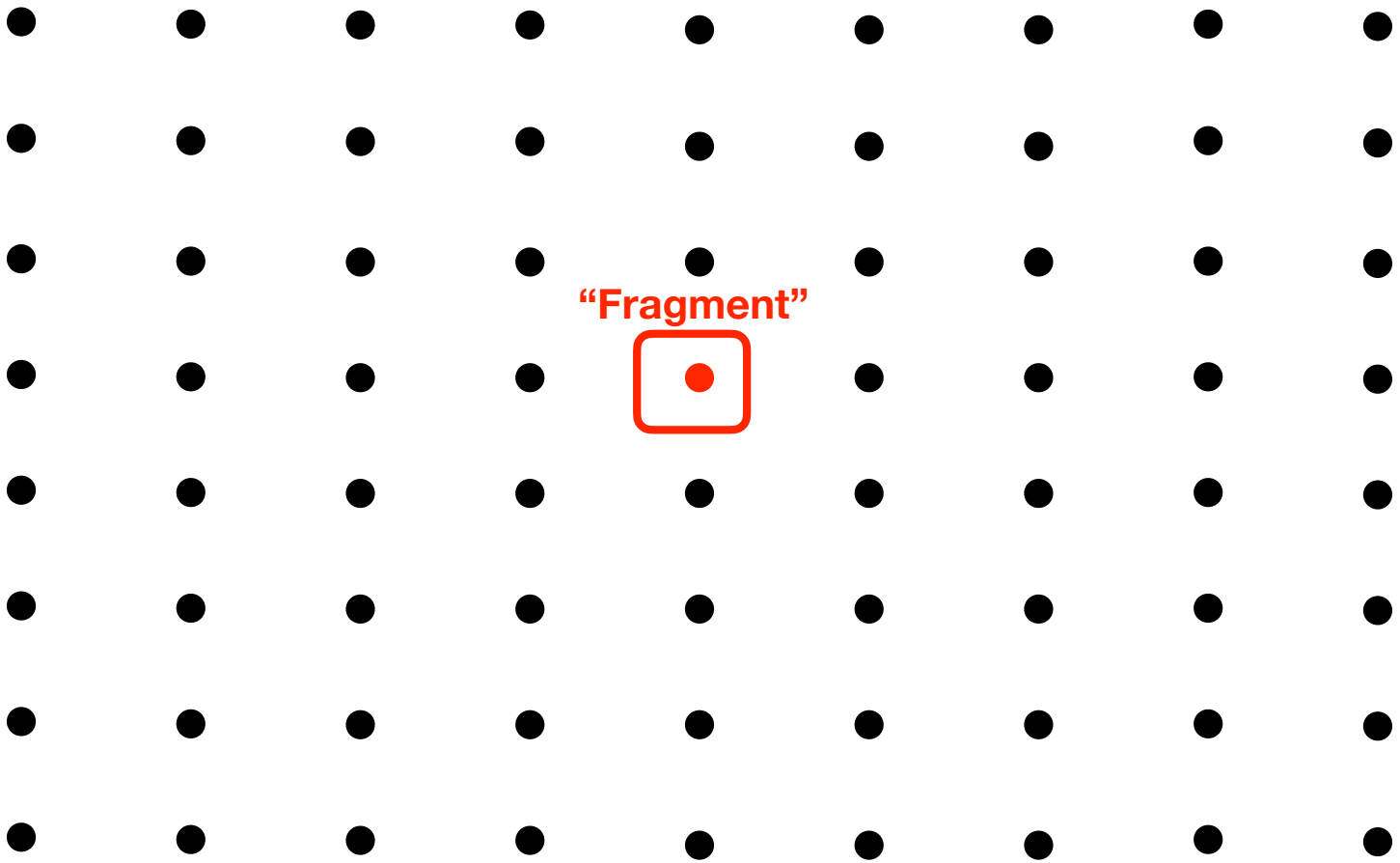
(Hubbard) model of a stretched 400-atom hydrogen ring



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

Single-orbital fragment

Original "lattice" representation



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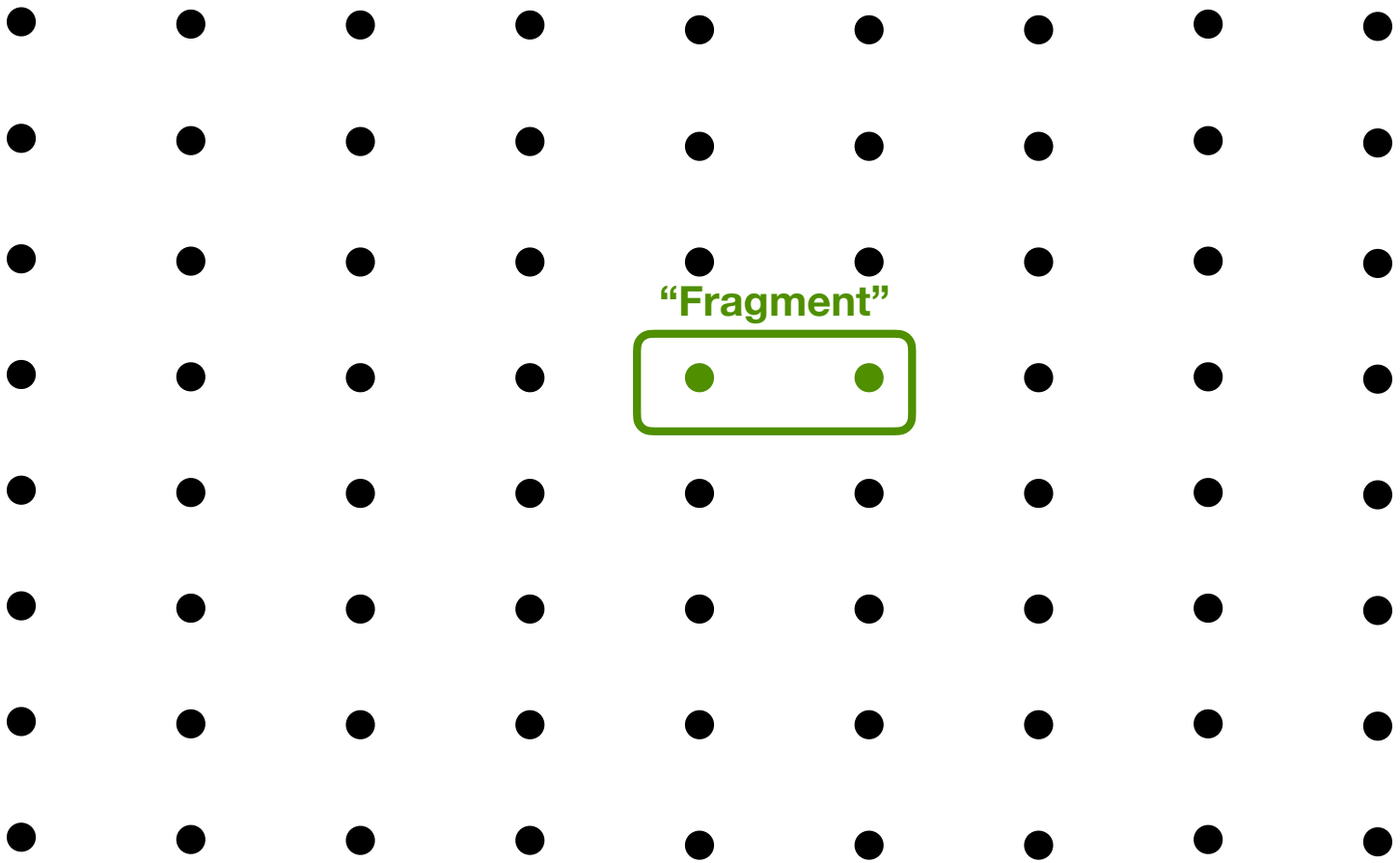
S. Wouters, C. A. Jiménez-Hoyos, Q. Sun, and G. K.-L. Chan, J. Chem. Theory Comput. 12, 2706 (2016).

Two-orbital fragment

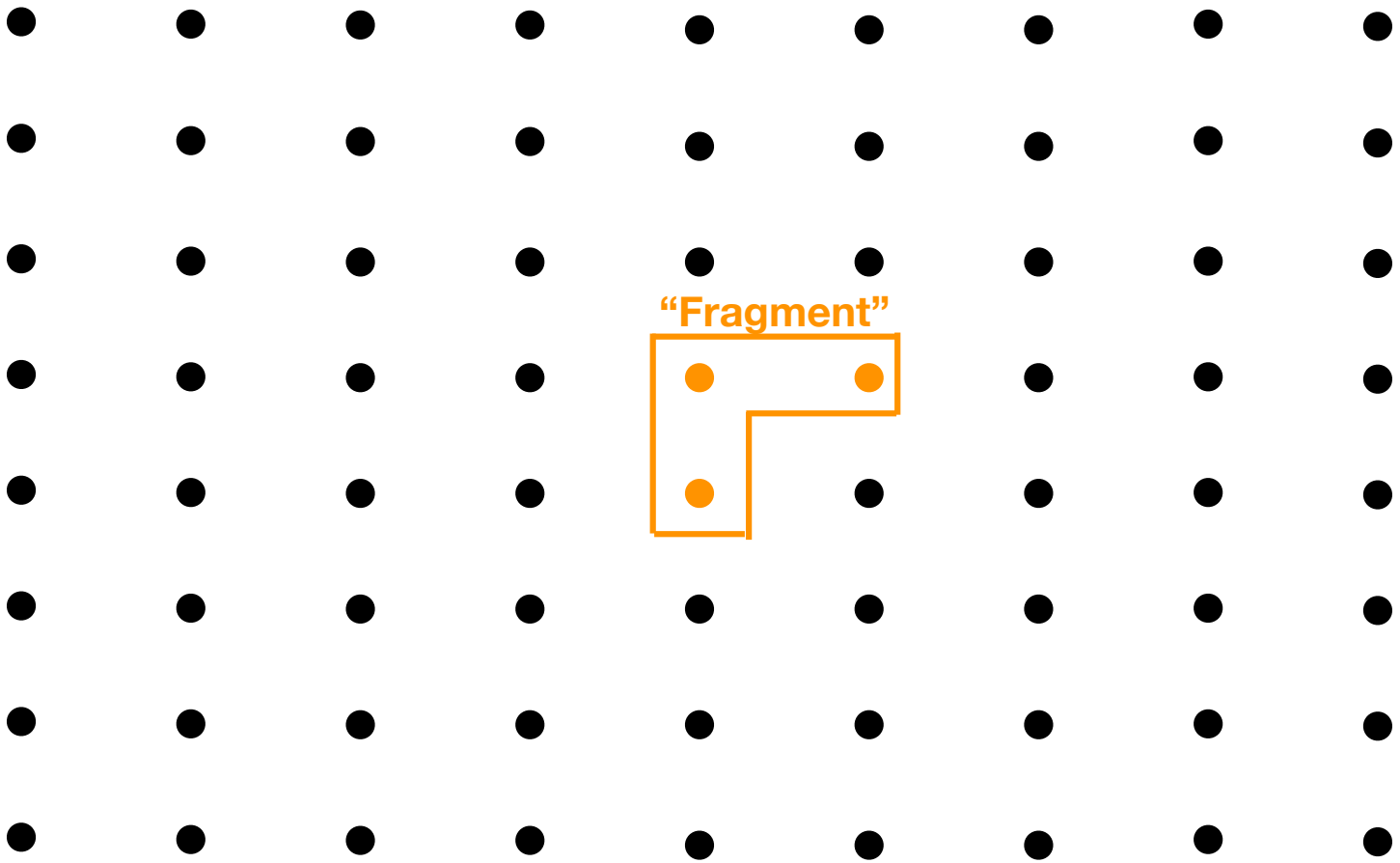
Original "lattice" representation



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).

Three-orbital fragment

Original "lattice" representation



G. Knizia and G. K.-L. Chan, Phys. Rev. Lett. ***109****, 186404 (2012).*
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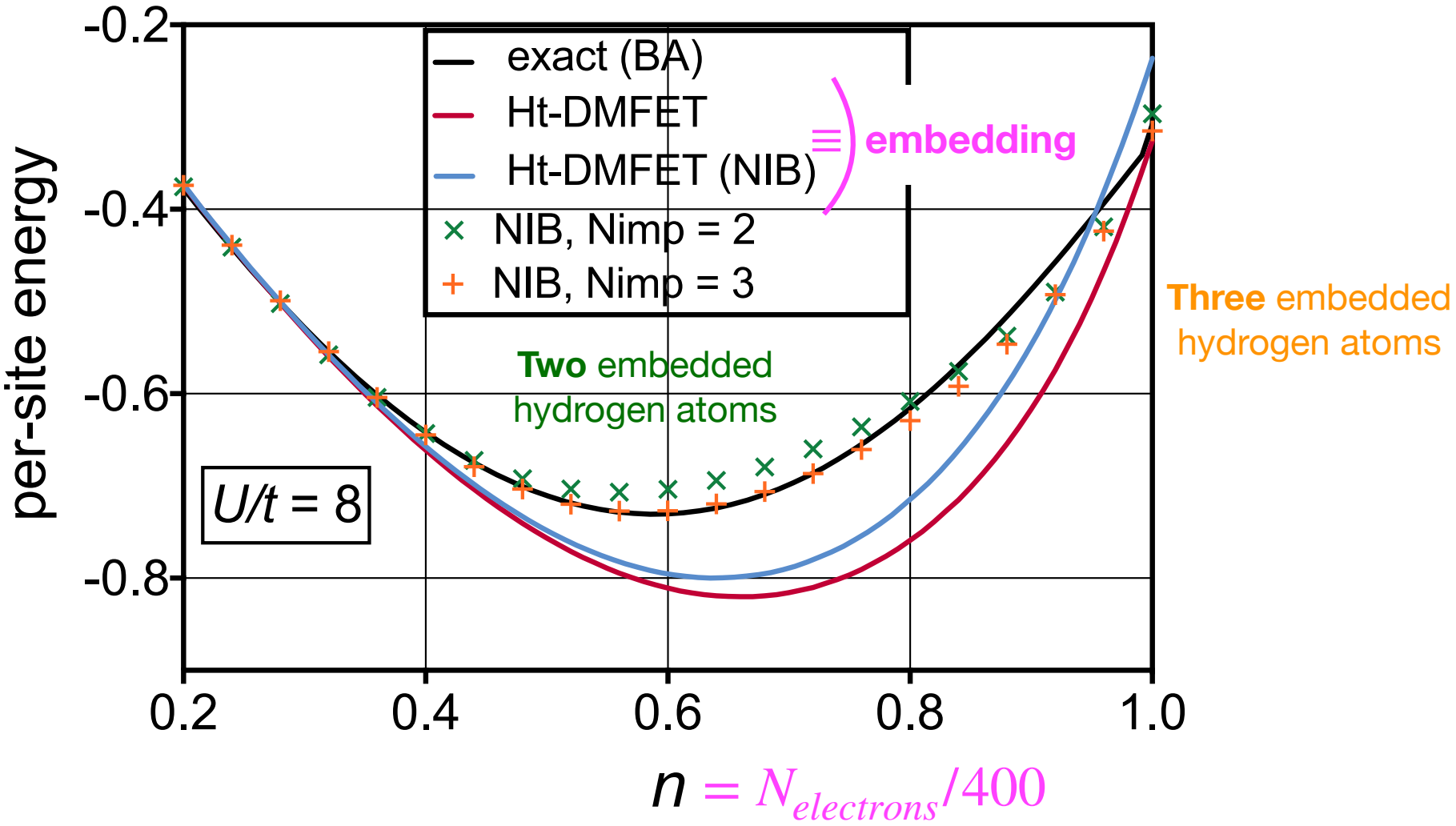
(Hubbard) model of a stretched 400-atom hydrogen ring



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

Thanks for your kind attention!

JCTC Journal of Chemical Theory and Computation

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Local Potential Functional Embedding Theory of Molecular Systems: Localized Orbital-Based Embedding from an Exact Density-Functional Perspective

Wafa Makhlouf,* Bruno Senjean, and Emmanuel Fromager

Cite This: *J. Chem. Theory Comput.* 2025, 21, 10293−10314 Read Online

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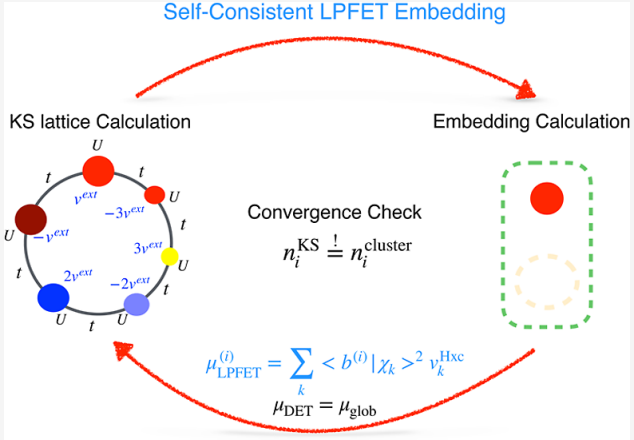
ABSTRACT: Localized orbital-based quantum embedding, as originally formulated in the context of density matrix embedding theory (DMET), is revisited from the perspective of lattice density functional theory (DFT). An in-principle exact (in the sense of full configuration interaction) formulation of the theory, where the occupations of the localized orbitals play the role of the density, is derived for any (model or ab initio) electronic Hamiltonian. From this general formalism we deduce an exact relation between the local Hartree-exchange-correlation (Hxc) potential of the full-size Kohn−Sham (KS) lattice-like system and the embedding chemical potential that is adjusted on each embedded fragment, individually, such that both KS and embedding cluster systems reproduce the exact same local density. When well-identified density-functional approximations (that find their justification in the strongly correlated regime) are applied, a practical self-consistent local potential functional embedding theory (LPFET), where the local Hxc potential becomes the basic variable, naturally emerges from the theory. LPFET differs from previous density embedding approaches by its fragment-dependent embedding chemical potential expression, which is a simple functional of the Hxc potential. Numerical calculations on prototypical systems show the ability of such an ansatz to improve substantially the description of density profiles (localized orbitals occupation numbers in this context) in strongly correlated systems.



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Effective Reconstruction of Expectation Values from Ab Initio Quantum Embedding

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

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

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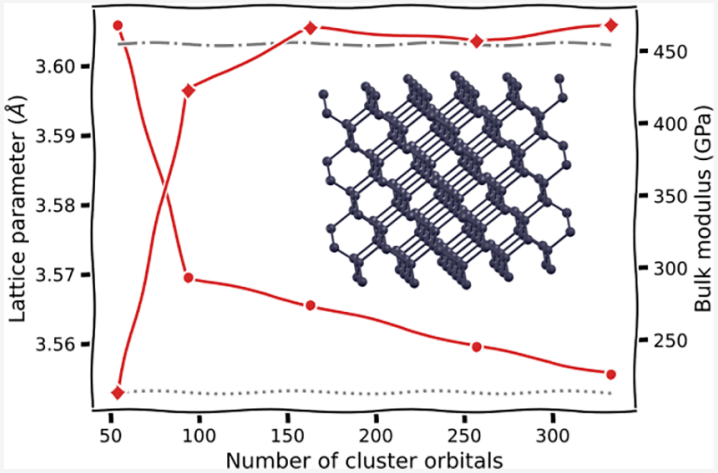
ABSTRACT: Quantum embedding is an appealing route to fragment a large interacting quantum system into several smaller auxiliary "cluster" problems to exploit the locality of the correlated physics. In this work, we critically review approaches to recombine these fragmented solutions in order to compute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

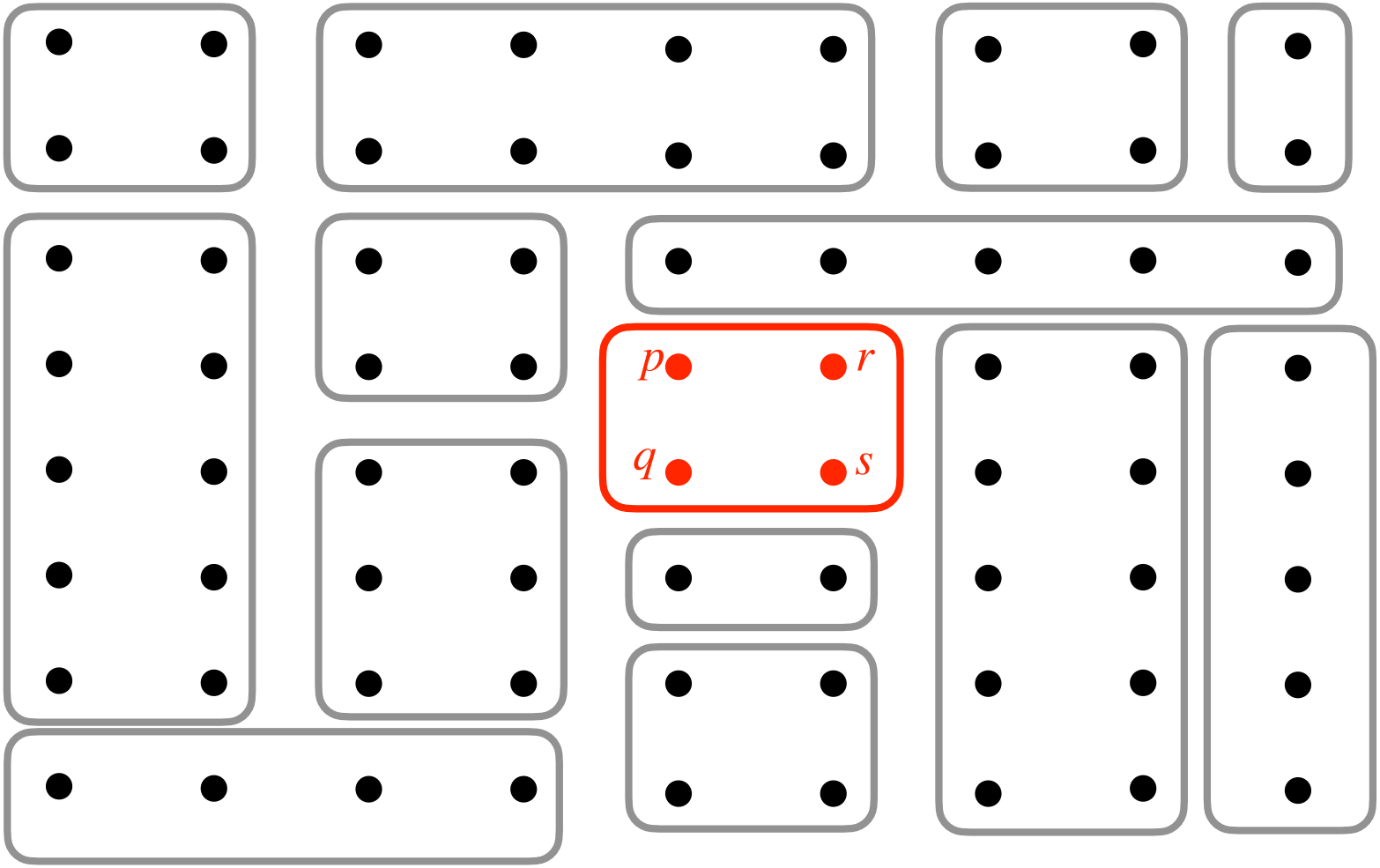


Local evaluation of the energy (in a localised spin-orbital basis)

So-called "lattice representation"

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

Fragmentation



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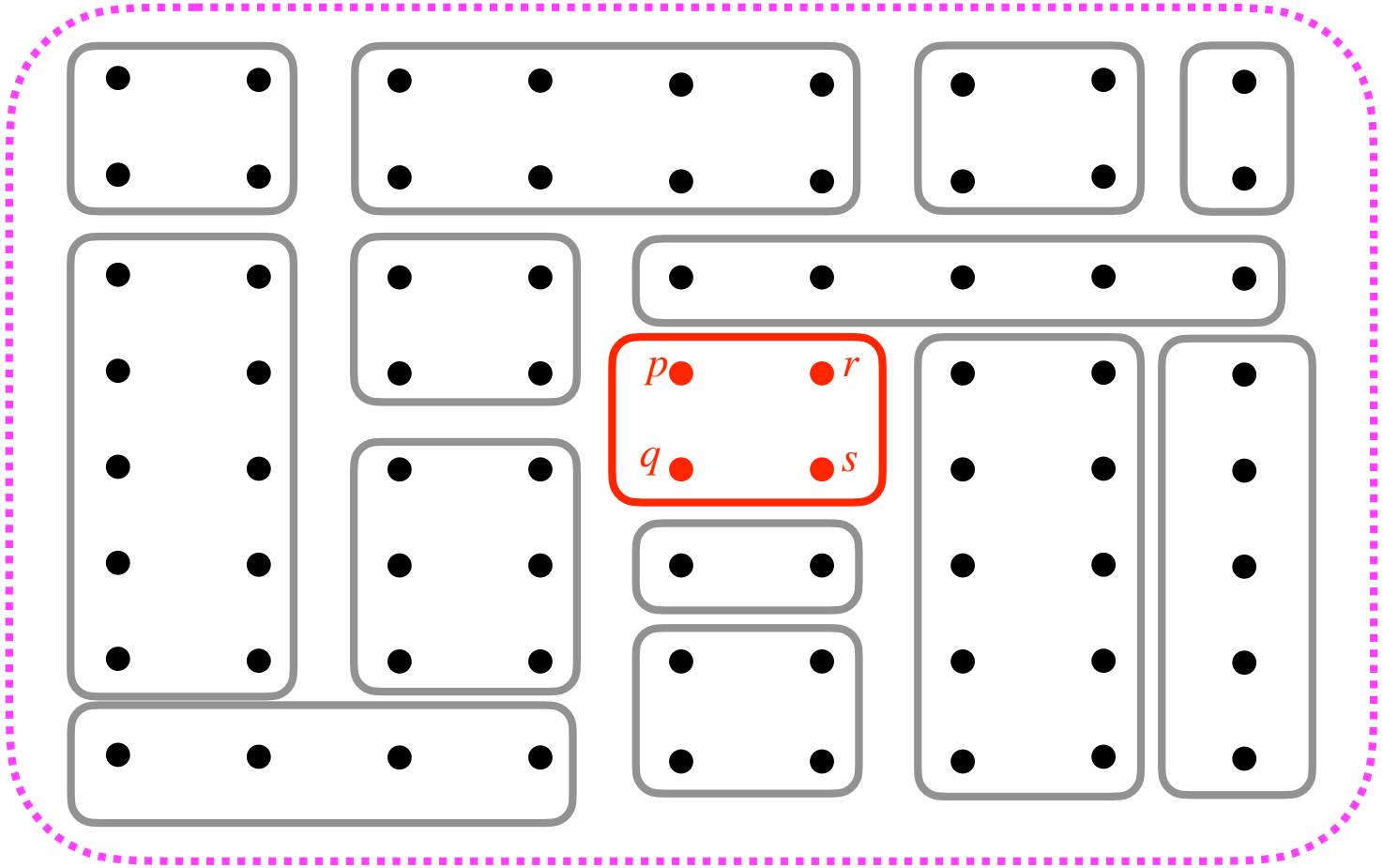
S. Wouters, C. A. Jiménez-Hoyos, Q. Sun, and G. K.-L. Chan, J. Chem. Theory Comput. 12, 2706 (2016).

N-representability problem

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

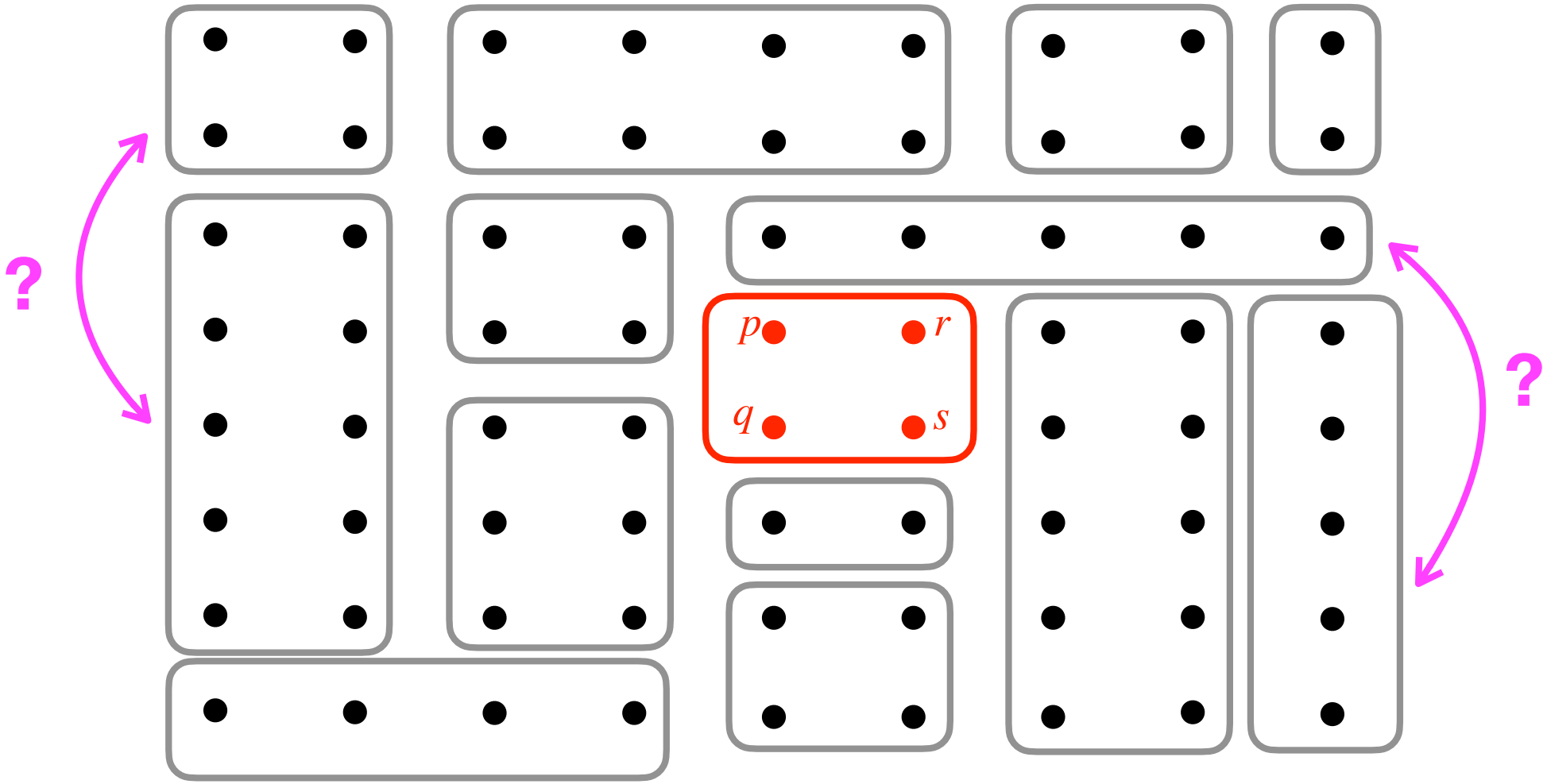
$$\langle \hat{c}_p^\dagger \hat{c}_q^\dagger \hat{c}_r \hat{c}_s \rangle_{clusters} \stackrel{?}{=} \langle \Psi | \hat{c}_p^\dagger \hat{c}_q^\dagger \hat{c}_r \hat{c}_s | \Psi \rangle$$



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

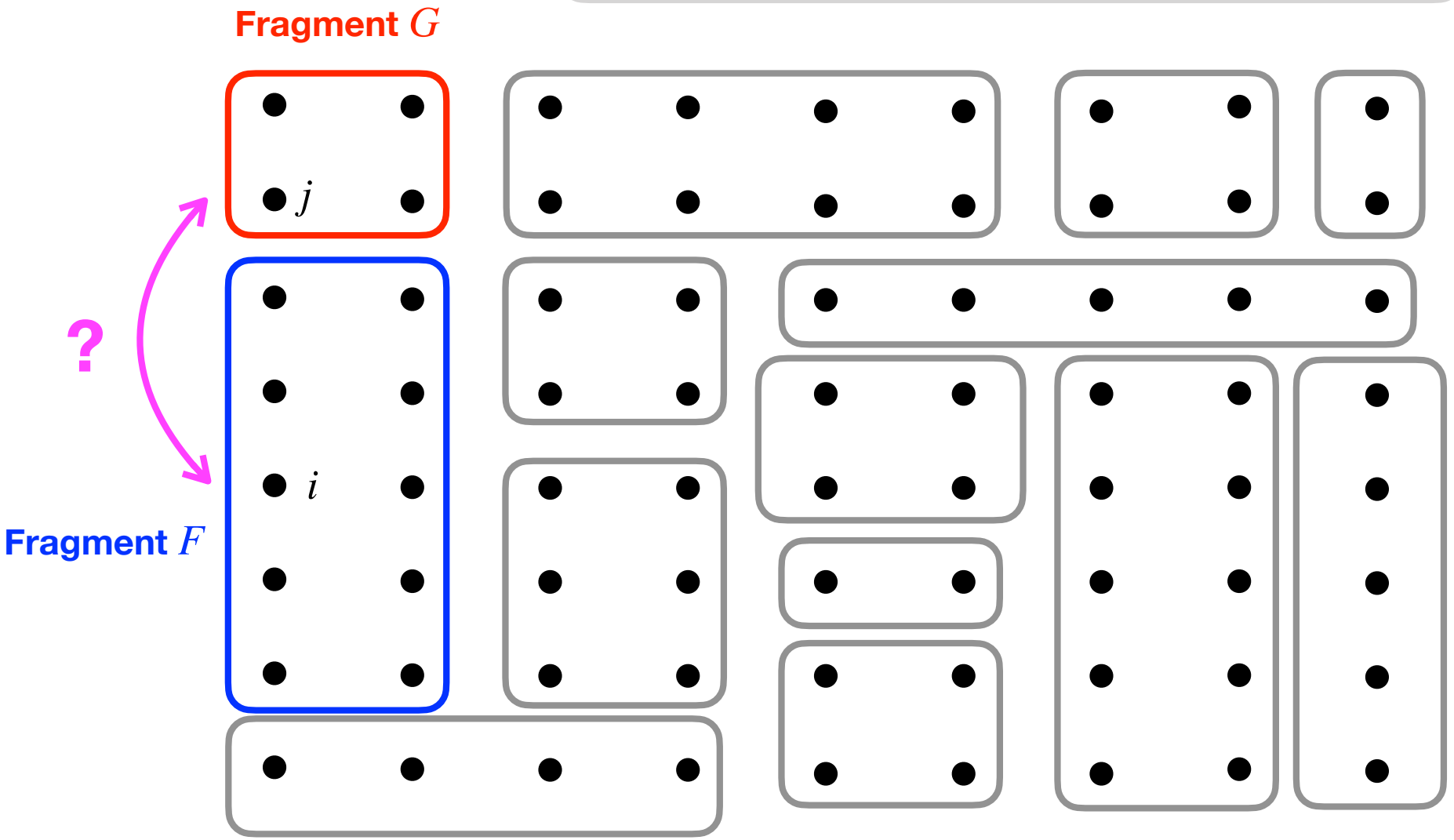
One-electron density matrix (1RDM)

Two-electron density matrix (2RDM)



"Democratic" evaluation of RDMs from embedding clusters

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



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