

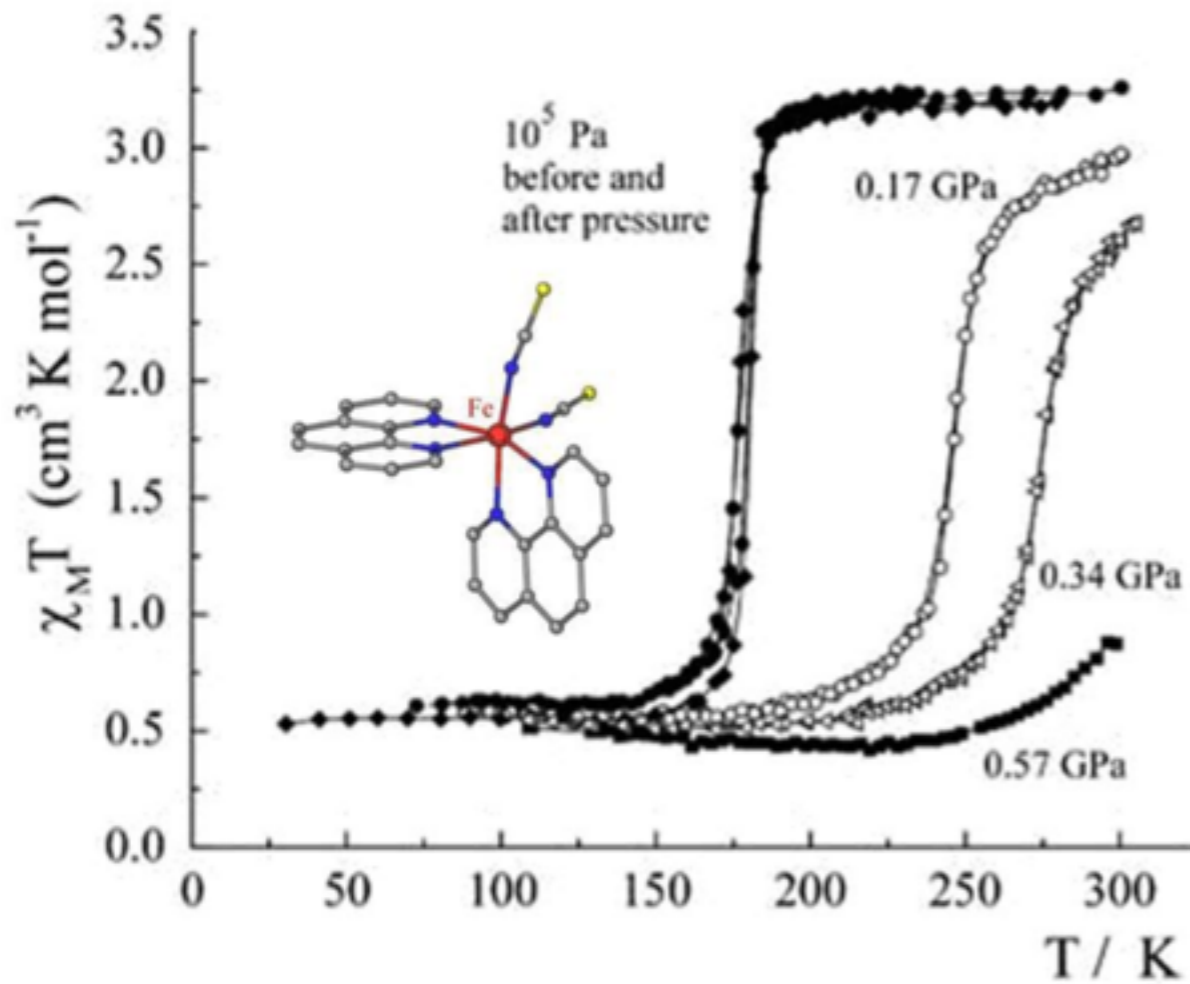
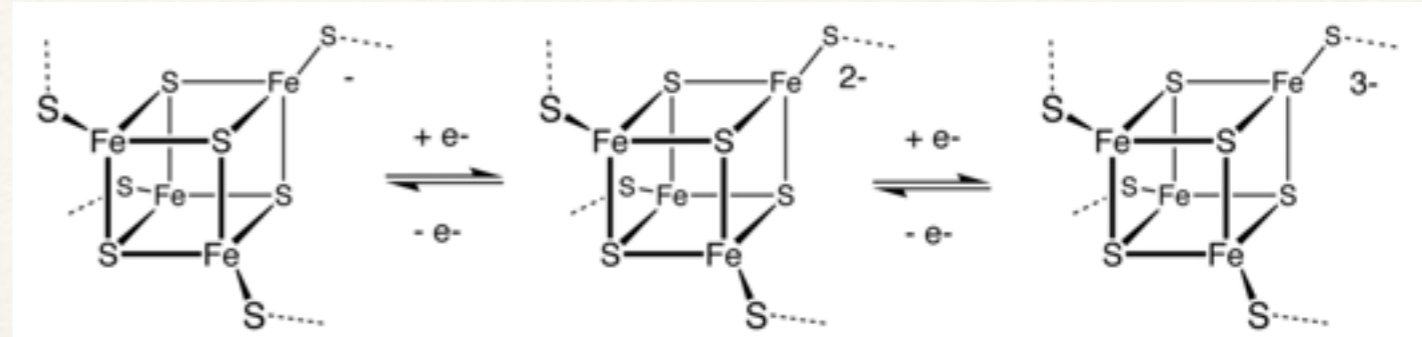
# Ab-initio Green's function Embedding methods

Dominika Zgid

T. N. Lan, A. A. Rusakov,

A. A. Kananenka, A. Welden, B. Winograd

# Chemically relevant problems

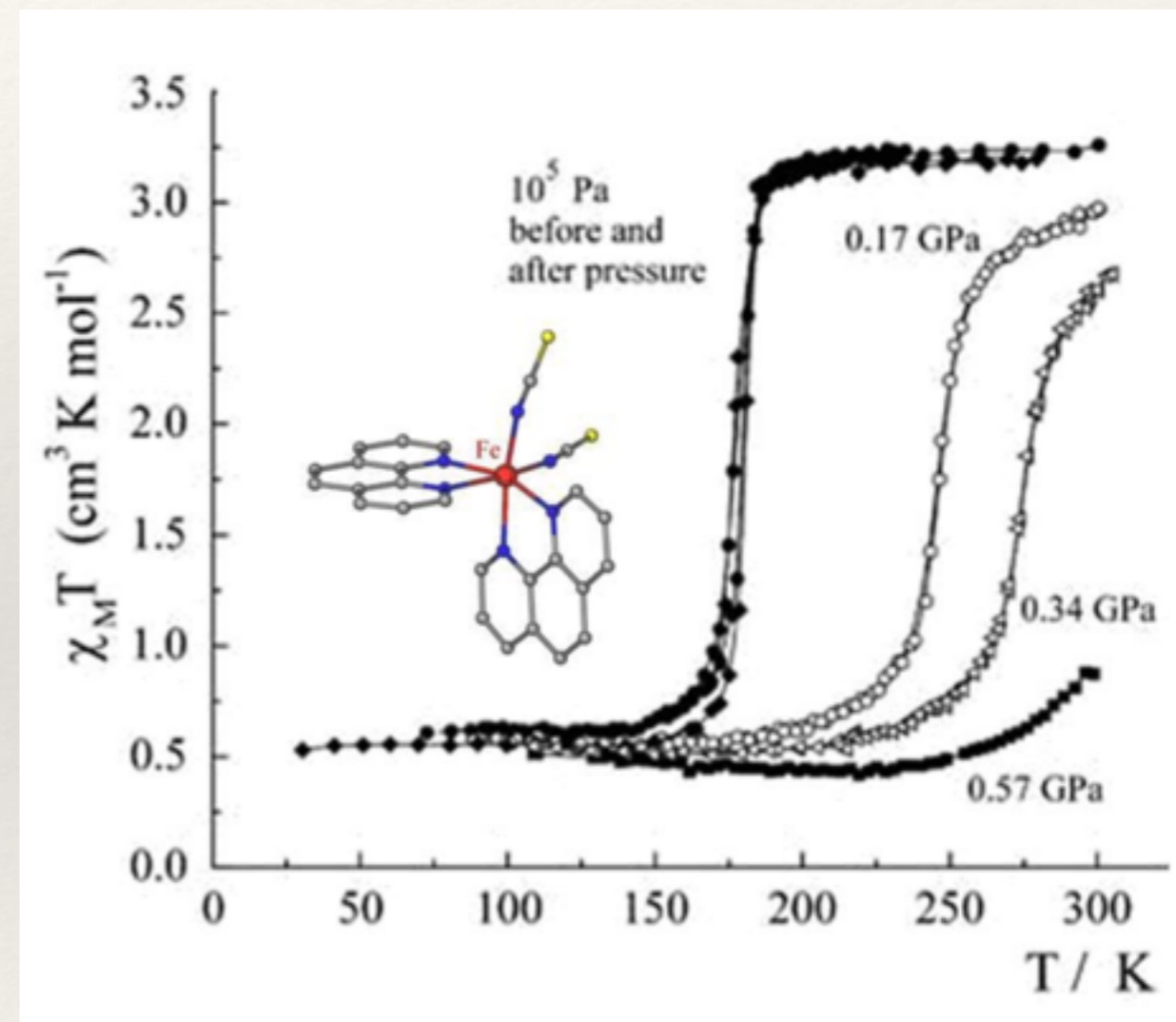
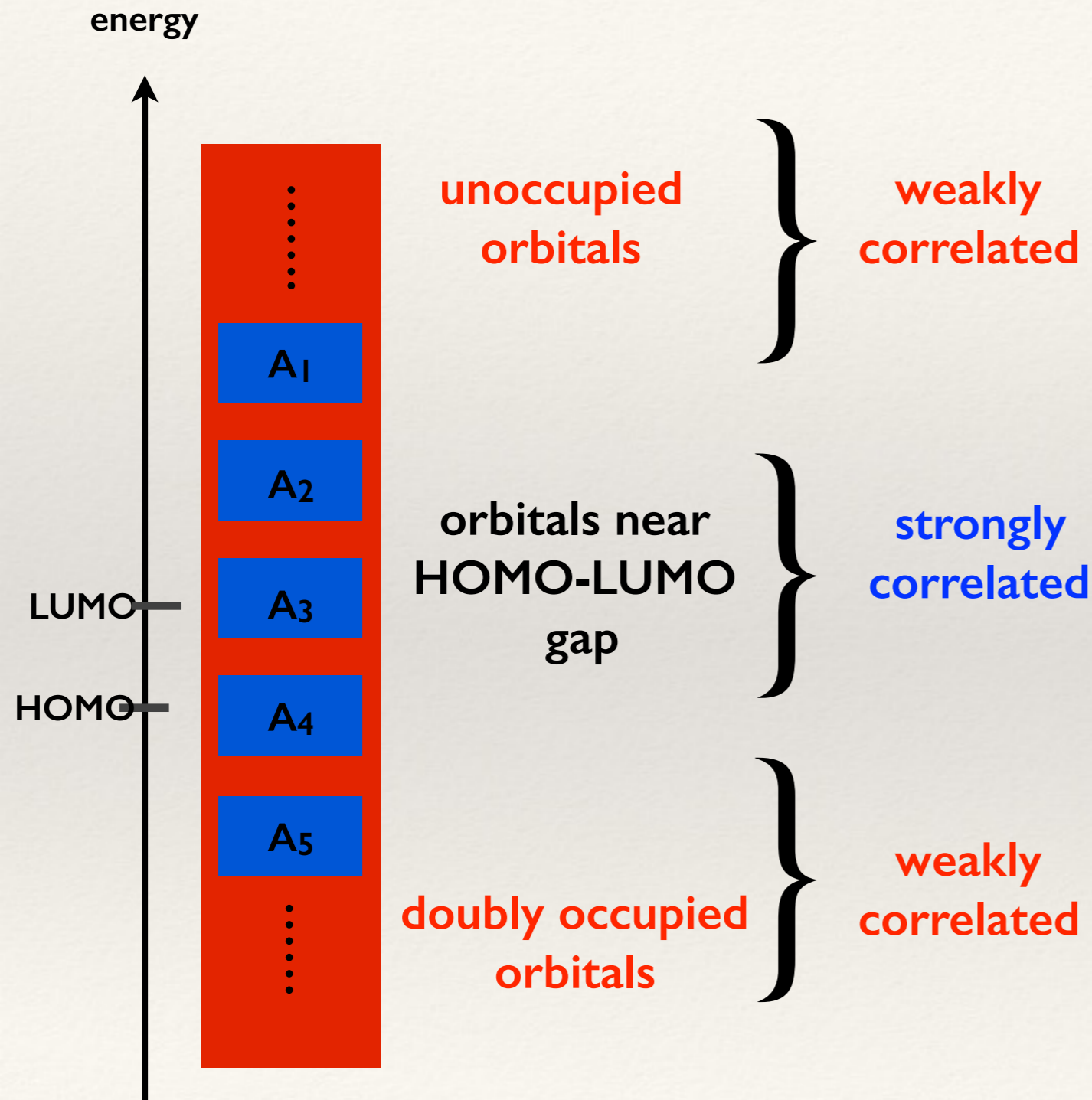


spin crossover molecules

active centers of proteins

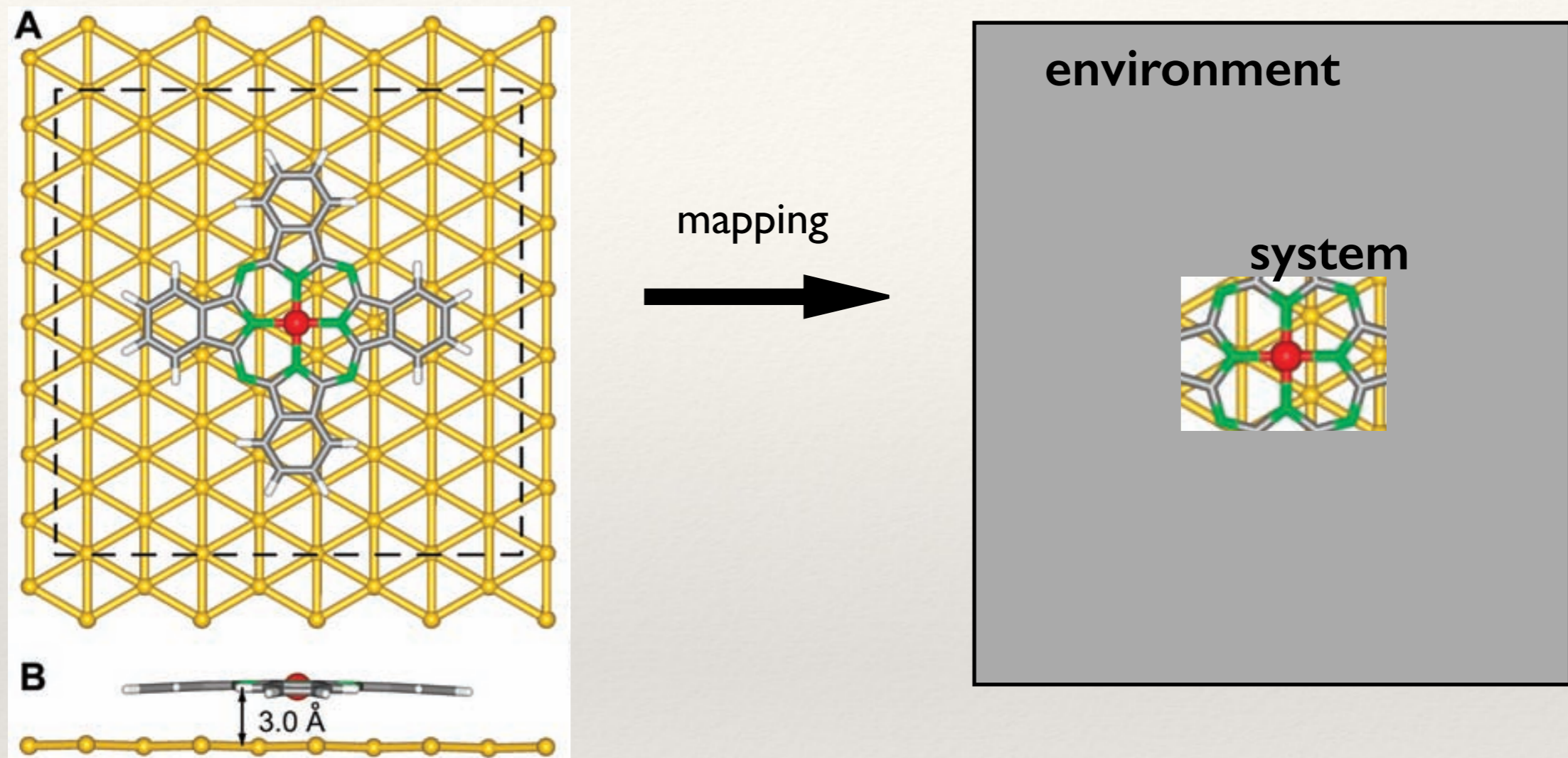
# Strongly correlated orbitals

How do we define a strongly correlated orbital?





# Can we describe it simply?

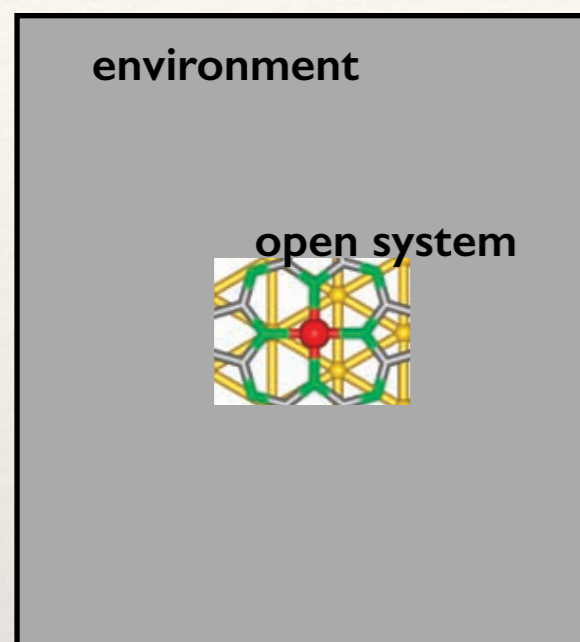


This procedure is called **embedding**

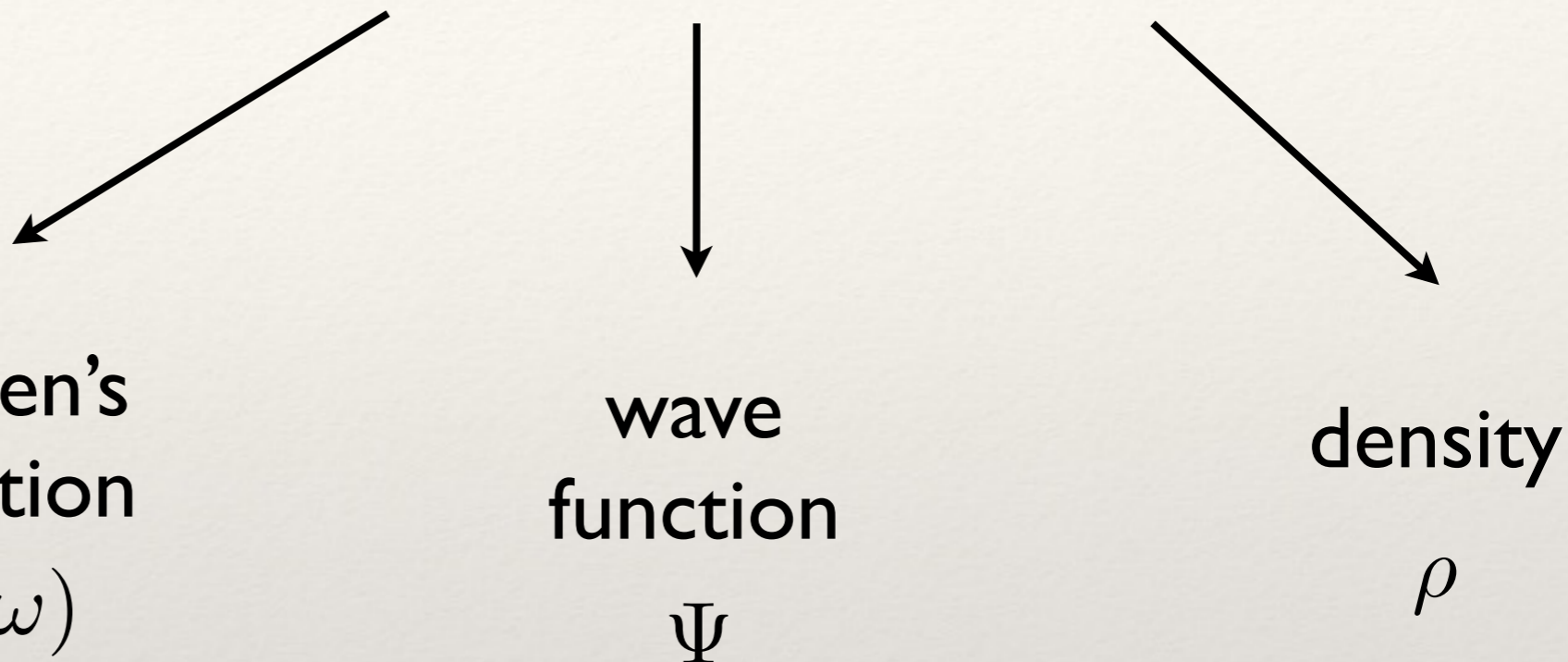
How to describe system and environment?



# Different types of QM/QM embedding approaches



object used in embedding



**spectroscopic quantities**

**thermodynamic quantities**

DMFT

SEET

**ground state quantities**

DMET

DFT embedding

# Building well defined approximations

How to find good approximate self-energies?

For Green's function we have a universal functional

**Luttinger-Ward functional (finite temperature)**

$$\Omega(G) = \frac{1}{\beta} \left\{ \Phi_{LW} - \text{Tr}[\Sigma G + \ln(\Sigma - G_0^{-1})] \right\}$$

grand potential

$$E[\rho] = F_{HK}(\rho) + \int dr V_{Ne}(r) \rho(r)$$

ground state energy

**universal functional**

**Hohenberg-Kohn functional (zero temperature)**



# Perturbative approximations to LW functional

A subset of skeleton diagrams present in the exact functional

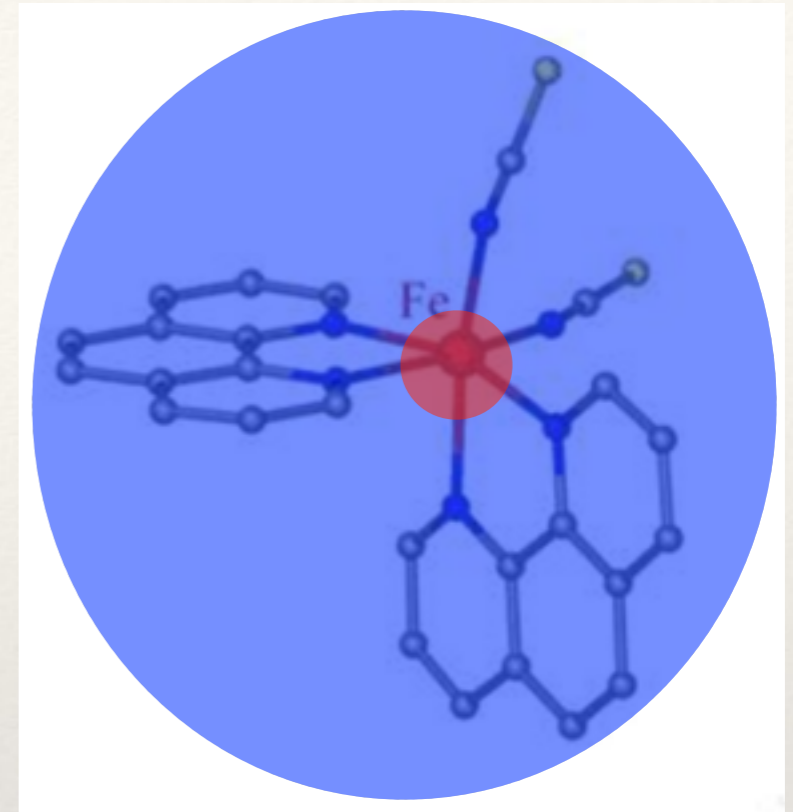
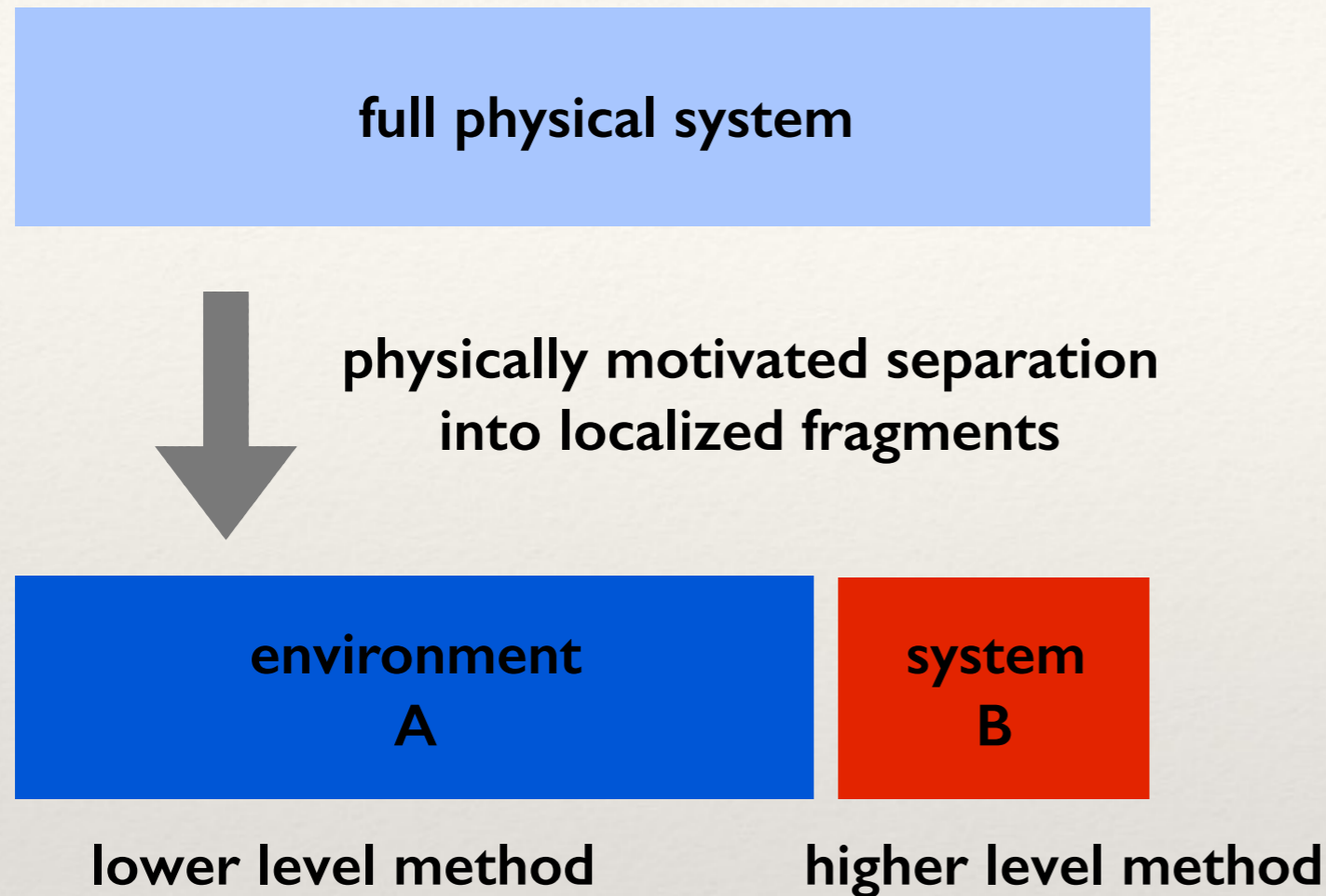
$$\begin{aligned}
 \Phi_{\text{GW}} &= -\frac{1}{2} \text{ (diagram)} - \frac{1}{4} \text{ (diagram)} - \frac{1}{6} \text{ (diagram)} + \dots \\
 \Sigma_{\text{GW}} &= \text{ (diagram)} + \text{ (diagram)} + \text{ (diagram)} + \dots \\
 \Phi_{\text{MP2}} &= -\frac{1}{2} \text{ (diagram)} - \frac{1}{4} \text{ (diagram)} - \frac{1}{4} \text{ (diagram)} \\
 \Sigma_{\text{MP2}} &= \text{ (diagram)} + \text{ (diagram)} + \text{ (diagram)}
 \end{aligned}$$

$$\frac{\partial \Phi_{\text{LW}}}{\partial G} = \Sigma$$

J. Chem. Phys. 122, 164102 2005

Approximations to Luttinger-Ward functional are used to evaluate self-energy

# Systems where perturbative series converges slowly



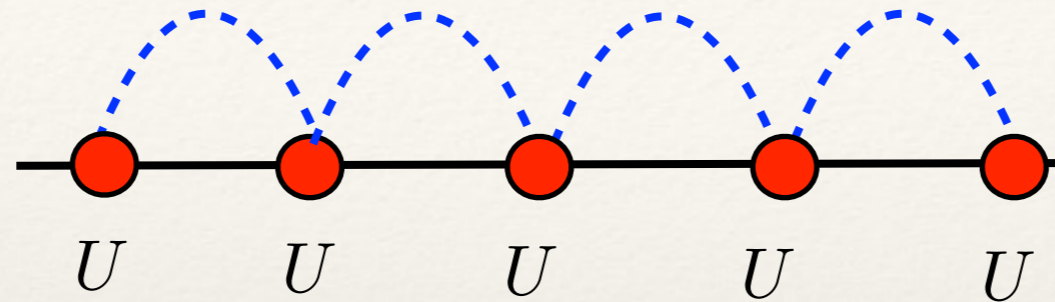
$$\Phi_{LW} = \Phi_{AB}^{low\ level} + \Phi_B^{high\ level} - \Phi_B^{low\ level}$$

$$\Sigma = \Sigma_{AB}^{low\ level} + \Sigma_B^{high\ level} - \Sigma_B^{low\ level}$$

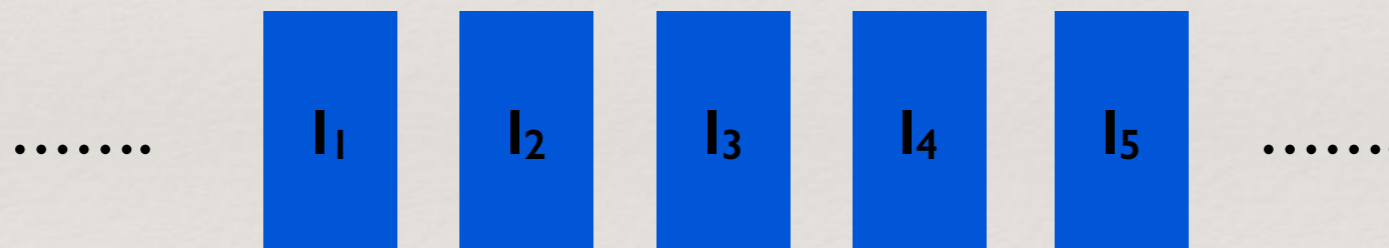


# Dynamical Mean Field Theory (DMFT)

$$H = -t \sum_{\langle i,j \rangle, \sigma} (c_{i\sigma}^\dagger c_{j\sigma} + c_{j\sigma}^\dagger c_{i\sigma}) + U \sum_{i=1}^N n_{i\uparrow} n_{i\downarrow}$$



physically motivated separation  
into localized fragments

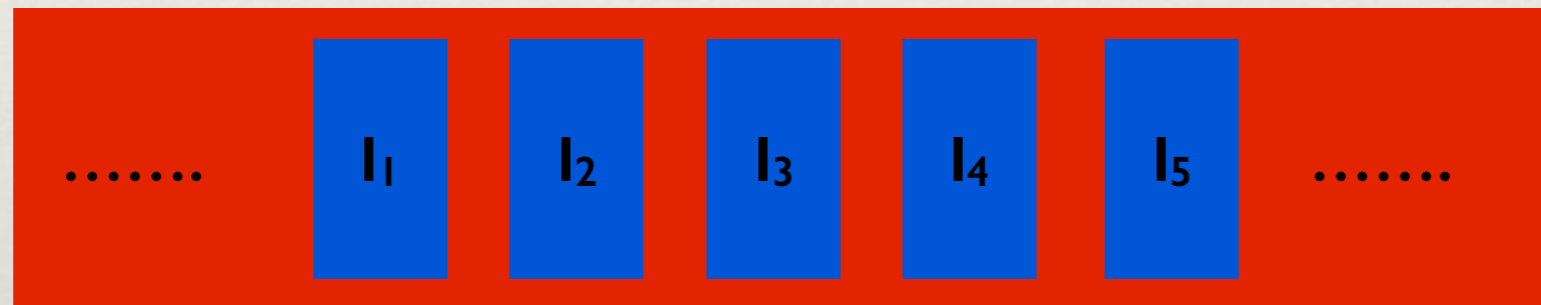
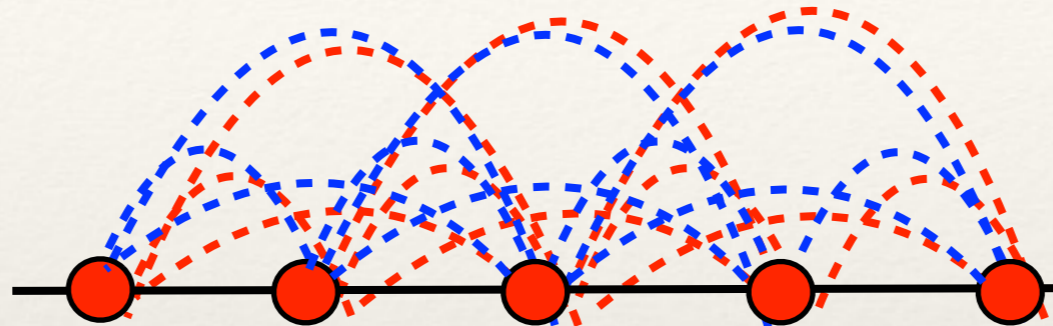


$$\Phi_{\text{DMFT}} = \sum_{j=1}^M [\Phi_I]_j$$

diagrams with all the  
interaction vertices inside orbital group I<sub>j</sub>

# LDA+DMFT or HF+DMFT

$$H = \sum_{ij} t_{ij} a_i^\dagger a_j + \frac{1}{2} \sum_{ijkl} v_{ijkl} a_i^\dagger a_k^\dagger a_j a_l$$



local contributions from group  $l_j$

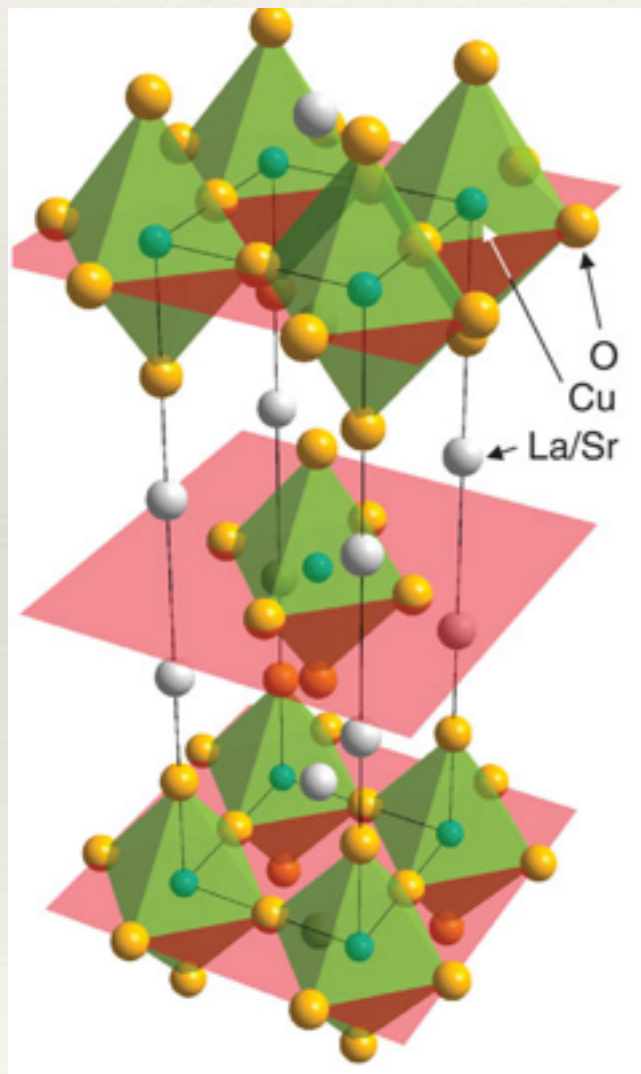
$$\Phi_{\text{DMFT+HF}} = \Phi_{\text{HF}}^{\text{tot}} + \sum_{j=1}^M ([\Phi^I]_j - [\Phi_{\text{HF}}^I]_j)$$

all the non-local contributions



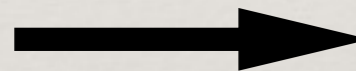
# Model Hamiltonian approach

## Realistic system

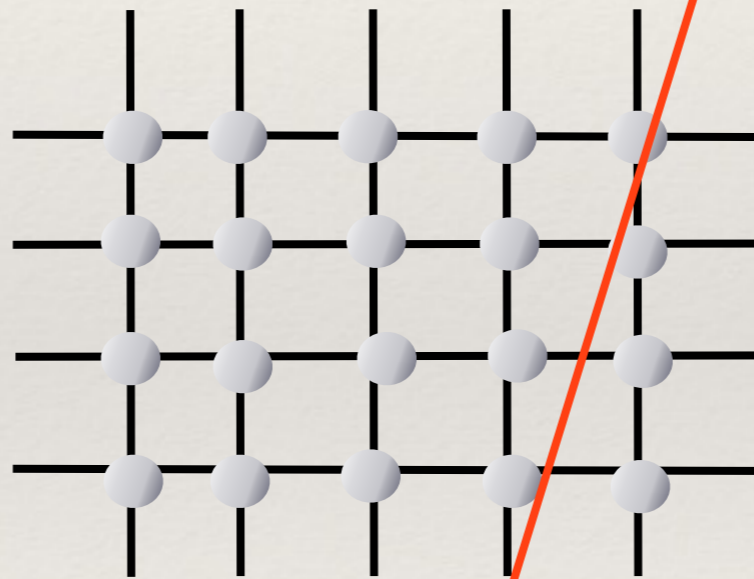


## Model system

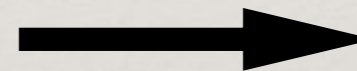
$$H = -t \sum_{\langle i,j \rangle, \sigma} (c_{i\sigma}^\dagger c_{j\sigma} + c_{j\sigma}^\dagger c_{i\sigma}) + U \sum_{i=1}^N n_{i\uparrow} n_{i\downarrow}$$



mapping  
to a low  
energy  
physics  
model  
system



effective interactions



Solving  
Model  
System

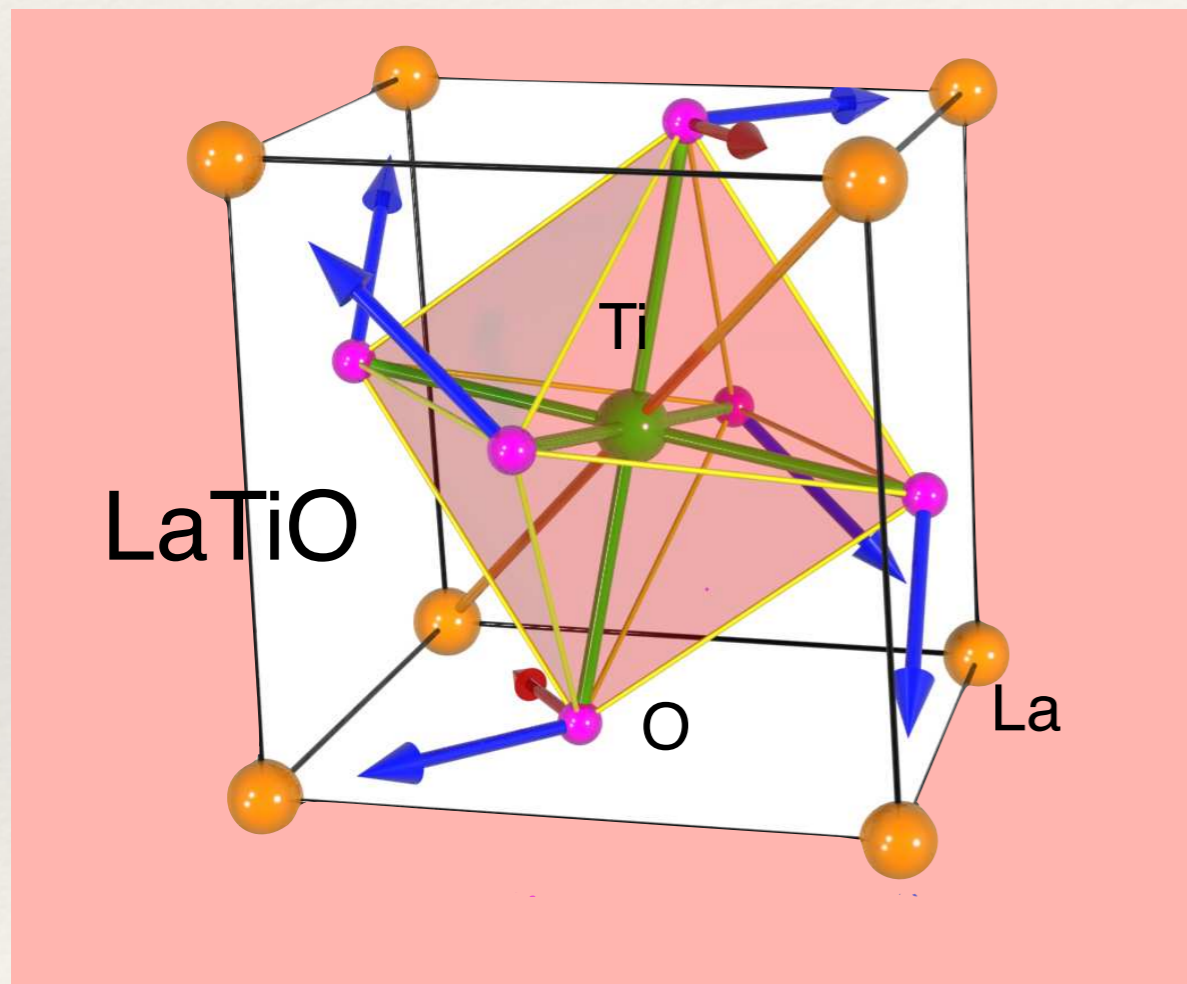
**approximate**

**controlled**

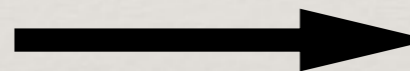
# Chemists' effective Hamiltonian approach

**Hamiltonian always remains unchanged**

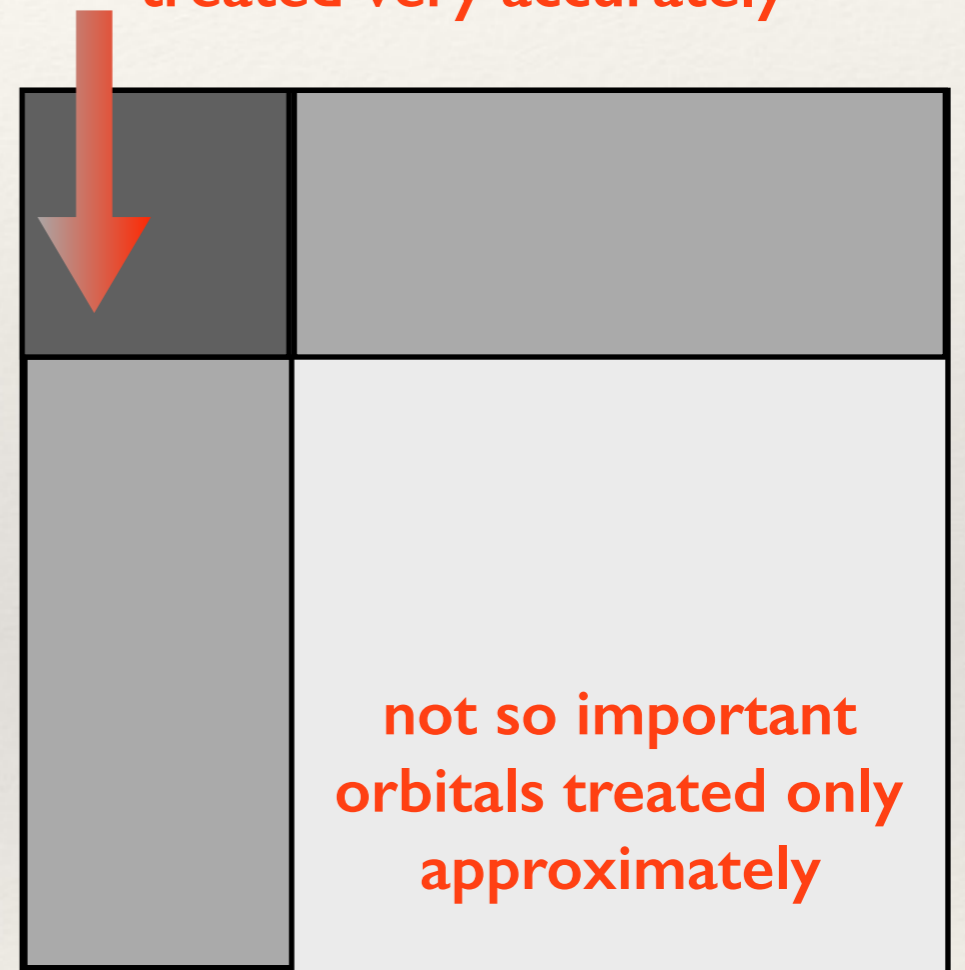
**wave functions or self-energies are approximated**



transforming  
to an  
effective  
Hamilton



important "dressed" orbital space  
treated very accurately

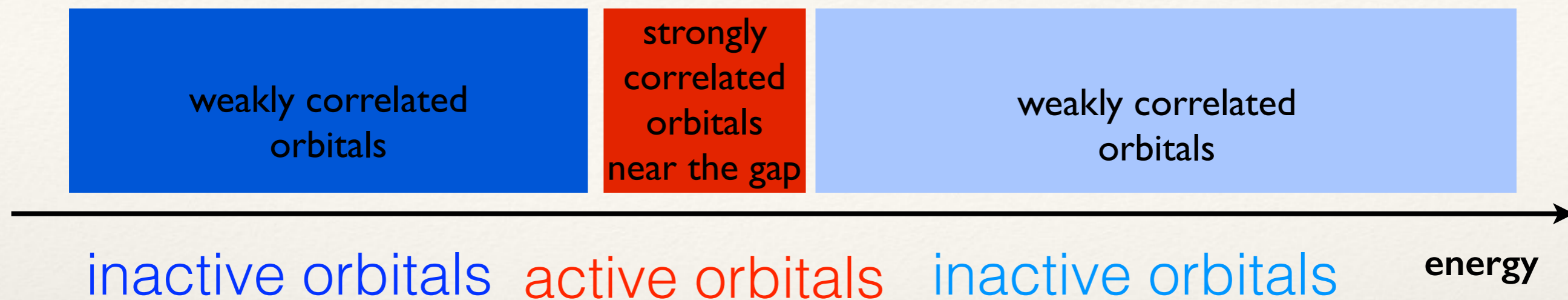


**controlled**

requires orbital  
transformation

effective  
Hamiltonian

# realistic molecular problems

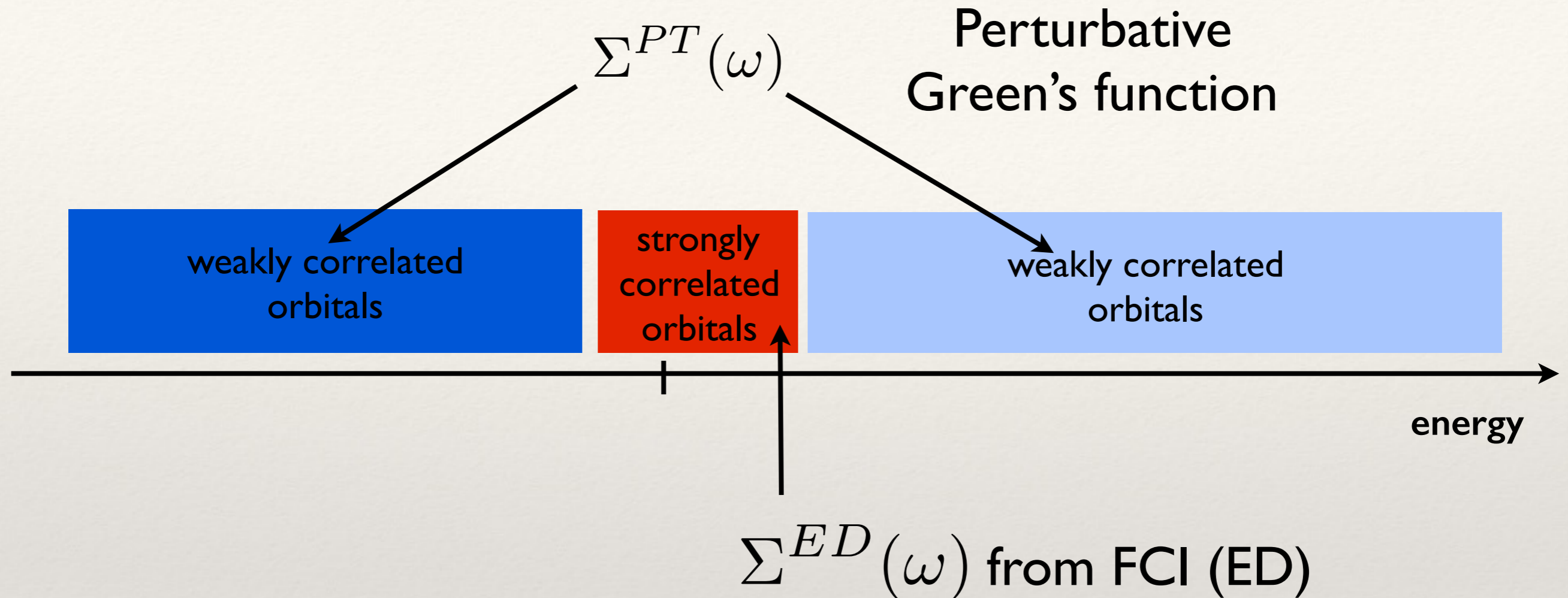


- separate different energy scales in realistic systems
- use different methods for weakly and strongly correlated orbitals
- be systematically improvable without any adjustable parameters
- maintain chemical accuracy

traditionally calculate ground state energy, perhaps couple of excited states



# Self-energy embedding

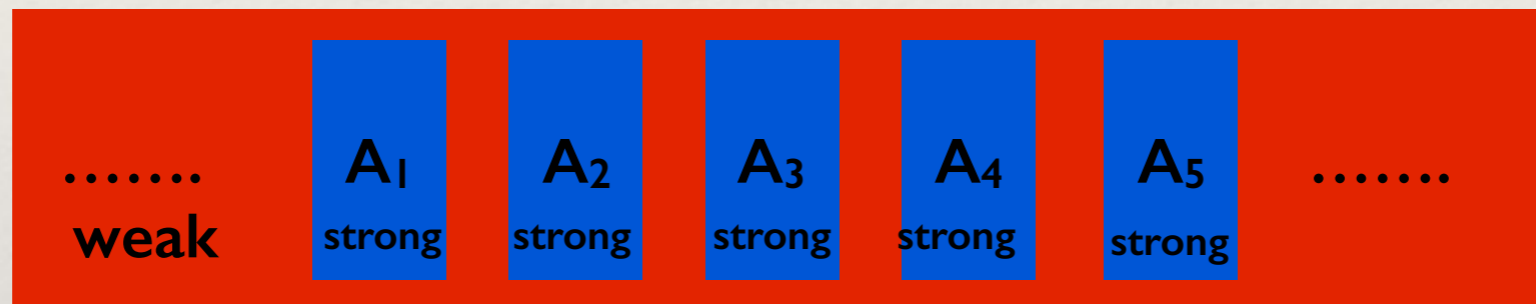
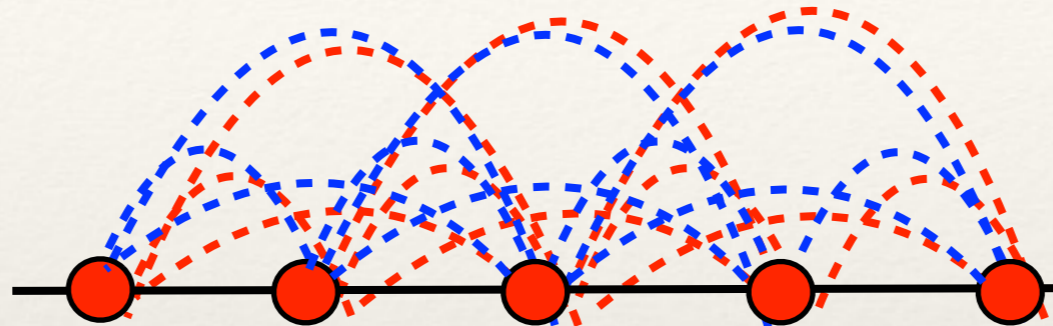


## Advantages

- no double counting of electron correlation when using PT
- no adjustable parameters in the Hamiltonian

# Self-energy Embedding Theory (SEET)

$$H = \sum_{ij}^N t_{ij} a_i^\dagger a_j + \sum_{ijkl}^N v_{ijkl} a_i^\dagger a_j^\dagger a_l a_k$$



$$\Phi^{\text{SEET}} = \Phi_{\text{weak}}^{\text{tot}} + \sum_{i=1}^M \left( [\Phi_{\text{strong}}^A]_i - [\Phi_{\text{weak}}^A]_i \right)$$

A. Kananenka, E. Gull, Dominika Zgid, Phys. Rev. B 91, 121111(R), 2015

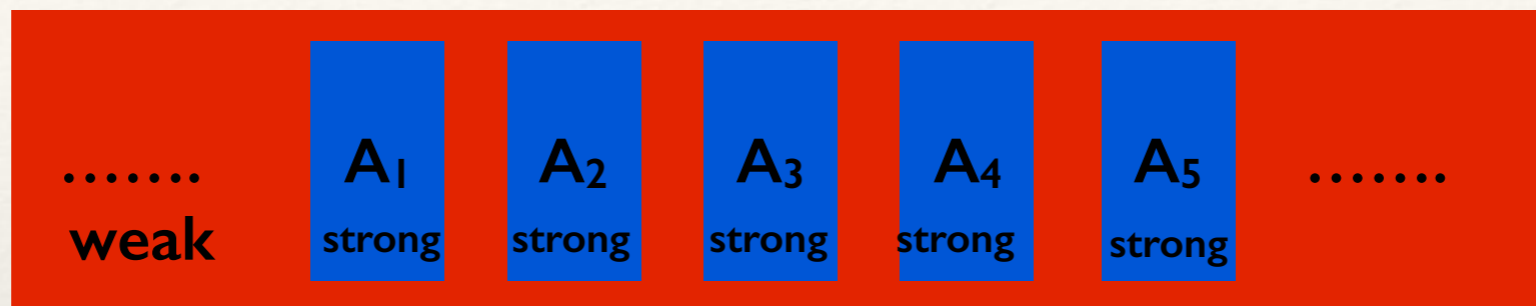
T.N. Lan, A. Kananenka, Dominika Zgid, JCP, 143, 241102 (2015)

T.N. Lan, A.A. Kananenka, Dominika Zgid, JCTC, 2016, 12 (10), pp 4856

Dominika Zgid, E. Gull, arXiv:1606.07454, New Journal of Physics, accepted

# Self-energy Embedding Theory (SEET)

$$\Phi^{\text{SEET}} = \Phi_{\text{weak}}^{\text{tot}} + \sum_{i=1}^M \left( [\Phi_{\text{strong}}^A]_i - [\Phi_{\text{weak}}^A]_i \right)$$



intractable problem

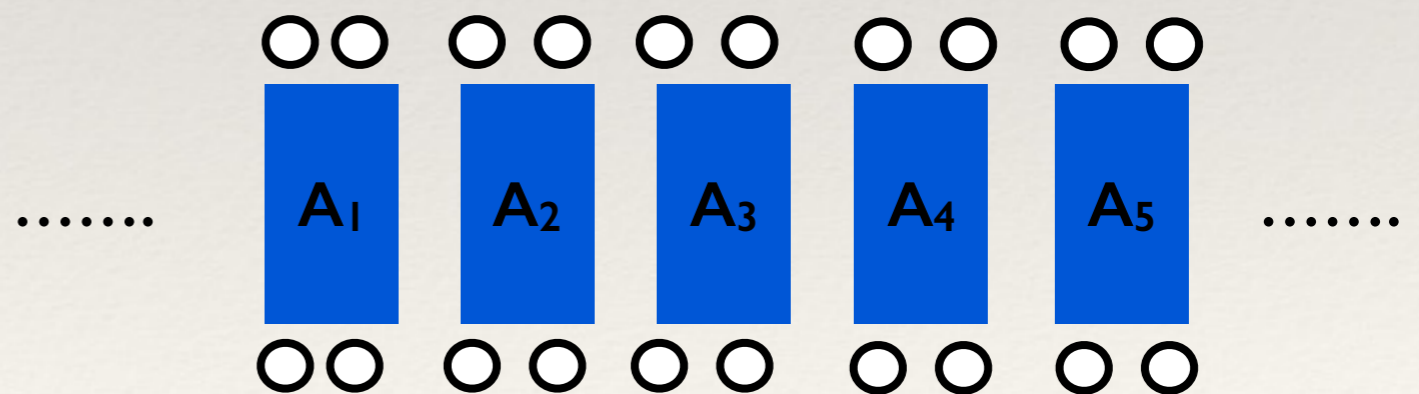


separates into a series of manageable calculations

low level perturbative method for the whole problem



high level method for impurity problems



$\Phi_{\text{weak}}^{\text{tot}}$   $[\Phi_{\text{weak}}^A]_i$

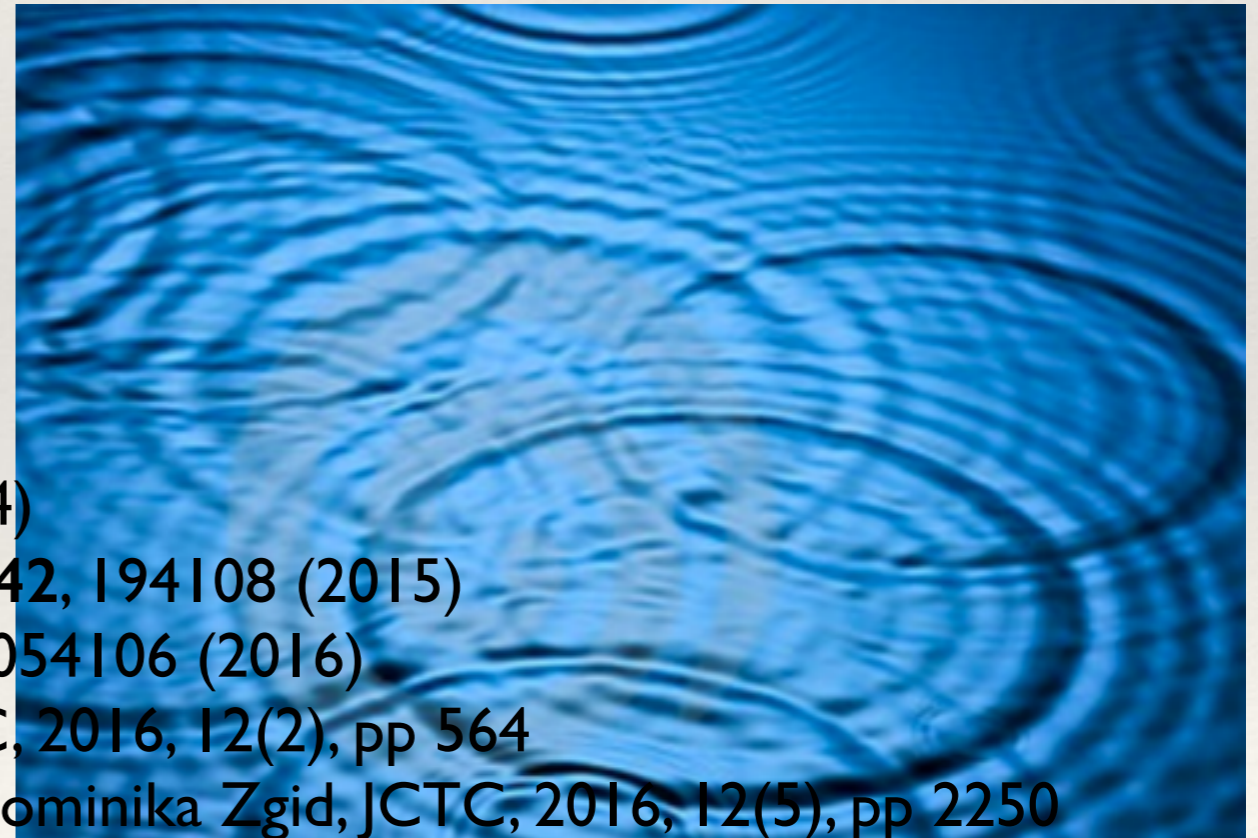
$[\Phi_{\text{strong}}^A]_i$



**separation onto manageable calculations**

# Self-consistent Green's function second order (GF2)

low level perturbative method for the whole problem



J.J. Phillips and Dominika Zgid, JCP **140**, 241101 (2014)

J.J. Phillips, A.A. Kananenka and Dominika Zgid, JCP **142**, 194108 (2015)

A.A. Rusakov and Dominika Zgid, J. Chem. Phys. **144**, 054106 (2016)

A.A. Kananenka, J.J. Phillips and Dominika Zgid, JCTC, 2016, 12(2), pp 564

A. A. Kananenka, A. R. Welden, T. N. Lan, E. Gull and Dominika Zgid, JCTC, 2016, 12(5), pp 2250

D. Neuhauser, R. Baer and Dominika Zgid, arXiv:1603.04141

A.R. Welden, A.A. Rusakov and Dominika Zgid, JCP **145**, 204106 (2016)



# Weakly correlated orbitals

$$\Phi_{\text{weak}}^{\text{tot}} \left[ \Phi_{\text{weak}}^A \right]_i$$

## Self-consistent Green's function second order (GF2)

$$\mathbf{G}(i\omega) = \left[ (\mu + i\omega)\mathbf{S} - \mathbf{F} - \Sigma(i\omega) \right]^{-1} \xrightarrow{\text{FFT}} \mathbf{G}(\tau)$$

$$\Sigma^{\text{bare}}(i\omega) = \text{[diagram: self-energy diagrams for bare case]}$$

no denominator  
AO orbitals

$$N_{\tau} n^5$$

$$\Sigma(i\omega) \xleftarrow{\text{IFFT}}$$

$$\Sigma_{ij}(\tau) = - \sum_{klmnpq} G_{kl}(\tau) G_{mn}(\tau) G_{pq}(-\tau) \times v_{imqk} (2v_{lpnj} - v_{nplj})$$

$$\Sigma^{\text{GF2}}(i\omega) = \text{[diagram: self-energy diagrams for GF2 case]}$$

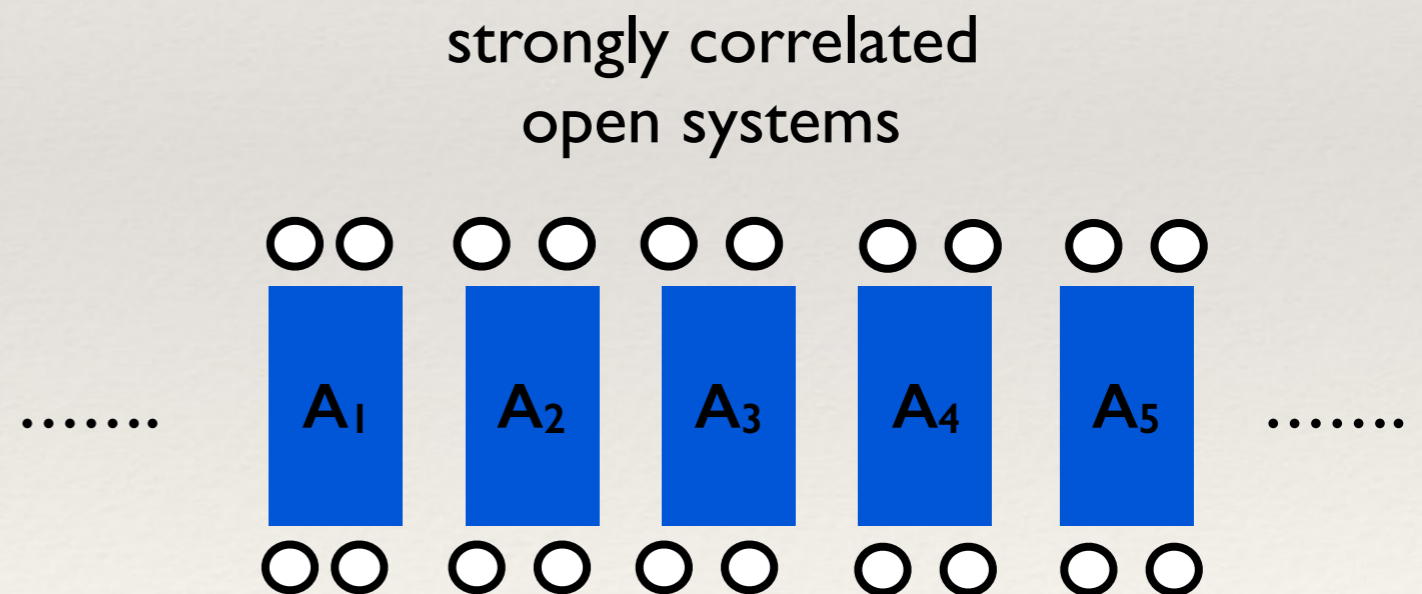
J.J. Phillips and Dominika Zgid, JCP 140, 241101 (2014)

A.A. Rusakov and Dominika Zgid, JCP, 144, 054106 (2016)

A.R. Welden, A.A. Rusakov and Dominika Zgid, JCP 145, 204106 (2016)



# High level methods for impurity problems




# Strongly correlated orbitals $[\Phi_{\text{strong}}^A]_i$

## Truncated ED versions from Quantum Chemistry

$$G_{kl}(\omega) = \langle \Psi_0 | a_k \frac{1}{\omega - (\hat{H} - E_0)} a_l^\dagger | \Psi_0 \rangle + \langle \Psi_0 | a_l^\dagger \frac{1}{\omega + (\hat{H} - E_0)} a_k | \Psi_0 \rangle$$

$$|\Psi_0\rangle = \phi_{\text{ref}} + \sum_i \overset{\text{singly excited}}{c_{1i}} \phi_{1i} + \sum_i \overset{\text{doubly excited}}{c_{2i}} \phi_{2i} + \cdots + \sum_i \overset{\text{n-tuply excited}}{c_{ni}} \phi_{ni}$$

  
decreasing contribution to wave function

- appropriate for realistic interactions
- can treat five d-orbitals or seven f-orbitals and many bath orbitals ~ 30

$$[\Sigma]_{\mu\nu} = [\Sigma_{strong}^{ED}]_{\mu\nu} + [\Sigma_{embedding}^{GF2}]_{\mu\nu}$$

chosen strongly  
correlated orbitals

local correlations  
described by an accurate  
method

non-local correlations described  
by a less accurate method

Let's come back to  
Self-energy embedding theory (SEET)

A. Kananenka, E. Gull, Dominika Zgid, Phys. Rev. B 91, 121111(R), 2015

T.N. Lan, A. Kananenka, Dominika Zgid, JCP, 143, 241102 (2015)

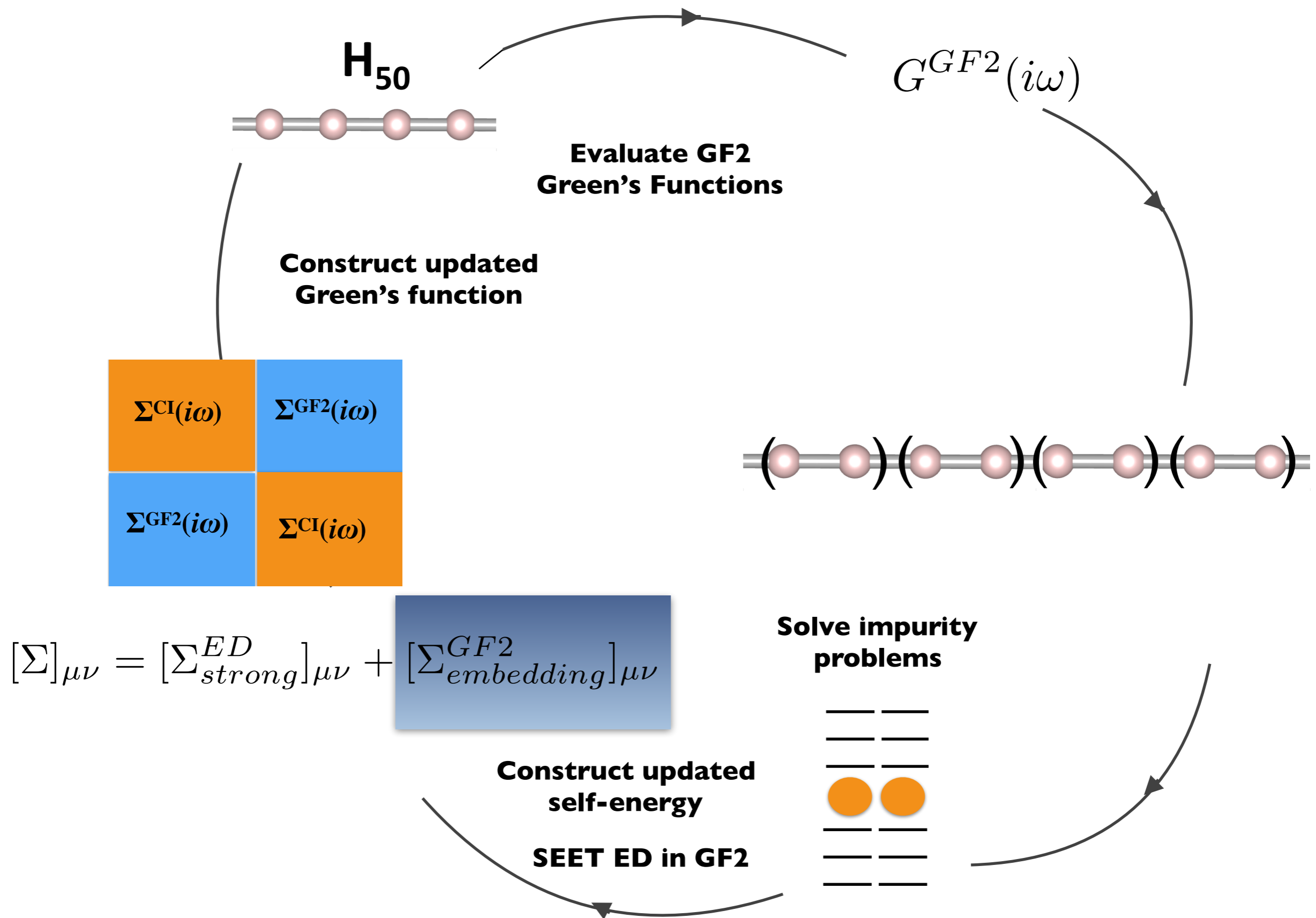
T.N. Lan, A.A. Kananenka, Dominika Zgid, JCTC, 2016, 12 (10), pp 4856

Dominika Zgid, E. Gull, New J. Phys. 19, 023047 (2017)

T.N. Lan, Dominika Zgid, arXiv:1703.06981, accepted to JCPL



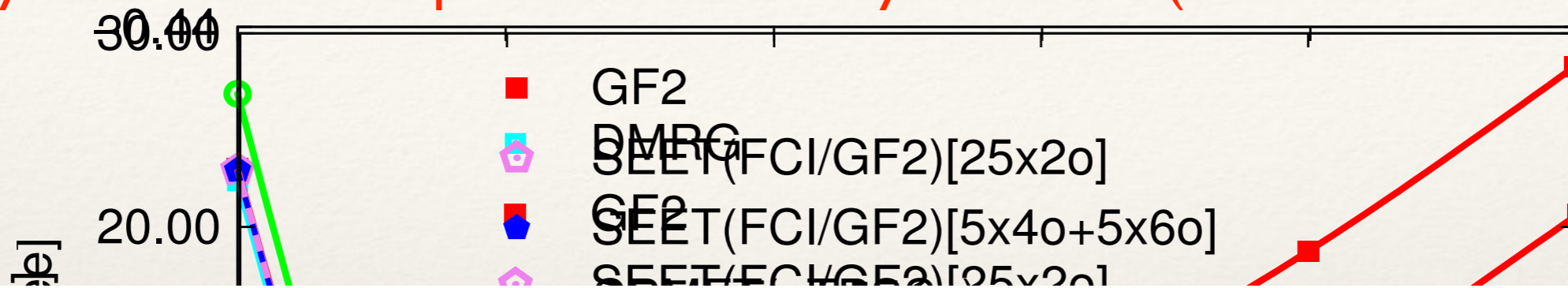
# SEET for molecules in localized basis



# SEET in localized orbitals

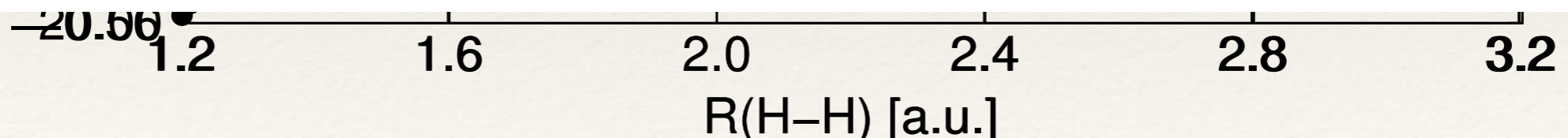
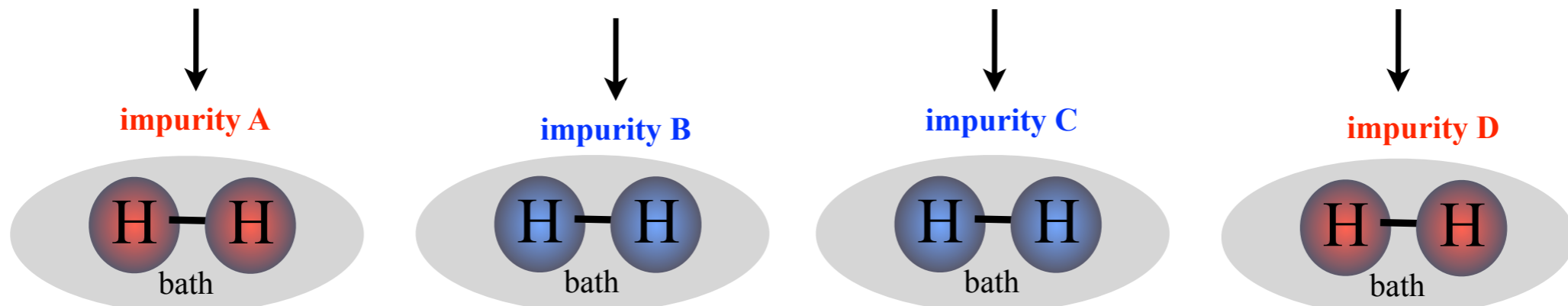
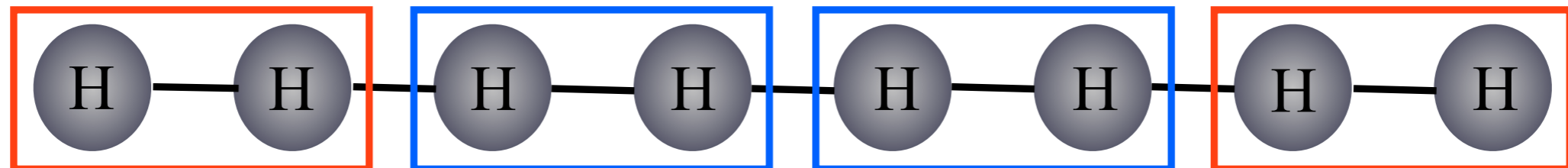
many strongly correlated electrons (50 orbitals, 50 electrons, STO-6G basis)

too many for traditional quantum chemistry methods (NEVPT2 or CASPT2)!!!



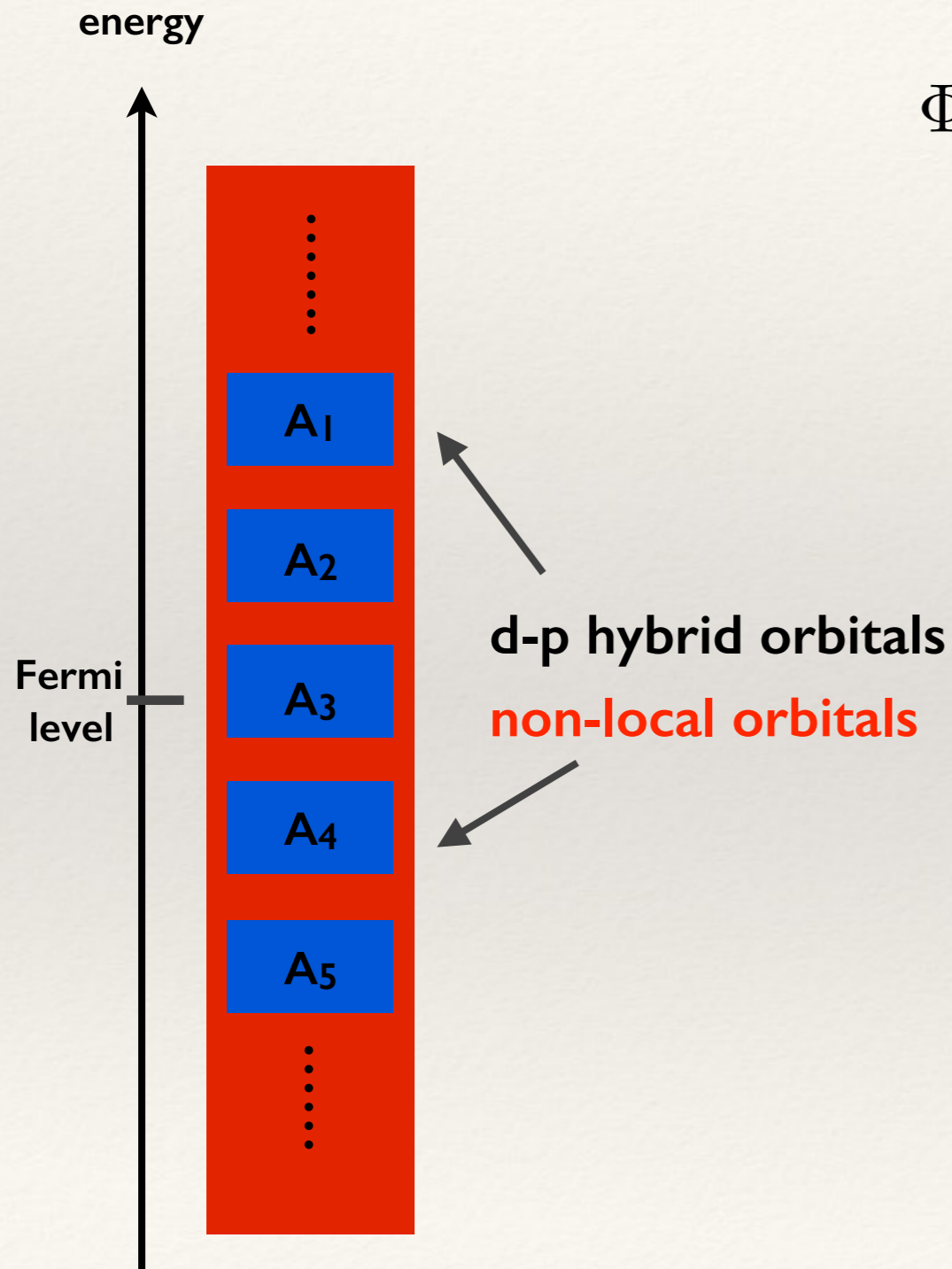
## Spatial impurity selection scheme

distance



# Is locality really crucial in SEET?

**No, separation of different energy scales is really important.**



$$\Phi^{\text{SEET}} = \Phi_{\text{weak}}^{\text{tot}} + \sum_{i=1}^M \left( [\Phi_{\text{strong}}^A]_i - [\Phi_{\text{weak}}^A]_i \right)$$

$$\Sigma^{\text{SEET}} = \begin{bmatrix} [\Sigma^A]_1 & \Sigma^{\text{int}} & \dots & \dots & \dots \\ \Sigma^{\text{int}} & [\Sigma^A]_2 & \Sigma^{\text{int}} & \dots & \dots \\ \dots & \dots & \dots & \dots & \dots \\ \dots & \dots & \Sigma^{\text{int}} & [\Sigma^A]_M & \Sigma^{\text{int}} \\ \dots & \dots & \dots & \Sigma^{\text{int}} & \Sigma^R \end{bmatrix}$$

$$[\Sigma^A]_i = \Sigma_{\text{weak}}^{\text{tot}} + ([\Sigma_{\text{strong}}^A]_i - [\Sigma_{\text{weak}}^A]_i)$$

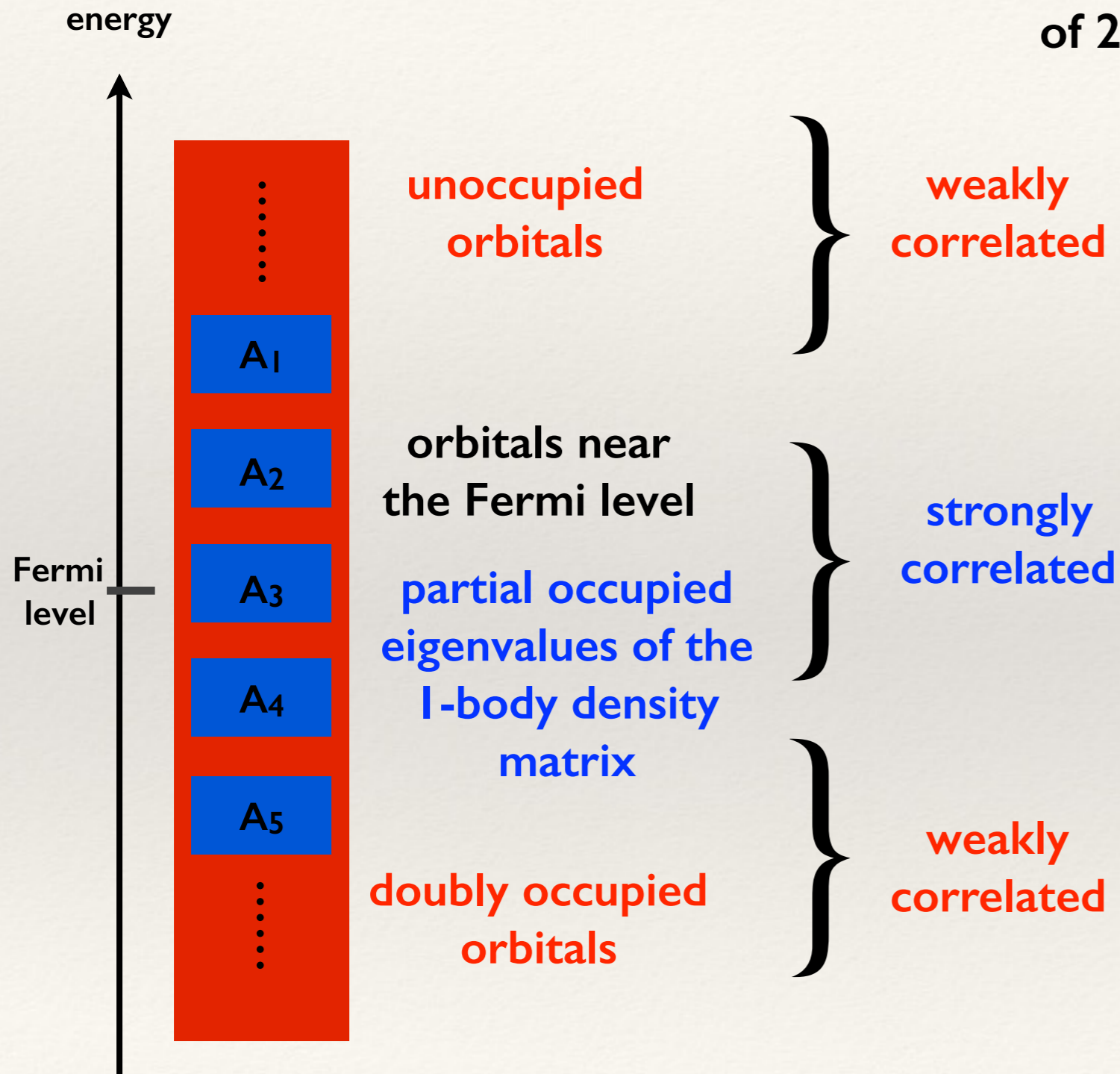
$$\Sigma^R = \Sigma_{\text{weak}}^R$$

$$\Sigma^{\text{int}} = \Sigma_{\text{weak}}^{\text{int}}$$

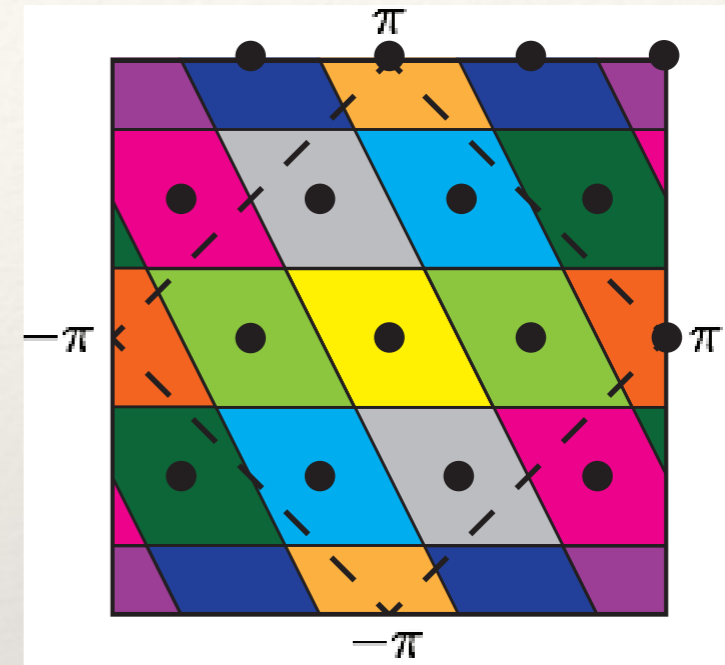


# Choosing strongly correlated orbitals automatically

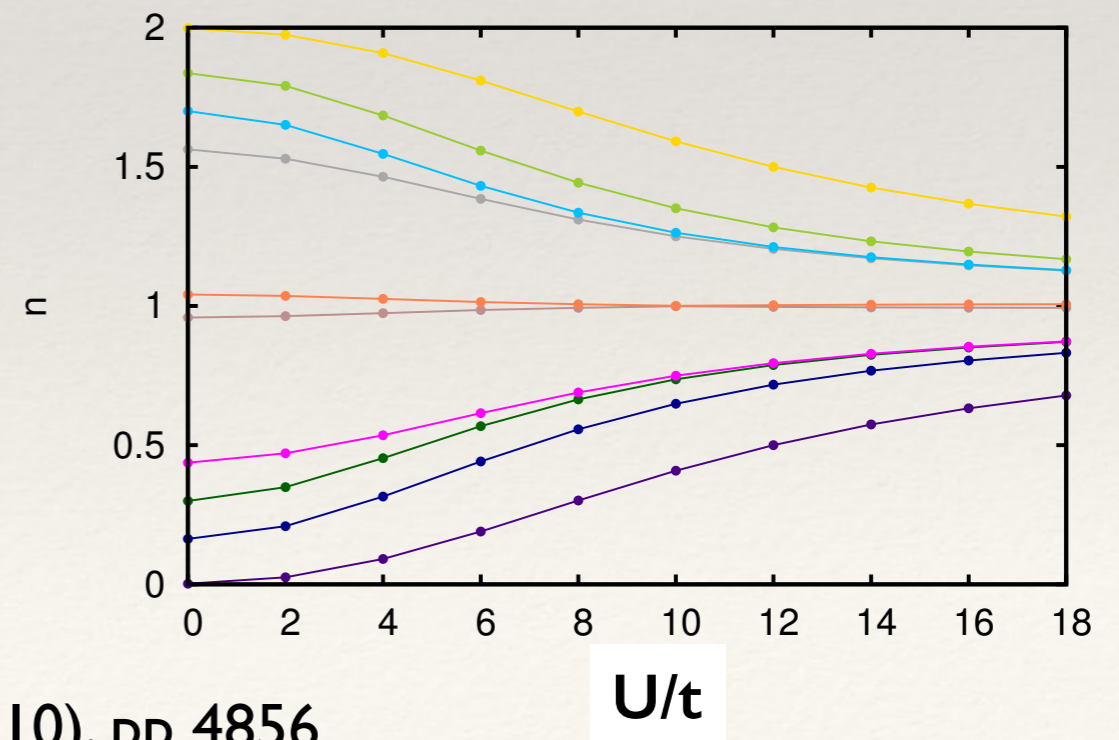
## How do we define a strongly correlated orbital?



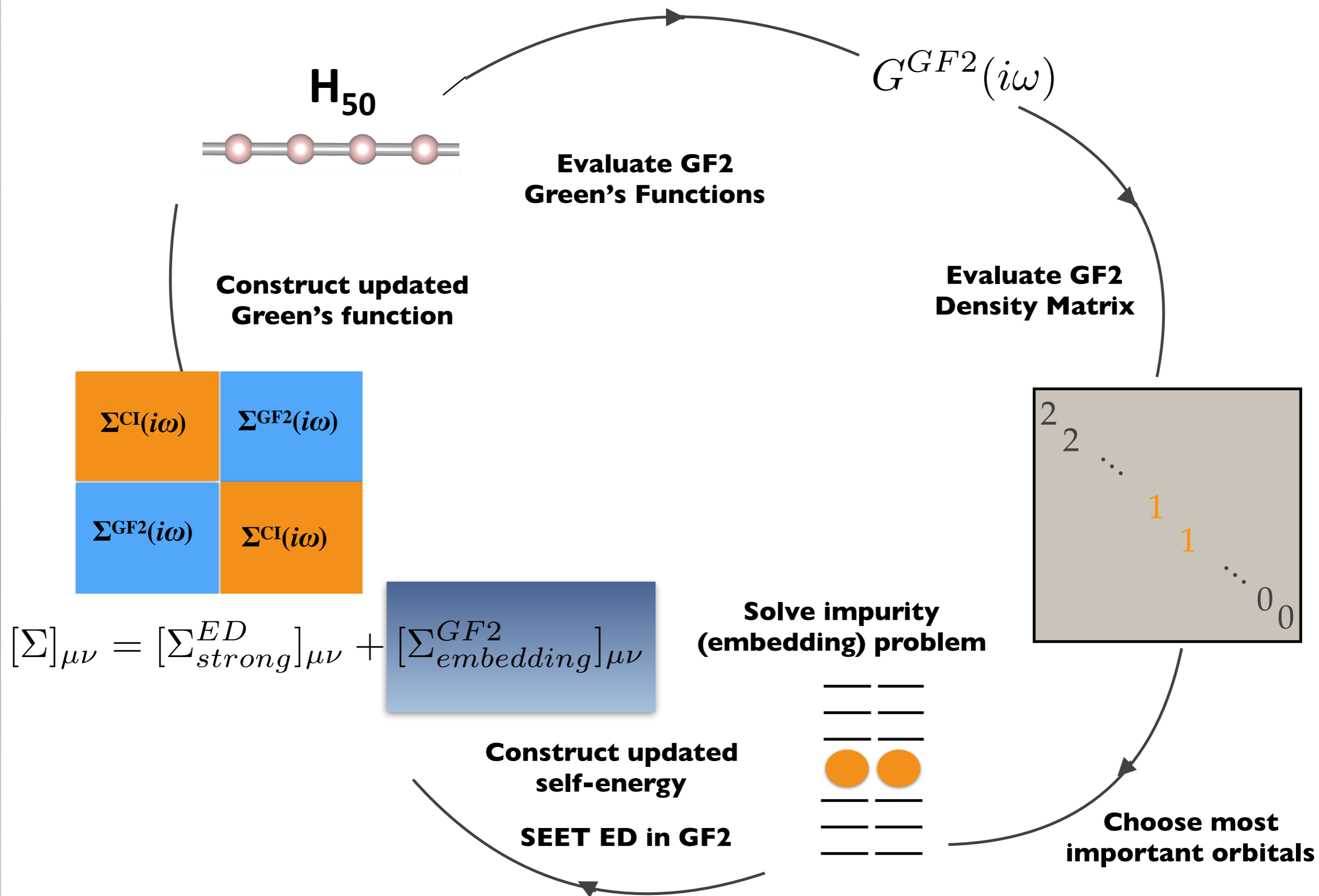
16-site patch  
of 2D Hubbard model in momentum space



Populations vs. interaction

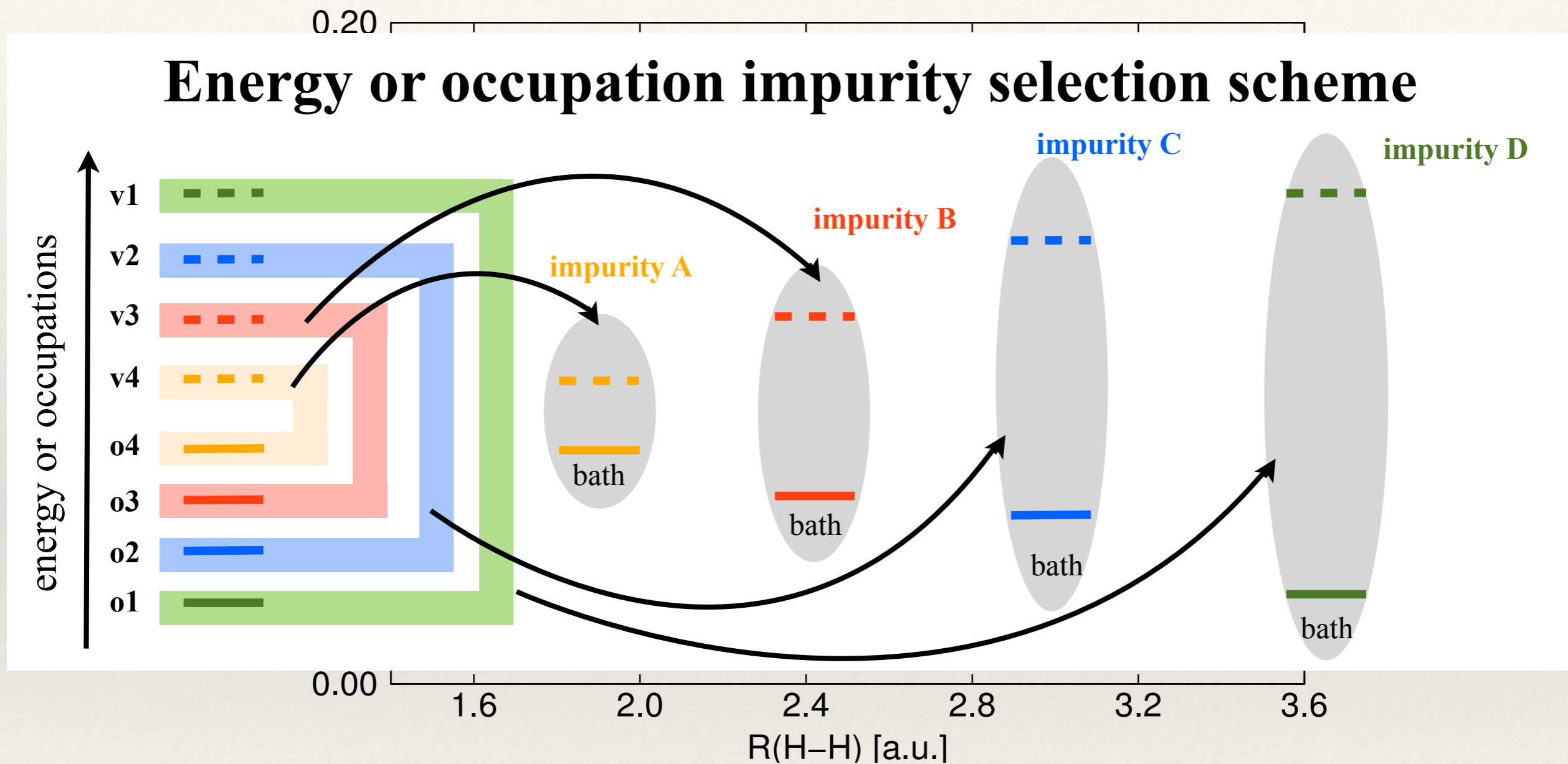


# SEET for molecules in energy basis



# SEET in energy basis

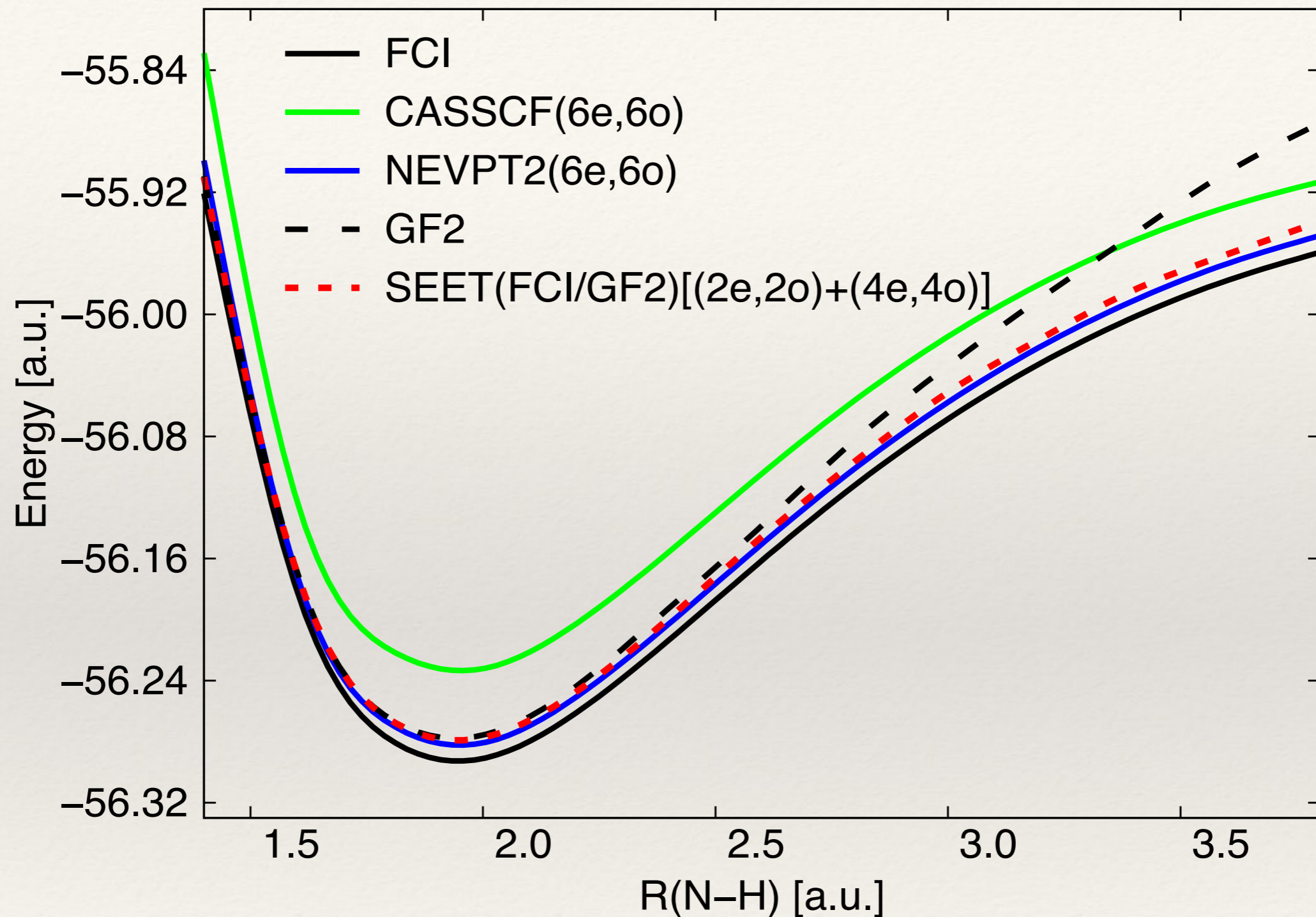
splitting strongly correlated orbitals into many groups  
is systematically improvable and converges well



H<sub>10</sub> stretching in cc-pVDZ basis (50 orbitals, 10 electrons)  
error w.r.t. DMRG



# SEET for molecules



NH<sub>3</sub> triple bond stretching in 6-31G basis (15 orbitals, 10 electrons)

# Structure of self-energy

$$\Sigma^{\text{SEET}} = \begin{bmatrix} \text{strong}_1 & \Sigma^{\text{int}} & \dots & \dots & \dots \\ \Sigma^{\text{int}} & \text{strong}_2 & \Sigma^{\text{int}} & \dots & \dots \\ \dots & \dots & \text{strong} & \dots & \dots \\ \dots & \dots & \dots & \text{strong}_M & \Sigma^{\text{int}} \\ \dots & \dots & \dots & \Sigma^{\text{int}} & \text{strong}_R \end{bmatrix}$$

The diagram shows a matrix structure for the self-energy  $\Sigma^{\text{SEET}}$ . The matrix is partitioned into blocks. Red blocks along the diagonal are labeled "strong" with subscripts 1, 2, ..., M, and R. Blue blocks are labeled  $\Sigma^{\text{int}}$ . Ellipses (...) indicate other elements in the matrix. The word "weak" is written in the upper-right and lower-left quadrants, indicating the nature of the interactions between the strongly correlated orbitals.

- What about a system with many strongly correlated orbitals?
- What if strongly correlated orbitals are divided into multiple groups?

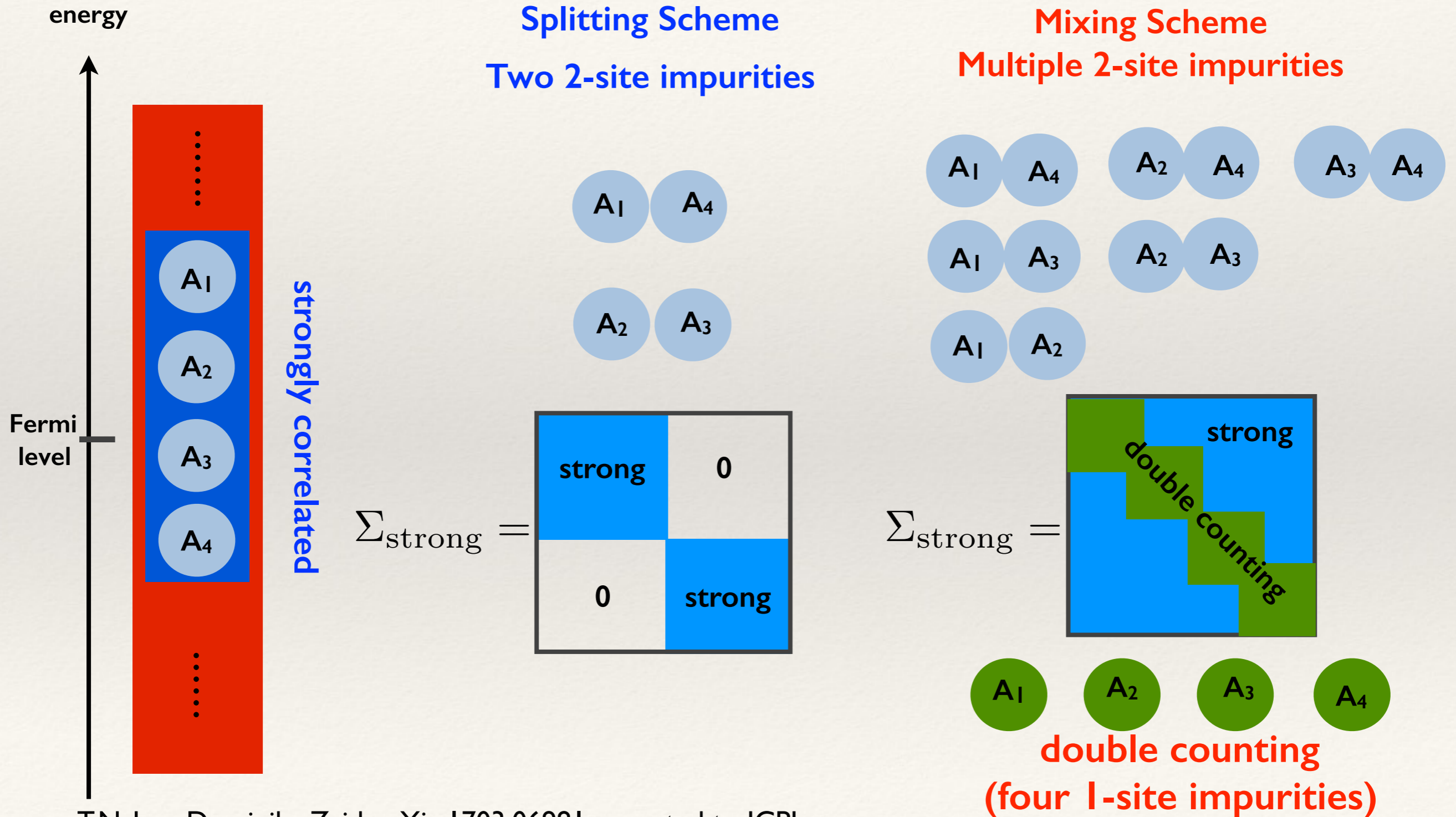
The accurately treated region is small.

Many strong interactions between orbitals are treated only perturbatively.

The accuracy of the calculations may not be sufficient!!!

# Recovering the self-energy fully

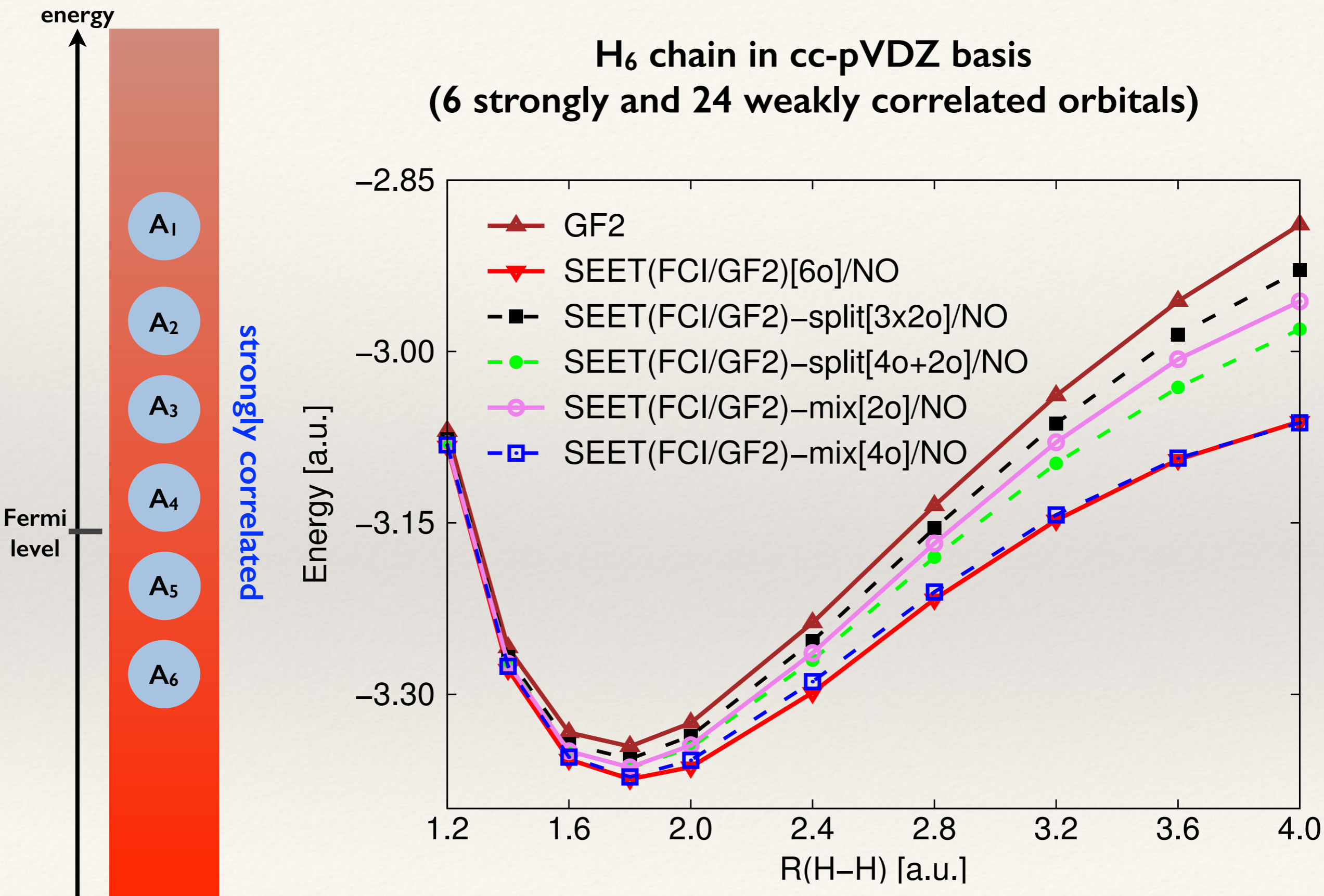
Problem: Assume we can build AIM with only 2 impurity orbitals





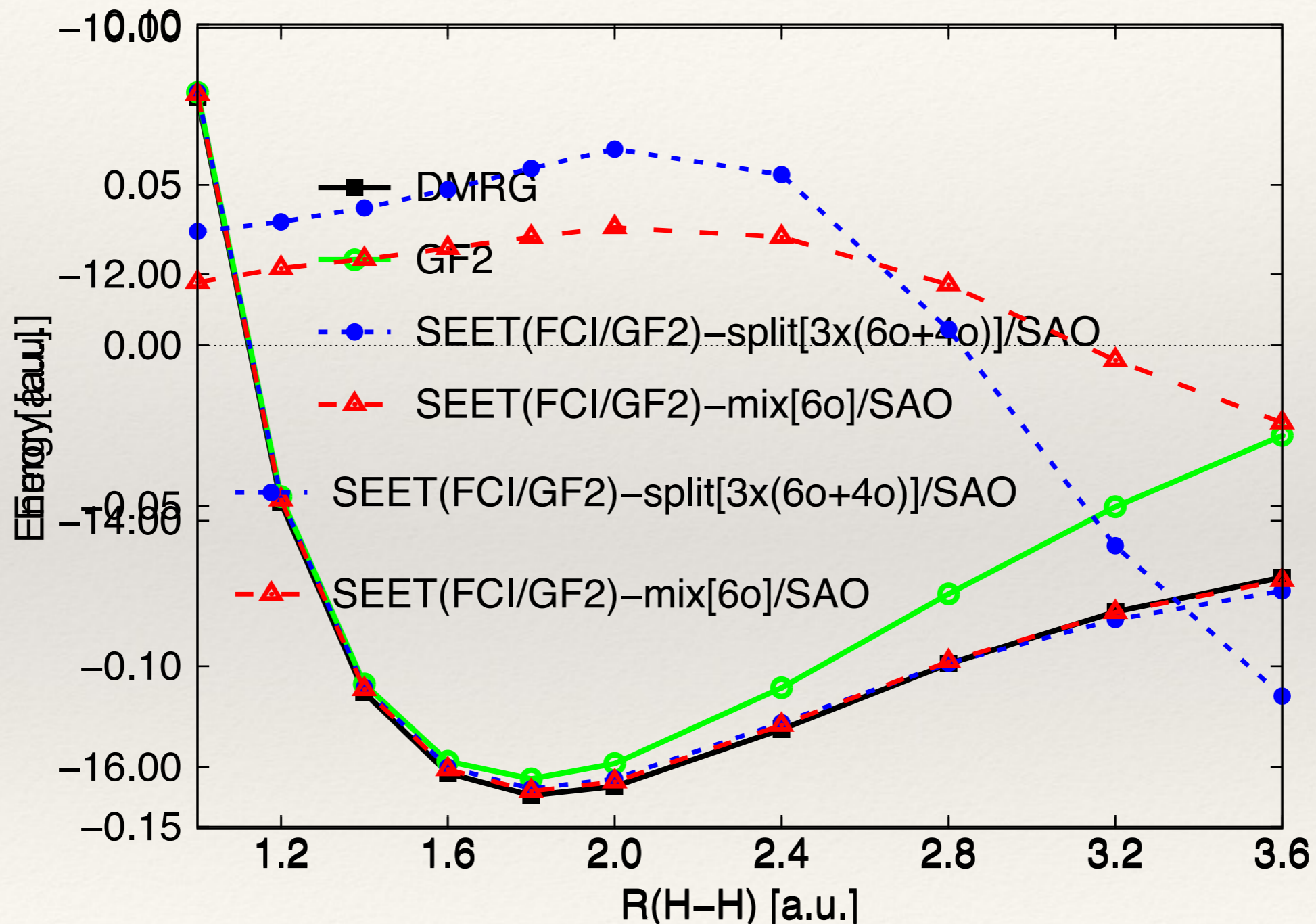
# Comparing splitting vs mixing SEET schemes

**H<sub>6</sub> chain in cc-pVDZ basis**  
**(6 strongly and 24 weakly correlated orbitals)**



# Comparing splitting vs mixing SEET schemes

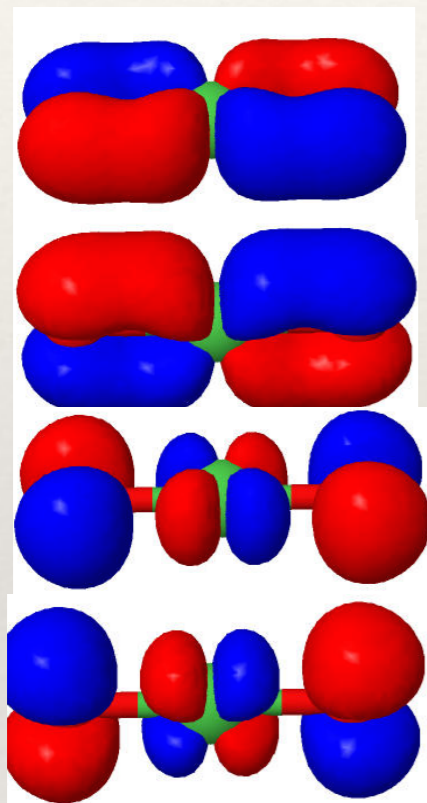
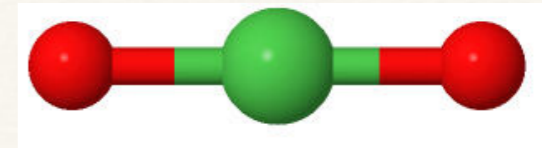
**H<sub>30</sub> chain in STO-3G basis  
(30 strongly correlated orbitals)**





# Comparing splitting vs mixing SEET schemes

Linear NiO<sub>2</sub> in cc-pVDZ basis  
(12 strongly and 59 weakly correlated orbitals)



## Occupation Numbers

SEET(FCI/HF)-mix(9o) CASCI(18e,12o)

1.79

1.79

1.79

1.79

0.46

0.47

0.46

0.47

## Electronic Energy [a.u.]

Hartree-Fock -1656.203

SEET(FCI/HF)-mix(9o): -1656.514

CASCI(18e,12o): -1656.512



# SEET for molecules vs Quantum Chemistry methods

## **NEVPT2 / CASPT2**

diagonalize and perturb

all strongly correlated orbitals  
are treated simultaneously

divergence of denominators  
when strong correlation present

PT2 describes only  
weak correlation

requires 1-, 2-, 3-, 4- RDM

## **SEET (FCI-in-GF2)**

perturb and diagonalize

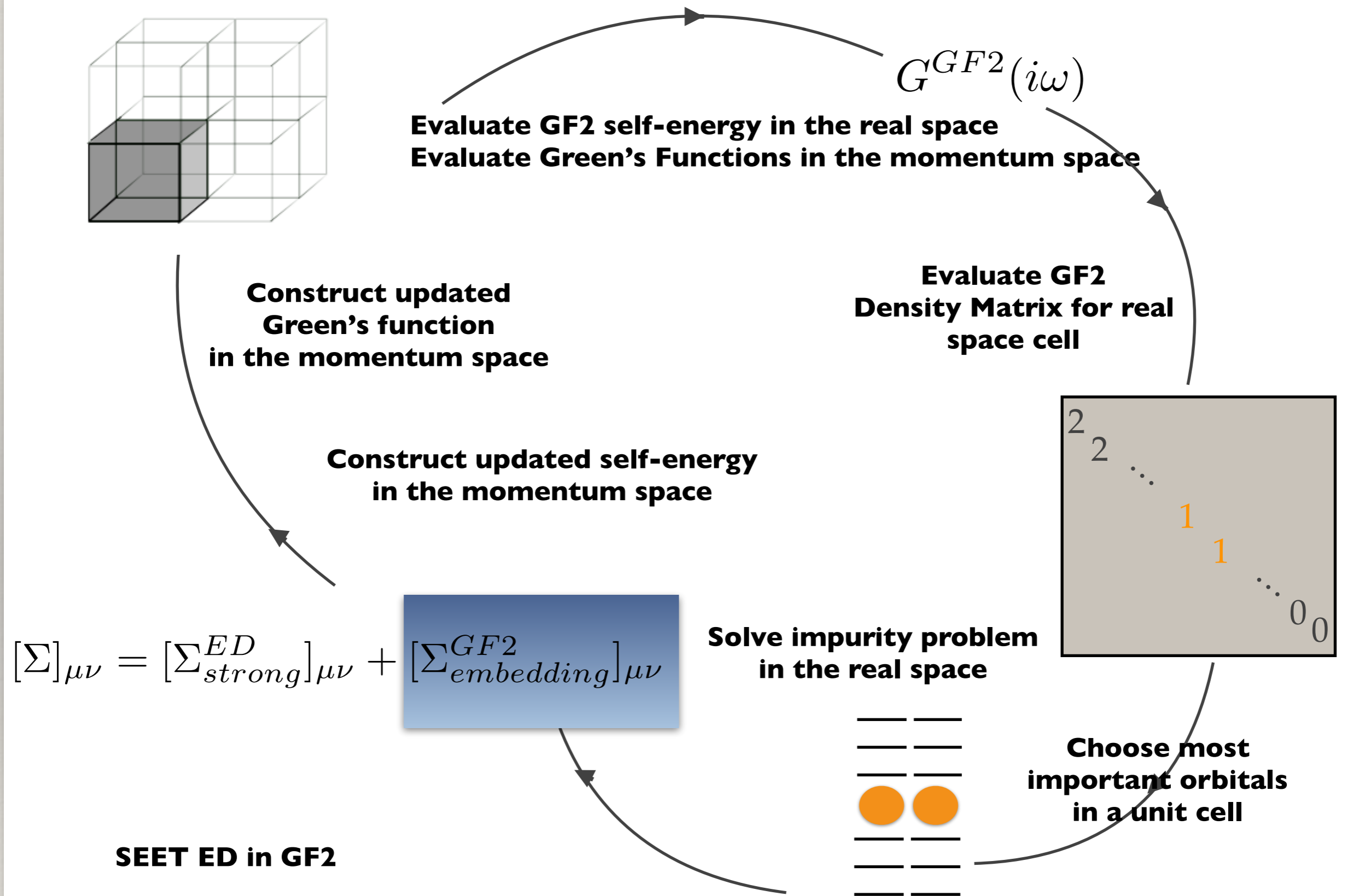
strongly correlated orbitals  
can be split among multiple impurities

no divergence

GF2 describes partially  
strong correlation

requires 1-body  
Green's functions

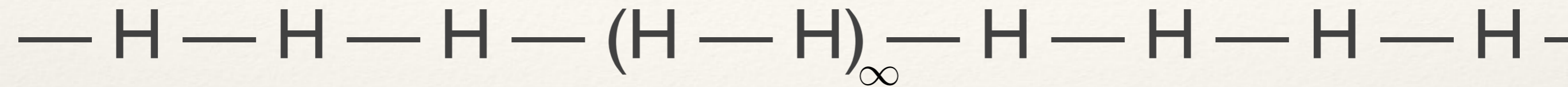
# Periodic systems with SEET



# Periodic SEET

Infinite 1D Hydrogen solid in STO-3G basis

$$H = \sum_{ij}^N t_{ij} a_i^\dagger a_j + \sum_{ijkl}^N v_{ijkl} a_i^\dagger a_j^\dagger a_l a_k$$

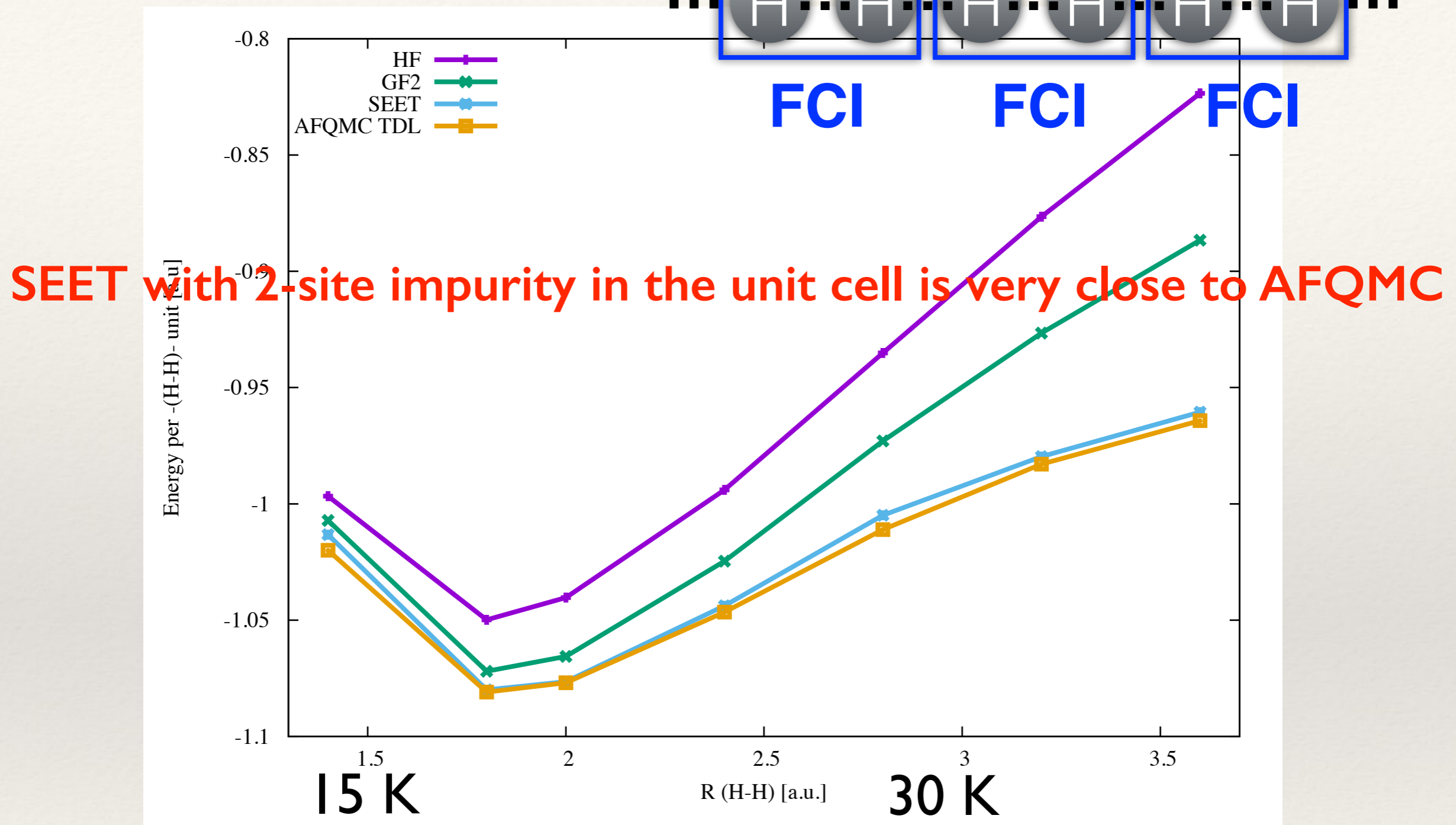
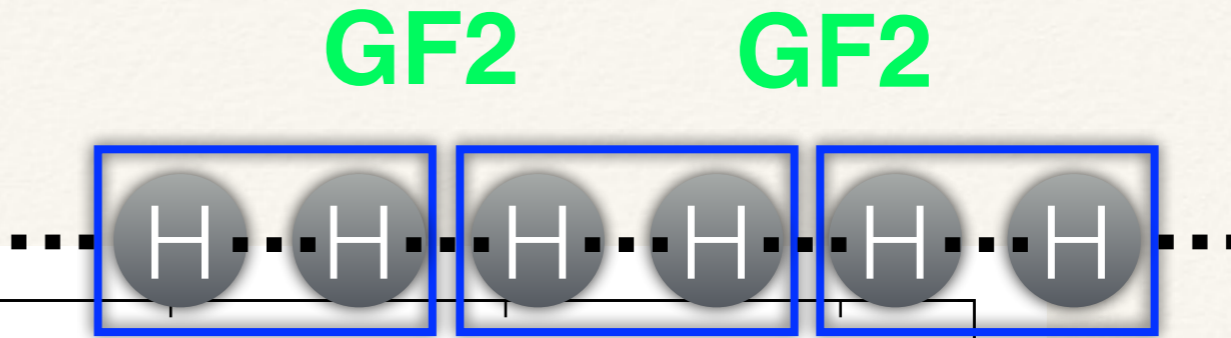


**Goal: To show that periodic SEET can give very accurate energies**

**Comparison with ground state TDL data from AFQMC (Shiwei Zhang)**

- SEET is a finite temperature method  
To be close to zero temp ground state we cool down our problem to  $\beta = 10000$  1/a.u. or 31.6 K
- Multiple physical phases are possible  
We need to be careful not be trapped in a metastable solution





AFQMC data from Simons Collaboration benchmark for H chains by Shiwei Zhang

T.N. Lan, A.A. Rusakov, Dominika Zgid, in preparation

# SEET key features

- SEET does not assume any mapping to a model Hamiltonian, it usually relies on a transformation to an effective Hamiltonian with energy scale separation.
- Self-energy is approximated, Hamiltonian is left unchanged.
- A systematic iterative approach yielding excellent energies can be easily constructed with SEET.
- Self-energy between weakly correlated orbitals can be easily included with GF2, strongly correlated orbitals are treated with truncated ED .
- SEET avoids some of the problems present in quantum chemistry methods.
- Iterative Green's function methods (GF2) can be used to choose strongly correlated orbitals.



# Acknowledgements



- my group



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