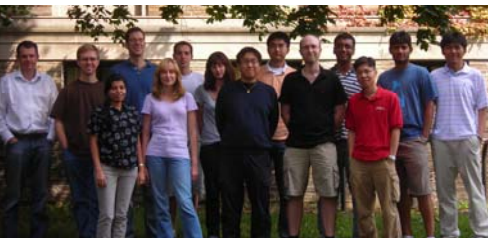


DMFT from a quantum chemistry perspective

Garnet Kin-Lic Chan

Dominika Zgid

Department of Chemistry and
Chemical Biology

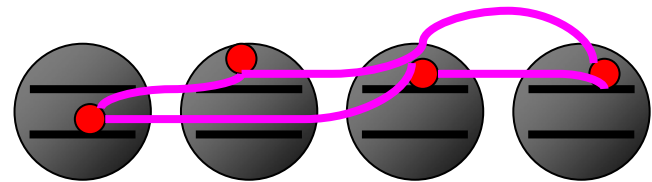
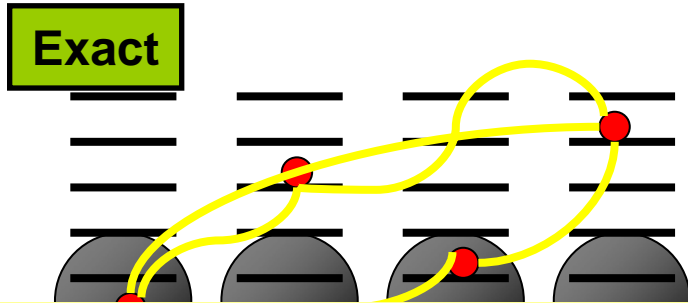


Cornell University

the David &
Lucile Packard
FOUNDATION



Four views of electronic structure



Some levels

All configurations, e.g. ED

Problem specific interactions



All levels

Convergent, structured wf ansatz

All interactions

- Chemistry energy scale is kT

- **Culture**

Fewer big problems,
many small problems

Method developers are
not generally method
users

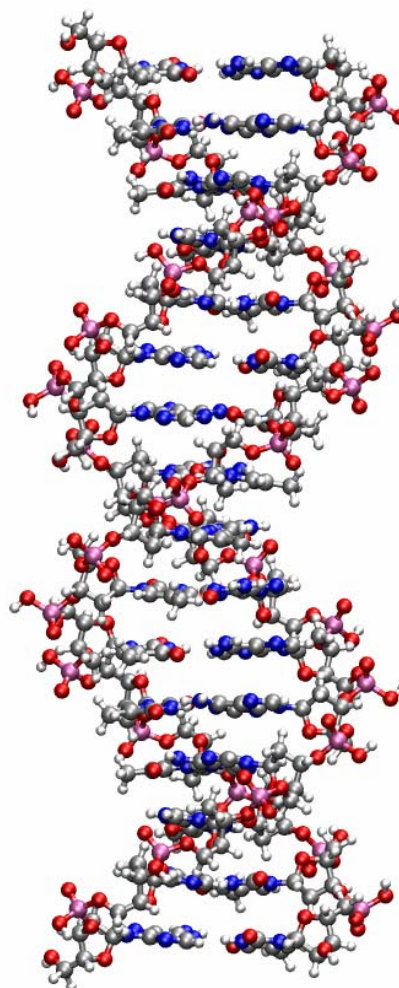
Weakly correlated quantum chemistry

Very accurate

Single water molecule vibrational spectrum

(010)	-0.32
(020)	-0.56
(030)	-0.78
(040)	-1.06
(050)	-1.41
(101)	0.60
(201)	1.23
(301)	2.05
(401)	2.74
(501)	4.65
(601)	5.94
(701)	6.46
All	1.90

Errors from expt
in 1/cm, micro eV!



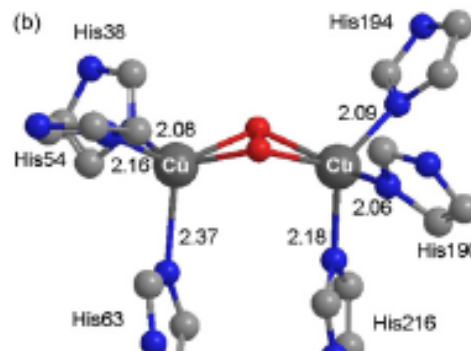
Very large

16 DNA base pairs

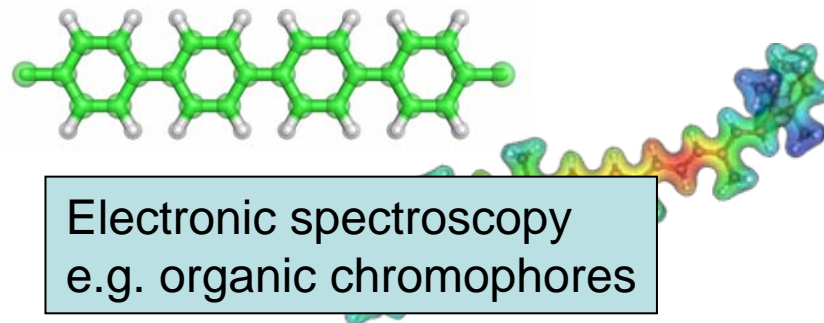
2nd order PT
total energy
1 month / 1 cpu

Strongly correlated molecular quantum chemistry

- e-e Coulomb energy \sim kinetic energy
- **Poor atomic overlap**
 - TM - d orbitals
 - stretched bonds
- **Excited states**
- **Low-dimensional electronic materials**

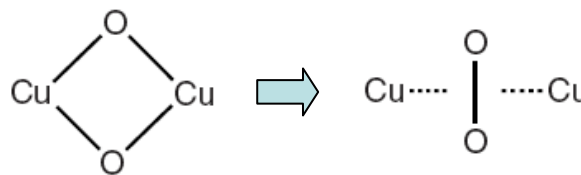
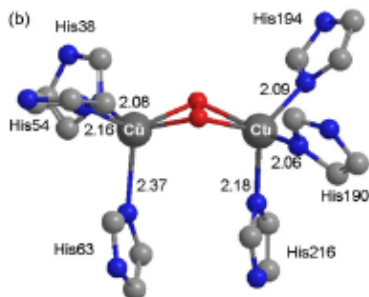


Making and breaking bonds:
e.g. TM catalysis

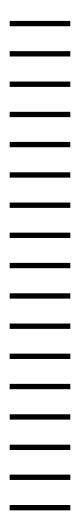


Electronic spectroscopy
e.g. organic chromophores

Strongly correlated QC in action: [Cu₂O₂]²⁺ isomerisation



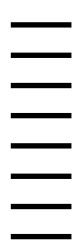
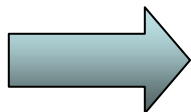
278 orbitals



canonical
transformation

(~ flow renormalisation)

new two-body (quartic) Hamiltonian



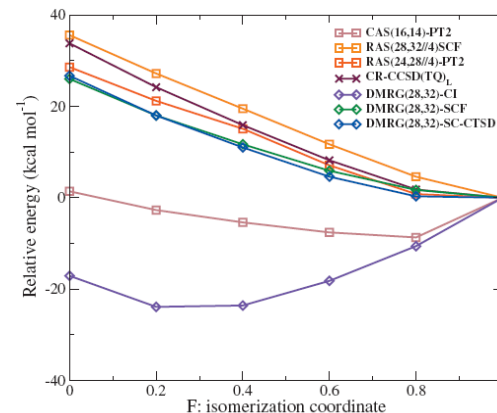
32 orbitals
Cu 3d/4d
O 2p/3p

ab-initio DMRG
(with all
interactions)

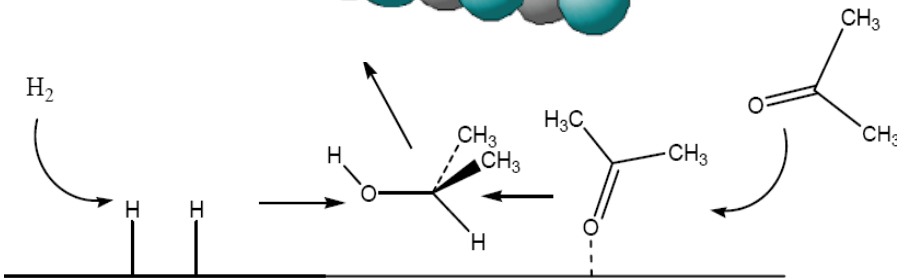
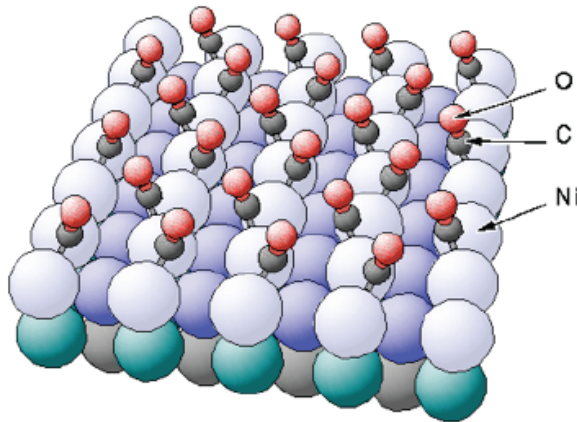
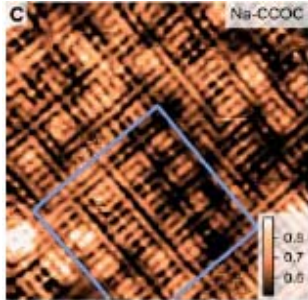


$$\overline{H} = H + [H, A] + \frac{3 \text{ body}}{2} [[H, A], A] + \frac{4 \text{ body}}{2} \dots$$

decoupling approximation



DMFT for quantum chemistry



- QC approaches correlation from local perspective
- DMFT provides natural bridge to extended systems
- Correlated solids
- **Molecules on surfaces**
- Spectroscopy and catalysis

Quantum chemistry for DMFT

- Experience with solvers
- (usually Hamiltonian formulation)
- Realistic interactions (with different philosophy)

Diagonalization

Flexible hierarchy to restrict Hilbert space e.g. RASCI

Resummed PT

Hierarchy to include more diagrams (TI PT) e.g. CC theory

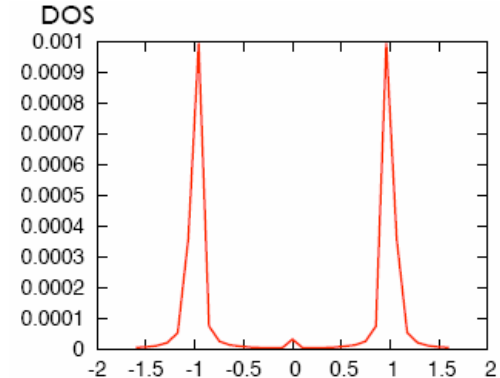
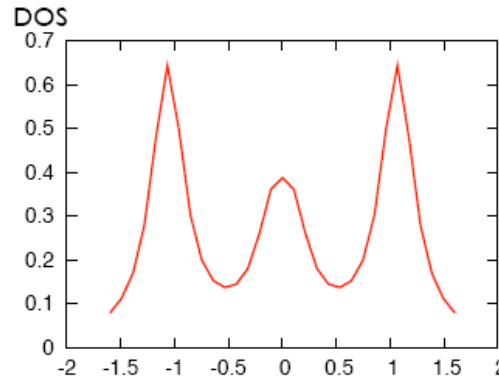
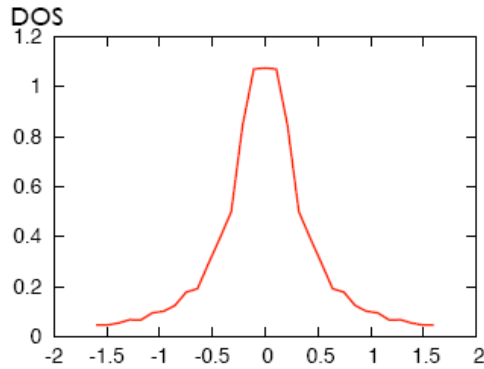
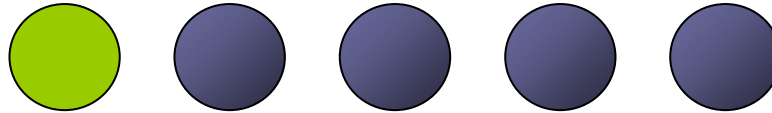
Variational wavefunctions e.g. MPS, Jastrow-det

Use with real interactions e.g. ab-initio DMRG

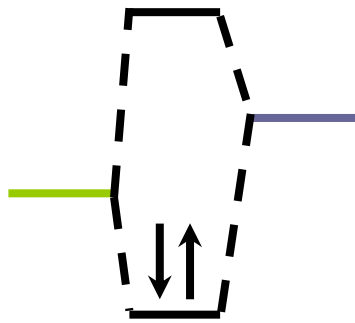


1. Restricted active space (diagonalisation) solver
2. Ab-initio DMFT, chemistry style

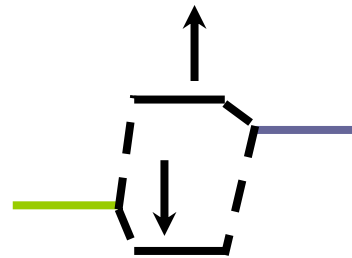
A simple QC solver



- exponential # configurations, but wavefunctions in 3 regimes are qualitatively simple



Hybridisation



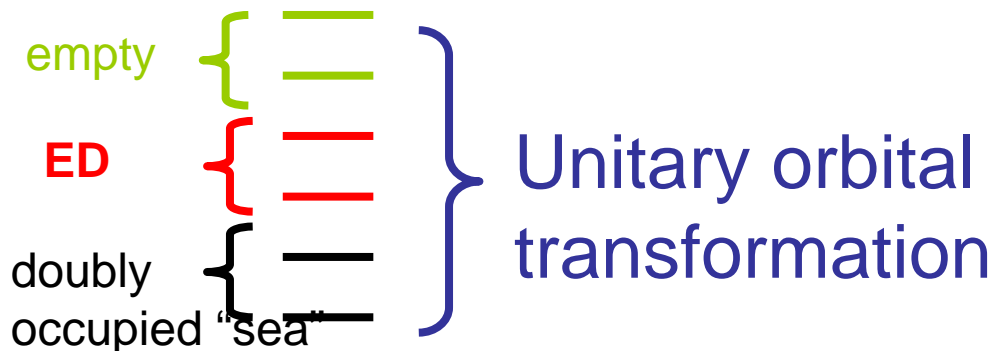
Partial hybridisation
AFM singlet



No hybridisation
AFM singlet

Active space

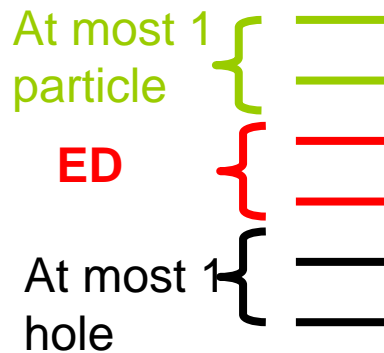
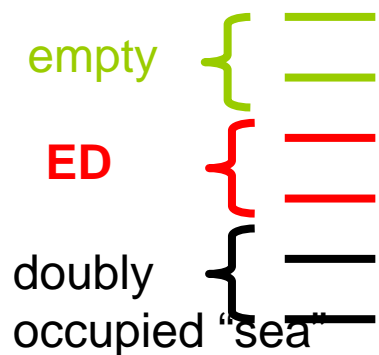
- “Optimally hybridized” orbitals (as function of t , U) -- **active space**
- Strong correlation method (e.g. ED) in small active space
- e.g. SIAM g.s. minimally described within 2 orbital active space



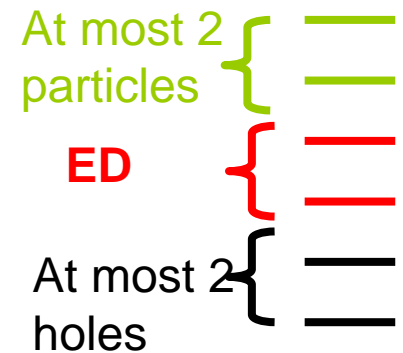
Optimise GS w.r.t.
1. Unitary transformation
2. Coefficients in ED

Restricted active space CI

- Although **external** orbitals less important, still want to include partially
- Restrict types of configurations



RASCIS

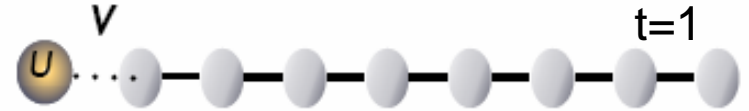


RASCISD

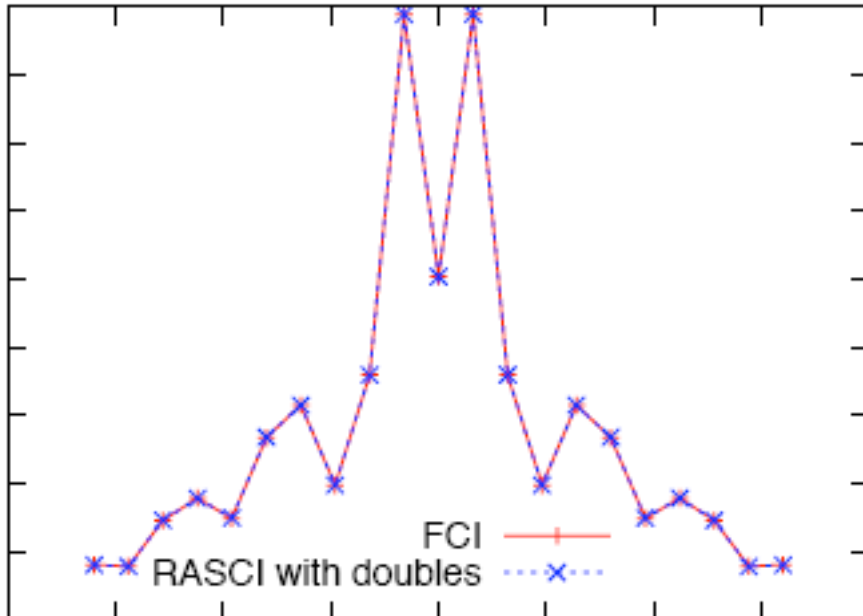
- Well-known flaws (extensivity) but cheap, cheerful, and systematically improvable

Single impurity Anderson model

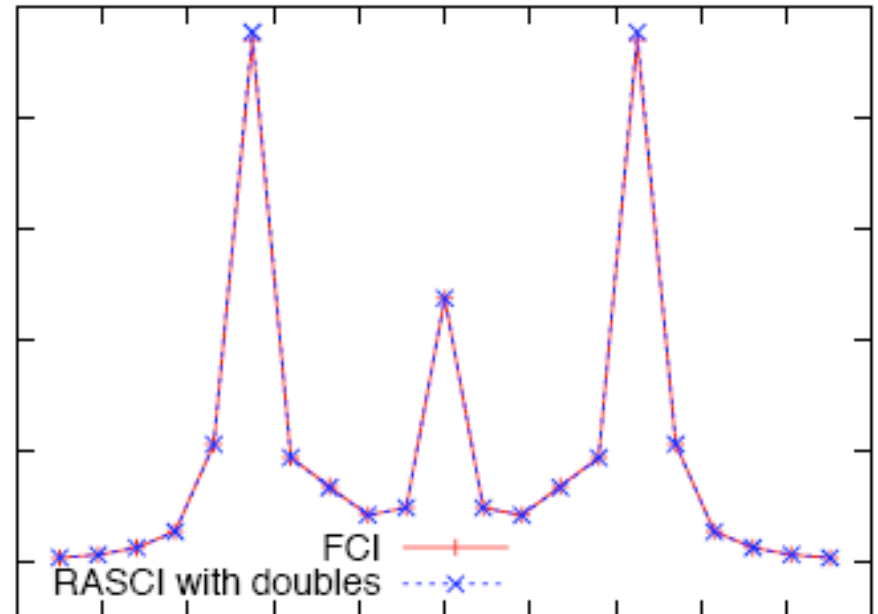
1 impurity, 9 bath orbitals



2 orbital active space; 2p/2h external space

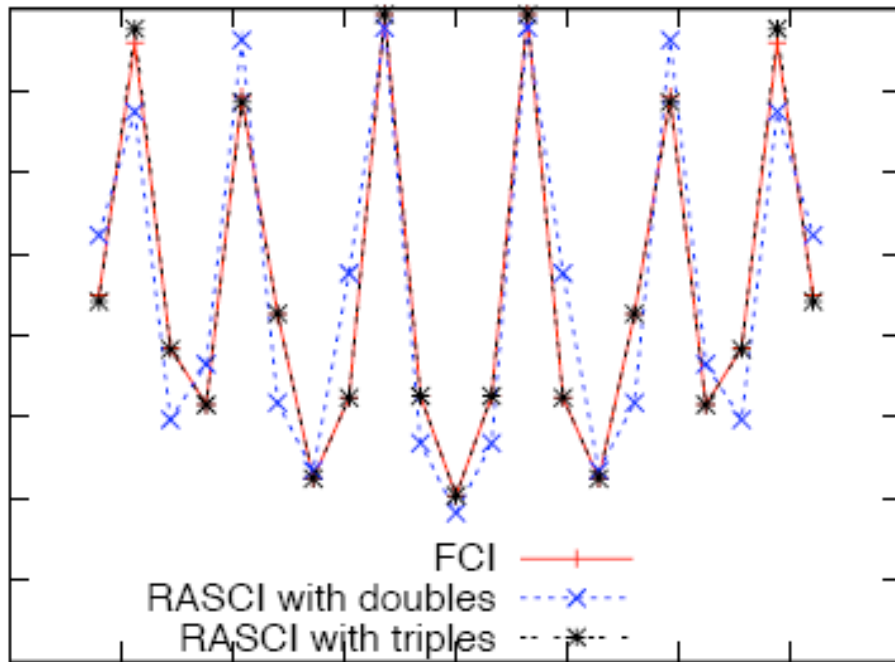


$U=1, v=1/2, t=1$

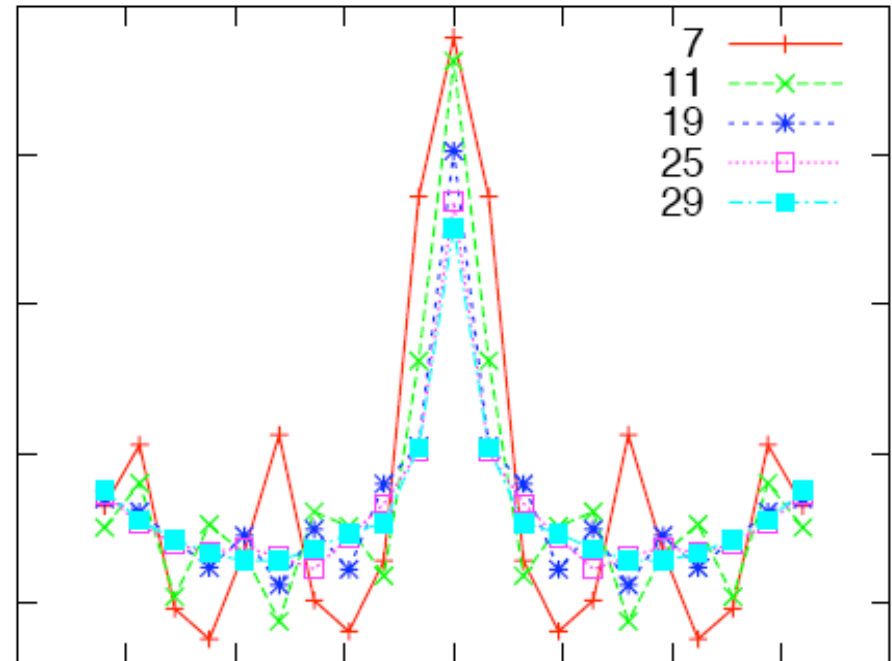


$U=4, v=1/2, t=1$

SIAM cont'd



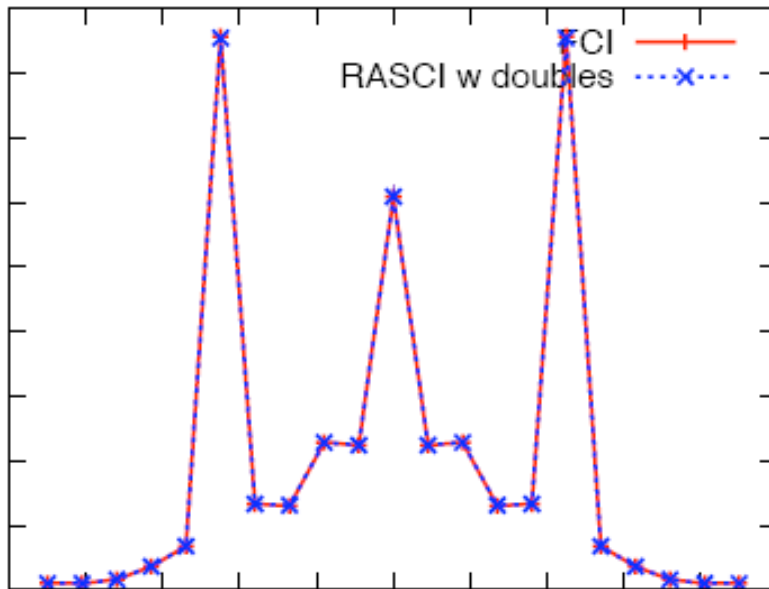
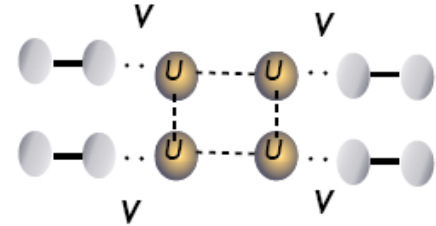
$U=8, v=2, t=1$



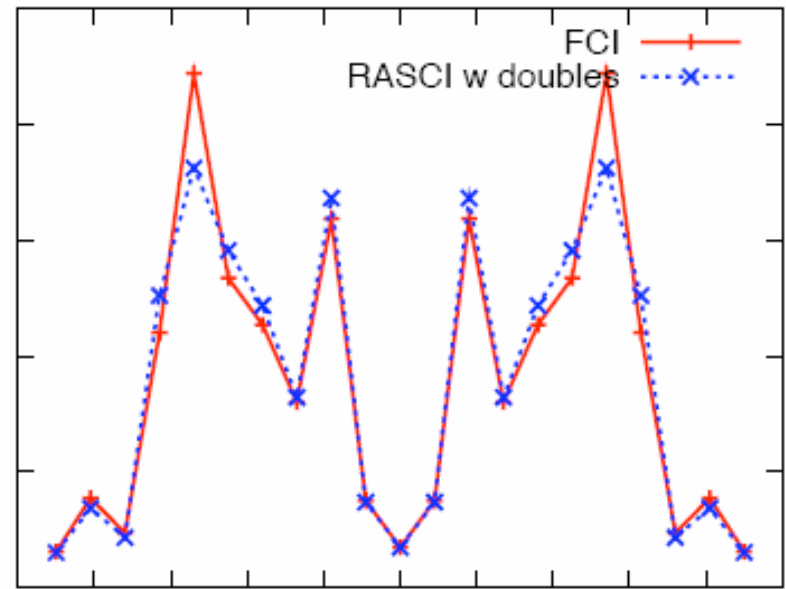
increasing
lattice size

Multi-impurity Anderson model

4 impurity, 8 bath orbitals

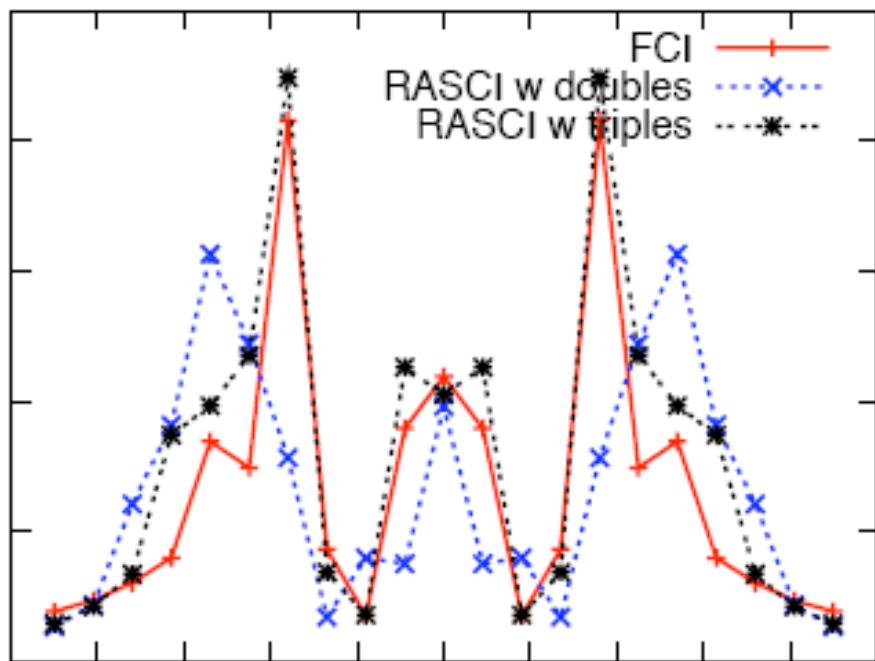


$U=1, v=1/2, t=1$

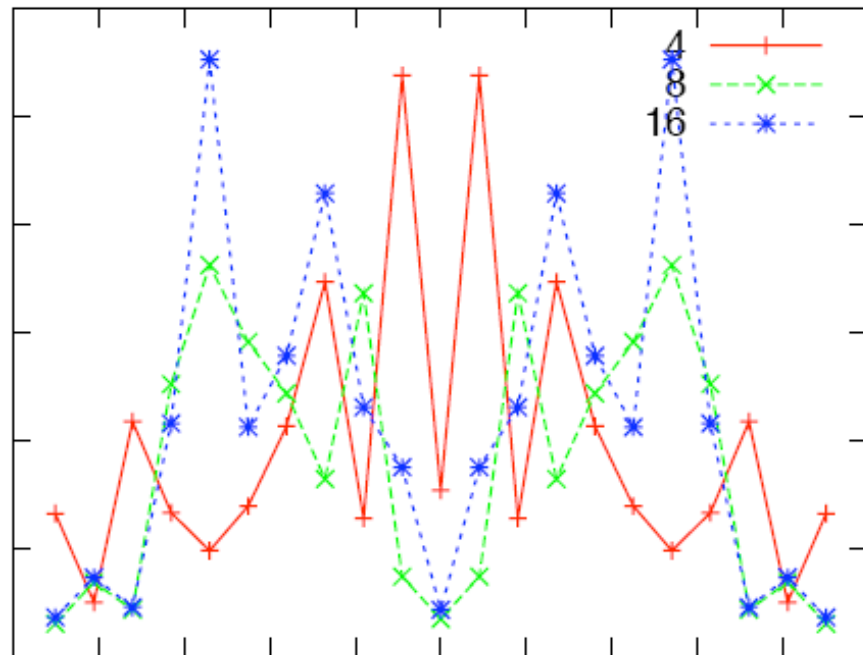


$U=4, v=1/2, t=1$

Multi-impurity cont'd

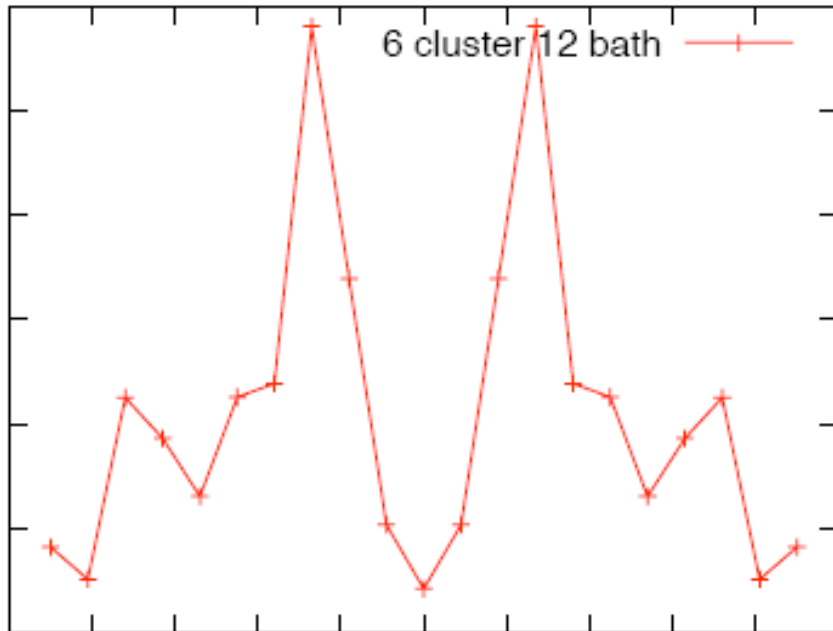


$U=8, v=2, t=1$

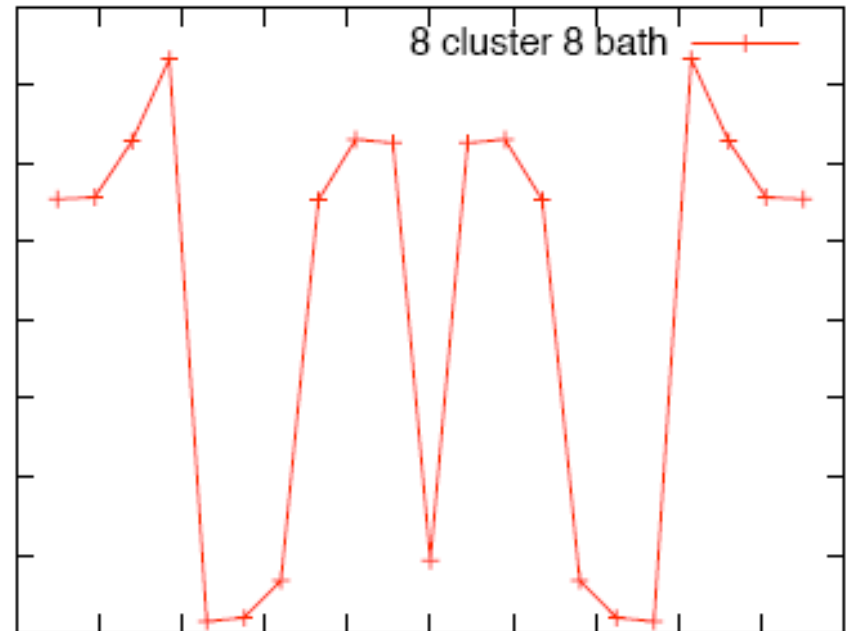


increasing
lattice size

Larger clusters



$U=4, v=0.5, t=1$



$U=8, v=0.5, t=1$

- What do these results mean?

Ab-initio QC DMFT

LDA+DMFT

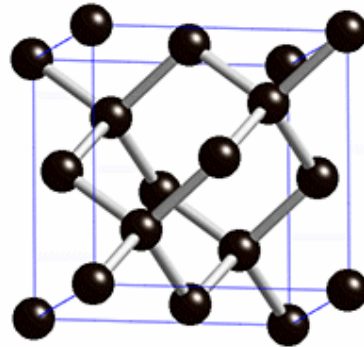
1. DMFT: local orbitals
2. LDA: all the rest
3. Fit screened interactions
4. Correct for double counting

QC+DMFT wishlist

1. Always diagrammatic controlled: **no DFT** **no double counting** **YES**
2. Local hamiltonian **v** **all** interactions **YES**
3. Local hamiltonian unscreened, screening via **v** **YES but v. small basis**
4. Long range Coulomb and screening **Only HF**

Diamond

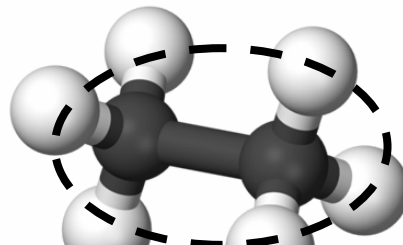
	Gap/eV
LDA	4.03
B3LYP	5.80
HF	12.17
GW	5.60



- Wide band-gap
- Correlations local

Stoll, PRB 46, 6700 "method of increments"

Cohesive energy LDA error 0.08 a.u.



X 4 0.130 a.u.

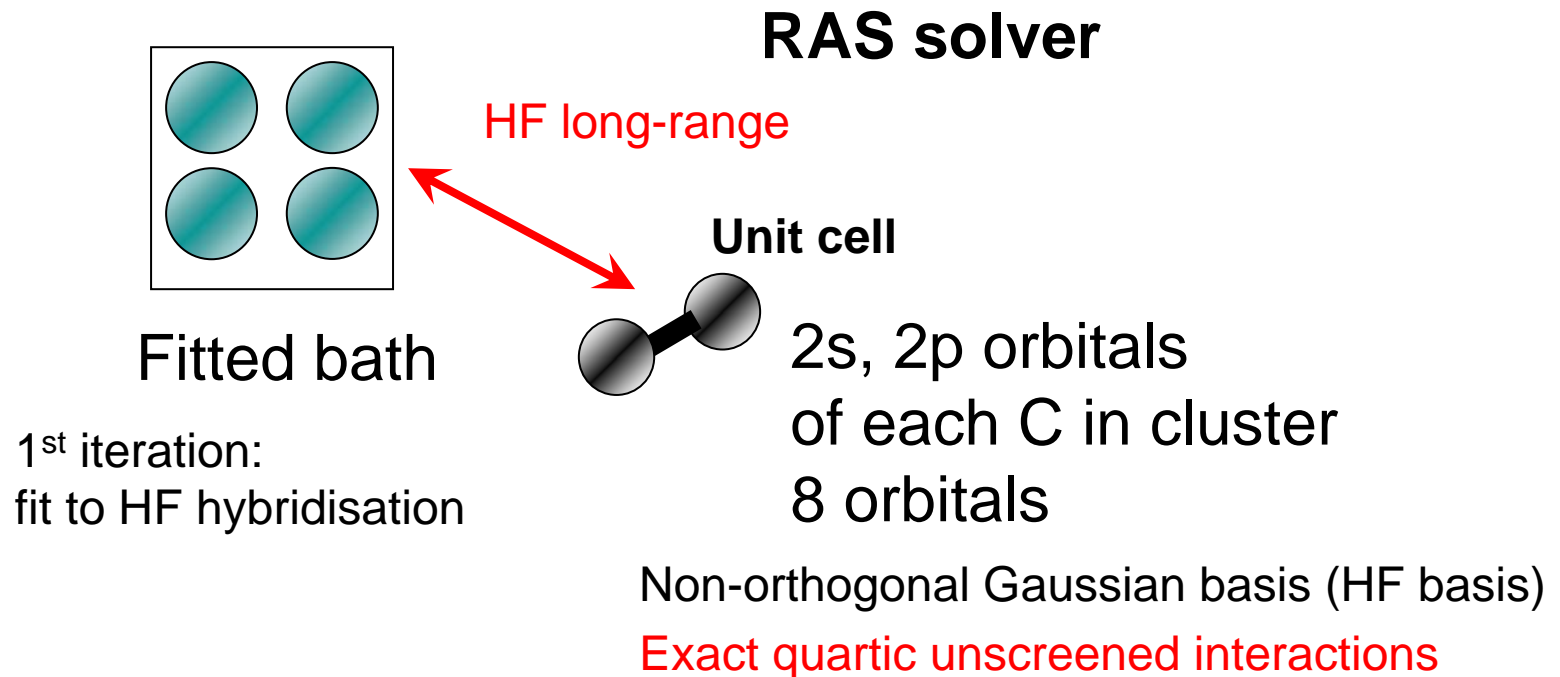
- **But challenging for DMFT?**
- **Multiorbital:** 2 C per cell, 8 valence orbitals
- **Strong hybridisation**

a.u.

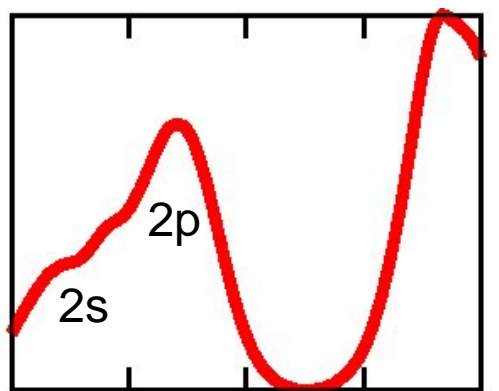
a.u.

Our setup

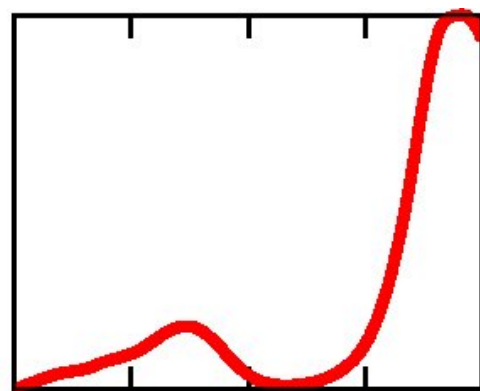
- Hamiltonian formulation (explicit bath)
- No self-consistency (yet)



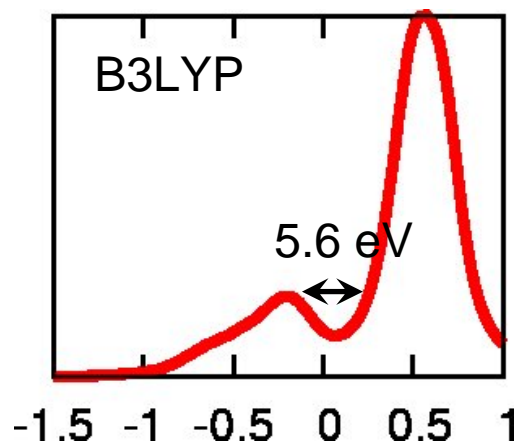
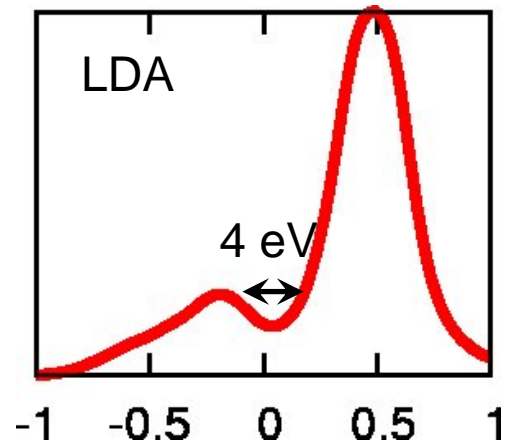
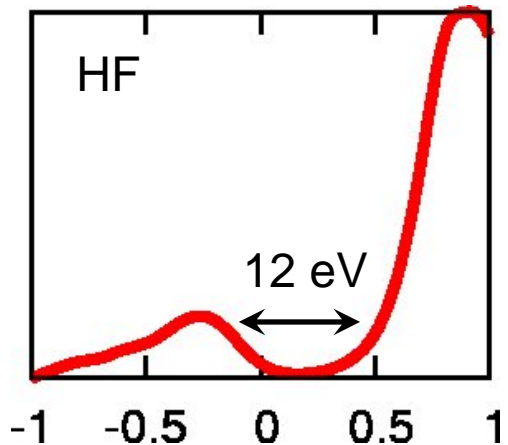
Diamond local spectral functions



$$-\frac{1}{\pi} \text{Im} \sum_k G_k^{-1} S_k$$



$$-\frac{1}{\pi} \text{Im} \sum_k G_k^{-1}$$



DMFT spectral functions

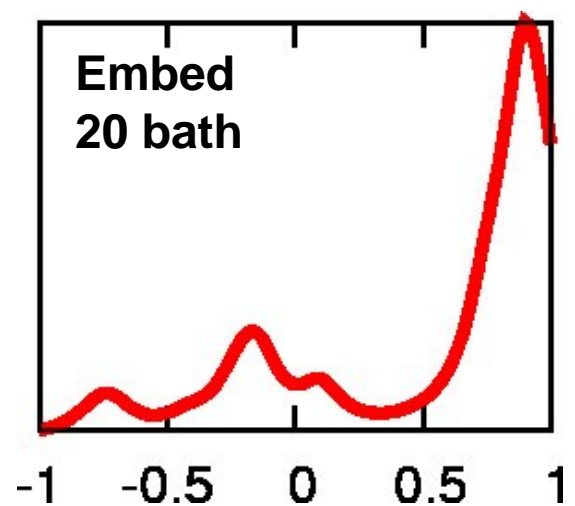
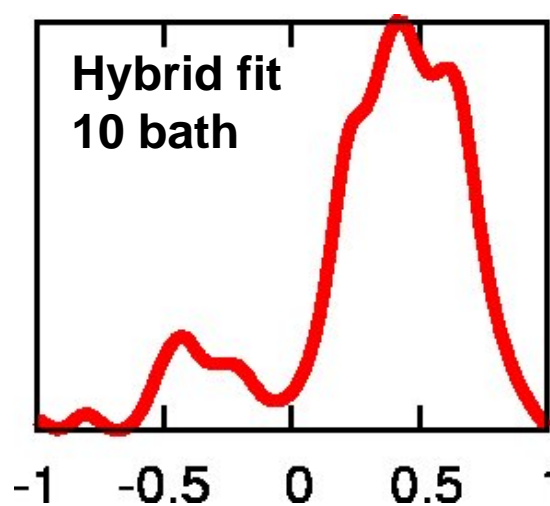
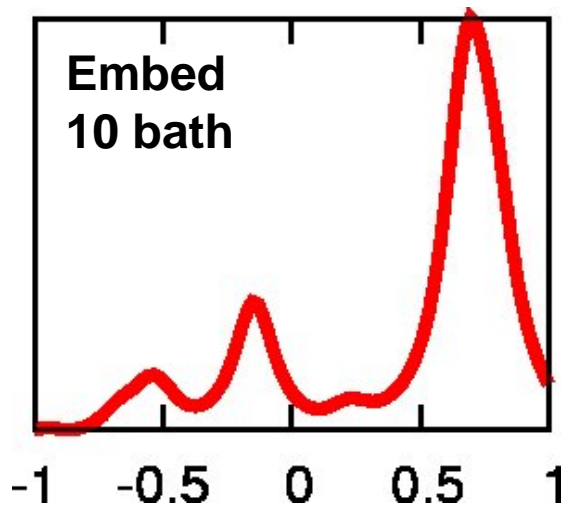
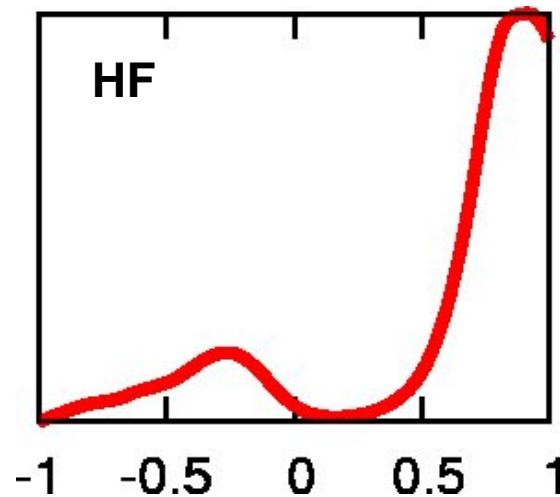
HF/STO-3G/8x8x8

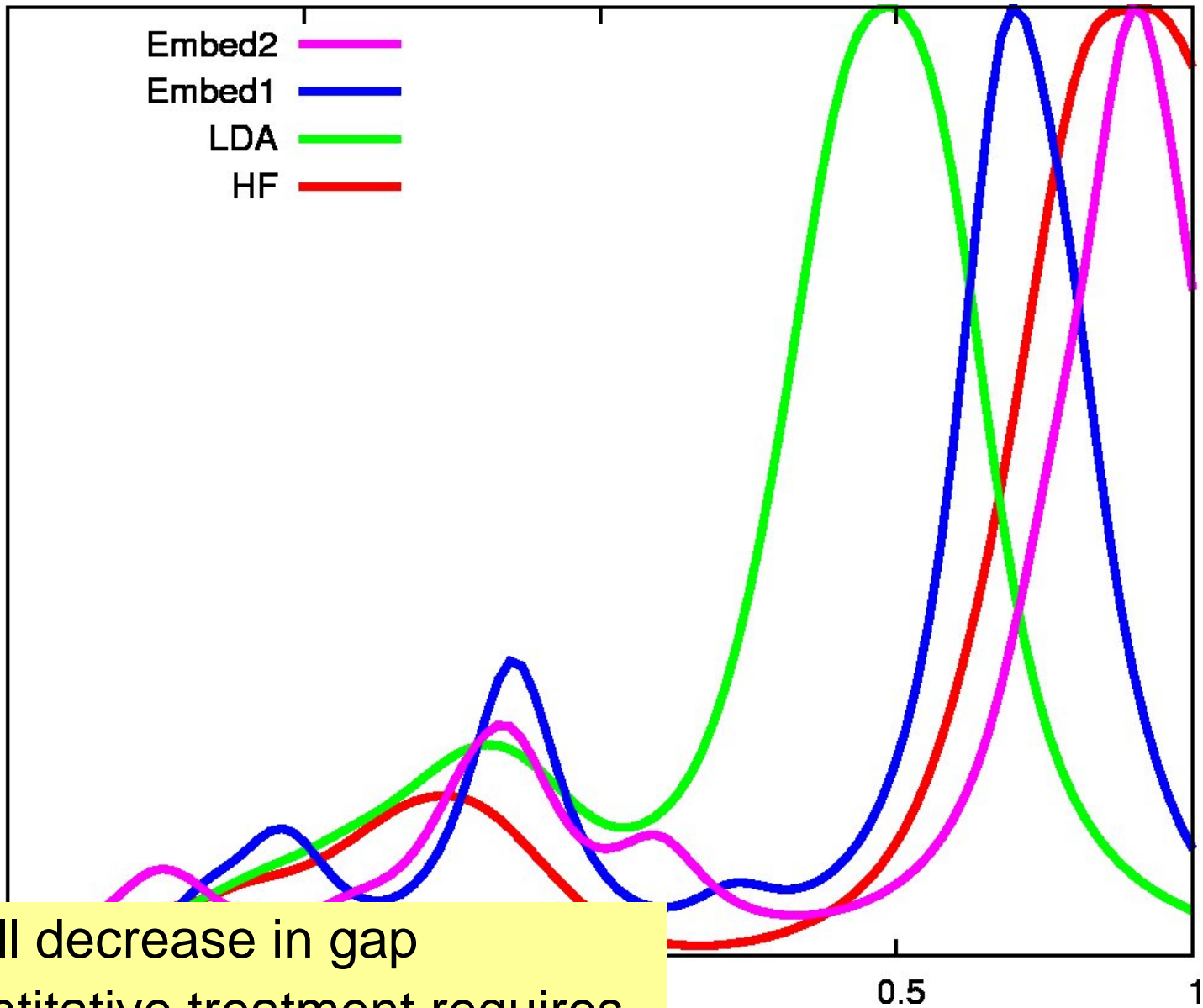
DMFT

CISD solver

Cluster: 2C unit cell

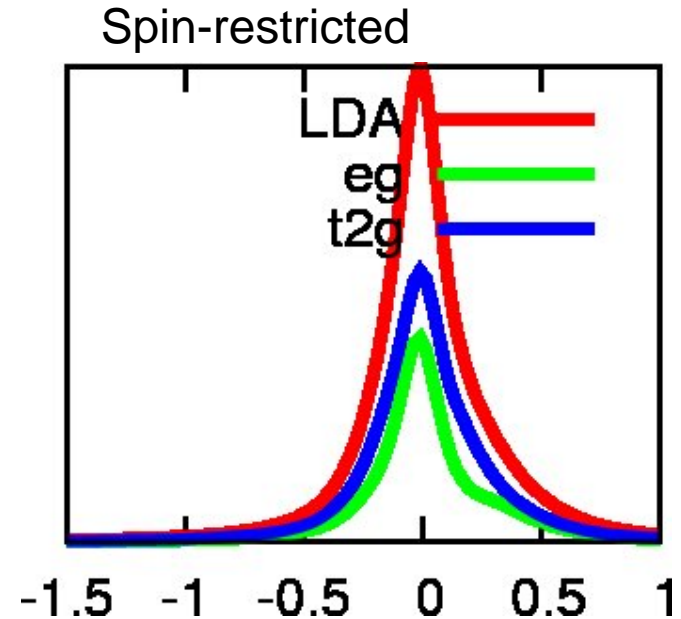
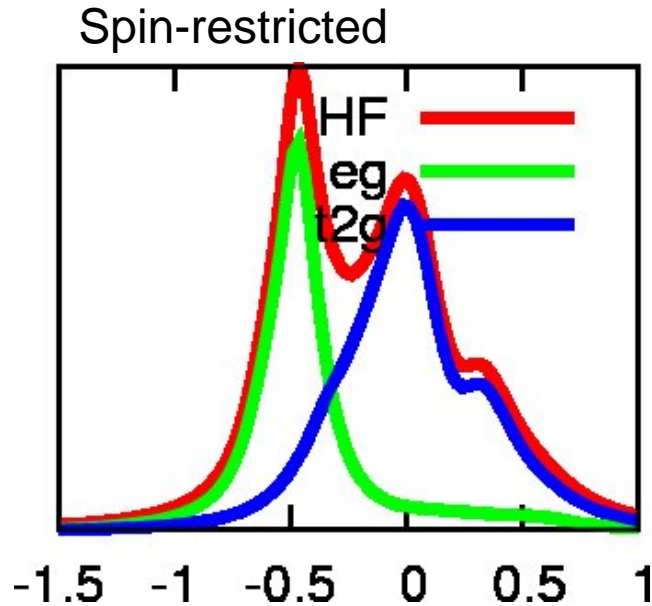
8 orbitals





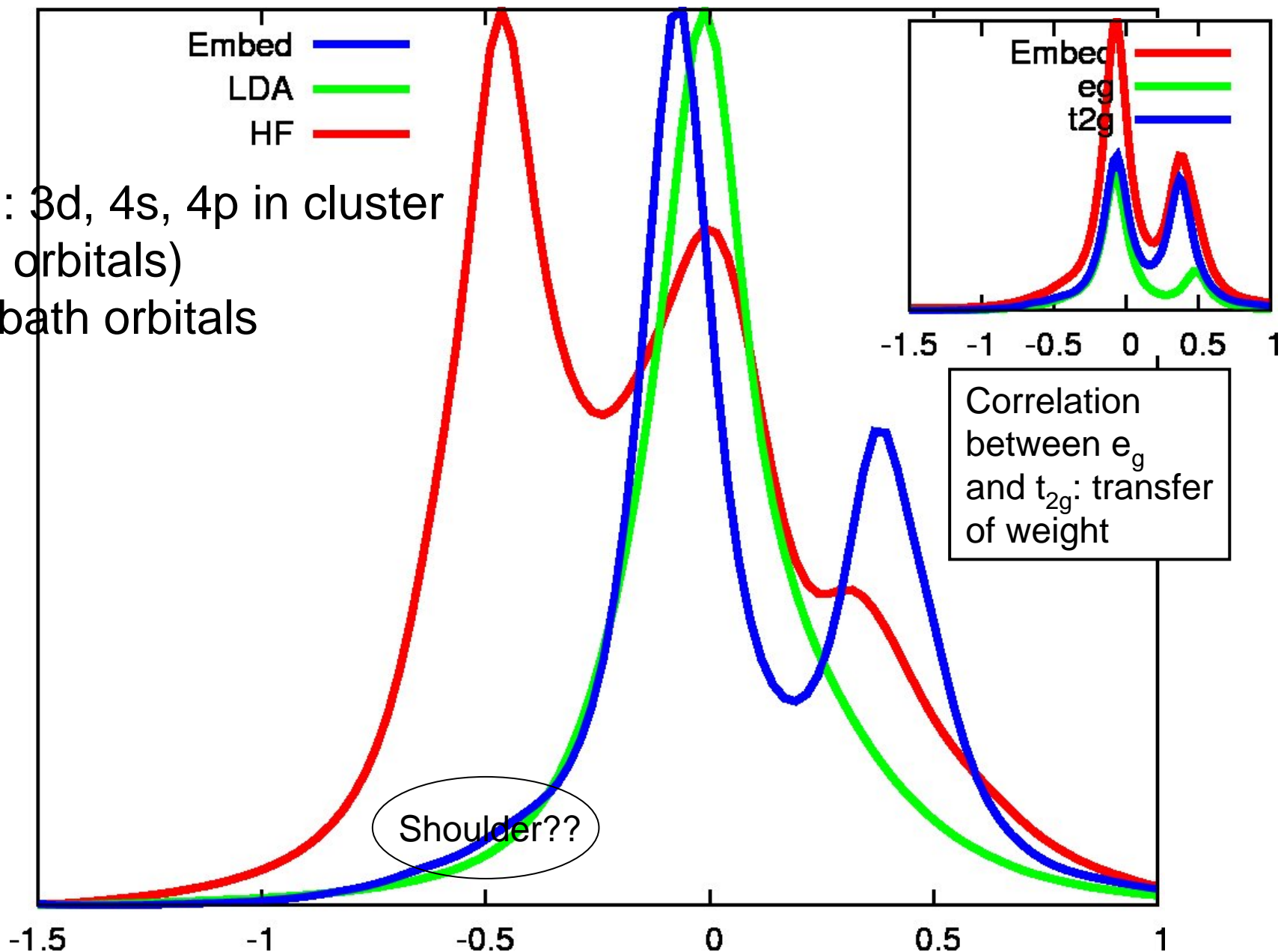
- Small decrease in gap
- Quantitative treatment requires larger basis in unit cell

FCC Nickel



- Classic problem for DMFT: 6eV satellite
- HF shows more basic problem: large splitting of t_{2g} and e_g !
- HF $U \sim 20$ eV, DMFT $U \sim 3$ eV

Ni: 3d, 4s, 4p in cluster
(9 orbitals)
5 bath orbitals



Conclusions

1. DMFT provides a natural way to extend QC techniques to extended problems
2. QC provides new solvers for DMFT and technology to handle realistic interactions
3. Look forward to fruitful exchange of ideas!