Weak interactions treated by DMC

Ryo Maezono

rmaezono@mac.com

School of Information Science,

Japan Advanced Institute of Science and Technology,
Ishikawa, Japan.

JAIST
JAPAN ADVANCED INSTITUTE OF SCIENCE AND TECHNOLOGY
1990

Collaborators

- Dr. Nguyen Thanh Cuong

  JAIST --> AIST (Tsukuba/National Institute)

  Initial/Trial WF preparations

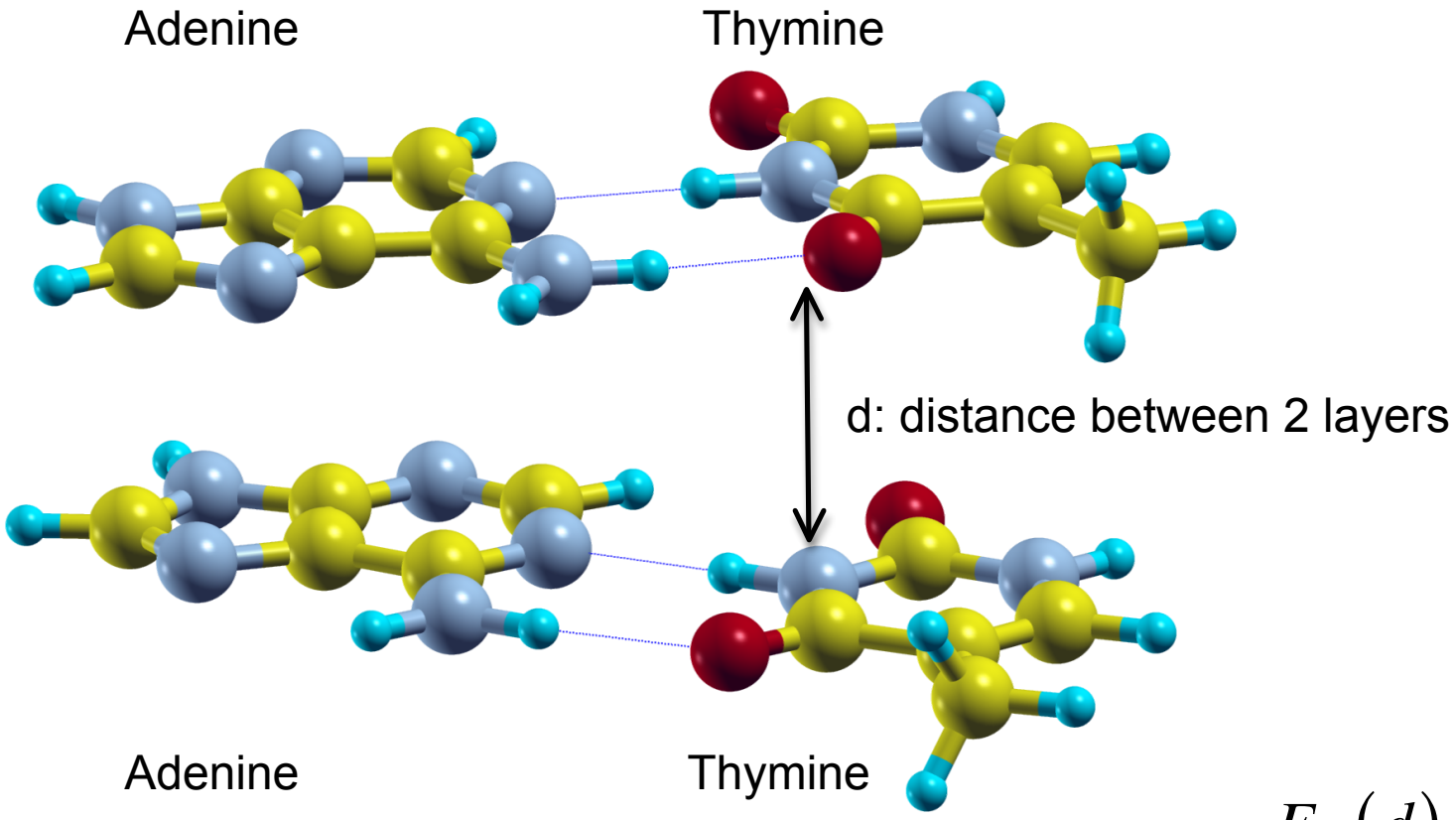
- Dr. John R. Trail

  JAIST

  Pseodo potentials

van der Waals Interaction between DNA Base Stacking

System


Adenine
Thymine
d: distance between 2 layers
Adenine
Thymine

$E_G(d)$

Background

R. Maezono, H. Watanabe, S. Tanaka, M.D. Towler and R.J. Needs, JPSJ 76, 064301 ('07).

FMO-QMC applied several years ago, but

(Glycine Trimer) it doesn't work well

$$E_{\text{total}} \approx \sum_{I=1}^{N} E_I + \sum_{I=2}^{N} \sum_{J=1}^{I-1} (E_{IJ} - [E_I + E_J])$$

$$= \sum E_{IJ} - (N-2) \sum_{I=1}^{N} E_I$$

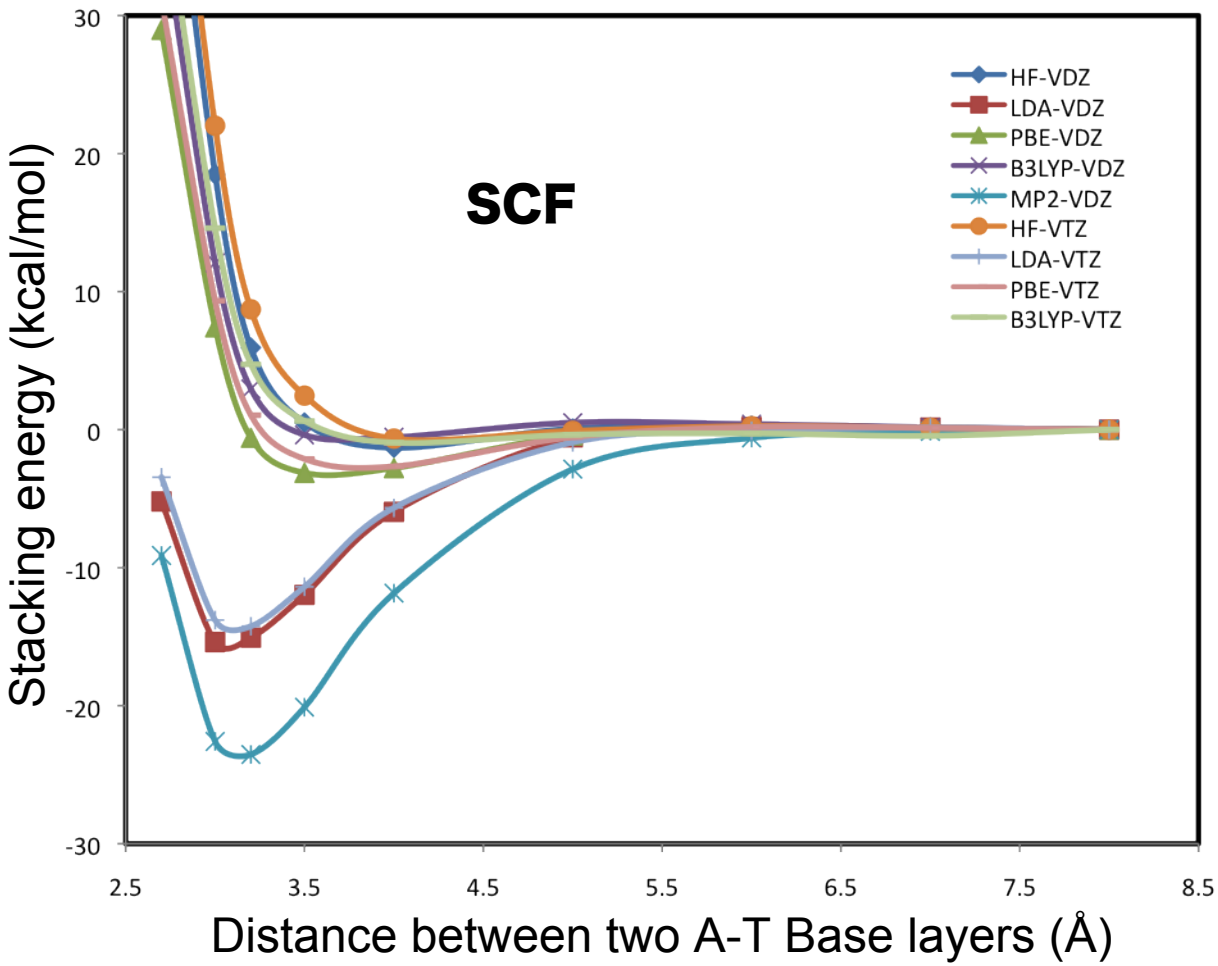
(Error-bar and bias get larger)

→ Whole calculation is possible, try it.

Computational Details

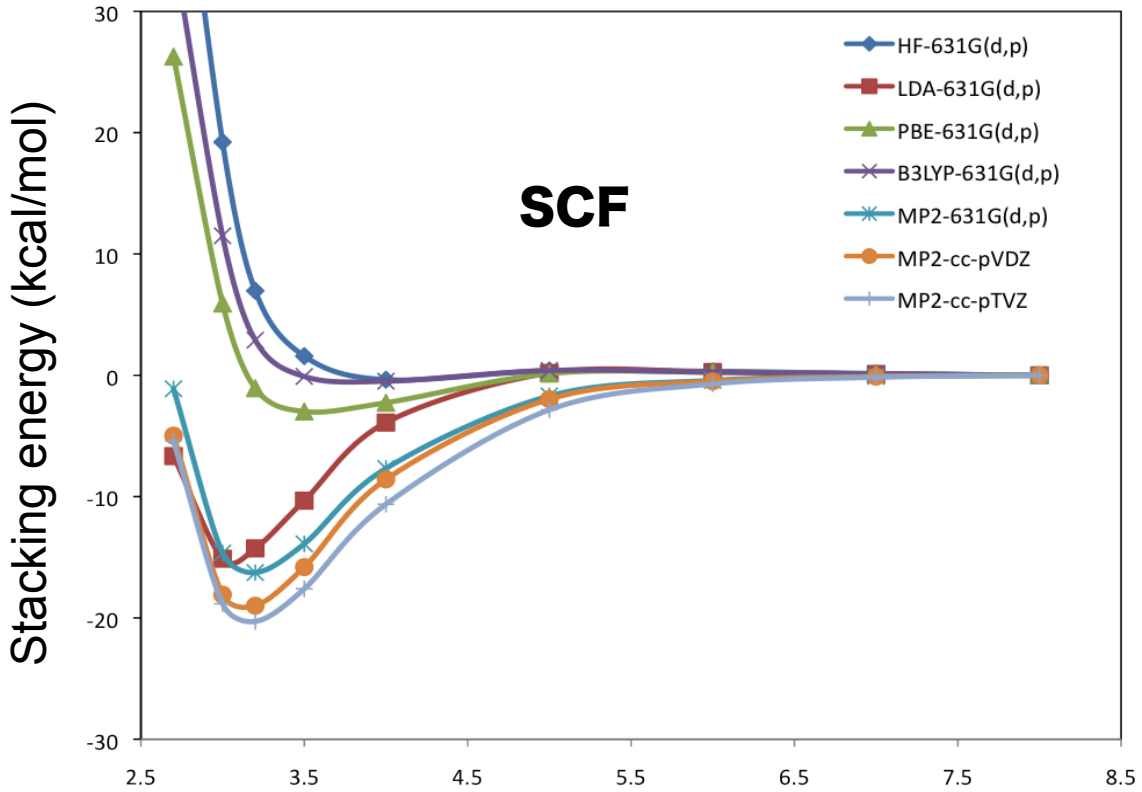
- Gaussian 03 software
- All electron
  - HF: 6-31G(d,p) basis set
  - DFT: LDA, PBE-PBE, B3LYP with 6-31G(d,p) basis set
  - MP2: 6-31G(d,p), cc-pVDZ, cc-pVTZ basis sets
- BFD Pseudo-potential with vdz, vtz basis sets
  - HF, DFT (LDA, PBE-PBE, B3LYP)
  - MP2 (only with vtz basis set)

BFD Pseudo potentials



Stacking energy = E(R)-E(R_0=8)

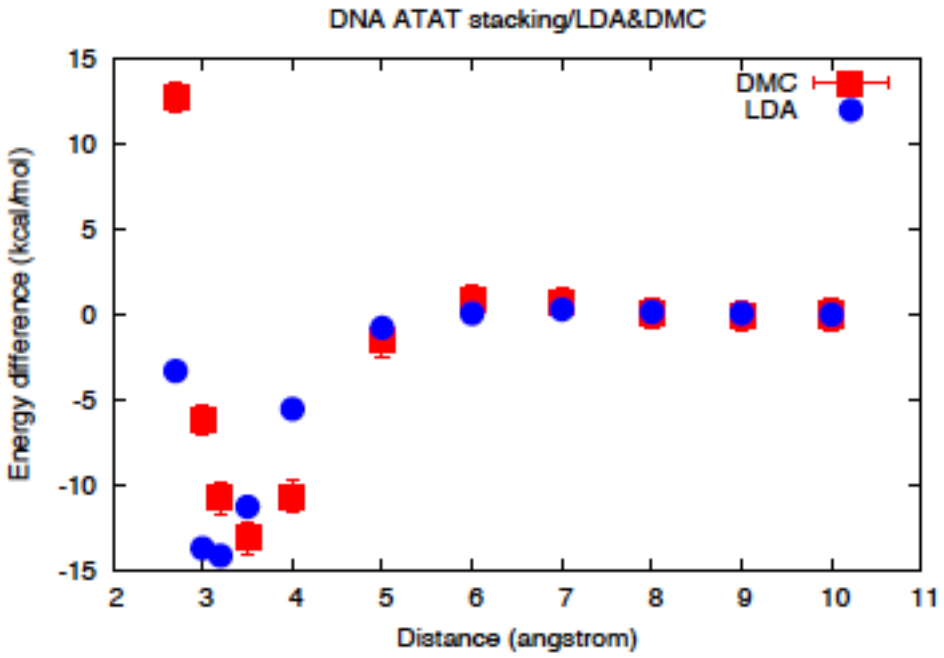
Results – All electron



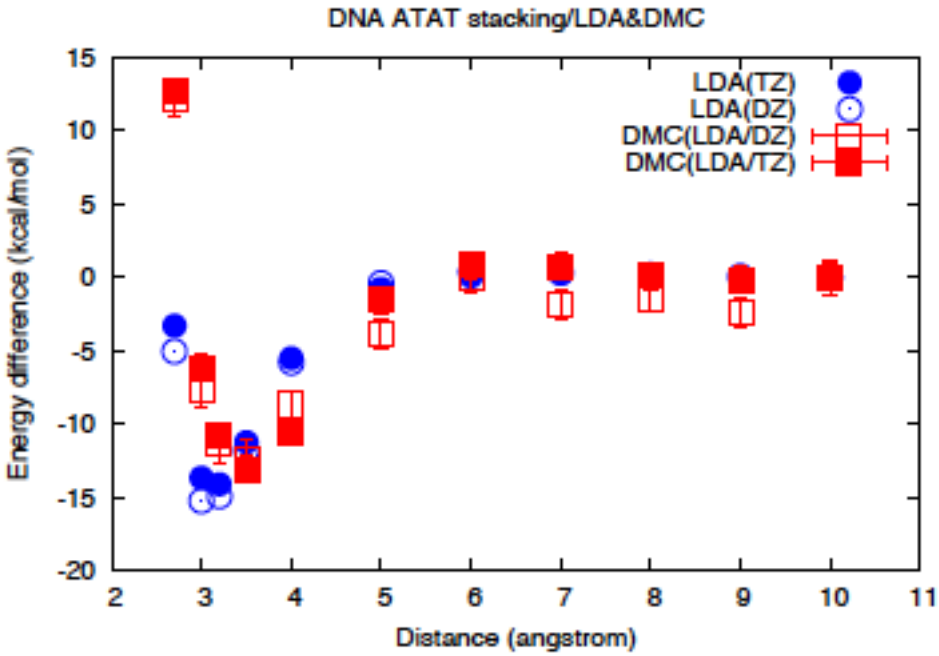
Distance between two A-T Base layers (Å)

Stacking energy = $E(R)-E(R_0=8)$

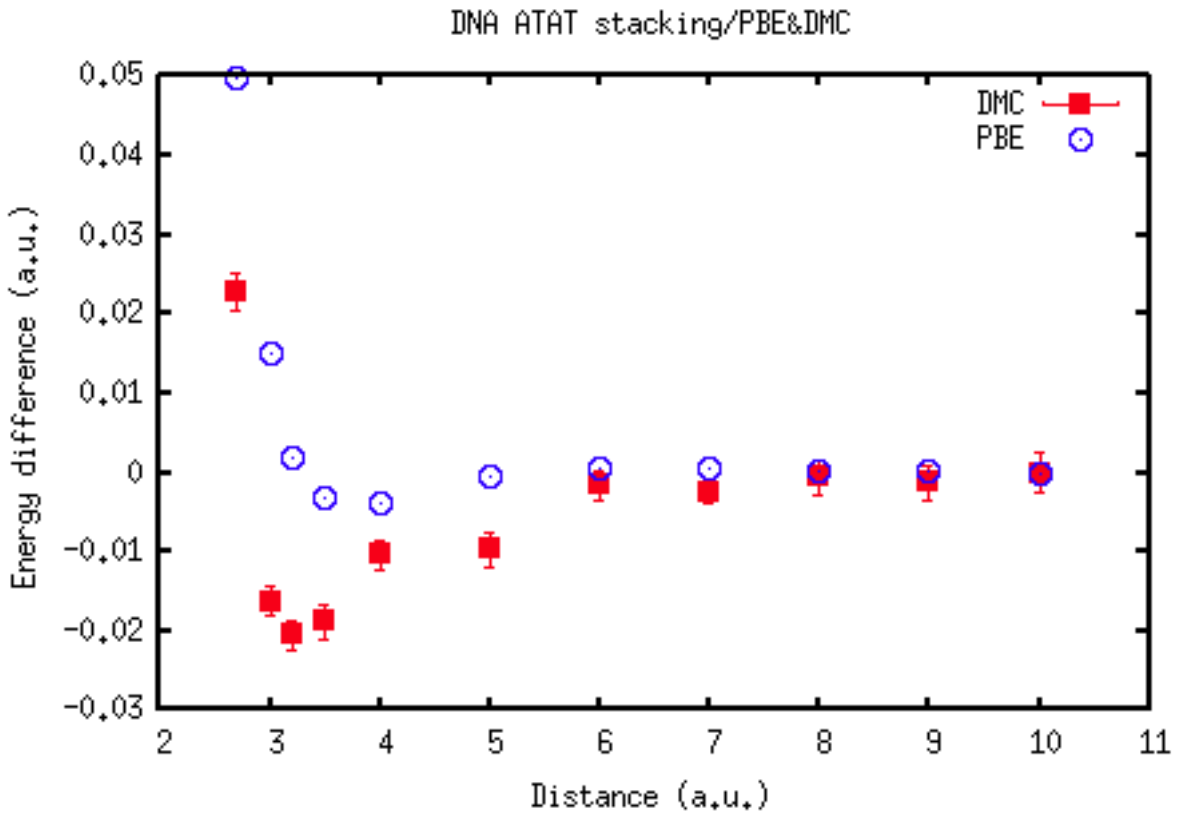
QMC/LDA trial nodes



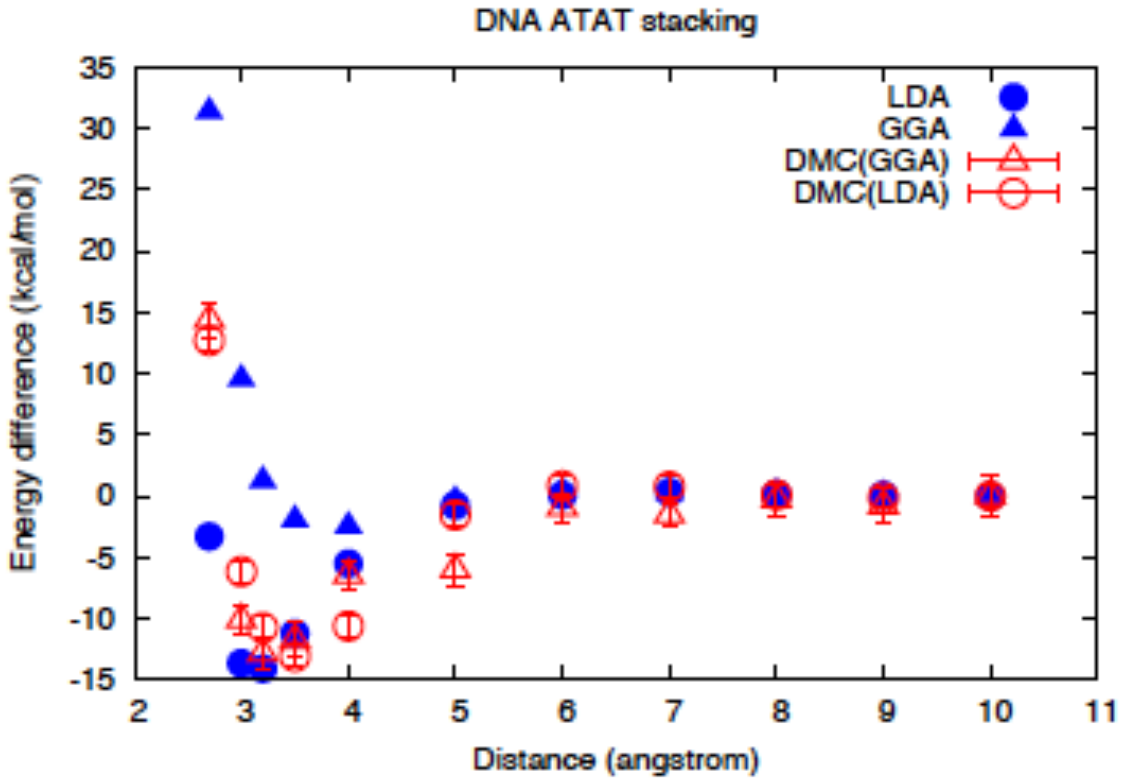
TZ and DZ


DNA ATAT stacking/LDA&DMC
Energy difference (kcal/mol)
Distance (angstrom)
LDA(TZ)
LDA(DZ)
DMC(LDA/DZ)
DMC(LDA/TZ)
15
10
5
0
-5
-10
-15
-20
2
3
4
5
6
7
8
9
10
11

QMC/GGA trial nodes

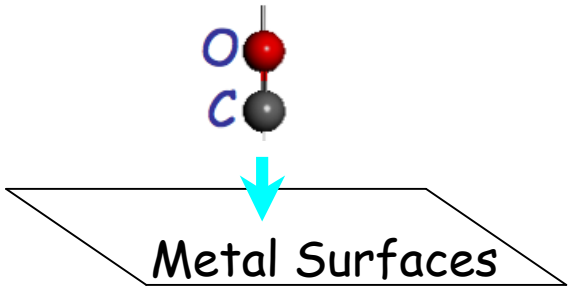


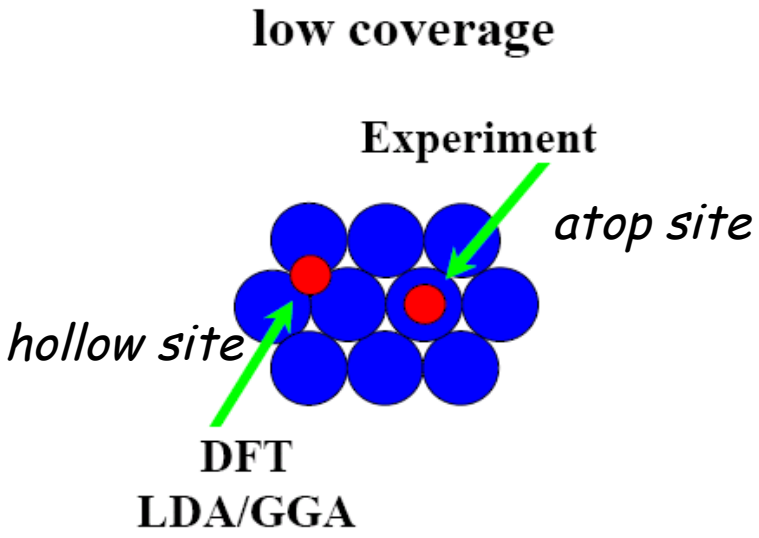
LDA & GGA


DNA ATAT stacking
Energy difference (kcal/mol)
Distance (angstrom)
LDA
GGA
DMC(GGA)
DMC(LDA)
35
30
25
20
15
10
5
0
-5
-10
-15
2
3
4
5
6
7
8
9
10
11

CO on Cu(111) surface

... Another example of weak interaction nature...





DFT fails to predict correct adsorption site

for several transition and nobel metal surfaces.

Discrepancies

Co	Ni	**Cu**
Rh	Pd	Ag
Ir	**Pt**	Au

J. Feibelman et.al., J. Phys. Chem. B **105** (2001) 4018

XC potentials

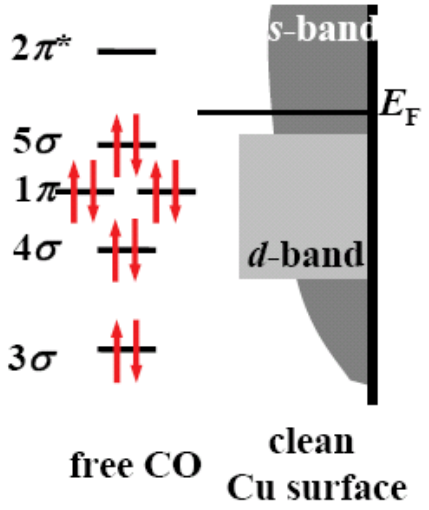
Non-local Exchange into account

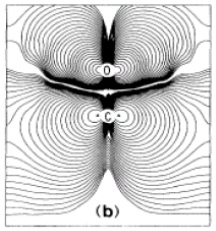
- **HSE** correct adsorption site for Cu, Rh
  but fail for Pt

- **B3LYP** correct adsorption site for Cu, Rh, Pt
  but not believed
  to give proper description for metallic systems

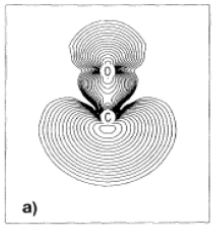
Electronic structure

CO ; Metal Surfaces





LUMO-2π*



HOMO-5σ

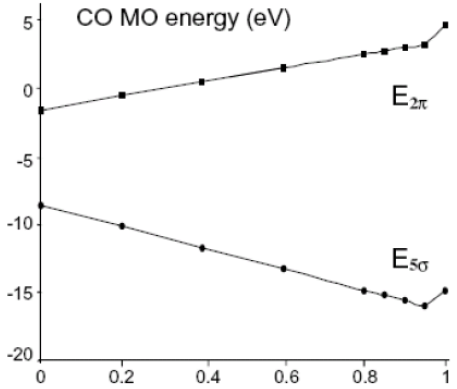
M. Gajdos et.al., Condens. Matter **16** (2004) 1141

Two channels of interaction

· $\pi^* - d$ (planer) ; strong / prefers HOLLOW

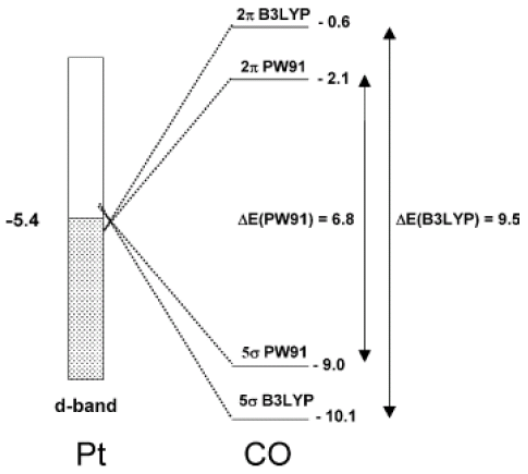
· $\sigma - d$ (z^2) ; weak, long-ranged / prefers TOP

XC dependence



The HOMO and LUMO energies of CO as a function of the amount of exact exchange in a hybrid functional.

Backdonation from the metal d states to 2π is most favoured with the PW91 functional -> a fcc site most stable one.



HOMO/LUMO GAP underestimated in LDA

→ [π*-d] channel pronounced to give Hollow site abs.

DFT challenges

Difficulty comes from the same origin...

Conventional XC being bad at

long-ranged weak interactions (vdW etc.)

--> Some DFT researchers are now trying with

XC designed for vdW.

QMC calculation

- Energy comparison

TOP site is properly predicted to be preferred?

- Charge density

How density is deformed as CO approaching to surface?

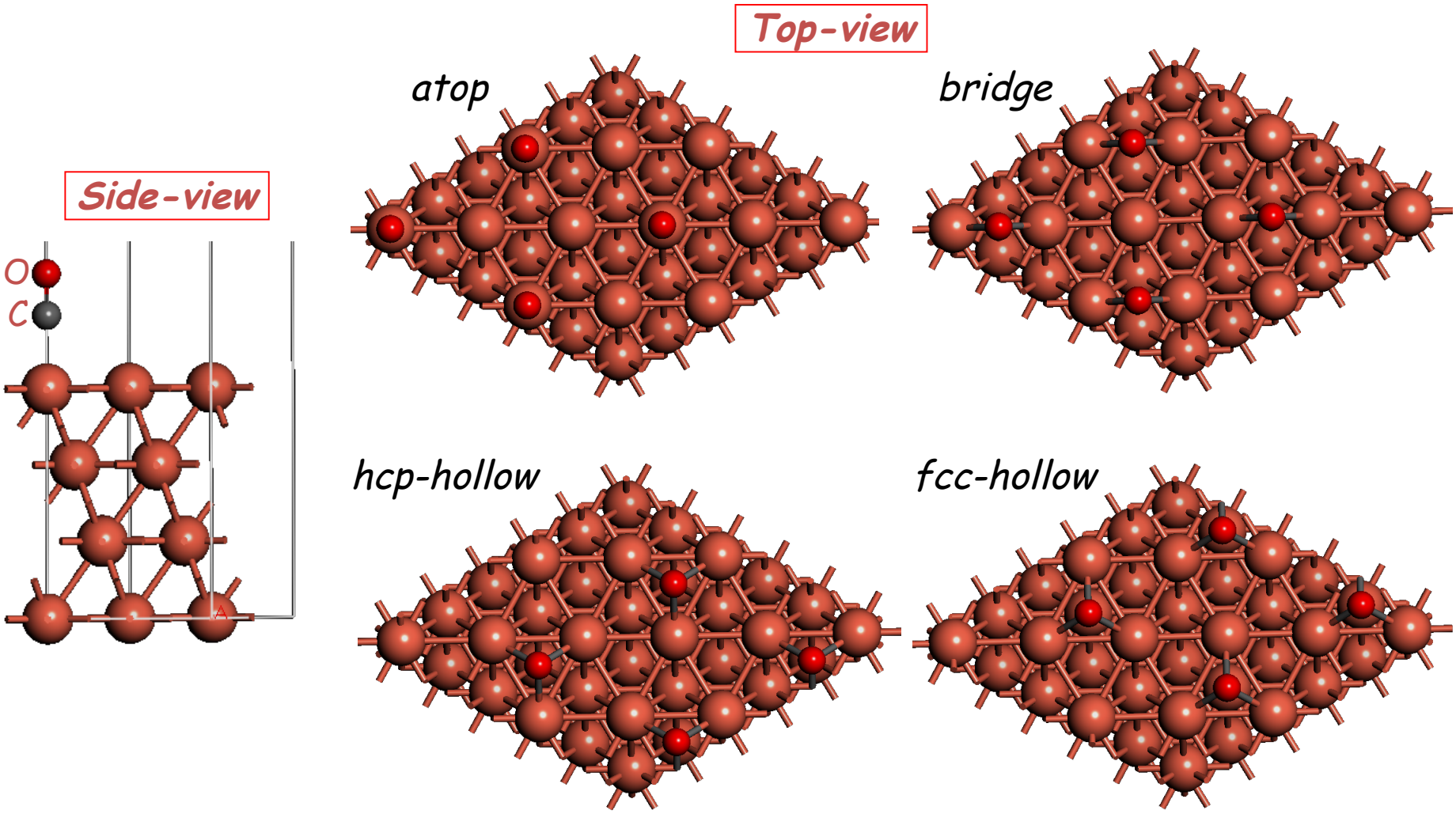
Comparison between DFT & QMC.

※ When FN-DMC reverses the result from initial guess DFT

what occurs on many-body WF?

(corresponding to HOMO-LUMO shift)

Absorption sites



Results so far

Energy (hartree/UnitCell)

	PBE-GGA	DMC (10k for stats.)
ATOP	-1817.8330	-1806.25(1)
BRIDGE	-1817.8335	-1806.24(1)
HOLLOW(HCP)	-1817.8341	-1806.23(1)
HOLLOW(FCC)	-1817.8345	-1806.20(1)

DFT for QMC trial WF

DFT with PWSCF code

- A slab model: Cu(111) -$\left(\sqrt{3}\times\sqrt{3}\right)-R30$
  with 4-layers (12 Cu atoms)

- PBE functional

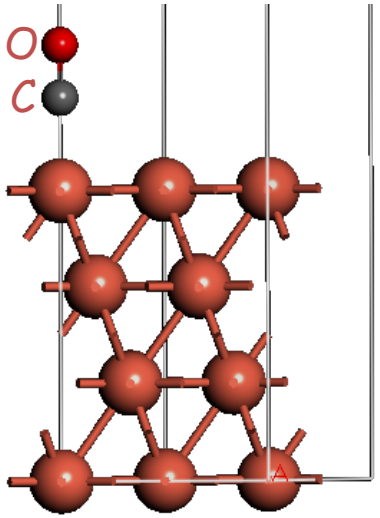
- Trail-Needs small core pseudo potential

  KB ghost --> s-local for Cu
  d-local for other

- E_{cutoff} = 250 Ry

- 2x2x1 *k*-mesh (shifted into L-pt)

  --> 816 electrons for QMC



Trail-Needs PP

Large Core for Cu: 11 electrons

E_{cutoff} (Ry)	E_{total}(Ry)
100	-1020.85296106
200	-1205.79813236
300	-1250.80554480
400	-1260.09948666
500	-1261.43336365
600	-1261.50965834
700	-1261.51931978
800	-1261.54014445

Small Core for Cu: 17 electrons

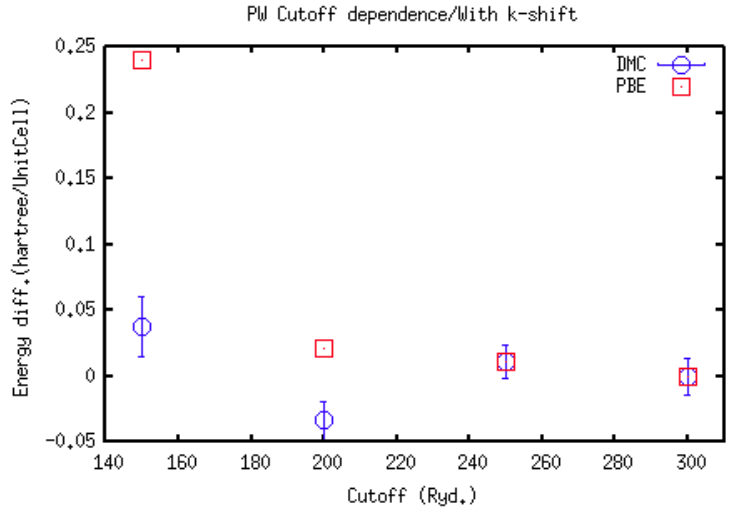
E_{cutoff} (Ry)	E_{total}(Ry)
100	-3569.17561370
200	-3592.34897908
300	-3592.39104215
400	-3592.40725712
500	-3592.40804109
600	-3592.40821798
700	-3592.40834096
800	-3592.40844810

Reducing Cutoff

500 Ryd. required for DFT to converge

--> Too large for QMC when converted to blip.

Less than 300 Ryd. is feasible



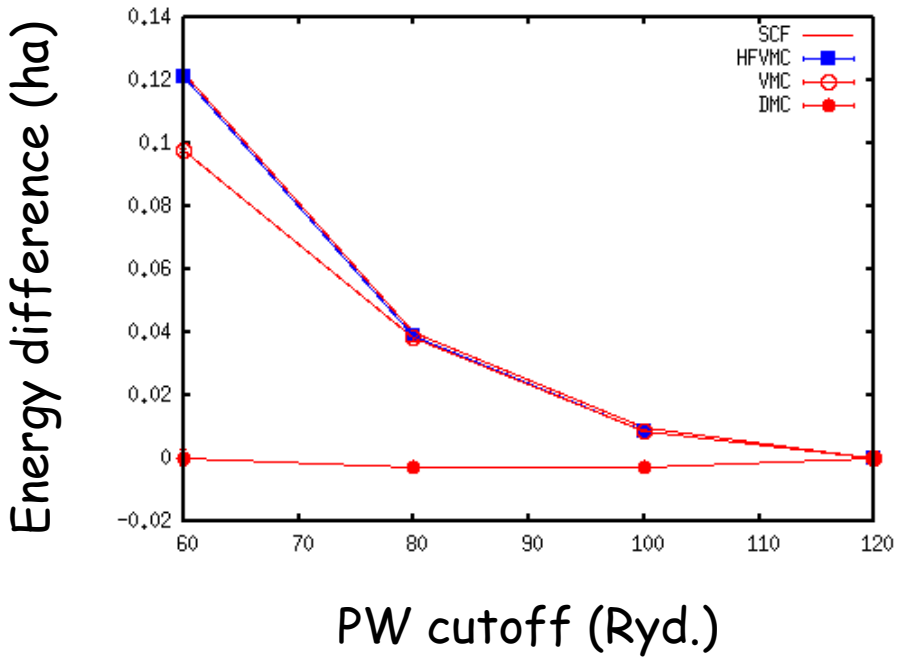
We can reduce it to 250 Ryd.

- E_{cutoff} = 250 Ry
- 2x2x1 *k*-mesh (shifted into L-pt)

--> 816 electrons for QMC

Reducing Cutoff

GaN442 case



QMC calculations

- Reducing cutoff

500 Ryd. required for DFT to converge

--> Too large for QMC feasible...

- T-move problem

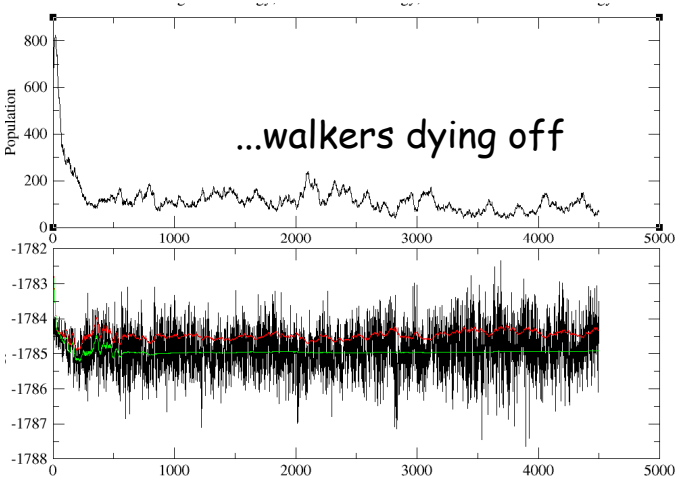
Turning off the scheme for stable pop. control.

- HPCF setup

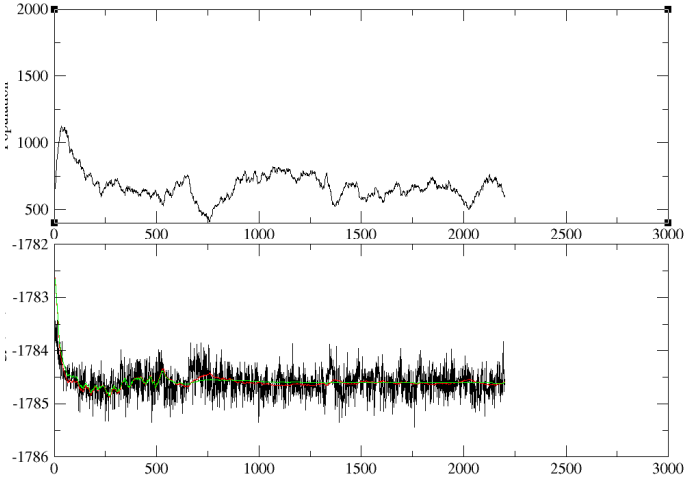
(# of bin files)/(MPI_IO)/(single prec.)

T-move problem

DMC for Cu substrate



with T-move



w/o T-move

Results so far

Energy (hartree/UnitCell)

	PBE-GGA	DMC (10k for stats.)
ATOP	-1817.8330	-1806.25(1)
BRIDGE	-1817.8335	-1806.24(1)
HOLLOW(HCP)	-1817.8341	-1806.23(1)
HOLLOW(FCC)	-1817.8345	-1806.20(1)

HPCF setup

PC cluster (100Ry./VMC/2nodes/8cores)

(# of bin files)/(MPI_IO)/(single prec.)

label	Time/block	CPU time	real time	Mem/CPU (MB)
1/F/F	14.3300	683.7300	3037.8542	2451
1/T/F	14.3101	652.3100	5247.8384	2451
2/F/F	62.4399	1168.9800	5050.0791	1225
2/T/F	62.0800	1370.0499	5585.0464	1225
8/F/F	74.3298	1975.8499	4694.2241	306
8/T/F	75.7101	1467.2600	1714.6511	306
8/T/T	75.0399	1365.8799	1564.9081	153

- MPI/IO quite effective with proper choice of '# of bin files"

  --> # of cores (not # of nodes) in PC cluster case

- Single prec. reduces file capacity but no CPU time.

HPCF setup

Cray XT5 (4nodes/32cores)

(# of bin files)/(MPI_IO)/(single prec.)

label	CPU time	real time
4/T/F	7236.7598	7237.3755
32/T/F	37691.1875	46593.4492

(100Ryd.)

Another test with 300 Ryd.

label	CPU time	real time
4/F/T	1625.4000	1674.2101
4/T/T	1775.5400	1822.2231

- MPI/IO not so effective in such well-designed HPCF.
- Proper choice of '# of bin files' = (# of nodes)

Future possible works

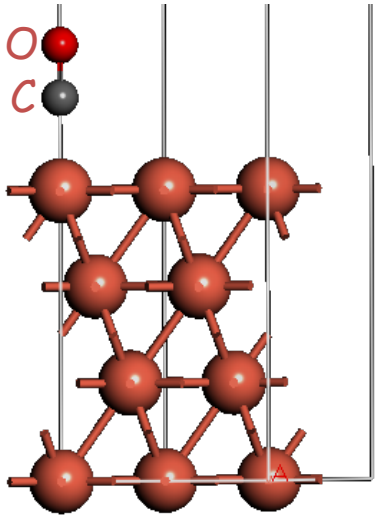
- CO on Ni-surface

  How induced spin polarization changes as CO approaches.

DFT calculation

DFT with PWSCF code

- A slab model: Cu(111) -$\left(\sqrt{3}\times\sqrt{3}\right)-R30$
  with 4-layers (12 Cu atoms)
- PBE functional
- PAW pseudopotential
- E_{cutoff} = 150 Ry
- 14×14 ×1 *k*-mesh



PAW-DFT results

Adsorption energy (eV) $E_{adsorption} = E_{CO-Cu(111)} - \left(E_{CO} + E_{Cu(111)}\right)$

Cu(111)	atop	bridge	hcp-hollow	fcc-hollow
4-Layers	-0.583 eV	-0.637 eV	-0.711 eV	-0.714 eV
7-Layers	-0.618 eV	-0.670 eV		

(※ Experiments : Atop -0.425 eV, -0.46 eV, -0.49 eV)

M. Gajdos et.al., Condens. Matter **16** (2004) 1141

- FCC-hollow predicted.
- Not enough converge; 4-layer to 7-layer but doesn't matter to the prediction
- Smaller difference between Atop & hollow than that of previous works

--> PAW works well