Quantum Monte Carlo in the Apuan Alps VII
28th July - 4th August 2012, Vallico Sotto, Tuscany, Italy

Materials Simulations Using Quantum Monte Carlo

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Cheng Ching (NCKU), Mei-Yin Chou (IAMS)
Pablo, Neil Drummond, Richard Needs (Cambridge)

Outline

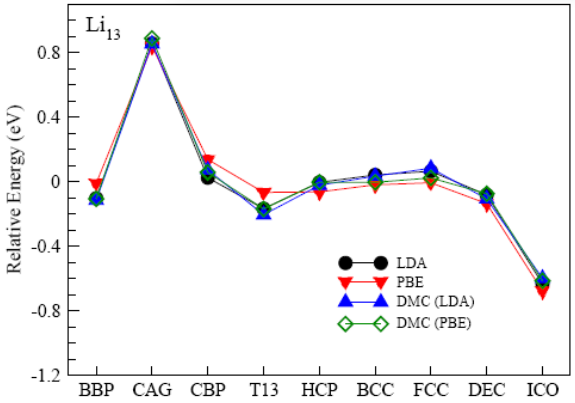
- *Motivation? Why using QMC?*
- *Material Simulations using QMC*
  - ✓ ***covalent and metallic clusters***
  - ✓ ***band gaps of TiO_2, MgO, NaCl***
  - ✓ ***surface adsorption on graphene & Al(100)***
  - ✓ ***interlayer binding of two BN sheets***
  - ✓ ***surface energy: $\Delta S(DMC) > \Delta S(LDA) > \Delta S(PBE)$***
  - ✓ ***O, OH & H_2O adsorption on surfaces***
  - ✓ ***CO adsorption on late TM (111) surfaces***

For Matertal Simulations:

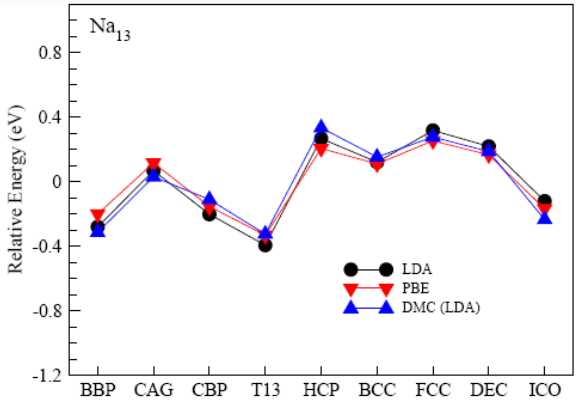
Density Functional Theory is a very powerful tool when the system is

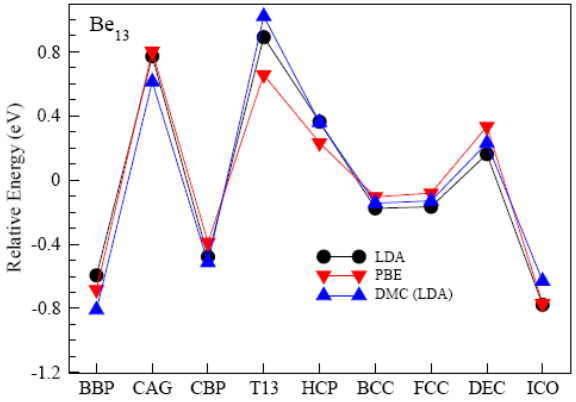
" well defined "

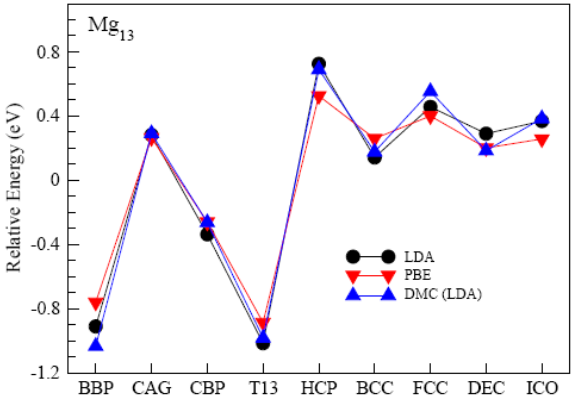
Simple metal Clusters

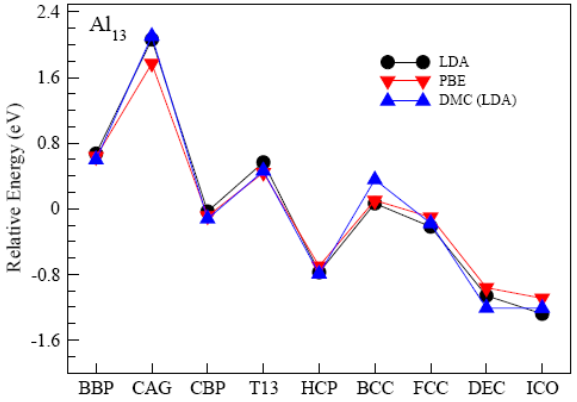


DFT is reliable in predicting the relative energy of simple metal clusters!





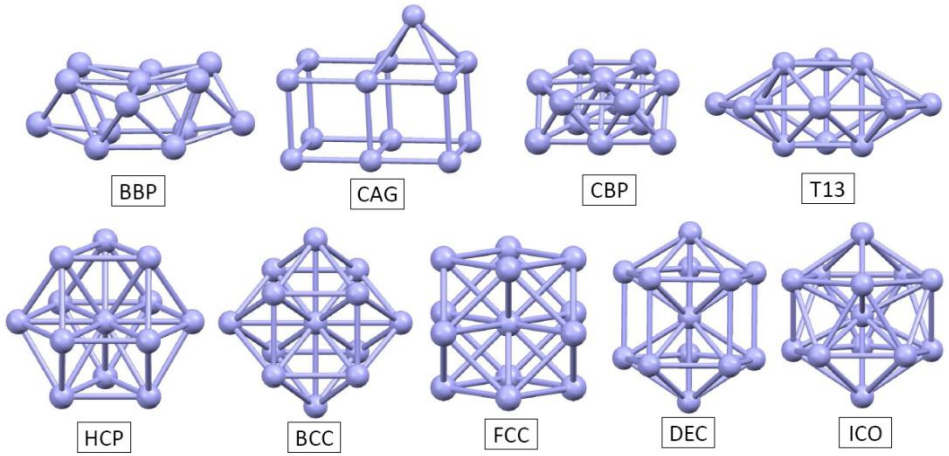




$$\cos\theta = \frac{\vec{\mathfrak{D}}^{\mathrm{DFT}} \cdot \vec{\mathfrak{D}}^{\mathrm{DMC}}}{|\vec{\mathfrak{D}}^{\mathrm{DFT}}||\vec{\mathfrak{D}}^{\mathrm{DMC}}|}$$

$$L = \frac{|\vec{\mathfrak{D}}^{\mathrm{DFT}}|}{|\vec{\mathfrak{D}}^{\mathrm{DMC}}|}$$

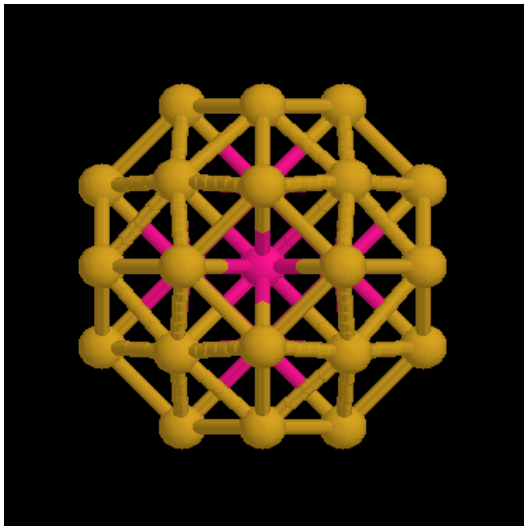
	(θ)		L	
Cluster	LDA	PBE	LDA	PBE
Li_{13}	4.25	12.23	1.02	1.02
Na_{13}	15.23	15.59	1.01	0.83
Be_{13}	11.57	16.77	0.97	1.09
Mg_{13}	6.76	7.87	0.98	0.81
Al_{13}	7.27	6.00	0.98	0.81

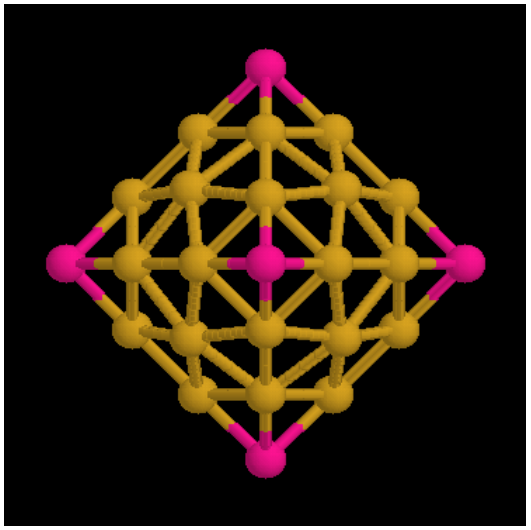


The CORRECT choice of Exchange-Correlation Approximation is a "BIG" issue in DFT !

DFT is very great, why bother using Quantum Monte Carlo ?

Which Au_{38} is a more stable structure ?

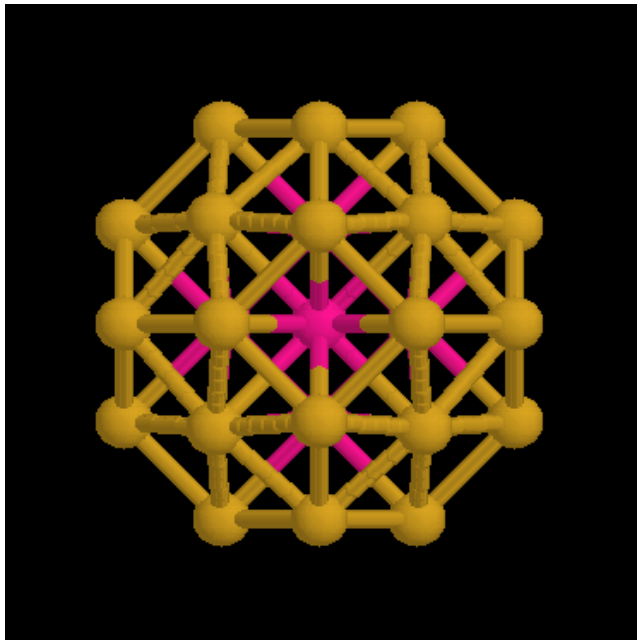


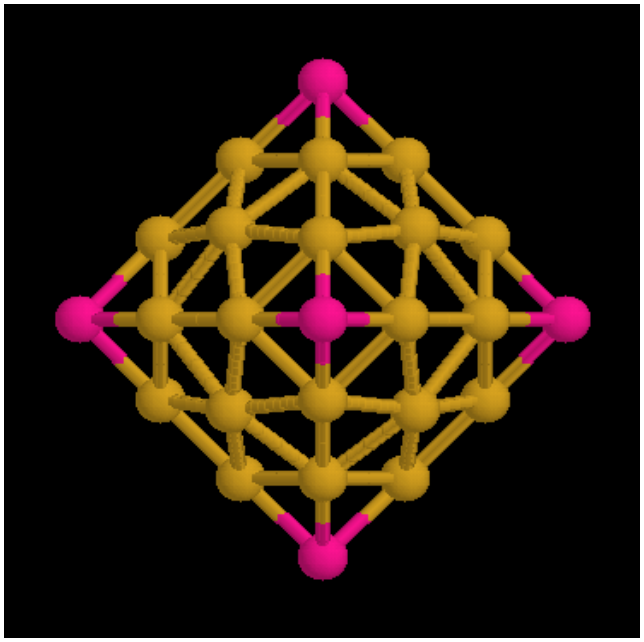


E_{fcc} = - 131.98 eV	(LDA)	E_{O_h} = - 130.81 eV
E_{fcc} = - 100.40 eV	(PBE)	E_{O_h} = - 101.86 eV
E_{fcc} = - 97.50 eV	(PW91)	E_{O_h} = - 99.02 eV

$\Delta E_{rel} > 2.5$ eV… need more accurate methods? QMC

Which Au_{38} is a more stable structure?





E_{fcc} = - 131.98 eV	(LDA)	E_{O_h} = - 130.81 eV
E_{fcc} = - 100.40 eV	(PBE)	E_{O_h} = - 101.86 eV
E_{fcc} = - 97.50 eV	(PW91)	E_{O_h} = - 99.02 eV
E_{fcc} = - 33541.66 eV	(QMC)	E_{O_h} = - 33541.58 eV

Here statistical error of DMC energy is ~ 0.2 eV, so the two structures are almost degenerate…!

PHYSICAL REVIEW B **77**, 235430 (2008)

First-principles study of metal adatom adsorption on graphene

Kevin T. Chan,[1,2] J. B. Neaton,[3] and Marvin L. Cohen[1,2]
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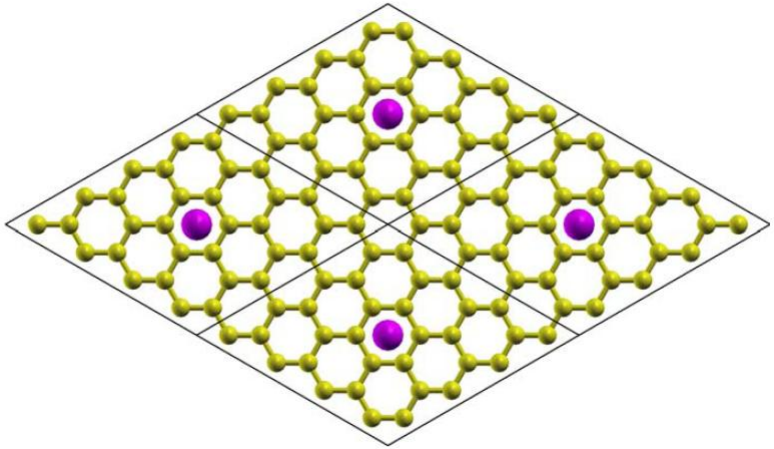
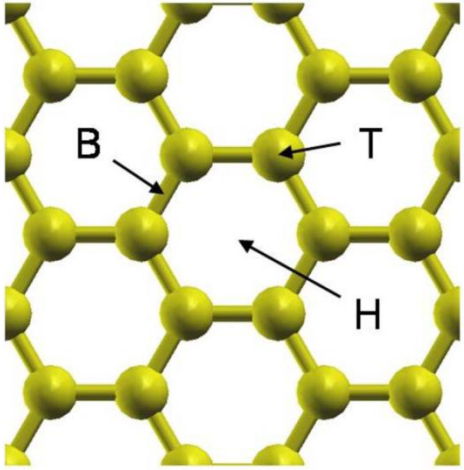
[3]*The Molecular Foundry, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA*
(Received 30 April 2008; published 20 June 2008)

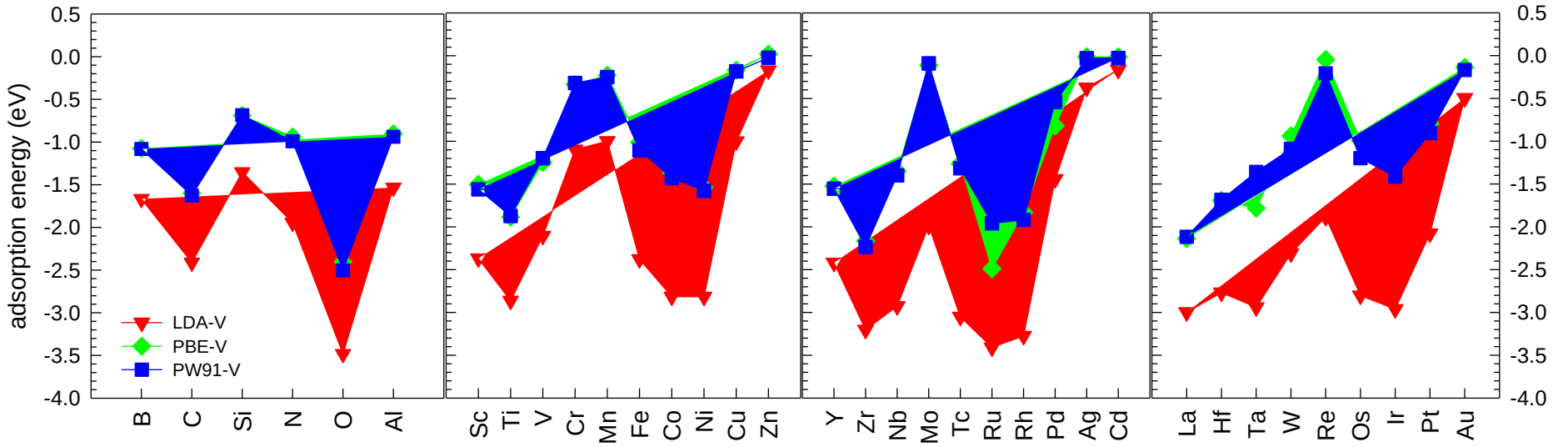
VASP-PBE

Li, Na, K, Ca, Al, Ga, In, Sn, Ti, Fe, Pd, Au





Single atom @ graphene

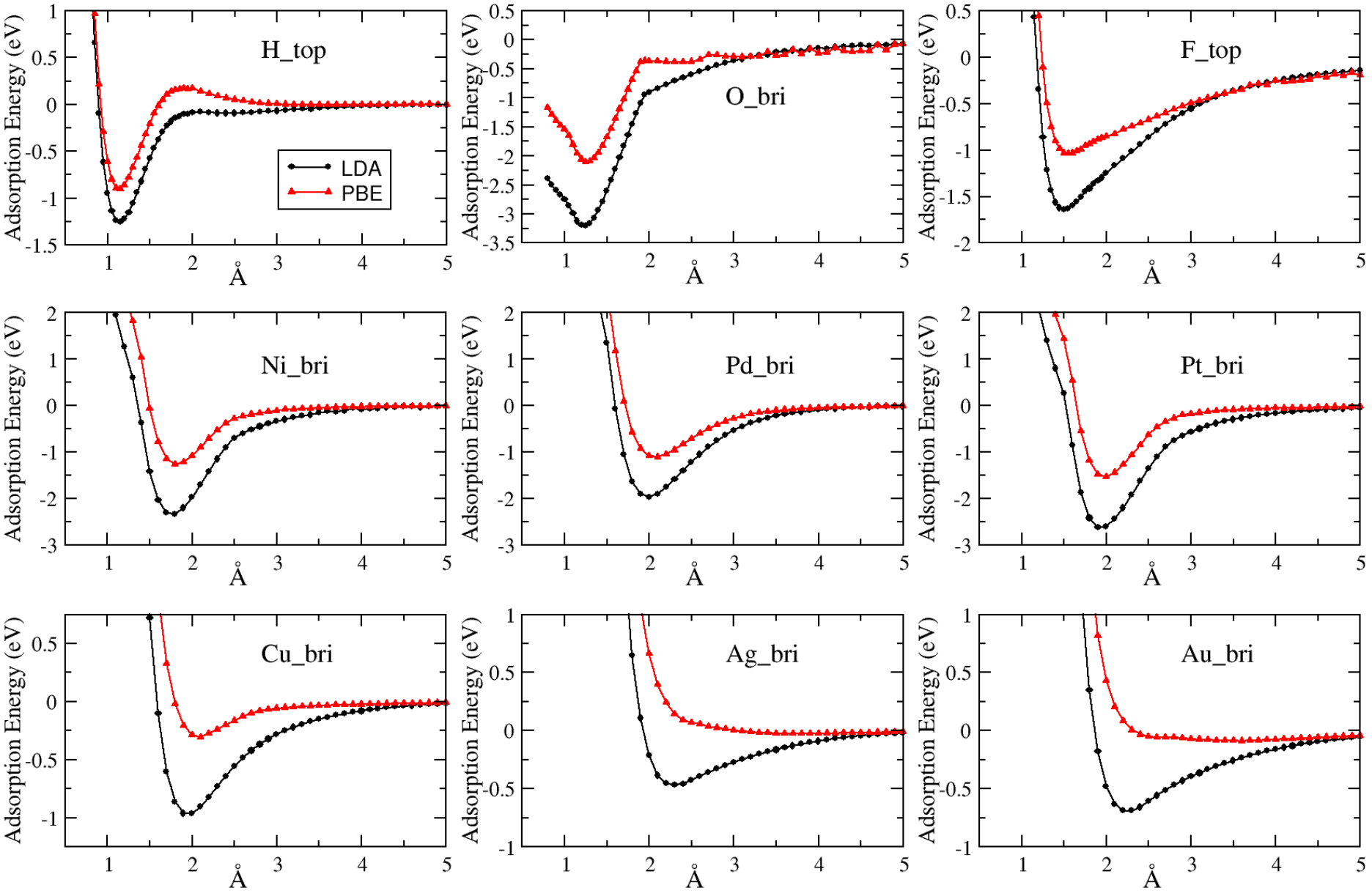


LDA & GGA predict different adsorption energy at preferred adsorption site!

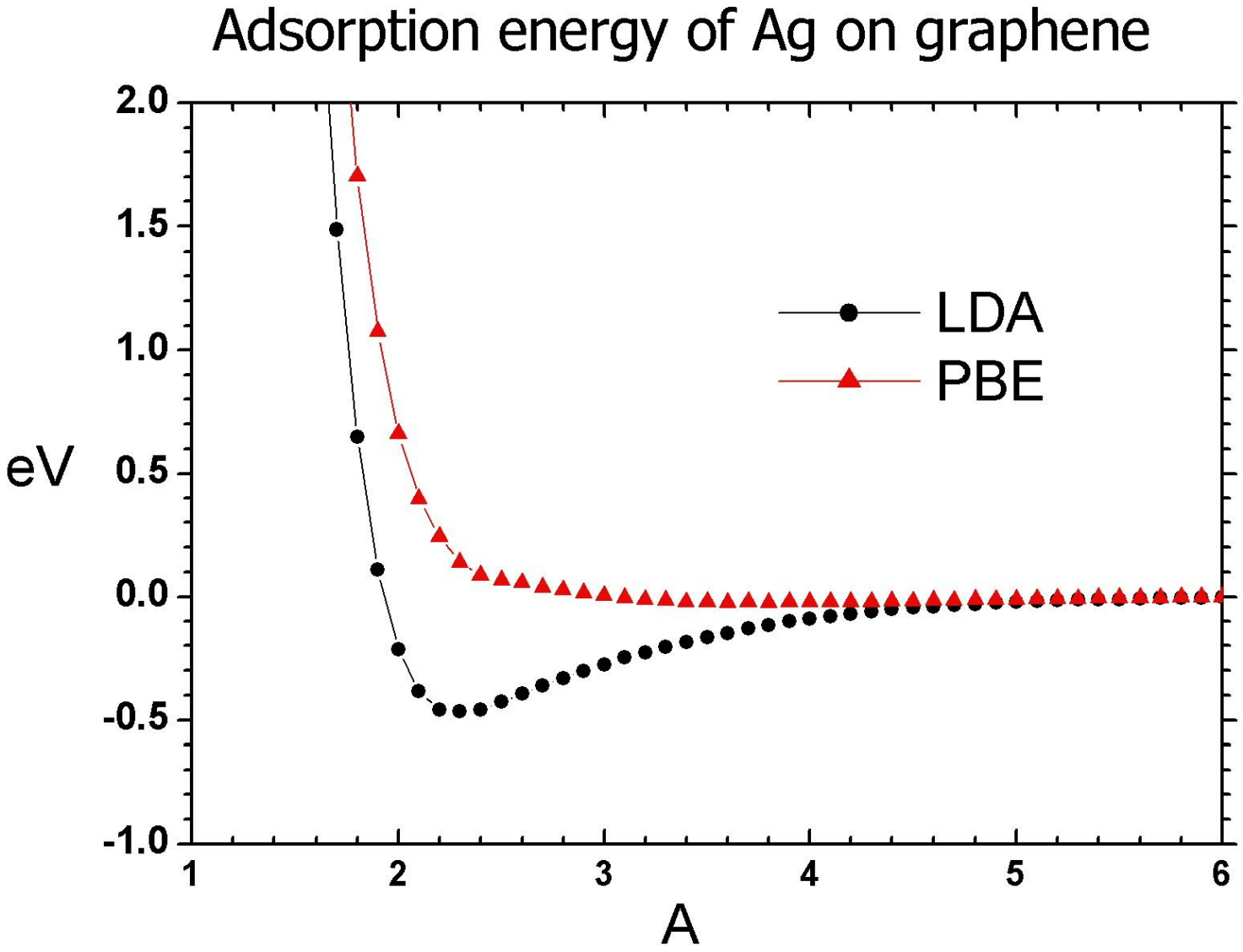
Except for Zn & Cd atom, the adsorption energy difference obtained by LDA and GGA is ranging from 0.4 ~ 1.8 eV.

QMC is needed to check the accuracy of exchange-correlation approximations !

Single atom@graphene (DFT reults)



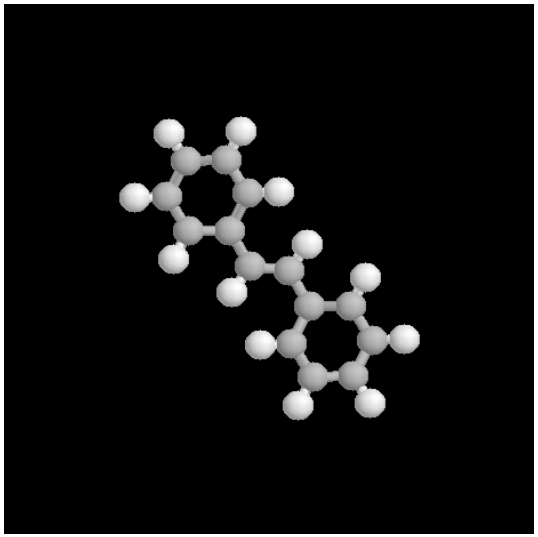
Need more accurate methods? QMC



DFT give wrong adsorption energy & geometry?

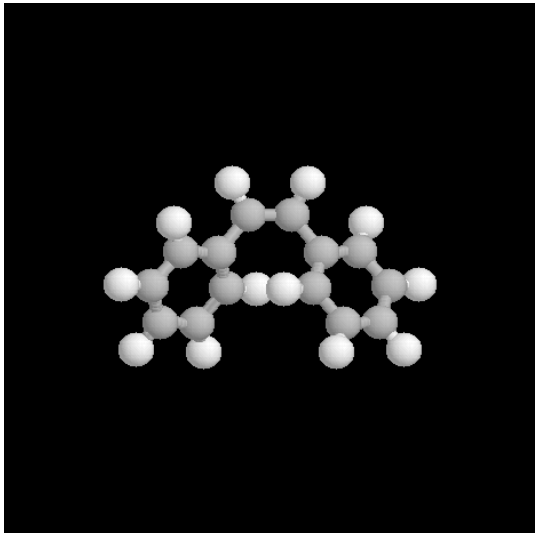
Need more accurate methods? QMC

trans-stilbene

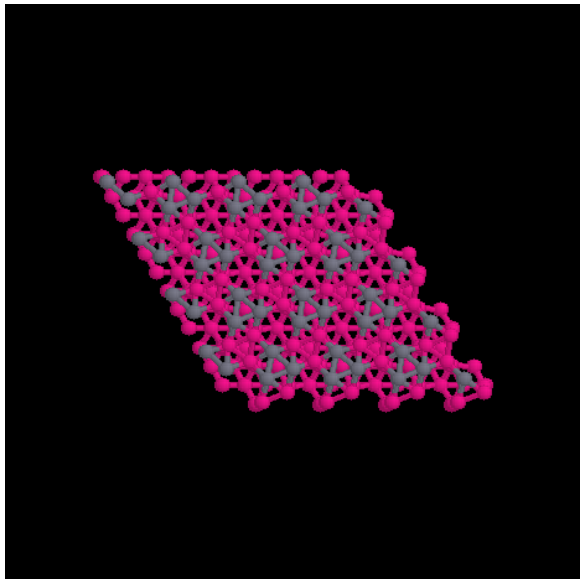


E_{trans}= 0.0 eV

cis-stilbene

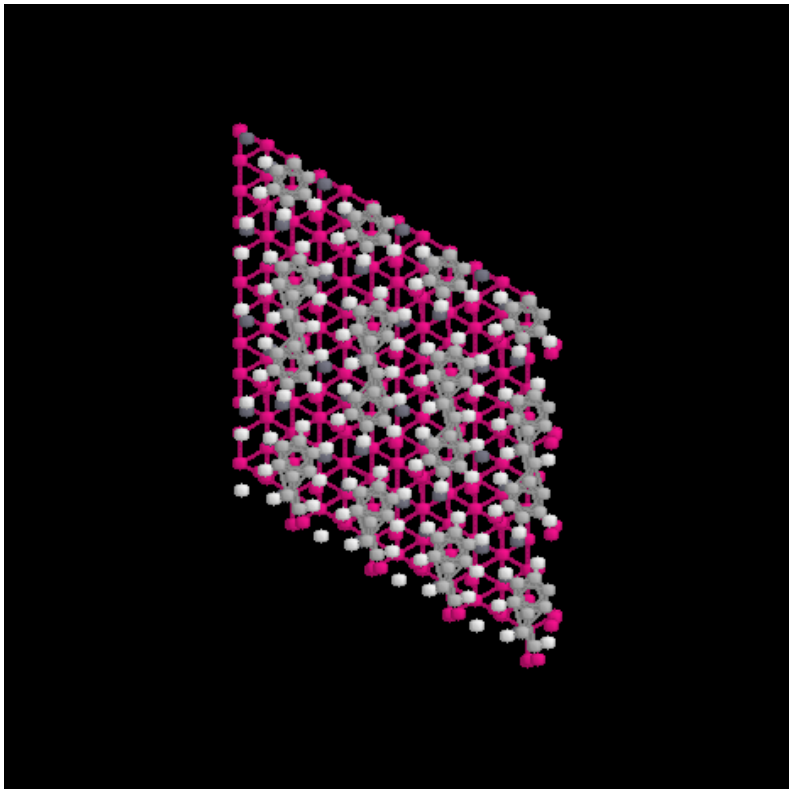


E_{cis}= 0.204 eV



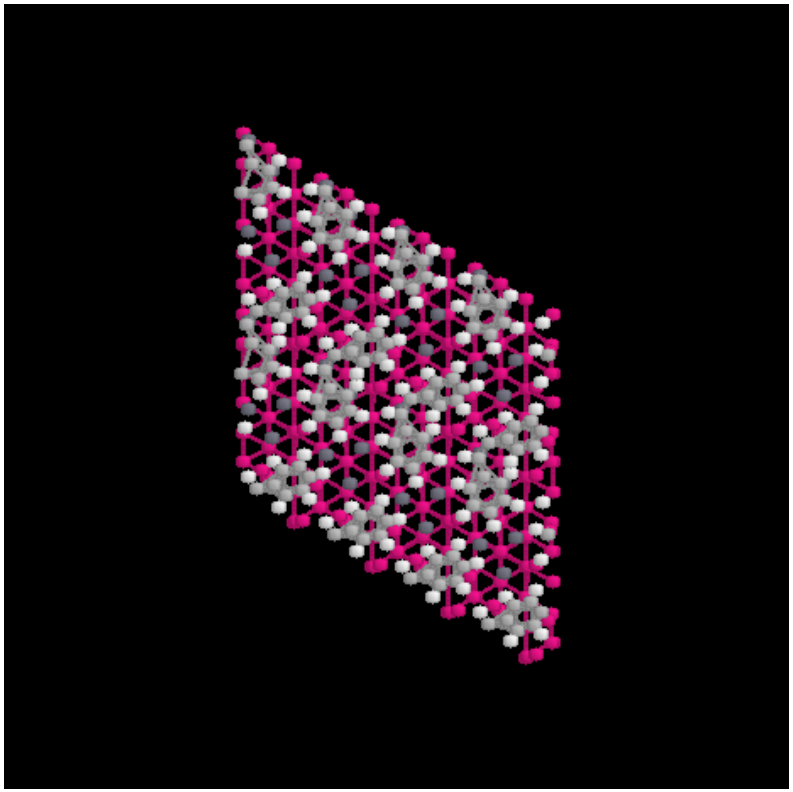
Ag-Ge(111)-IET

trans-stilbene/Ag-Ge(111)



E_{ads}= 1.059 eV *(LDA)*

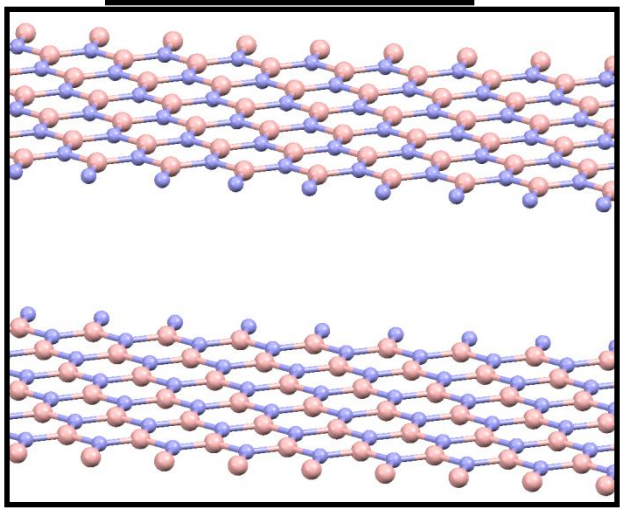
cis-stilbene/Ag-Ge(111)



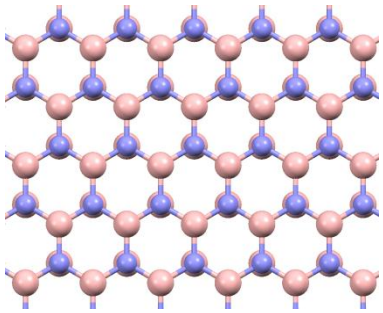
E_{ads}= 0.887 eV *(LDA)*

LDA agrees expt., but… E_{ads} ~ 0.40 & 0.20 eV (PW91)
and thus DFT has little (or no) predicting power!!!

Boron nitride sheet



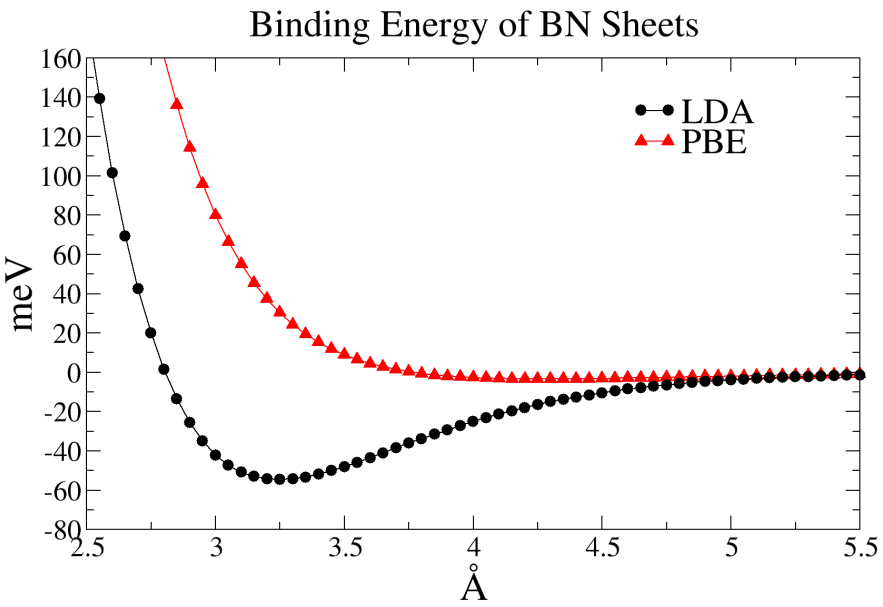
Side view



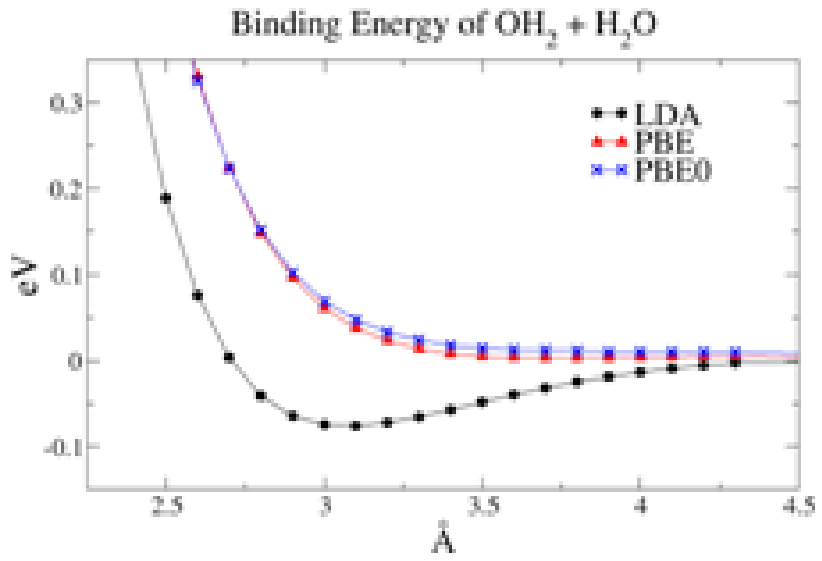
B atom

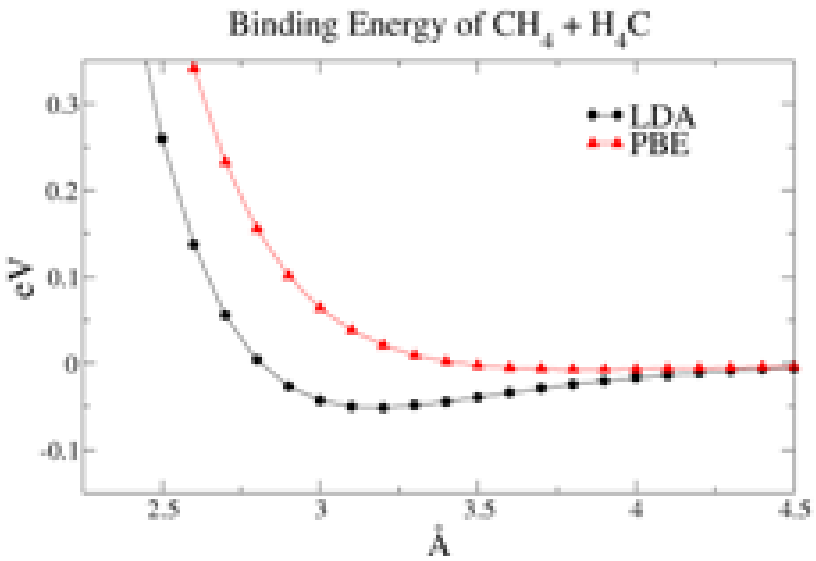
N atom

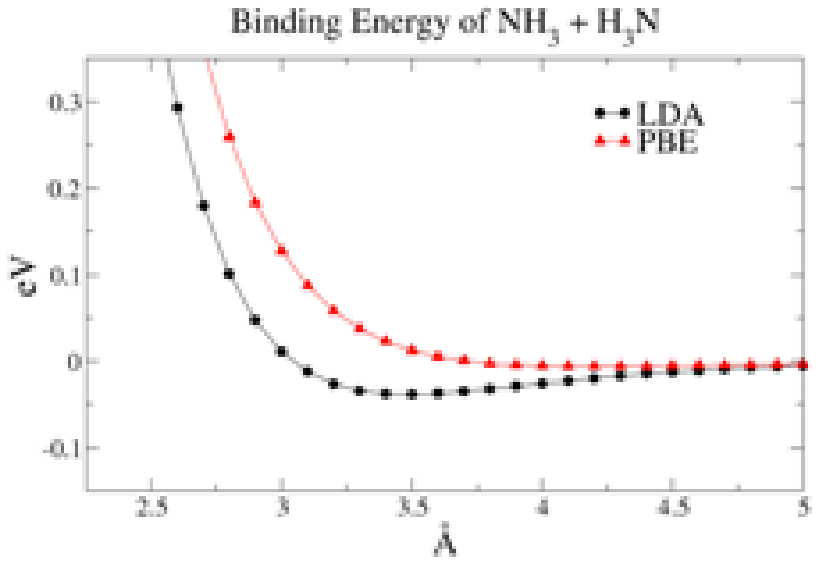
Top view

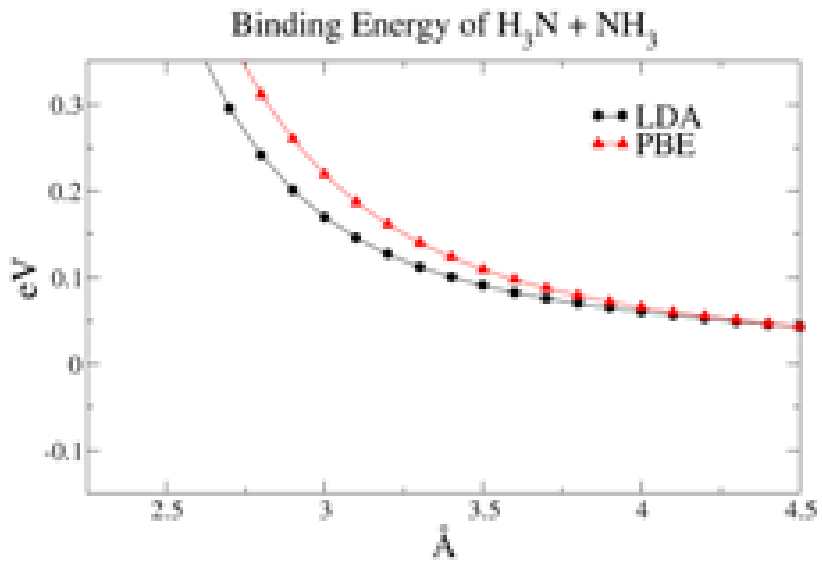


LDA is more correct than GGA by judging from QMC!





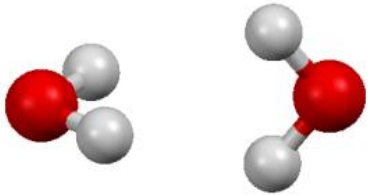


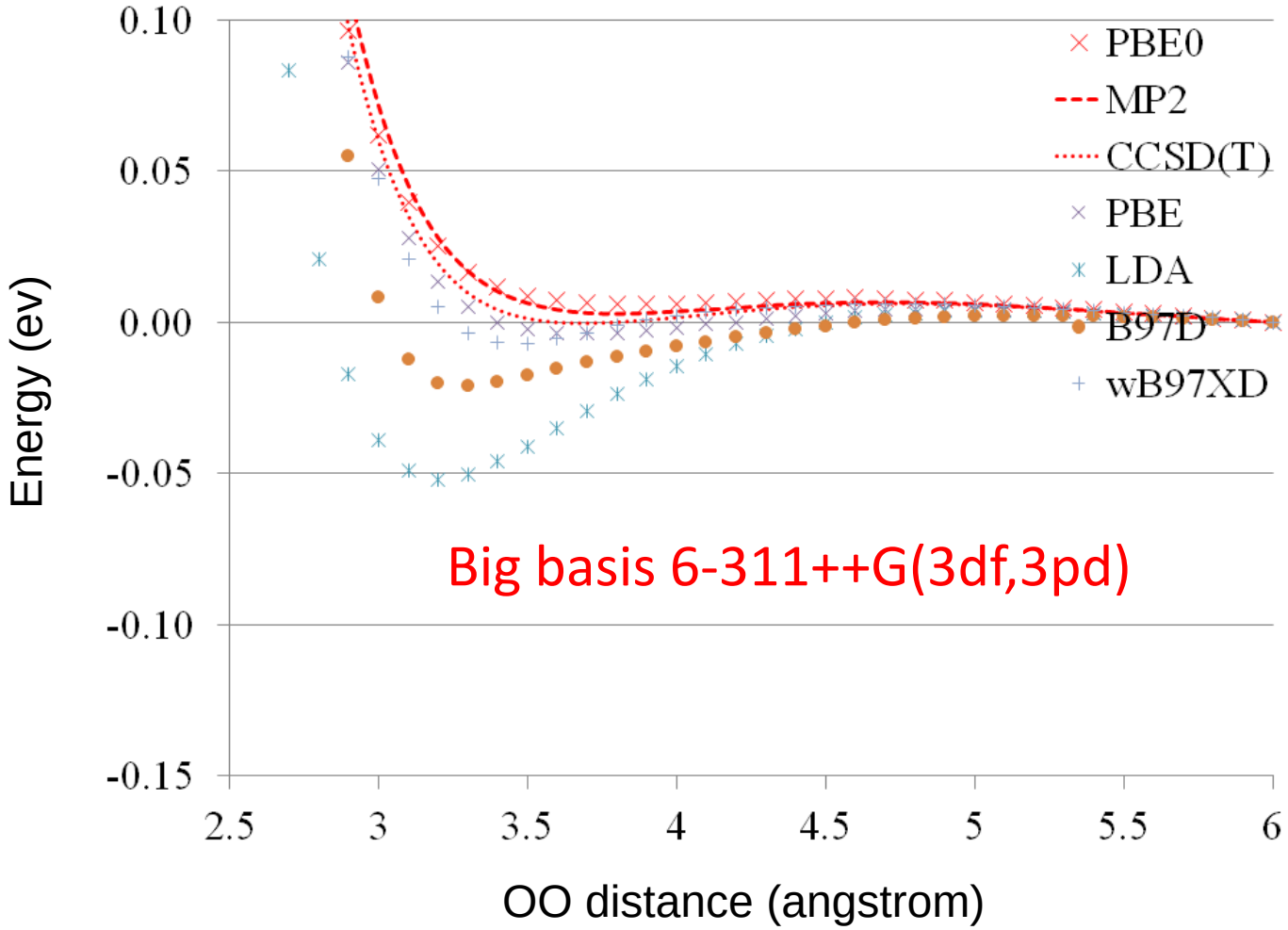


GGA is perhaps more correct than LDA!

Water dimer interaction (results from Dr. Kaito)

GGA (PBE) is more match with CCSD(T) than LDA





Applications of *Ab Initio* Random Structure Searching

Richard Needs

University of Cambridge, UK

Chris Pickard

University College London, UK

QMC in the Apuan Alps 2009, Vallico Sotto, Italy, 25 July – 1st August 2009

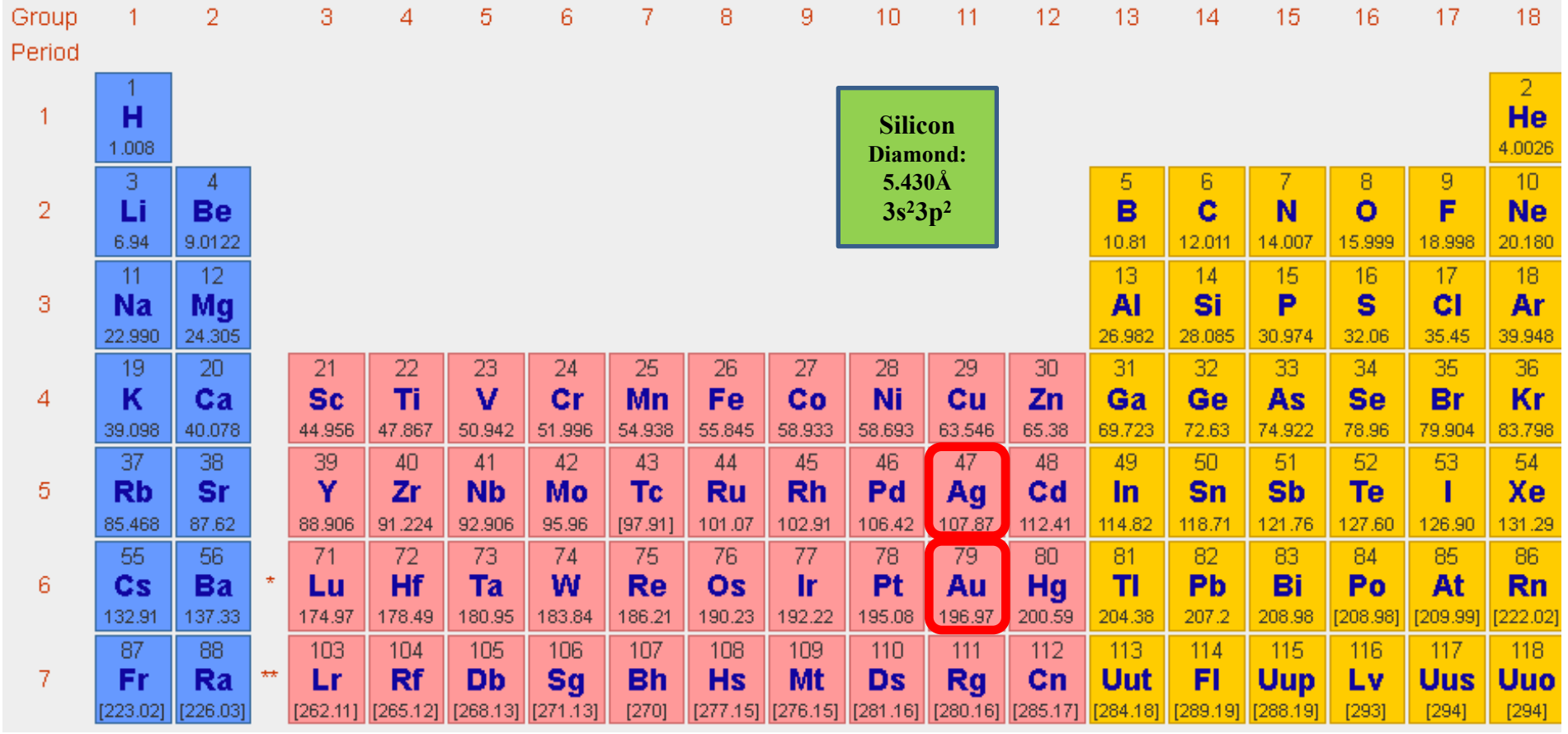
Ab Initio Random Structure Searching

- Make a random unit cell
- Throw the required numbers of each atom type into the cell at random
- Relax under the quantum mechanical forces and stresses
- Repeat until happy or computing credits run out
- Look at lowest-energy or other interesting structures

Pickard and Needs, Phys Rev Lett 97, 045504 (2006)

"As it's your first day we're going to start you on something easy"

We have try very hard to train ourself to become a sniffer dog in global structure search

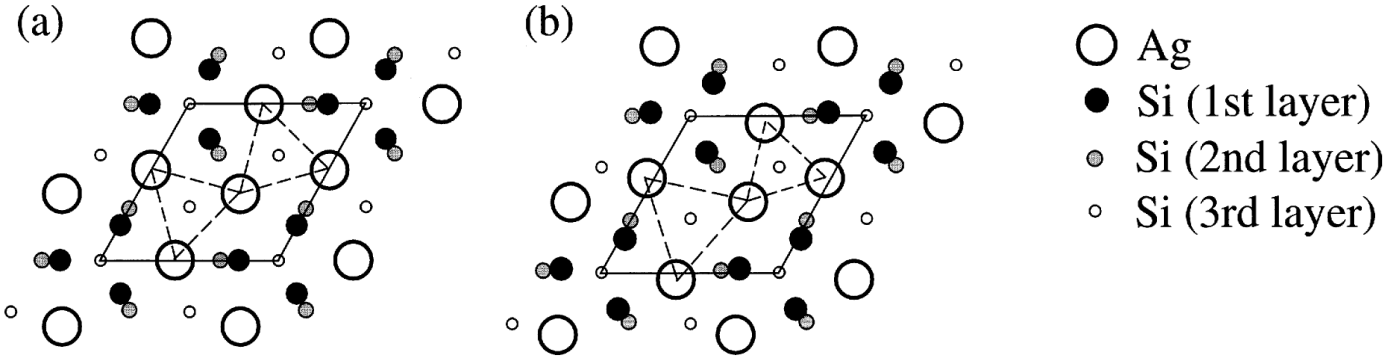


Study of adsorbate-induced √3×√3 reconstruction on Si(111)

Silver
FCC : 4.09Å
$5s^1 4d^{10}$

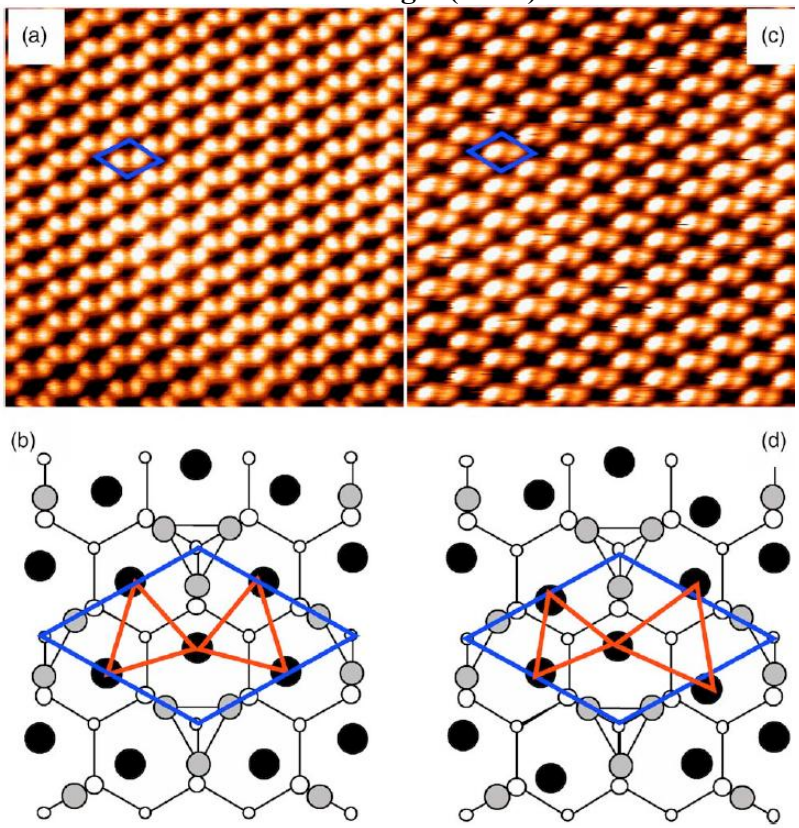
Gold
FCC : 4.08Å
$6s^1 4f^{14} 5d^{10}$

1ML Ag/Si(111)-√3×√3 (IET)



Honeycomb-Chained Triangle (HCT)

InEquivalent Triangle (IET)

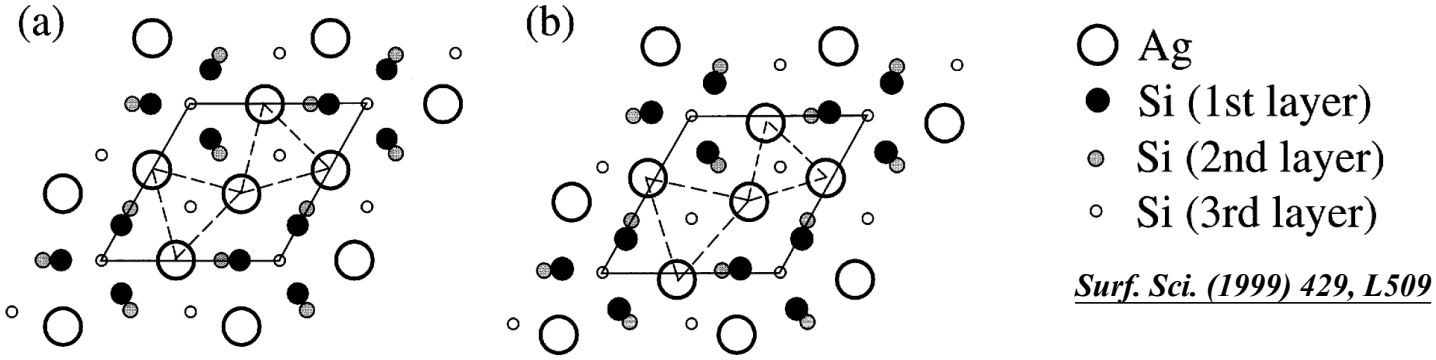


a) STM image at RT, Vs=−0.6 V and I=1.0 nA, 84×84 Å.
b) HCT model.

c) STM image obtained at the same area as image (a), Vs=−0.3 V and I=0.3 nA, 84×84 Å.
d) IET model.

H. M. Zhang *et al*., Phys. Rev. B **74**, 201304 (R) (2006)

1ML Ag/Si(111)-√3×√3 (IET)

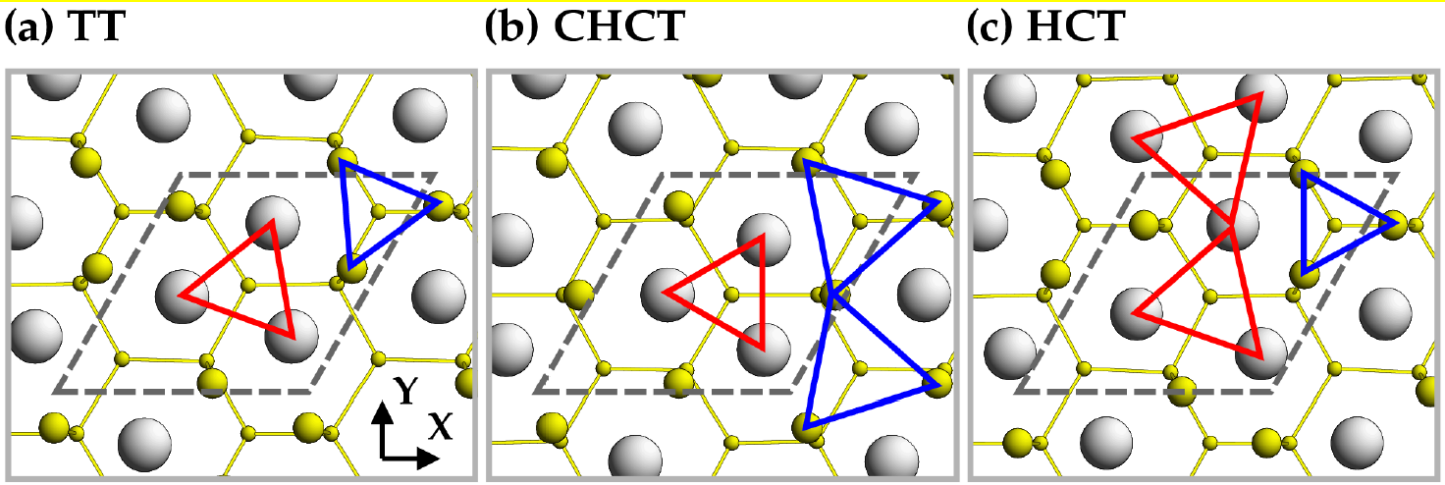


Honeycomb-Chained Triangle (HCT)

InEquivalent Triangle (IET)

Surf. Sci. (1999) 429, L509

1ML Au/Si(111)-√3×√3 (CHCT)



Twisted Trimer (TT)

Conjugate-Honeycomb-Chained Trimer (CHCT)

Honeycomb-Chained Trimer (HCT)

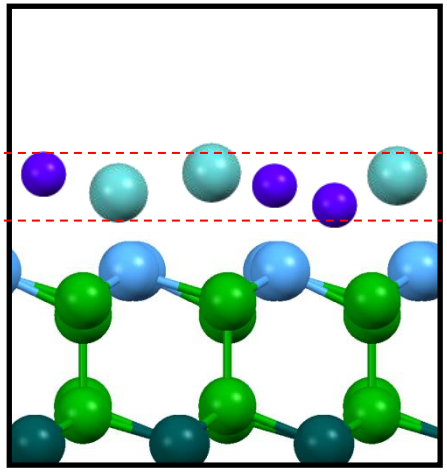
J. Y. Lee *et al*., J. Krean Phys. Soc. **55**, 2460 (2009)

M. Chester and T. Gustafsson, Surf. Sci. **256**, 135 (1991)

Y. G. Ding *et al*., Surf. Sci. **275**, L691 (1992)

H. M. Zhang *et al*., Phys. Rev. B **66**, 165402 (2002)

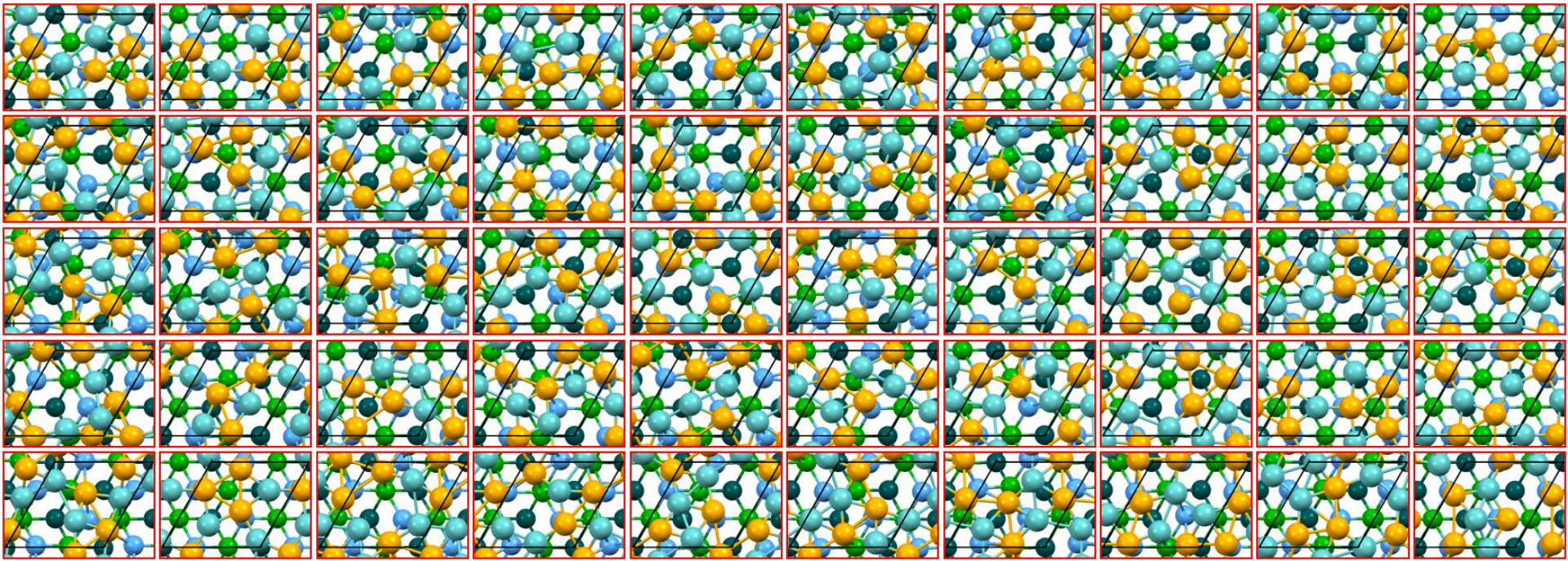
AIRSS calculation



Adsorbate atom
Si - surface
Si - 1st layer (T1 site)
Si - 2nd & 3rd layer (T4 site)
Si - 4th layer (H3 site)

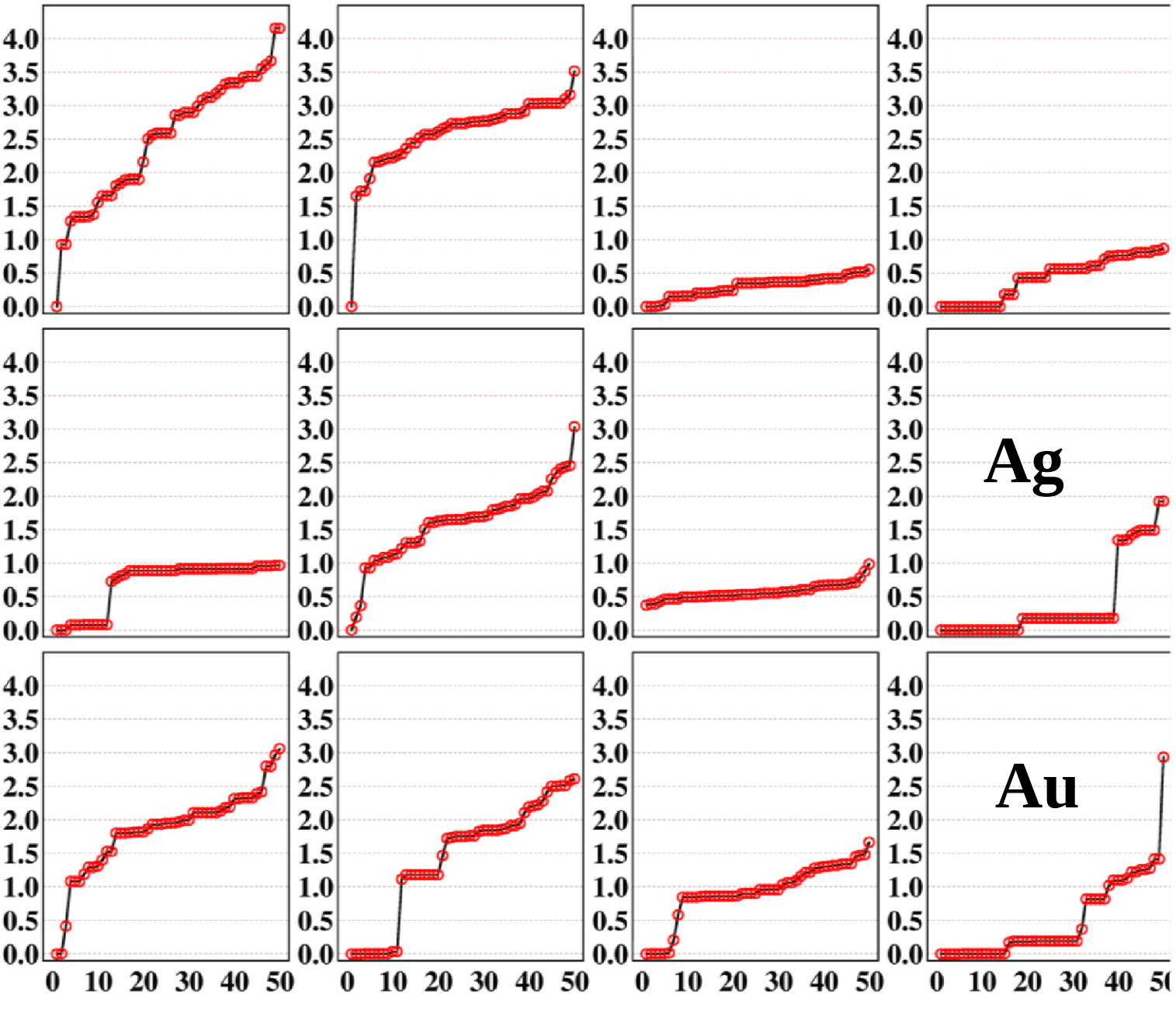
Constrains

- The distance between any two adatom is more than 2.1Å
- Z-axis range : 1.5~3.0Å above surface Si atom



preliminary studies (AIRSS results)

1	1 H 1.008	
2	3 Li 6.94	4 Be 9.01
3	11 Na 22.990	12 Mg 24.3
4	19 K 39.098	20 Ca 40.0
5	37 Rb 85.468	38 Sr 87.6
6	55 Cs 132.91	56 Ba 137.
7	87 Fr [223.02]	88 Ra [226.

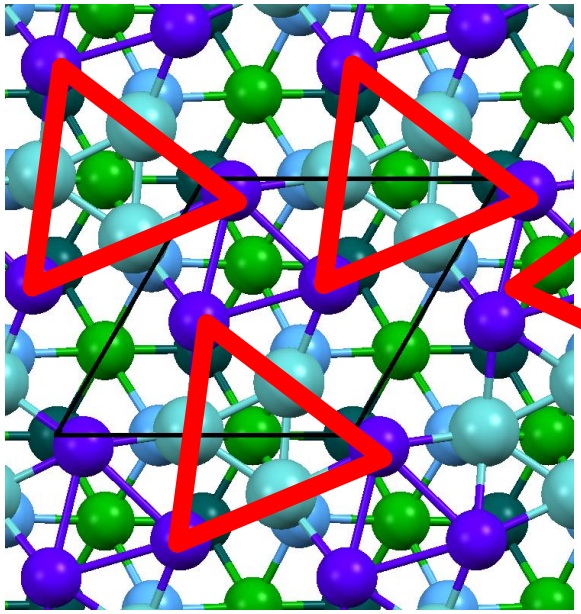


AIRSS results

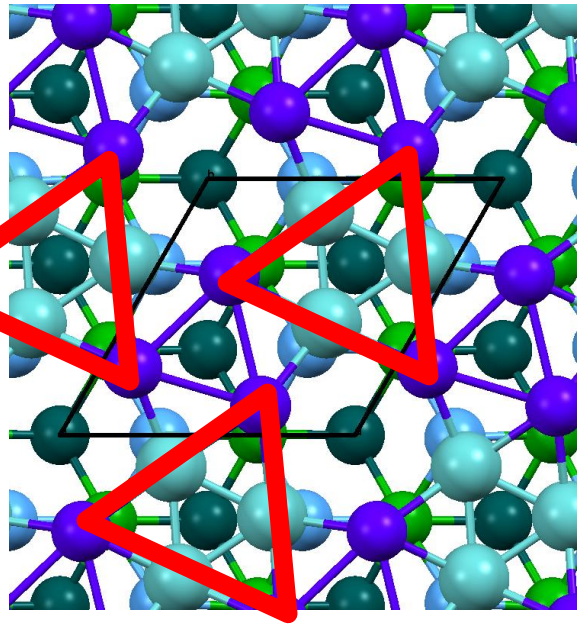
47 銀 Silver 107.8682

2 8 18 18 1

[Kr]5s^1 4d^{10}

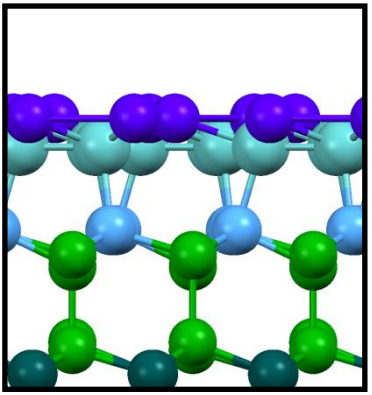


IET

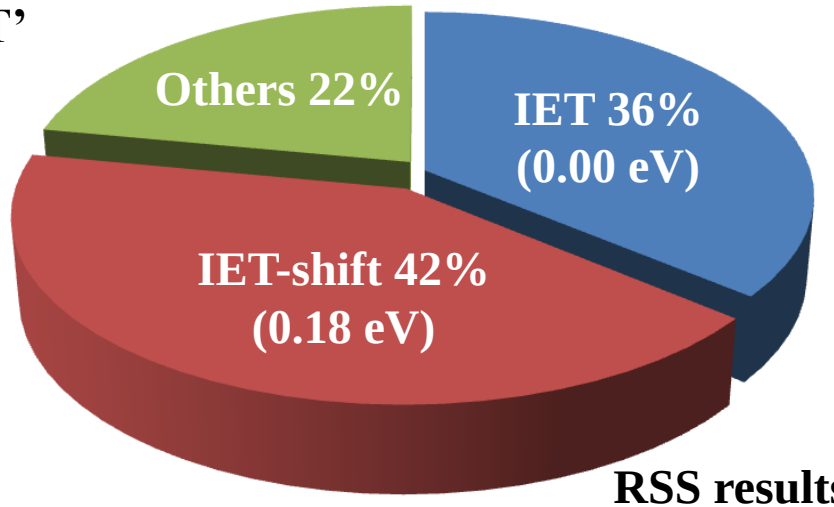


IET’

	PBE	LDA
IET	0.000	0.000
HCT	0.037	0.138
CHCT	1.164	0.764



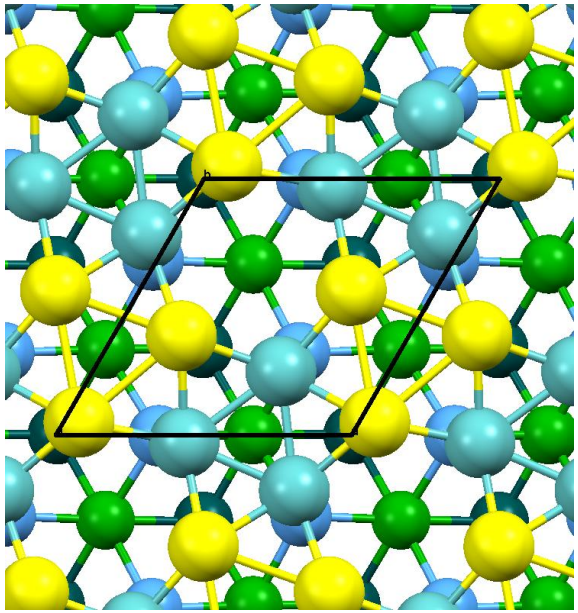
- Ag atom
- Si - surface
- Si - 1st layer (T1 site)
- Si - 2nd & 3rd layer (T4 site)
- Si - 4th layer (H3 site)



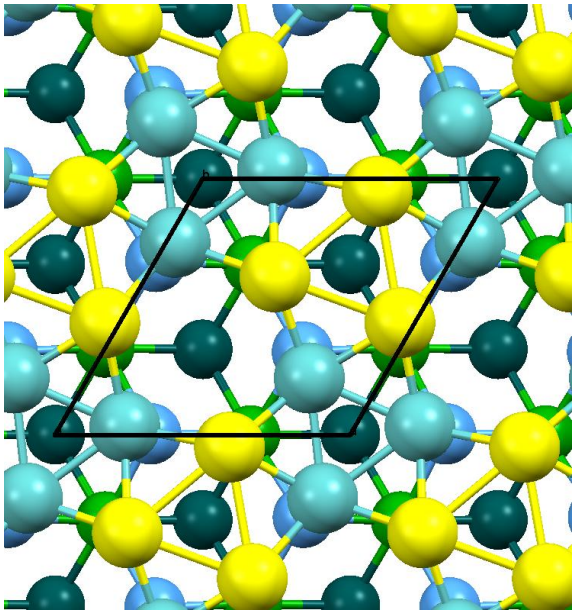
RSS results (PBE)

AIRSS results

79 金 Gold 196.966569
2 8 18 32 18 1
[Xe]6s^1 4f^{14} 5d^{10}

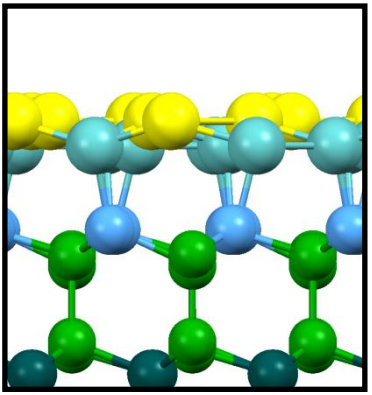


IET

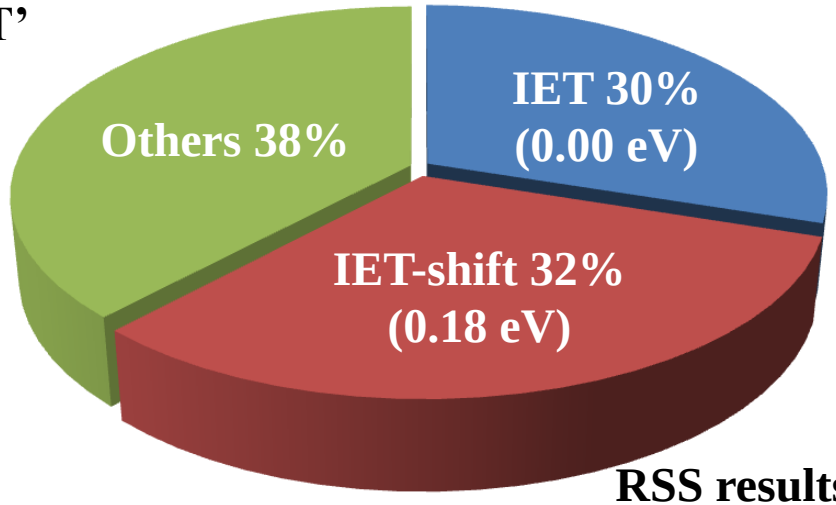


IET’

	PBE	LDA
IET	**0.000**	
HCT	0.081	
CHCT	0.084	



- Au atom
- Si - surface
- Si - 1st layer (T1 site)
- Si - 2nd & 3rd layer (T4 site)
- Si - 4th layer (H3 site)



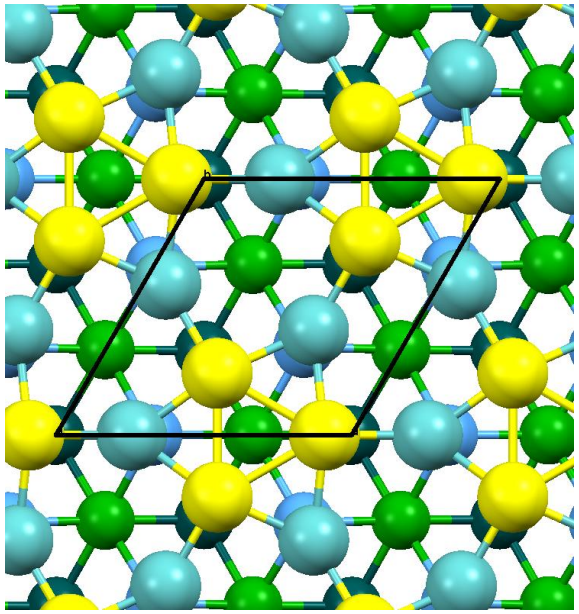
RSS results (PBE)

79 金 Gold 196.966569

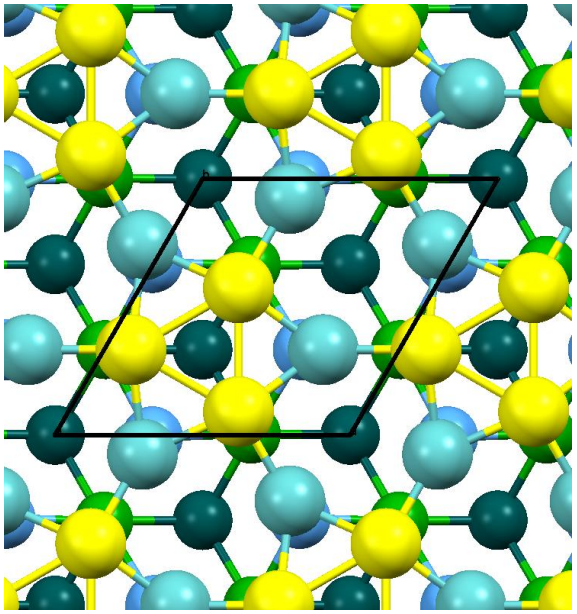
2 8 18 32 18 1

[Xe]6s^1 4f^{14} 5d^{10}

AIRSS results *(PES is unknown from DFT ?)*

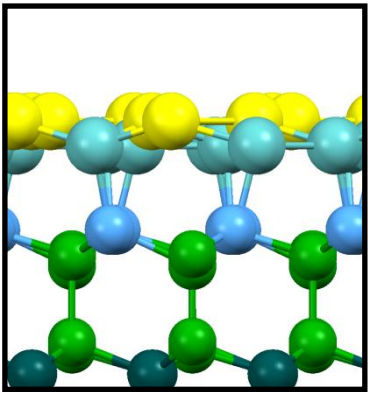


CHCT



CHCT'

	PBE	LDA
IET	**0.000**	→ CHCT
HCT	0.081	0.453
CHCT	0.084	**0.000**



- Au atom
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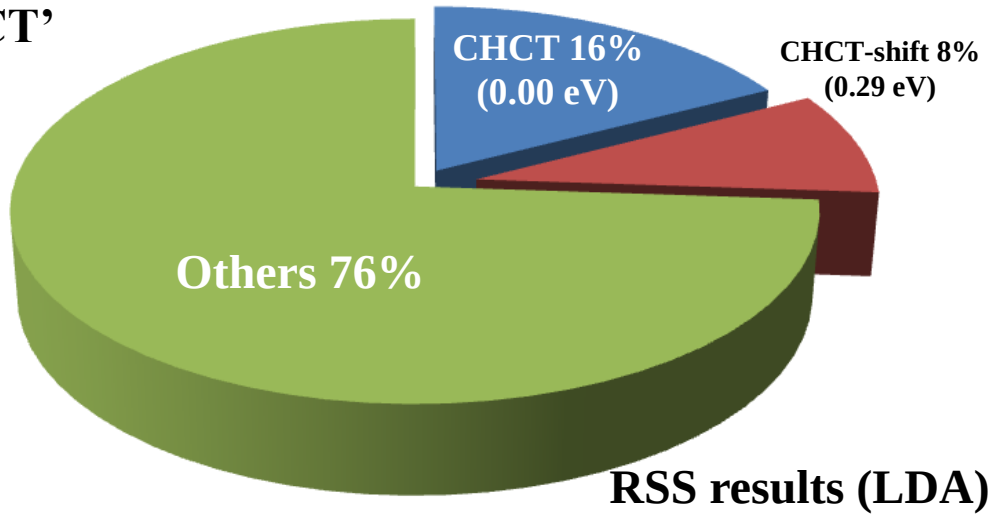
- Si - 4th layer (H3 site)

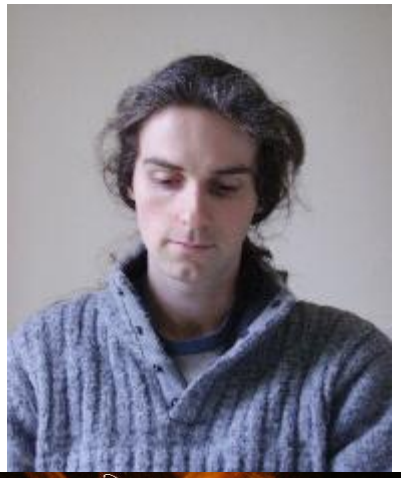


RSS results (LDA)

CASINO code : QMC Methods

http://www.tcm.phy.cam.ac.uk/~mdt26/casino2.html

R.J. Needs, M.D. Towler, N.D. Drummond and P. López Ríos, CASINO version 2.3 User Manual, University of Cambridge, Cambridge (2008).

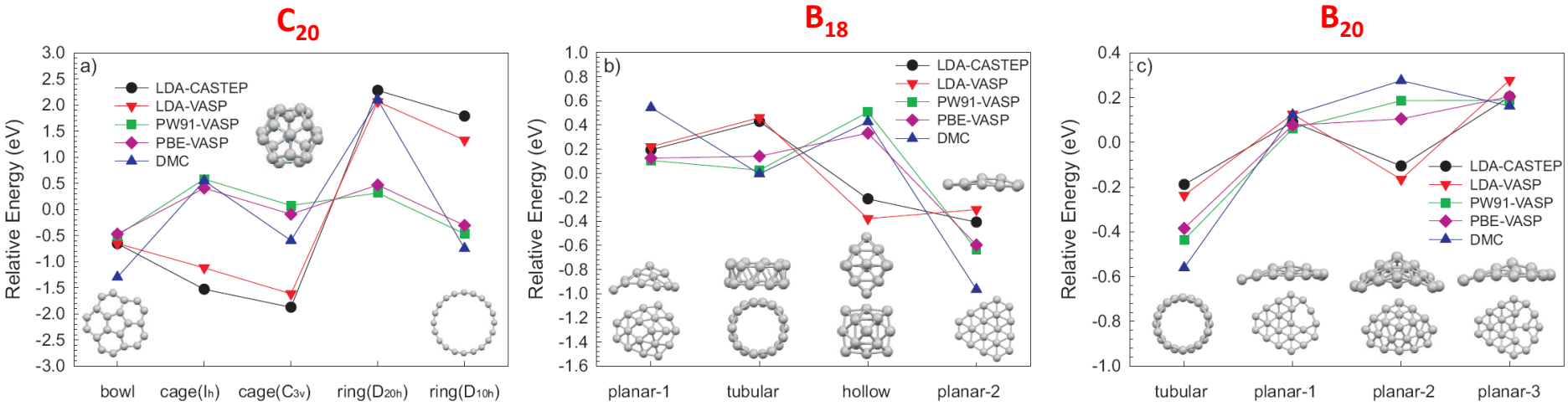


Outline

- Motivation? Why using QMC?
- Material Simulations using QMC
  - ✓ **covalent and metallic clusters**
  - ✓ band gaps of TiO_2, MgO, NaCl
  - ✓ surface adsorption on graphene & Al(100)
  - ✓ interlayer binding of two BN sheets
  - ✓ surface energy: $\Delta S(DMC) > \Delta S(LDA) > \Delta S(PBE)$
  - ✓ O, OH & H_2O adsorption on surfaces
  - ✓ CO adsorption on late TM (111) surfaces

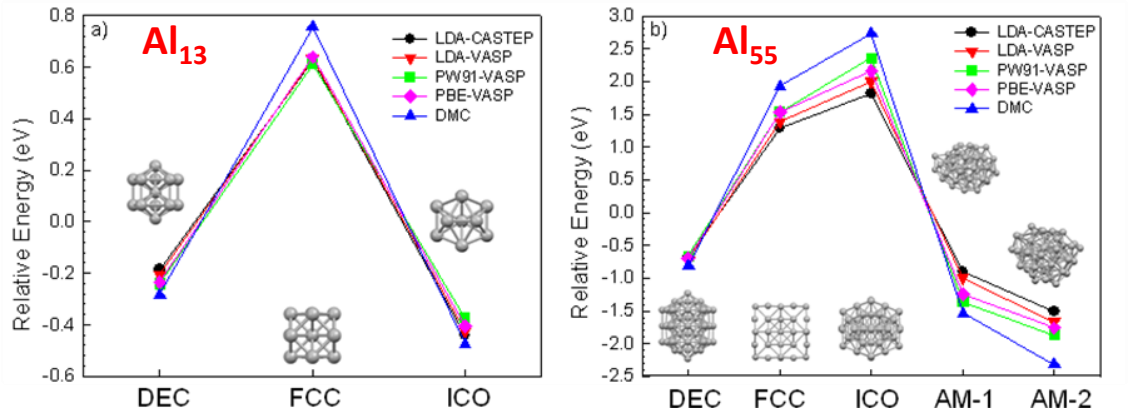
C_{20}, B_{18}, B_{20}, Al_{13} and Al_{55} Clusters

I. Covalent clusters



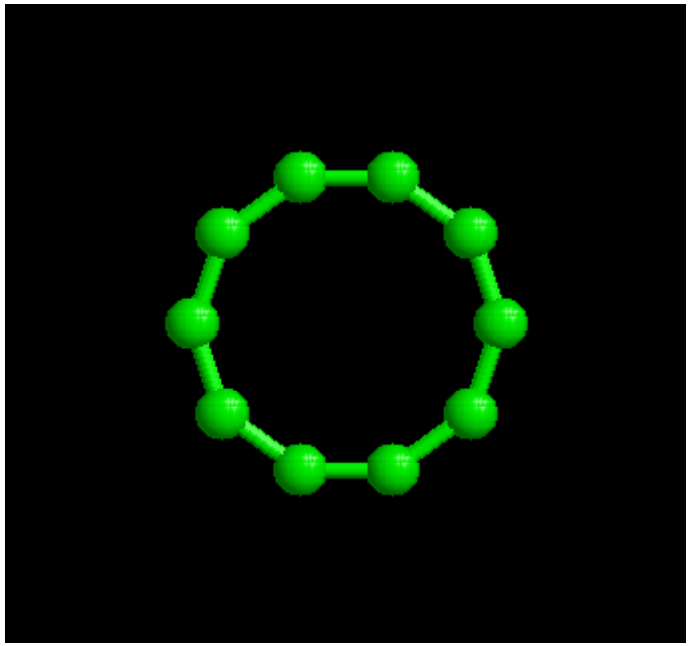
LDA & PBE are inadequate in predicting the relative energy of covalent clusters

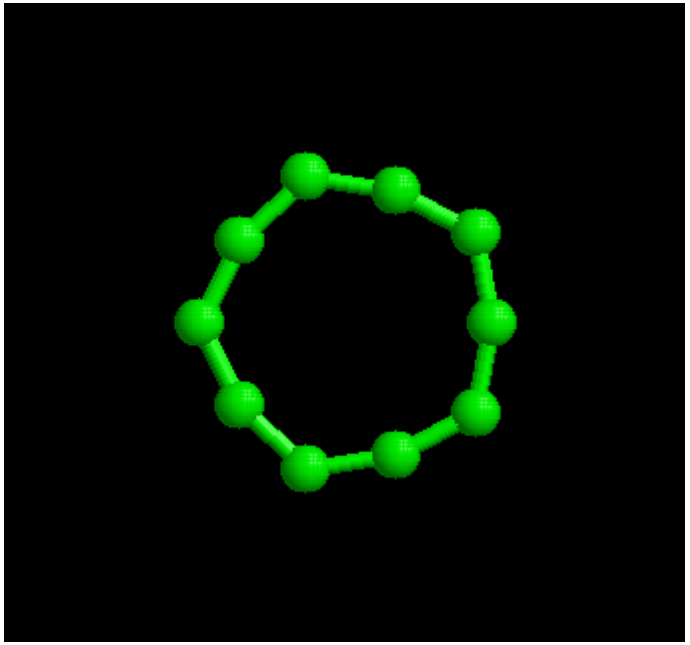
II. Simple Metal clusters



DFT is reliable in predicting the relative energy of simple metal clusters

C_{10} : 2D PES





D_{10h} D_{5h}

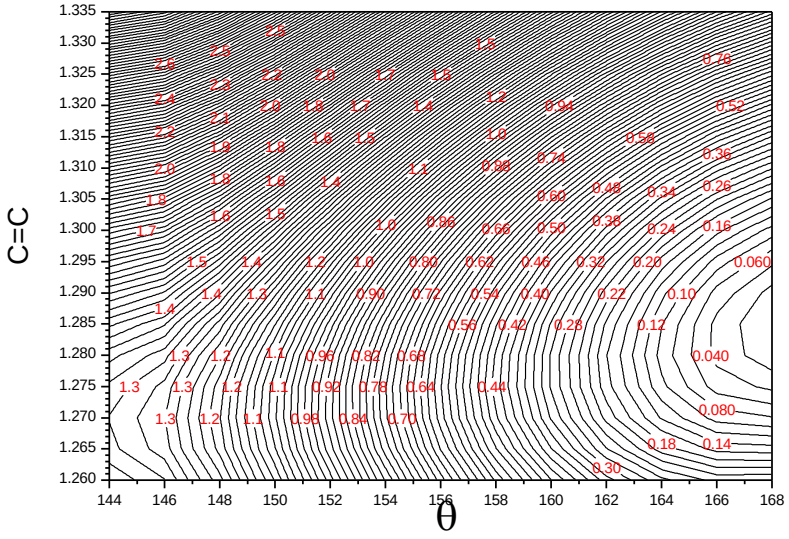
$\Delta(E)$	= 0.079	eV	CASTEP – LDA
	= 0.189 (20)	eV	DMC (DFT geometry)
6-311+g	= 0.174	eV	B3LYP
cc-pVDZ	= 0.295	eV	B3LYP
cc-pVTZ	= 0.160	eV	B3LYP
cc-pVQZ	= 0.147	eV	B3LYP

How about Quantum Chemistry Methods: HF, MP2, MP4, CCSD(T)?

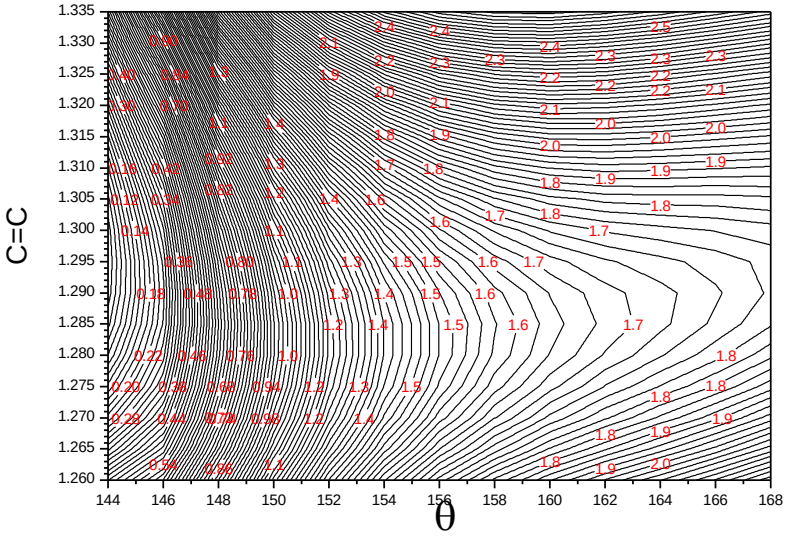
High level methods are more important than increasing local basis sets!

cc-pVTZ

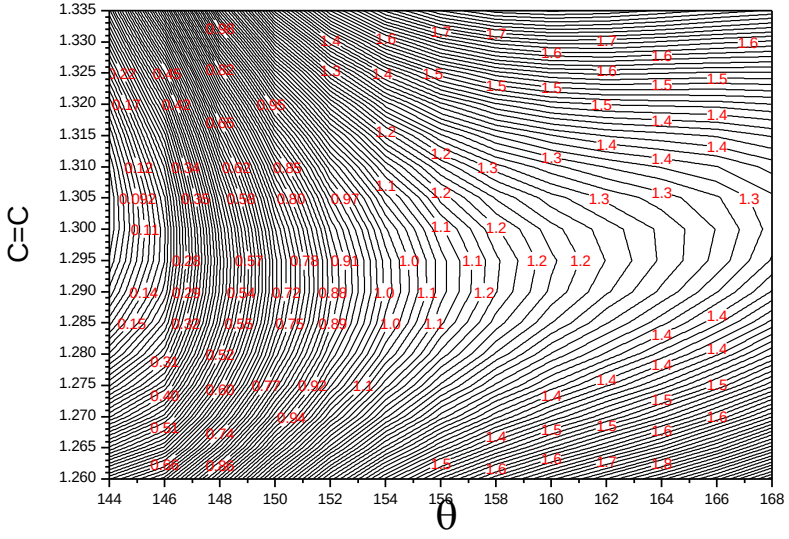
HF



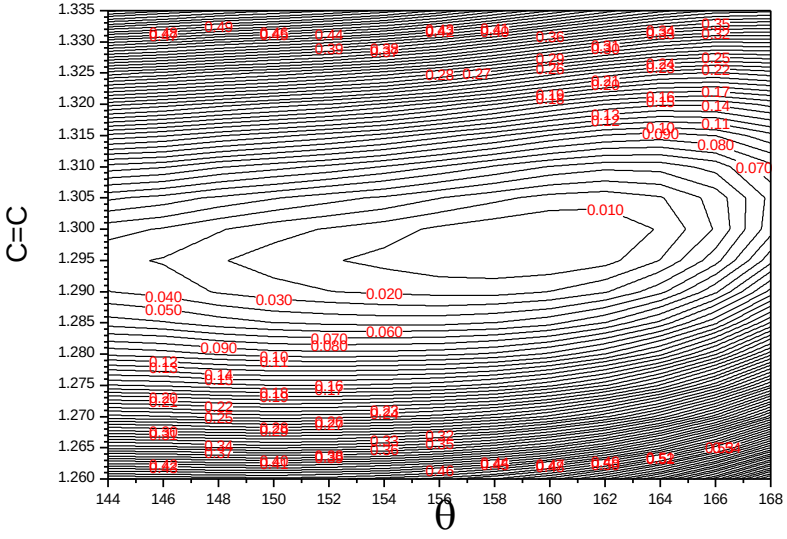
MP2



MP4

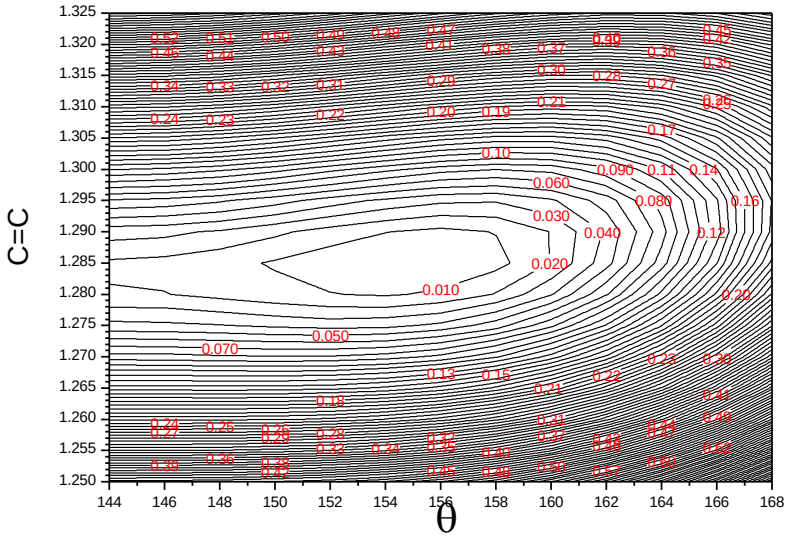


CCSD (T)

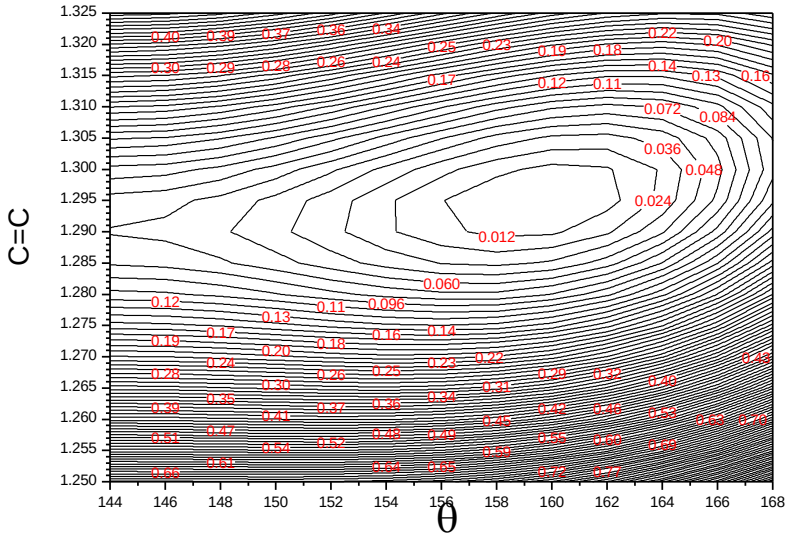


DFT with XCs are better than HF, MP2 and MP4

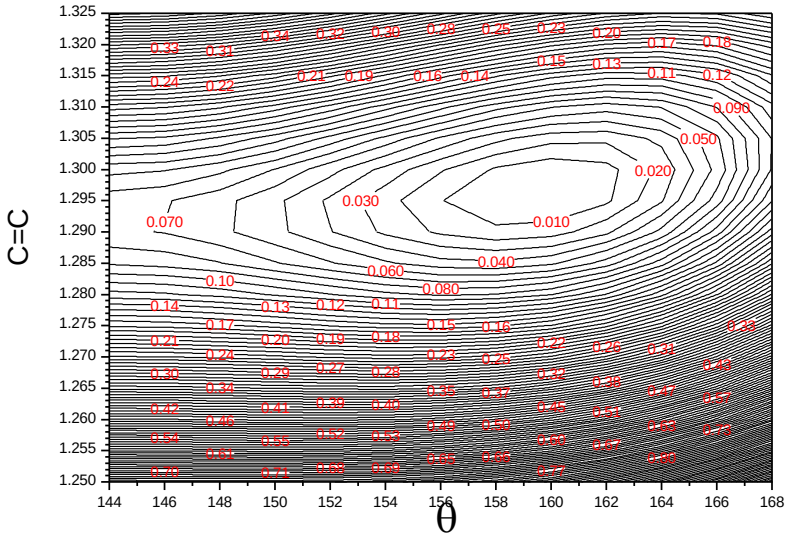
LDA



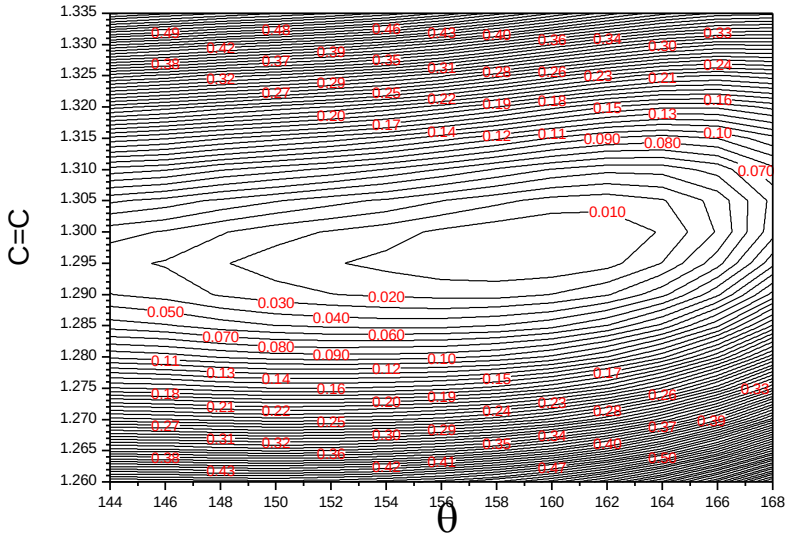
PW91



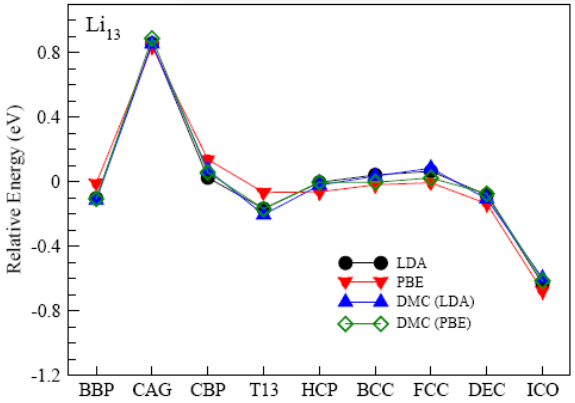
PBE



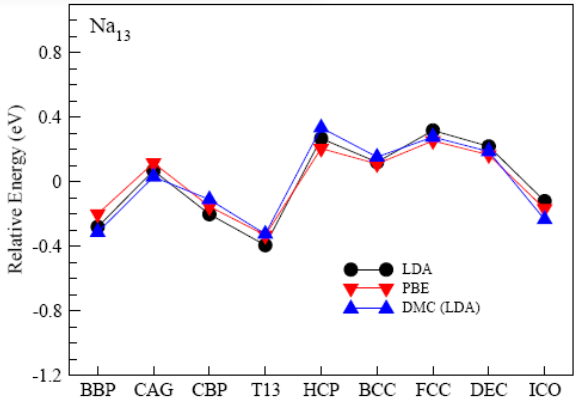
CCSD(T) cc-pVTZ

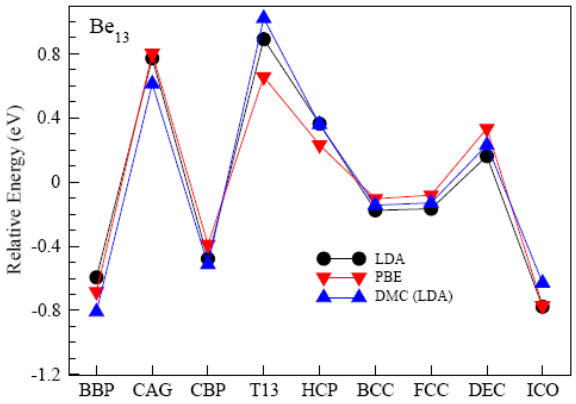


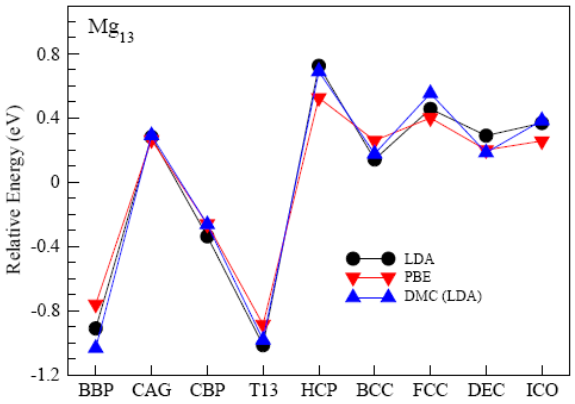
Quantum Monte Carlo Studies of 13-atom Simple Metallic Clusters

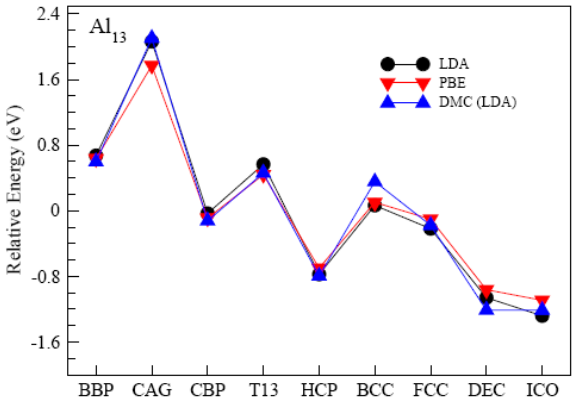


DFT is reliable in predicting the relative energy of simple metal clusters!





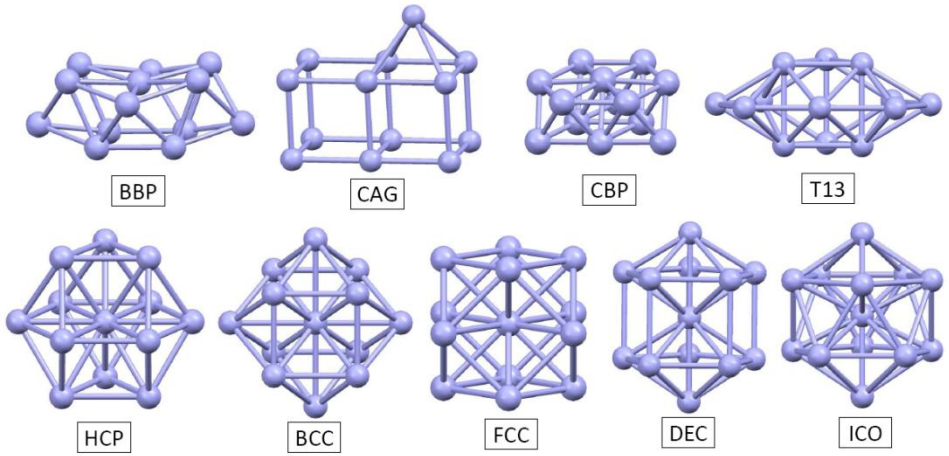




$$\cos\theta = \frac{\vec{\mathfrak{D}}^{\mathrm{DFT}} \cdot \vec{\mathfrak{D}}^{\mathrm{DMC}}}{|\vec{\mathfrak{D}}^{\mathrm{DFT}}||\vec{\mathfrak{D}}^{\mathrm{DMC}}|}$$

$$L = \frac{|\vec{\mathfrak{D}}^{\mathrm{DFT}}|}{|\vec{\mathfrak{D}}^{\mathrm{DMC}}|}$$

	(θ)		L	
Cluster	LDA	PBE	LDA	PBE
Li_{13}	4.25	12.23	1.02	1.02
Na_{13}	15.23	15.59	1.01	0.83
Be_{13}	11.57	16.77	0.97	1.09
Mg_{13}	6.76	7.87	0.98	0.81
Al_{13}	7.27	6.00	0.98	0.81



Methodology

A n-dimensional displacement vector

$$\vec{\mathfrak{D}}^{A}_{M(a)}$$ ← XC functional

M : metal element
(a) : semi-core state

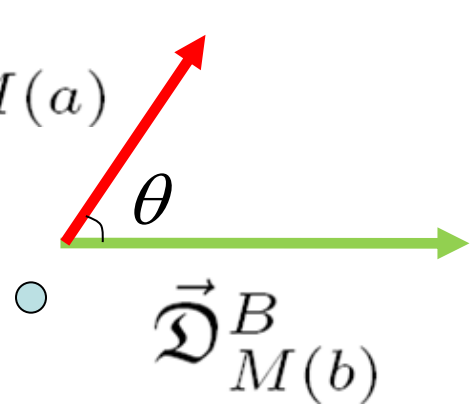
$$\vec{\mathfrak{D}} = (r_1, r_2, \ldots, r_n)$$ Here, n=9

The relative energy definition :

$$r_i = E_i - \bar{E}$$

E_i : the total energy of a certain isomer

$\bar{E}$: the average energy of all the isomers



$$\cos(\boldsymbol{\theta}) = \frac{\vec{\mathfrak{D}}^{A}_{M(a)} \cdot \vec{\mathfrak{D}}^{B}_{M(b)}}{(|\vec{\mathfrak{D}}^{A}_{M(a)}||\vec{\mathfrak{D}}^{B}_{M(b)}|)} \qquad \boldsymbol{L} = \frac{|\vec{\mathfrak{D}}^{A}_{M(a)}|}{|\vec{\mathfrak{D}}^{B}_{M(b)}|}$$

If cos(θ) & L = 1, then DFT and DMC energies differ only by a constant energy shift.

"LSDA" and "PBE" energy correlation parameters are with respect to DMC, while "DMC" is with respect to SJB-DMC.

	$\cos\theta$			L			σ (eV)	
Cluster	LSDA	PBE	DMC	LSDA	PBE	DMC	LSDA	PBE
Li_{13}	0.9973	0.9773	0.9973	1.02	1.02	0.99	0.03	0.08
Na_{13}	0.9649	0.9632	–	1.01	0.83	–	0.06	0.07
Be_{13}	0.9797	0.9574	0.9994	0.97	1.09	0.99	0.12	0.17
Mg_{13}	0.9930	0.9906	0.9999	0.98	0.81	1.01	0.07	0.13
Al_{13}	0.9972	0.9976	0.9998	0.98	0.85	1.01	0.08	0.13

$$\cos\theta = \frac{\vec{\mathfrak{D}}^{\mathrm{DFT}} \cdot \vec{\mathfrak{D}}^{\mathrm{DMC}}}{\left|\vec{\mathfrak{D}}^{\mathrm{DFT}}\right| \left|\vec{\mathfrak{D}}^{\mathrm{DMC}}\right|} \qquad L = \frac{\left|\vec{\mathfrak{D}}^{\mathrm{DFT}}\right|}{\left|\vec{\mathfrak{D}}^{\mathrm{DMC}}\right|} \qquad \sigma^2 = \frac{1}{n}\left|\vec{\mathfrak{D}}^{\mathrm{DFT}} - \vec{\mathfrak{D}}^{\mathrm{DMC}}\right|^2$$

1. *LSDA and PBE functionals are reasonably reliable for studying the energetics of simple metallic clusters.*
2. *PBE predicts smaller values of L (Na_{13}, Mg_{13}, and Al_{13}) and thus tends to give smaller energy difference than DMC.*
3. *Backflow lowers the DMC energies but does not affect the relative stabilities of the clusters.*

Outline

- Motivation? Why using QMC?
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  - ✓ **covalent and metallic clusters**
  - ✓ **band gaps of TiO_2, MgO, NaCl**
  - ✓ **surface adsorption on graphene & Al(100)**
  - ✓ **interlayer binding of two BN sheets**
  - ✓ **surface energy: $\Delta S(DMC) > \Delta S(LDA) > \Delta S(PBE)$**
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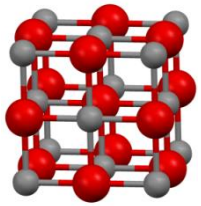
  - ✓ **CO adsorption on late TM (111) surfaces**

Band Gap by DMC :

MgO (32)

256 electrons



	LDA	DMC	GW	EXP.
E_{gap} (eV)	5.65	8.0(2)	8.2[a]	7.8[b]

a. *A. Yamasaki et al. Phys. Rev. B 66, 245108 (2002)*
b. *R. C. Whited et al. Solid State Commun. 13, 1903 (1973)*

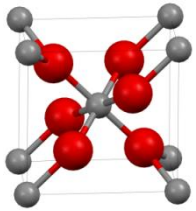
NaCl (32)

512 electrons

	DMC	EXP.
E_{gap} (eV)	8.1(3)	8.9

TiO_2 (16+32)

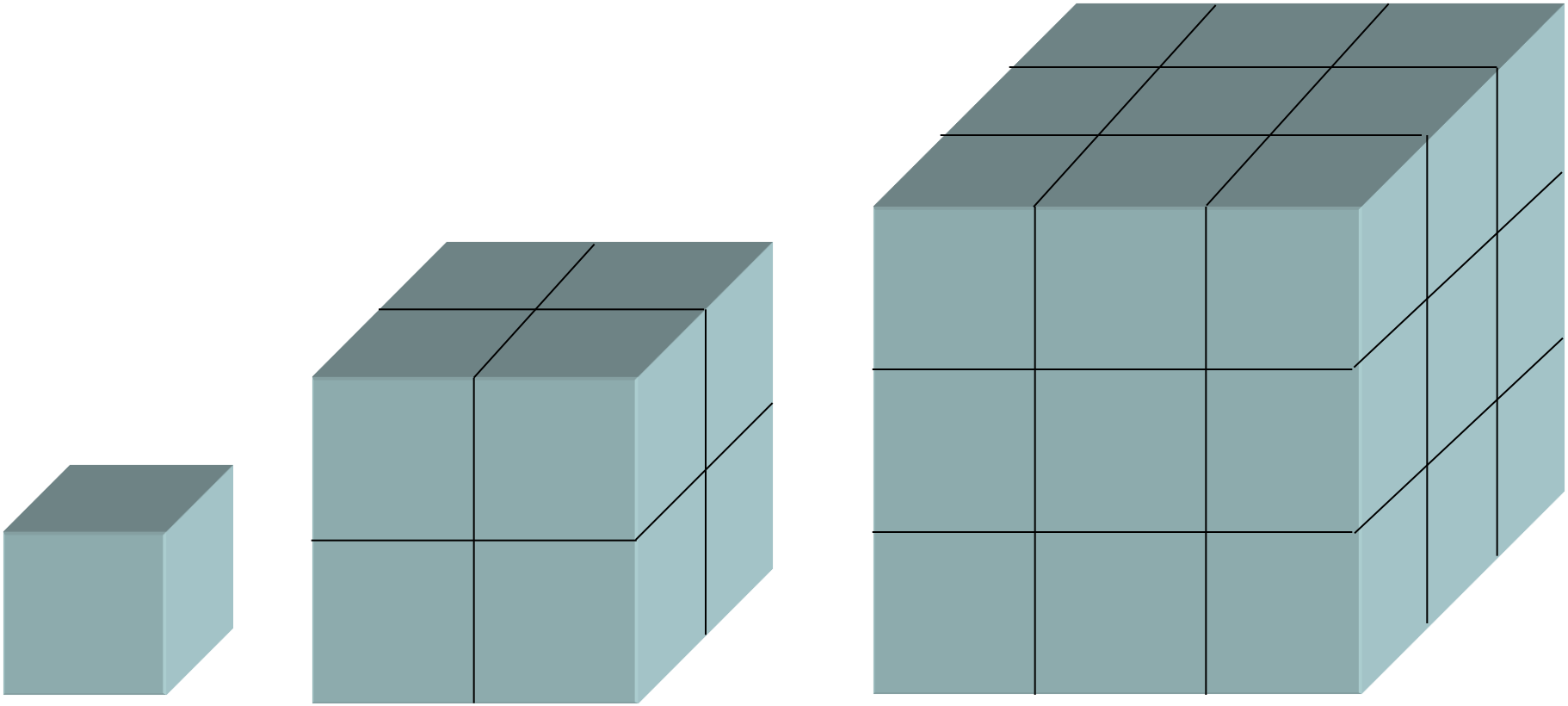
384 electrons



	LDA	DMC	GW	EXP.
E_{gap} (eV)	0.48	3.8(3)	3.78[a]	3.1[b]

a. *M. Van Schilfgaarde et al. Phys. Rev. Lett. 96, 226402 (2006)*
b. *A. Amtout and R. Leonelli Phys. Rev. B 51, 6842 (1995)*

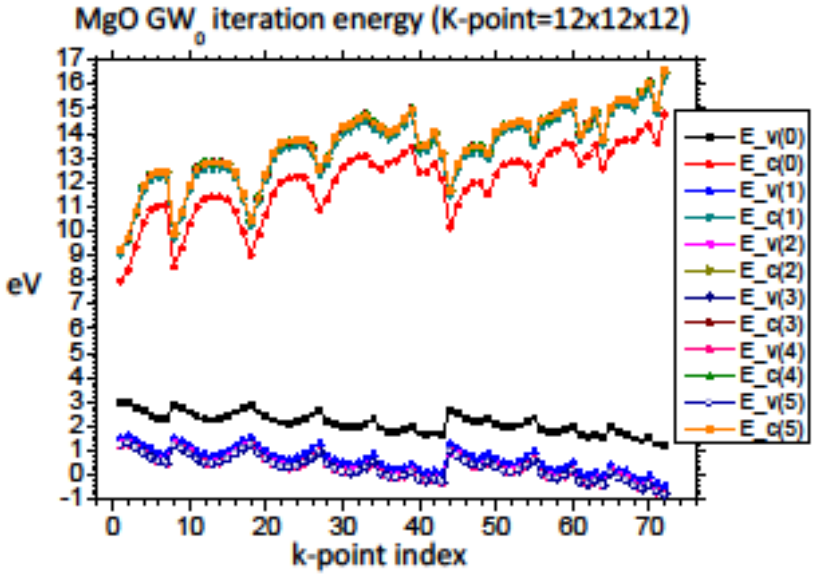
Supercell

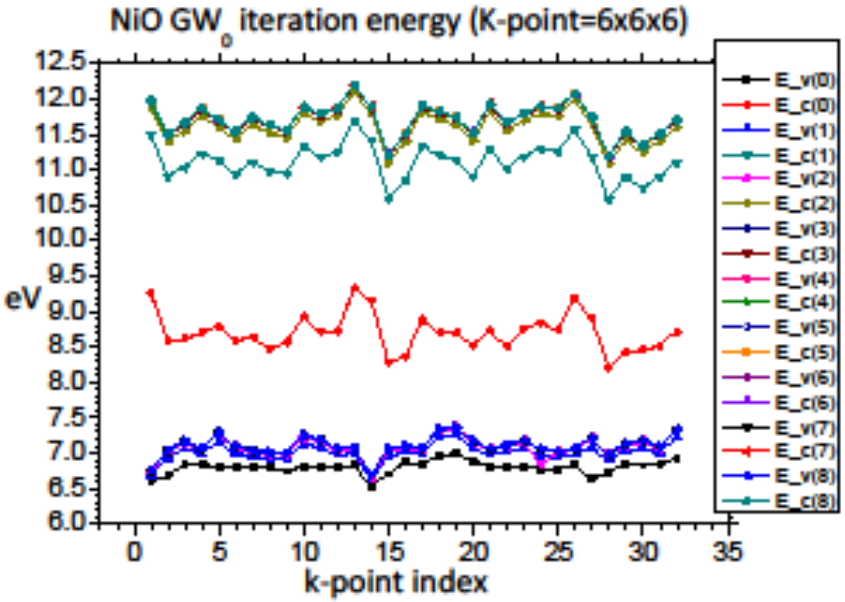


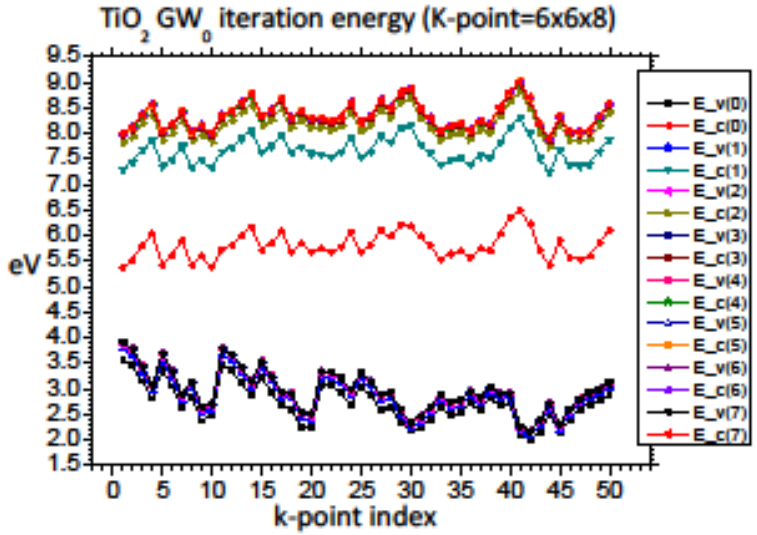
Unit cell
GW

2x2x2
DMC

3x3x3
DMC







For band gap calculations, try "NOT" to use QMC, but use GW calculations!

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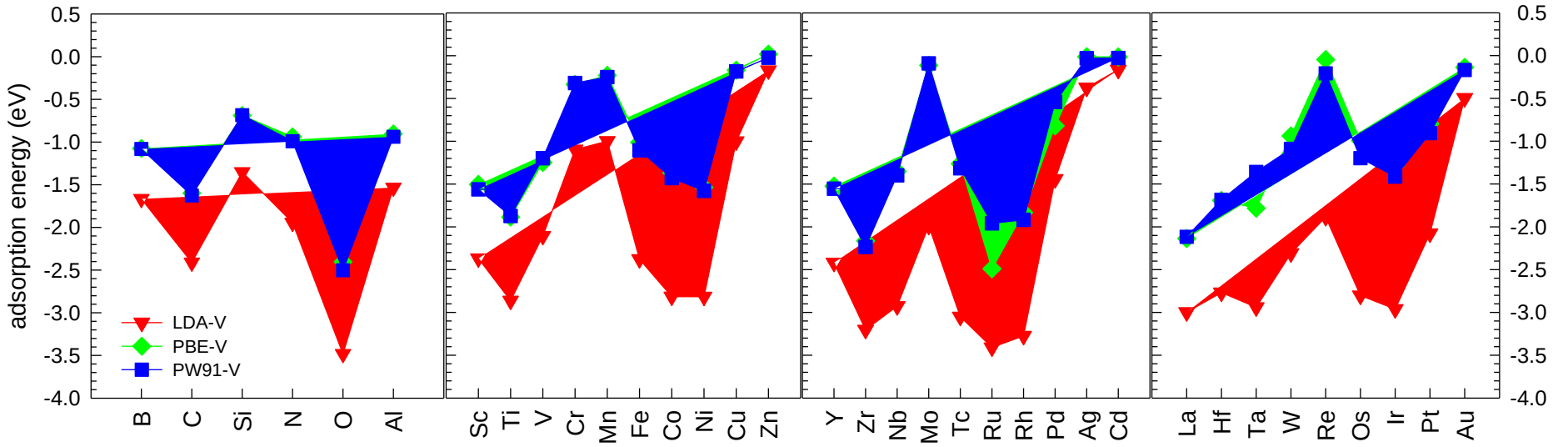
Single atom @ graphene



LDA & GGA predict different adsorption energy at preferred adsorption site!

Except for Zn & Cd atom, the adsorption energy difference obtained by LDA and GGA is ranging from 0.4 ~ 1.8 eV.

QMC is needed to check the accuracy of exchange-correlation approximations !

PHYSICAL REVIEW B **77**, 235430 (2008)

First-principles study of metal adatom adsorption on graphene

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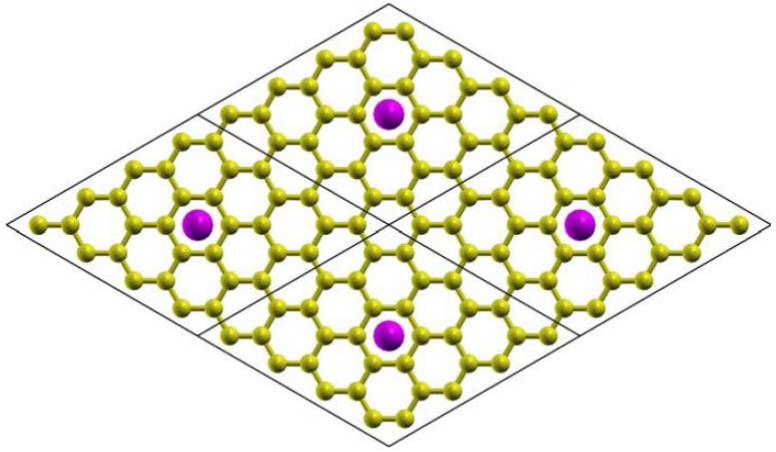
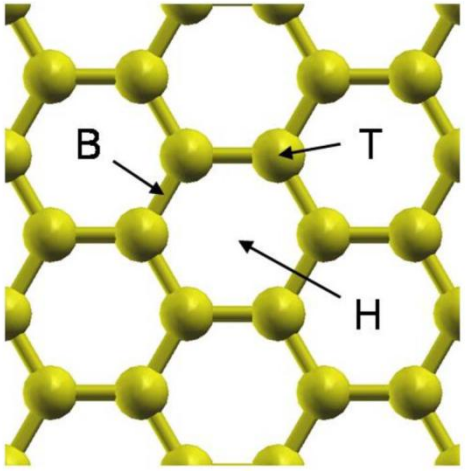
[2]*Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA*
[3]*The Molecular Foundry, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA*
(Received 30 April 2008; published 20 June 2008)

VASP-PBE

Li, Na, K, Ca, Al, Ga, In, Sn, Ti, Fe, Pd, Au





DFT : primitive unit cell with the k-point set summation
DMC: many-body unit cell with only one special k-point

O adsorption on Graphene

- **K-point = (-1/2,1/2) (1/2,1/2) 2x2x1**
- **E_ads(DFT) = -3.130 -3.679 -3.405 eV**
- **E_ads(DMC) = -1.059 -1.816 -1.437 eV**

- **K-point = (0,0) (-1/3,1/3) (1/3,0) (1/3,1/3) 3x3x1**
- **E_ads(DFT) = -3.190 -4.158 -3.373 -3.031 -3.451 eV**
- **E_ads(DMC)= -1.151 -2.298 -1.476 -0.919 -1.499 eV**

Over-binding effect predicted by LDA is ~ 2eV

In order to check the dependence of binding energies on the "special k-point", here we show the DFT and DMC adsorption energy results of single O atom on graphene (see table below).

(eV)	E(0,0)	E(-1/3,1/3)	E(1/3,0)	E(1/3,1/3)	Twist ave.
E_ads(DMC)-E_ads(DFT)	2.039	1.860	1.897	2.112	1.952

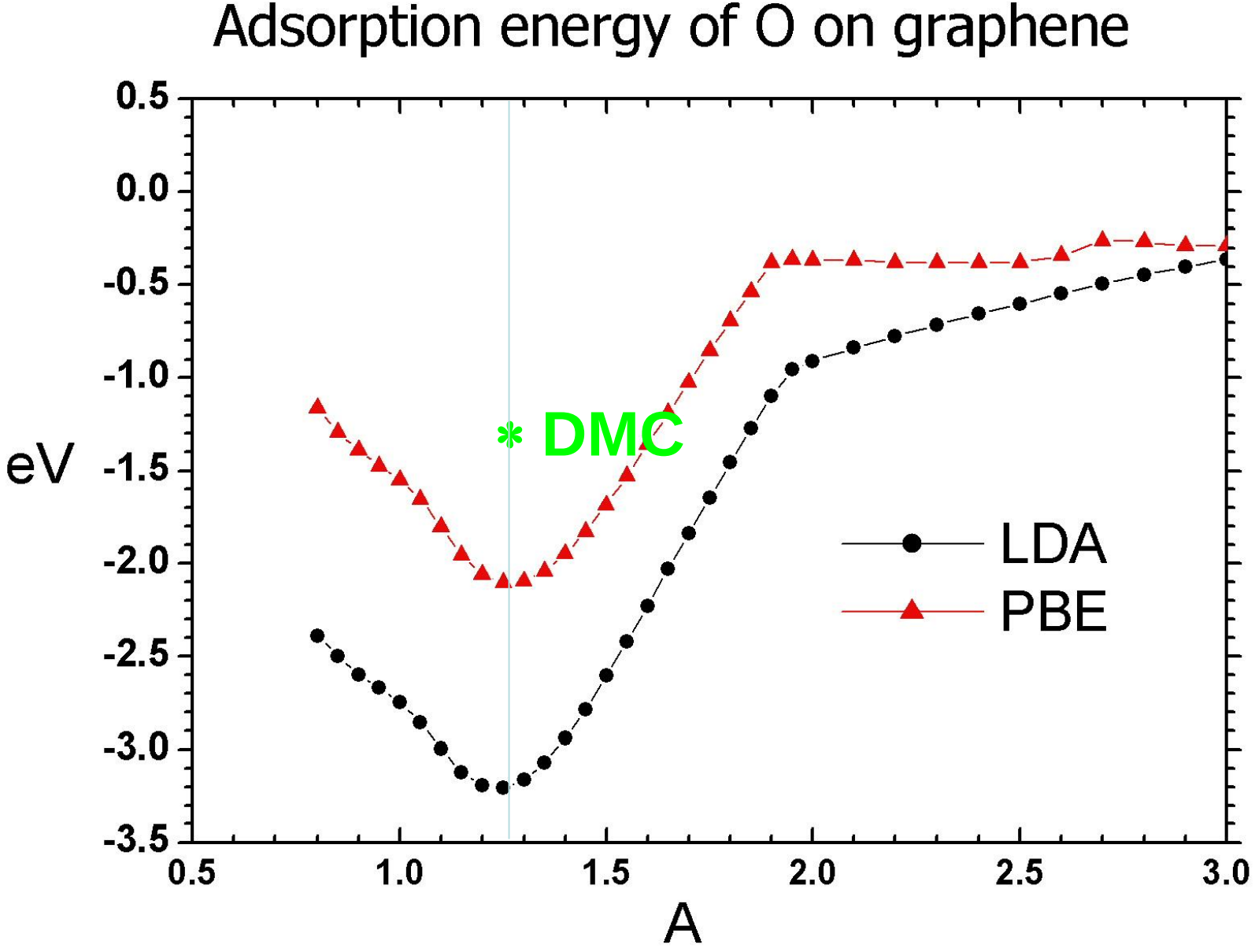
Twist ave. =E(0,0)/9+E(-1/3,-1/3)*2/9+E(1/3,0)*4/9+E(1/3,1/3)*2/9

(eV)	E(-1/2,1/2)	E(1/2,1/2)	Twist ave.	(1/2,0) Zone
E_ads(DMC) -E_ads(DFT)	2.071	1.863	1.968	1.811

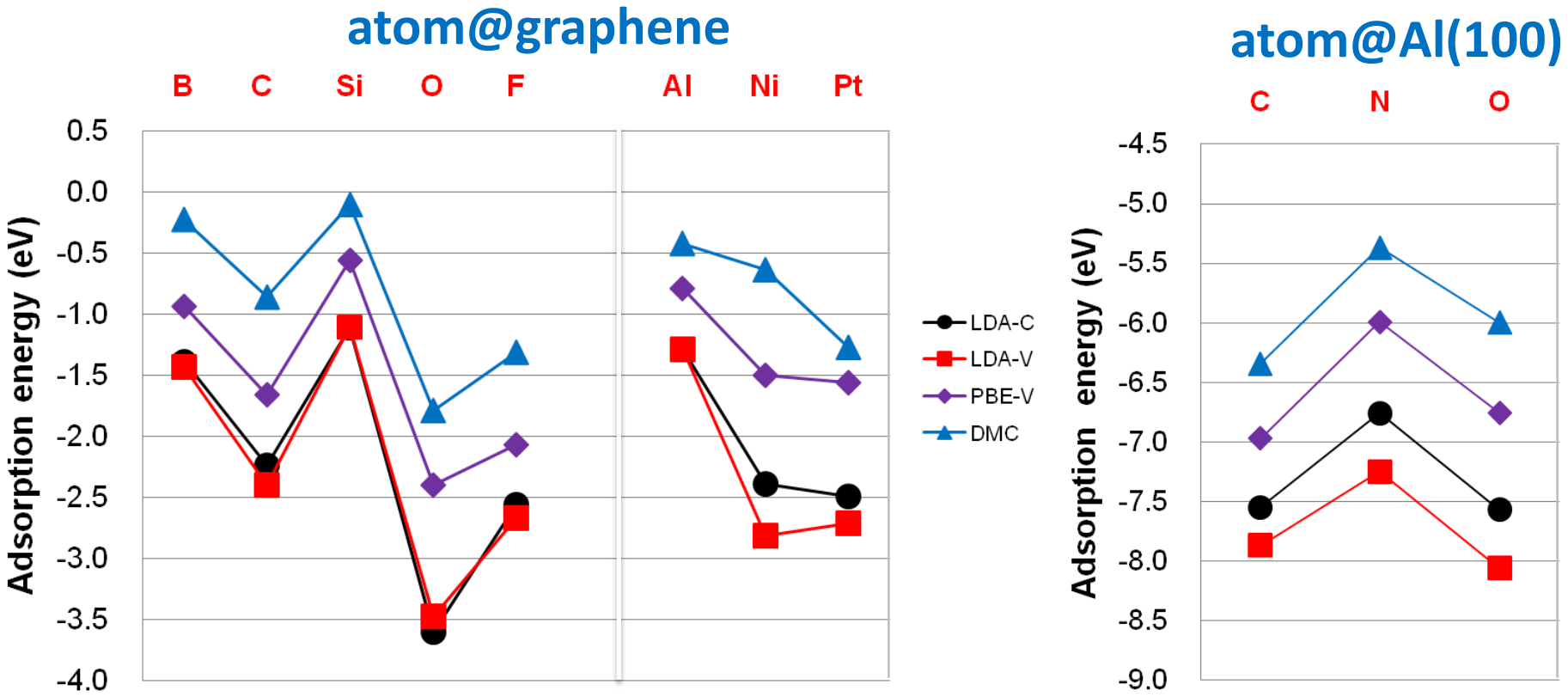
Twist ave. =E(-1/2,1/2)*1/2+E(1/2,1/2)*1/2

1. E(p,q) means the adsorption energy difference obtained at special k-point (p,q)
2. (0,0) , (-1/3,1/3) , (1/3,0) and (1/3,1/3) are four symmetry irreducible k points obtained from the Monkhorst-Pack 3x3 k-point set.
3. (-1/2,1/2) and (1/2,1/2) are two symmetry irreducible k points obtained from the Monkhorst-Pack 2x2 k-point set.
4. The twist average is the weighted average from independent special k points.

From above table, one can see the binding energy difference obtained from DFT and DMC is nearly independent of the choice of the special k point and this good property has ensured the correctness of the DMC results based on one selected special k point.


Adsorption energy of O on graphene
0.5
0.0
-0.5
-1.0
-1.5
-2.0
-2.5
-3.0
-3.5
eV
* DMC
LDA
PBE
0.5
1.0
1.5
2.0
2.5
3.0
A

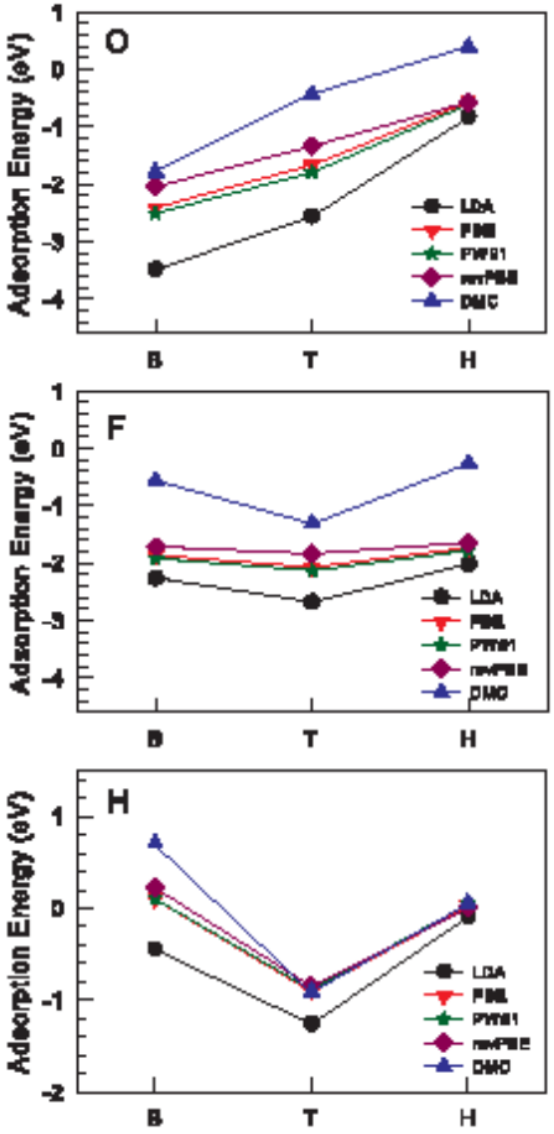
Single atom@graphene & Al(100)



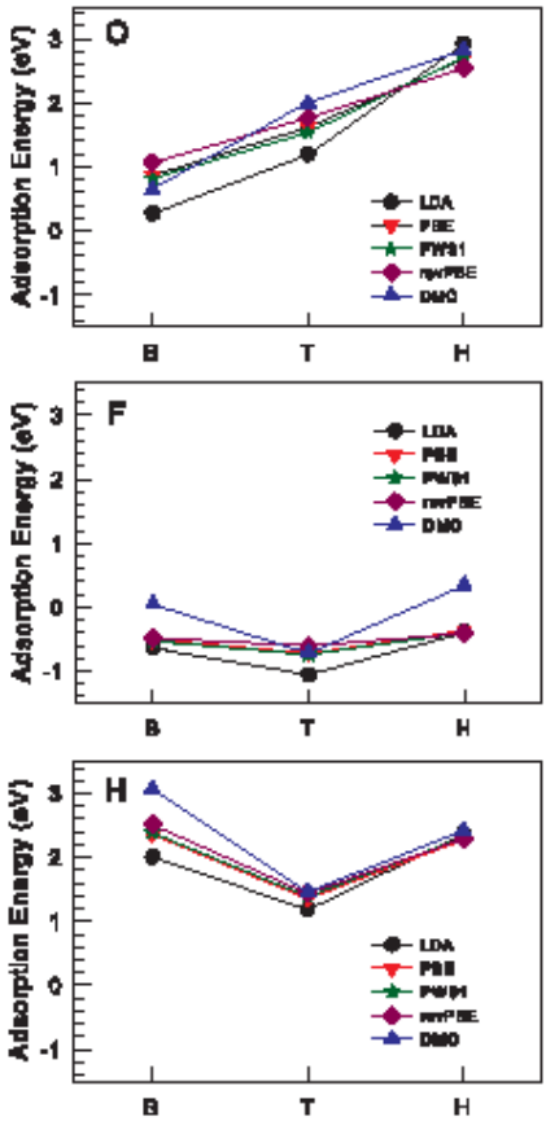
LDA overbinding 0.9~1.8 eV
GGA overbinding 0.3~0.9 eV

LDA overbinding ~1.5 eV
GGA overbinding ~0.7 eV

Adsorption energies of a single O, F and H atom at different adsorption sites on graphene are compared.

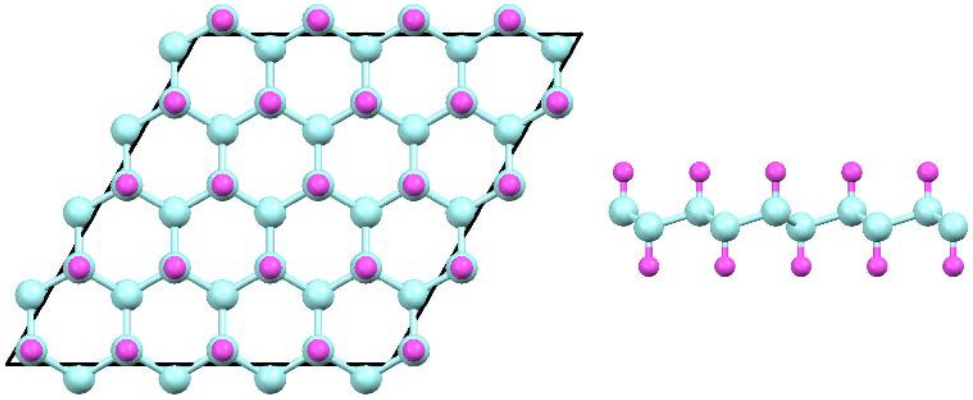


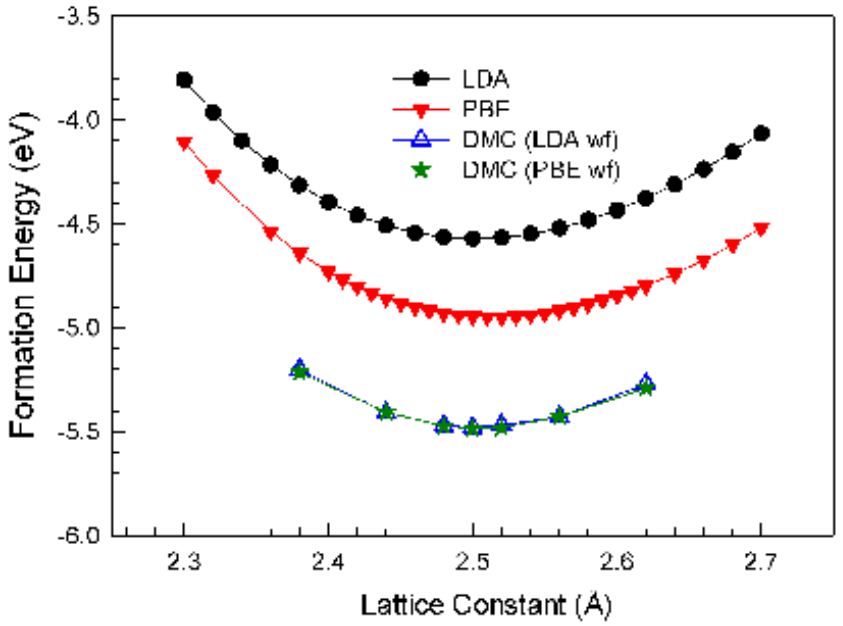
energies with respect to an isolated atom



energies with respect to an isolated molecule

Formation energies of graphane as a function of the lattice constant





1. *The DMC calculation gives a lattice constant of 2.50 ˚A, which is greater than that of graphene (2.46 ˚A).*
2. *This value is larger than the reported experimental value of 2.42 ˚A in a TEM measurement. This could be arisen from the substrate interaction.*

Outline

- Motivation? Why using QMC?
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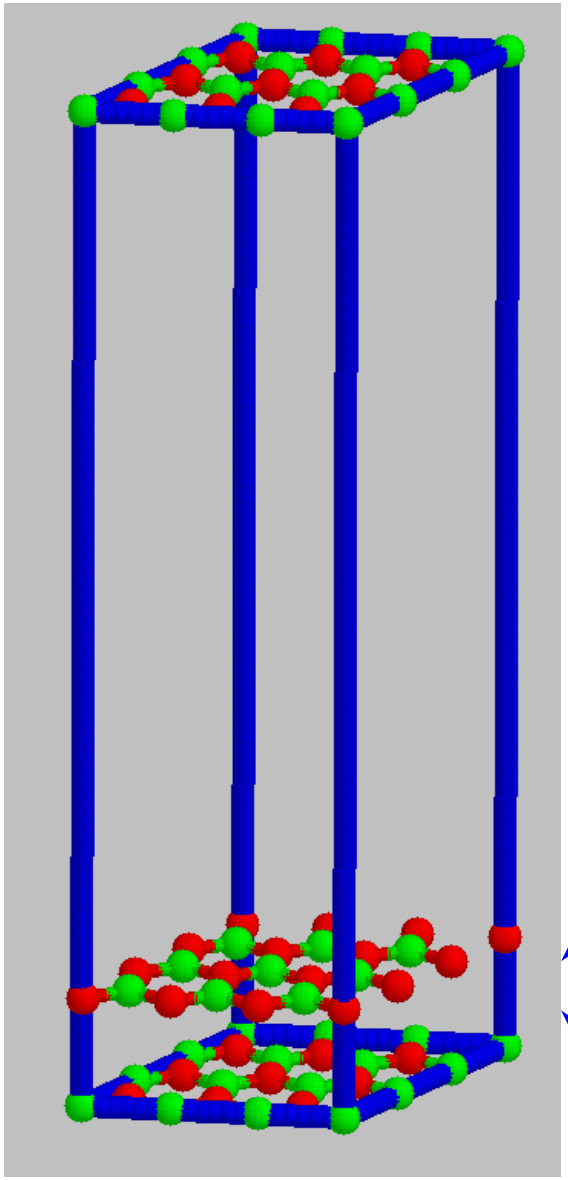
  - ✓ covalent and metallic clusters
  - ✓ band gaps of TiO_2, MgO, NaCl
  - ✓ surface adsorption on graphene & Al(100)
  - ✓ **interlayer binding of two BN sheets**
  - ✓ surface energy: $\Delta S(DMC) > \Delta S(LDA) > \Delta S(PBE)$
  - ✓ O, OH & H_2O adsorption on surfaces
  - ✓ CO adsorption on late TM (111) surfaces

BN bilayer : supercell structure

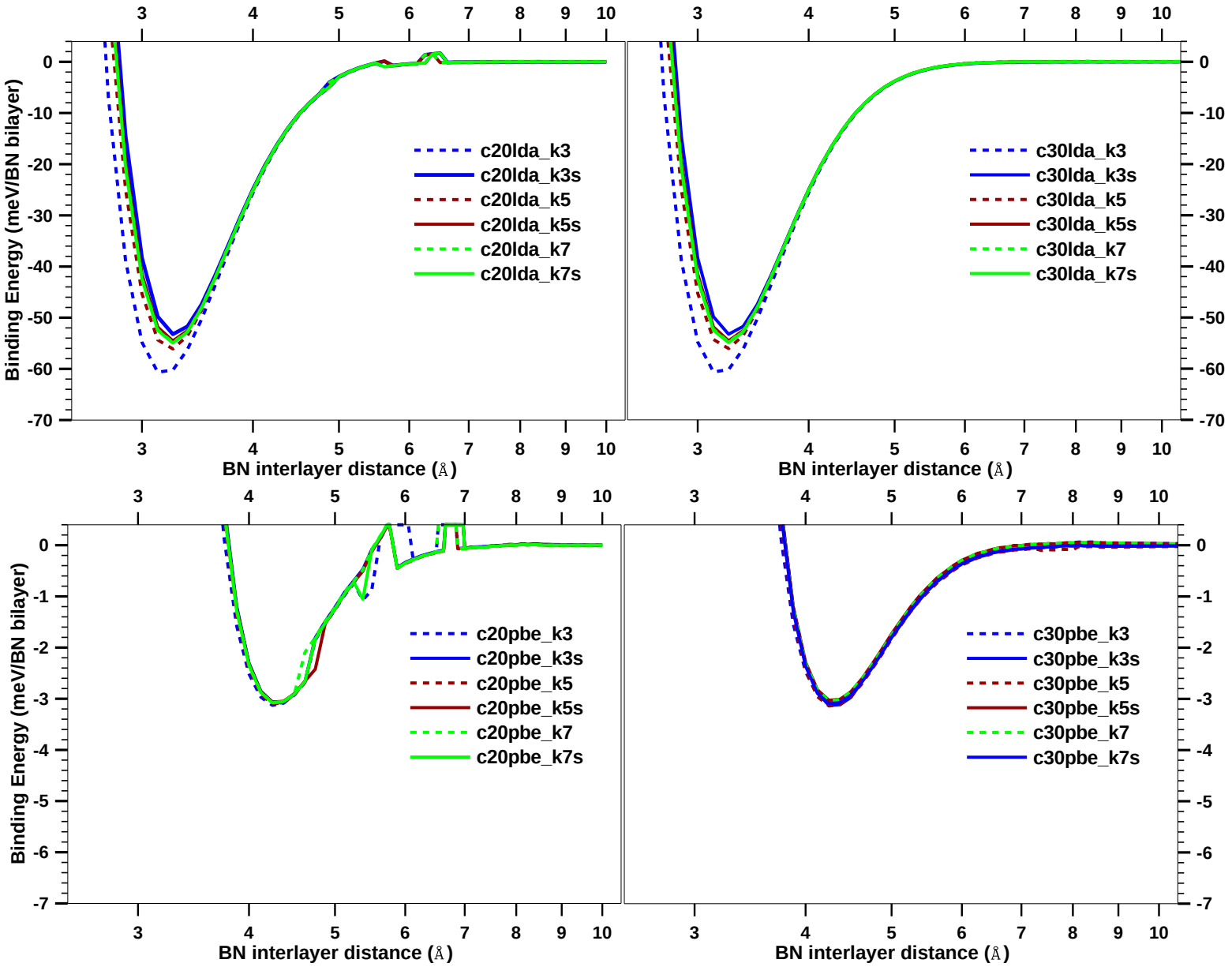


c=30Å

d : bilayer distance

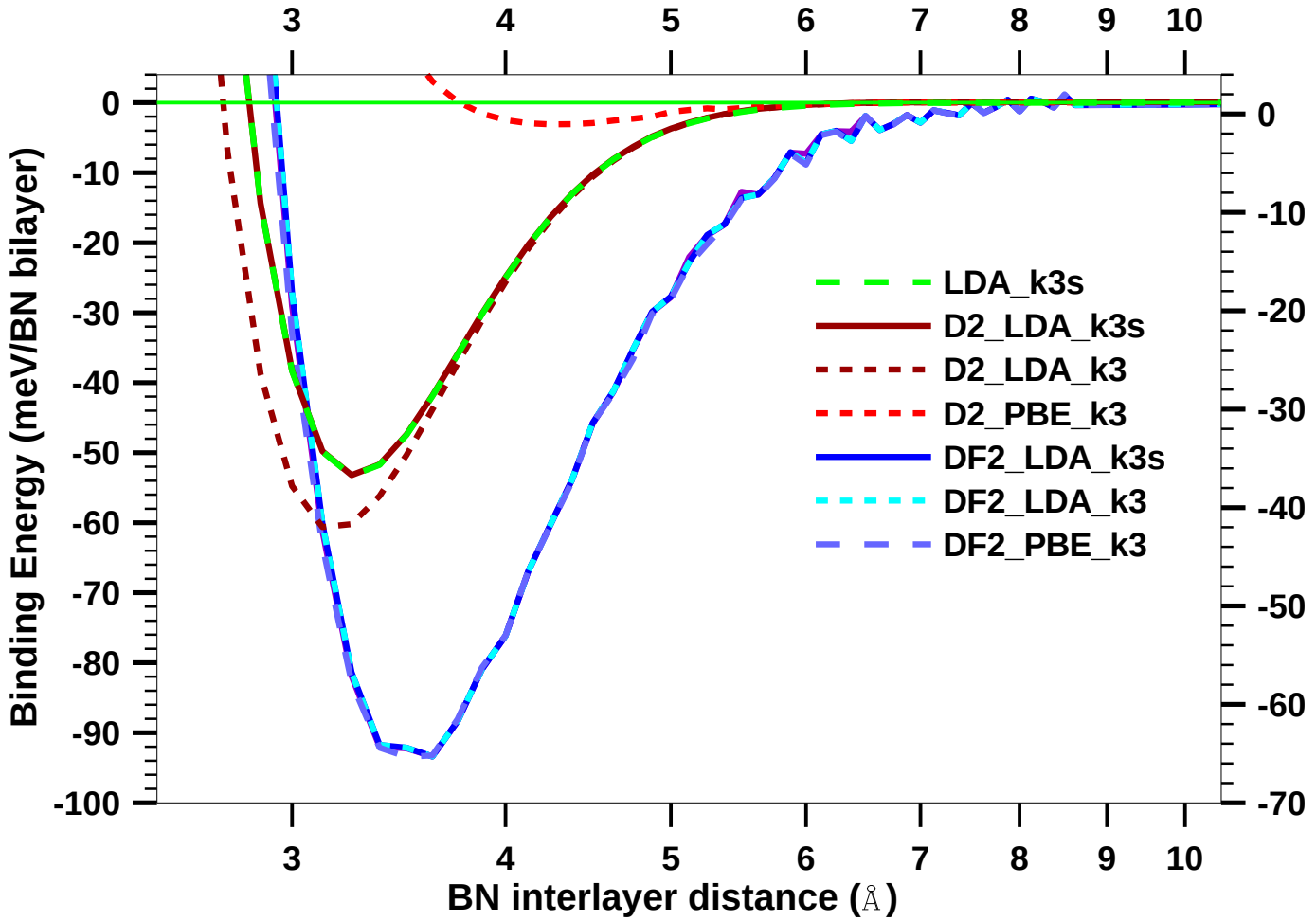
Worked done by Dr. Cheng Ching (NCKU)

DFT_LDA & DFT_GGA : effect of c and k points



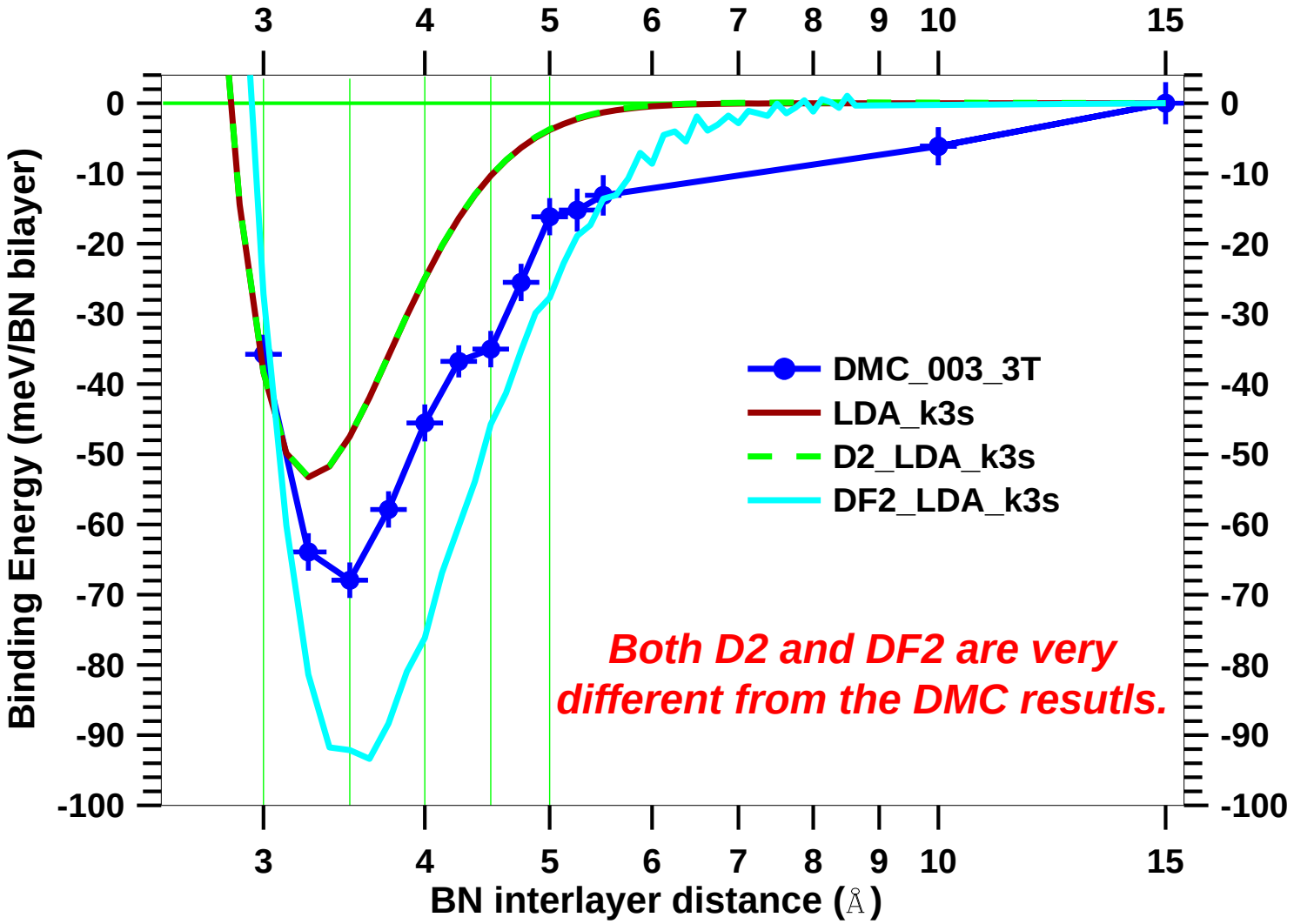
DFT_vdW : D2 and DF2 (and LDA)

- D2: S. Grimme, ``*Semiempirical GGA-type density functional constructed with a long-range dispersion correction*", J. Comp. Chem. 27, 1787 (2006).
- DF2: K. Lee, E. D. Murray, L. Kong, B. I. Lundqvist, and D. C. Langreth, Phys. Rev. B **82**, 081101 (2010).



DMC v.s. vdW_DFT v.s. LDA

- D2: S. Grimme, J. Comp. Chem. 27, 1787 (2006).
- DF2: K. Lee, E. D. Murray, L. Kong, B. I. Lundqvist, and D. C. Langreth, Phys. Rev. B **82**, 081101 (2010).



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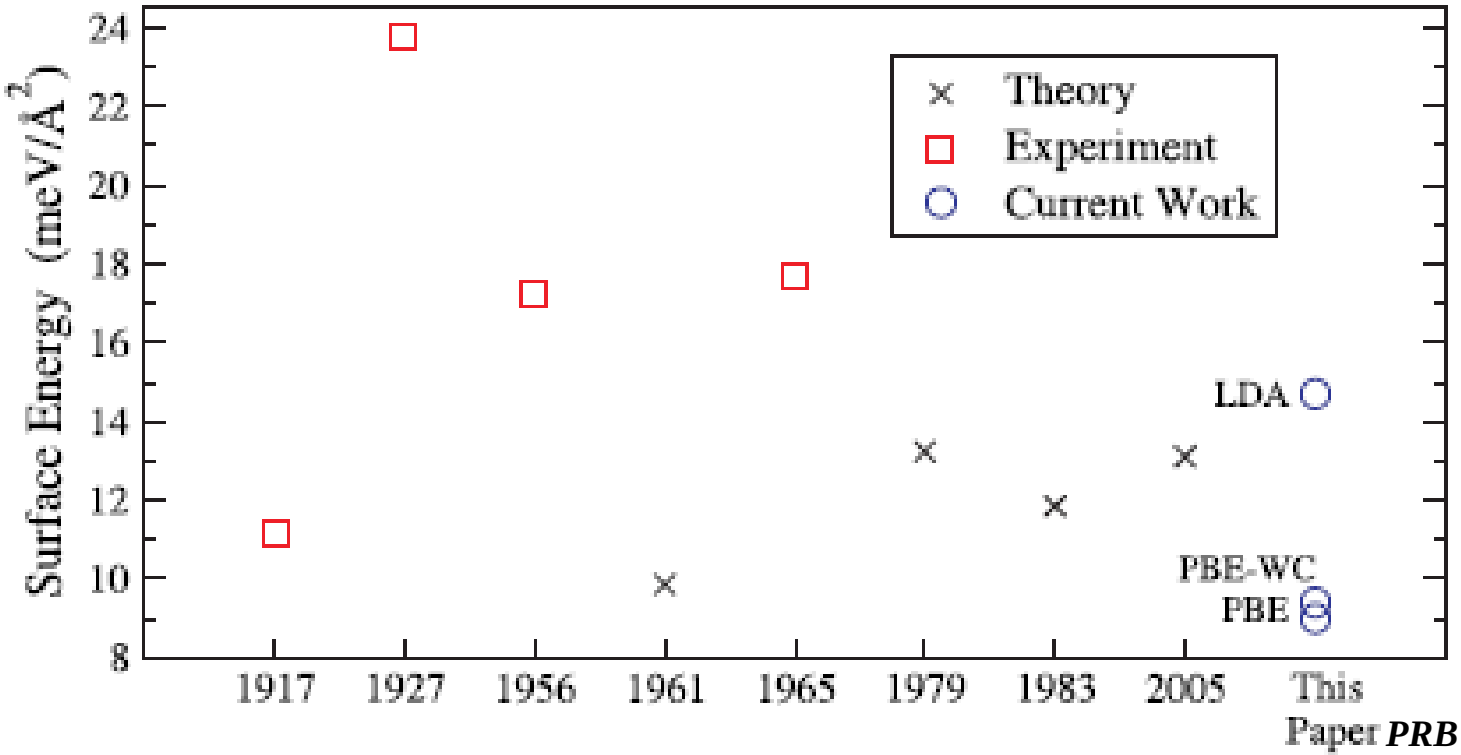
  - ✓ ***O, OH & H_2O adsorption on surfaces***
  - ✓ ***CO adsorption on late TM (111) surfaces***

Why study surface energy?

- *Surface energy is a fundamental quantity !*
- *Surface energy is difficulty to measure !*



PRB 76, 075401 (2007)

Can one obtain reliable Surface Energy using QMC?

INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **18** (2006) L435–L440 doi:10.1088/0953-8984/18/35/L01

LETTER TO THE EDITOR

The energetics of oxide surfaces by quantum Monte Carlo

D Alfè[1,2,3] and M J Gillan[2,3]

Abstract

Density functional theory (DFT) is widely used in surface science, but for some properties the predictions depend strongly on the approximation used for exchange–correlation energy. We note recent suggestions that the widely used generalized gradient approximation (GGA) is inferior to the local density approximation (LDA) for the surface formation energy σ of both transition metals and oxides. We report quantum Monte Carlo calculations of σ for the MgO(001) surface which support the accuracy of LDA for this case, and indicate that GGA is too low by ∼30%. We point out the potentially important implications of this result for nanoscience modelling.

MgO(001) – surface energy

DFT input : (with exp. lattice constant a_0=4.21Å)

1. **periodic cell dimension : surface** $a_0/\sqrt{2} \times a_0/\sqrt{2} \times 5a_0$ **(5 MgO layers + 5 vacuum)**
   bulk1 $a_0/\sqrt{2} \times a_0/\sqrt{2} \times 2a_0$ **(4 MgO layers)**
   bulk2 $a_0/\sqrt{2} \times a_0/\sqrt{2} \times 5a_0$ **(10 MgO layers)**

   Energy difference per MgO for bulk1 and bulk2 is only 2.7 meV, thus it is safe to use surface and bulk1 to calculate the surface energy.
2. **Ecut : 3000 eV**
3. **XC functional : LDA**

DMC input : (following DFT input)

1. **supercell : 2x2x1**
2. **time step = 0.01**
3. **number of moves = 30,000**

Exp. : 1.04 ~1.20 joule/m^2

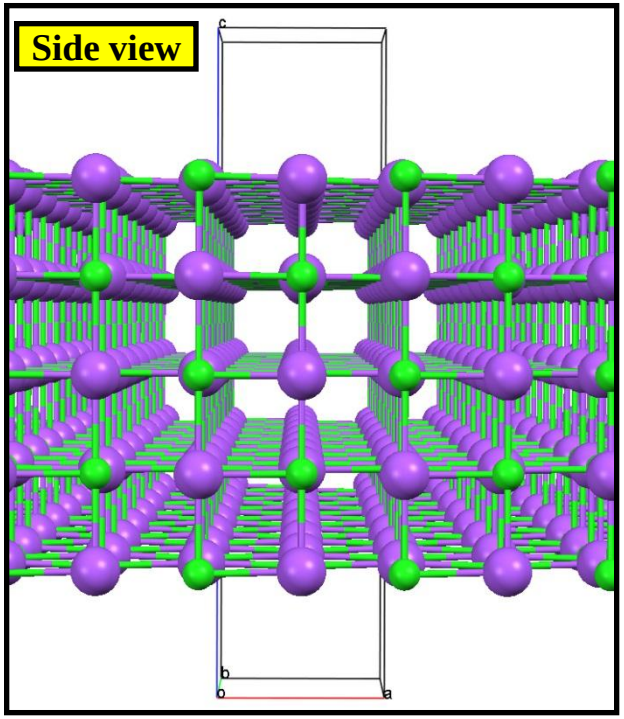
Surface formation energy (joule/m^2)

LDA-221K	LDA-661K	PBE-221K	PBE-661K	DMC-221K (He-core)	DMC-221K (Ne-core)
1.094	1.179	0.735	0.860	1.238	1.181

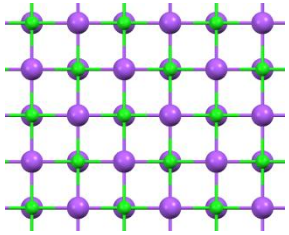
1. *LDA-221K means the DFT-LDA calculation using 2x2x1 k-point mesh*
2. *DMC result is using He-core for Mg pseudopotential*
3. *DMC-2e result is using Ne-core for Mg pseudopotential*
4. *DMC & DMC-2e statistical error are about 0.05 joule/m^2*

NaCl

Side view



Top view

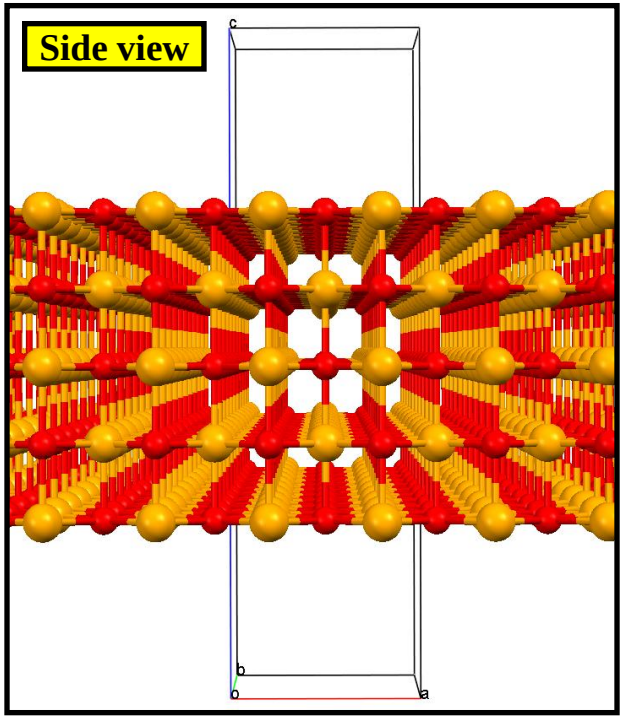


Na atom

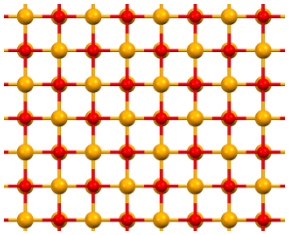
Cl atom

MgO

Side view



Top view

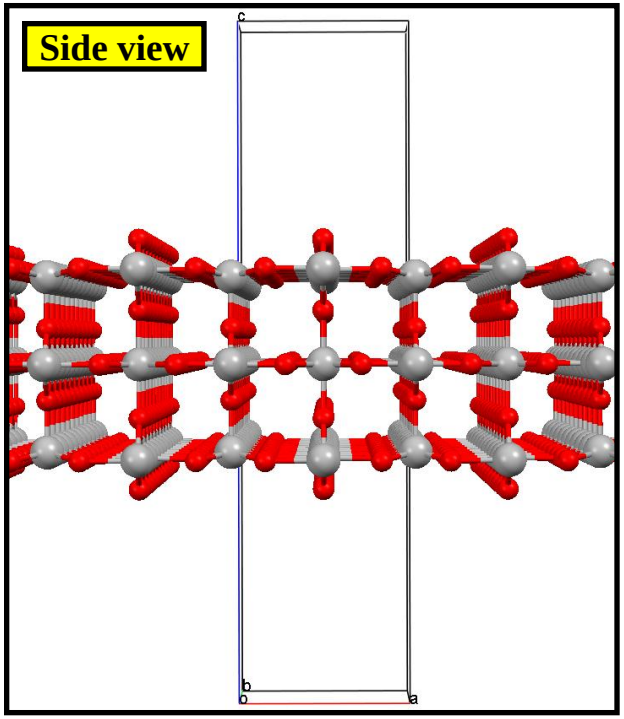


Mg atom

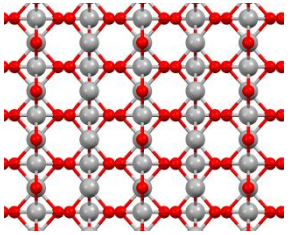
O atom

TiO_2

Side view



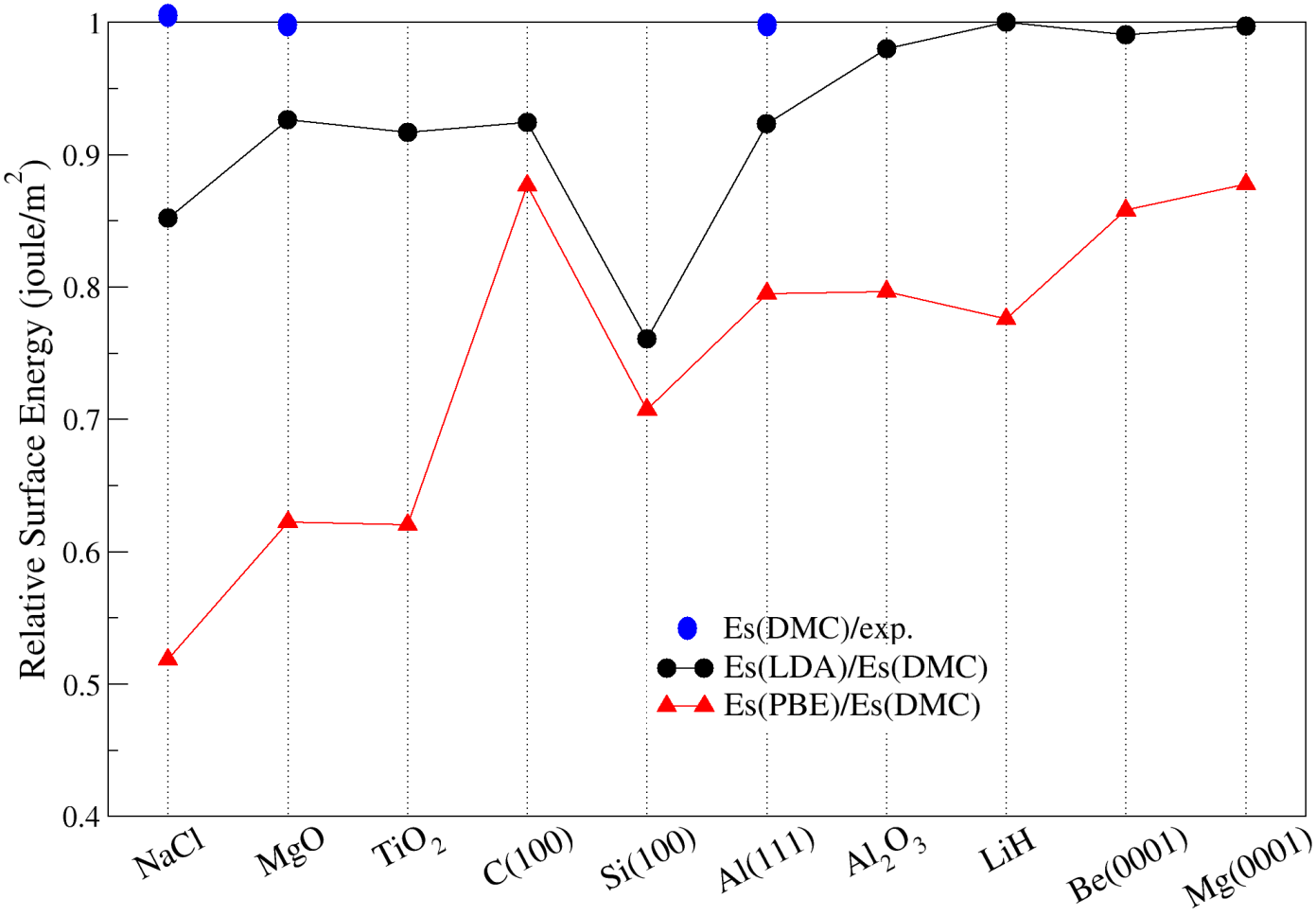
Top view



Ti atom

O atom

ΔS(DMC) > ΔS(LDA) > ΔS(PBE)



(1) For NaCl, MgO and Al(111), DMC results reproduce experimental data accurately.
(2) The surface energies predicted by LDA and PBE functionals are underestimated.

ELSEVIER

Surface Science 385 (1997) 386–394

surface science

ΔS(DMC) > ΔS(LDA)> ΔS(PBE) > ΔS(Expt) ???

A systematic study of the surface energetics and structure of TiO_2(110) by first-principles calculations

S.P. Bates *, G. Kresse, M.J. Gillan

INSTITUTE OF PHYSICS PUBLISHING

JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **18** (2006) 4207–4217

doi:10.1088/0953-8984/18/17/009

The energetics and structure of rutile TiO_2(110)

A Kiejna[1], T Pabisiak[1] and S W Gao[2]

These numbers are in line with the recent results obtained with the same code (GGA-PW91: 0.56 J m^{-2} [11]). Earlier calculations [3–9] gave substantially larger values of σ, falling in the ranges 1.10 J m^{-2} and 0.83 J m^{-2} (LDA, 3L and 6L slabs, respectively [3]), 0.84 J m^{-2} (LDA, 6L [8]), 0.73 J m^{-2} (GGA-PW91, 7L [6]), 0.80 J m^{-2} (GGA-PW91, 6L [9]), 0.81 J m^{-2} (GGA-PW91, 3L [7]); 1.14 J m^{-2}, and 0.82–0.84 J m^{-2} (3L, LDA, and GGA, respectively [4]), 0.84 J m^{-2} (GGA, 3L [5]), with the exception of a considerably lower value of 0.31 J m^{-2}, reported for a 6L slab calculation within GGA-PBE [8]. The empirical estimate of the surface energy is 0.28–0.38 J m^{-2} [29]. In most cases cited above the overestimation of the surface

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Adsorption and dissociation of ammonia on Au(111) surface: A density functional theory study

Table 1
Adsorption energy[a] of different groups on the gold surface (kJ/mol)

	Top	Bridge	hcp	fcc
NH_3	−25.94 (−26[b])			−11.72
NH_2	−174.27	−199.01		−194.23
NH			−329.09	−349.07
N	−291.94		−463.31	−489.82
H_2O	−10.81			
OH	−206.78	−224.84	−201.30	−203.34
O	−286.60		−391.74	−409.84
H	−266.44	−280.12	−285.06	−289.64

[a] Only minimal energies are listed.
[b] See literature [23].

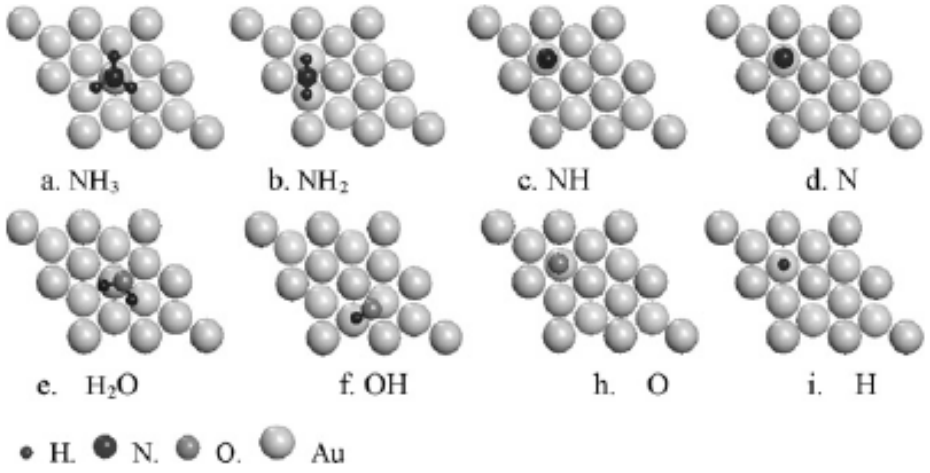


Fig. 1. Adsorbed different groups on top, bridge, fcc positions on Au(1 1 1) surfaces.

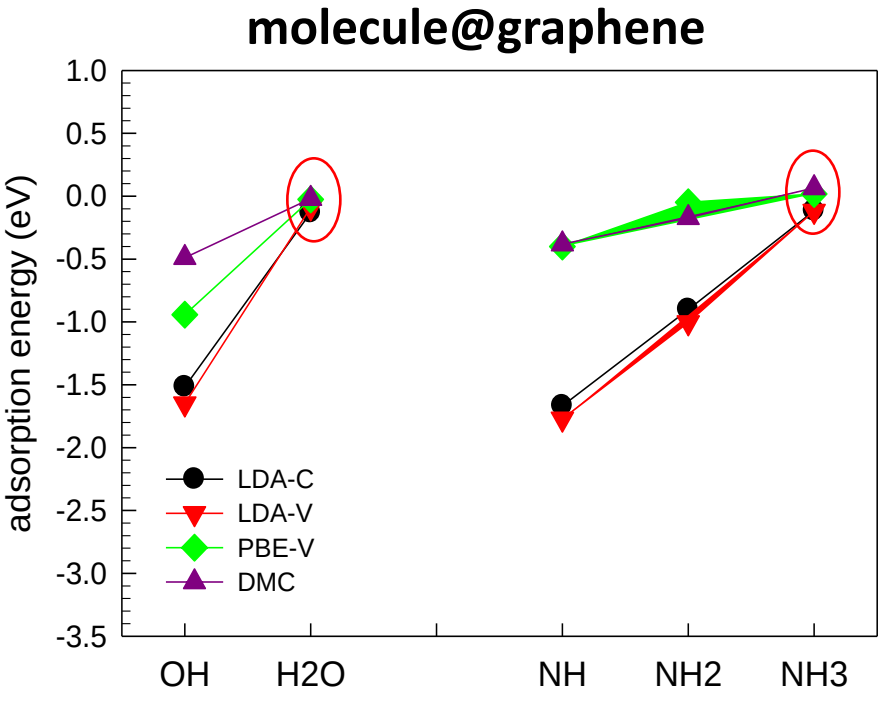
R. Liu et al., Applied Surface Science 254 (2008) 5706–5710

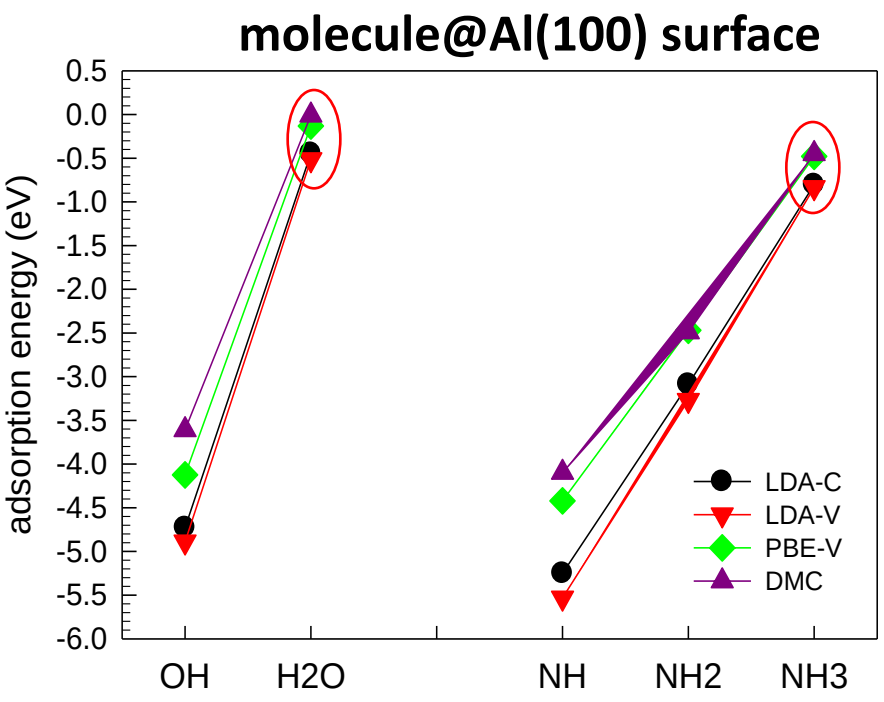
NH_3 and H_2O dehydrogenation:

- **Adsorption structures**
- **Adsorption energies**
- **Reaction barriers**
- **Energy Profiles**

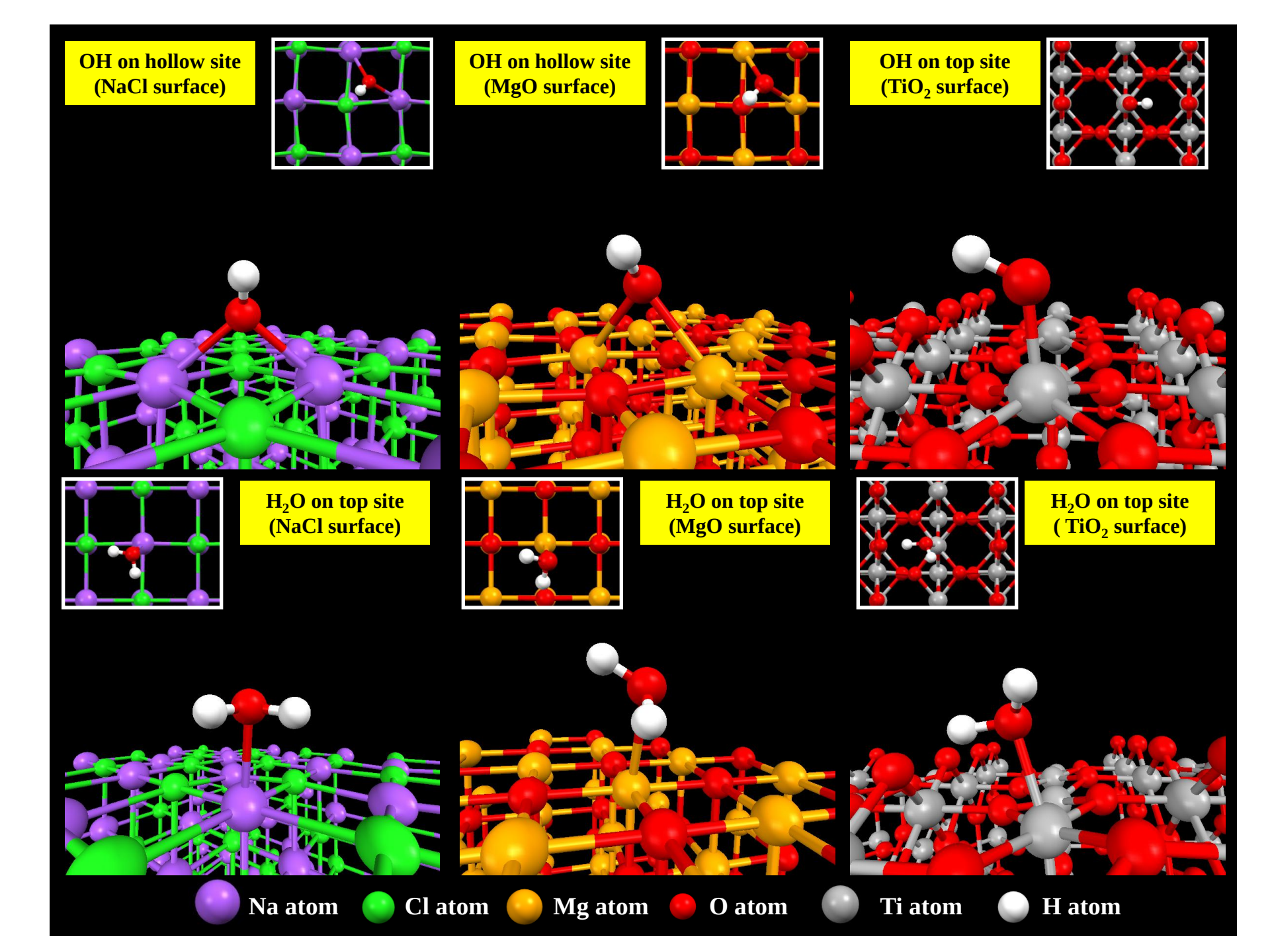
If DFT will give correct results?

Surface Adsorption

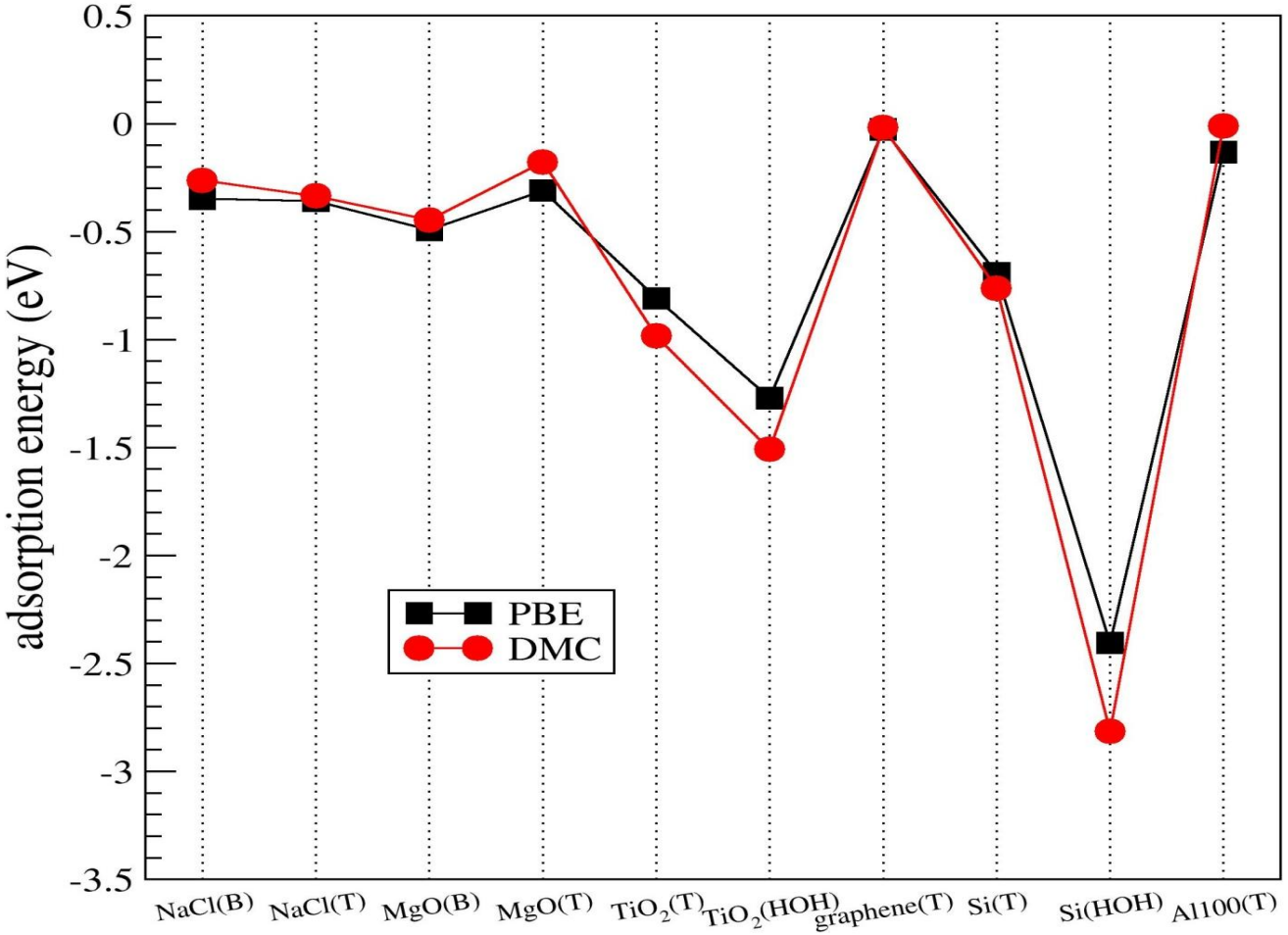




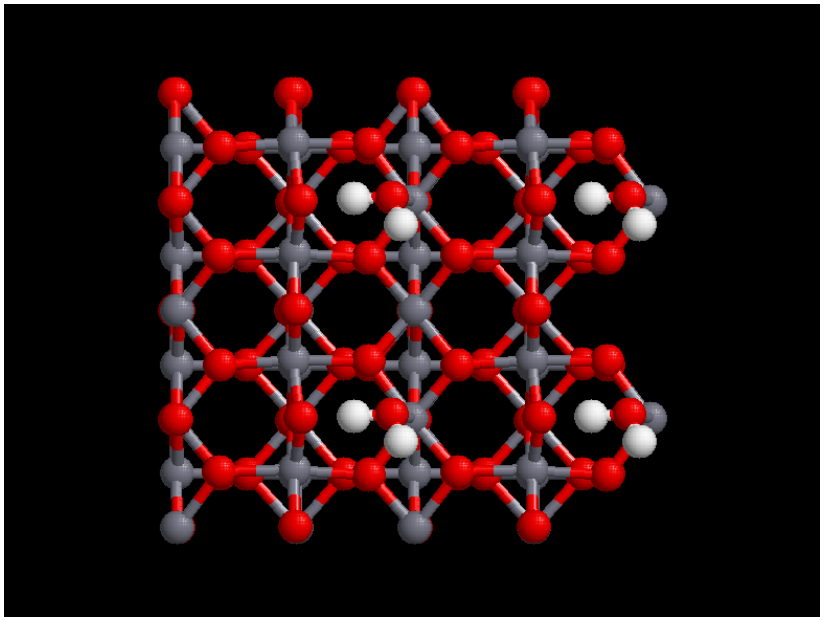
For OH adsorption : LDA and GGA have predicted over binding effects. Now the question is that: "*Will this effect be observed on the other surfaces?*".

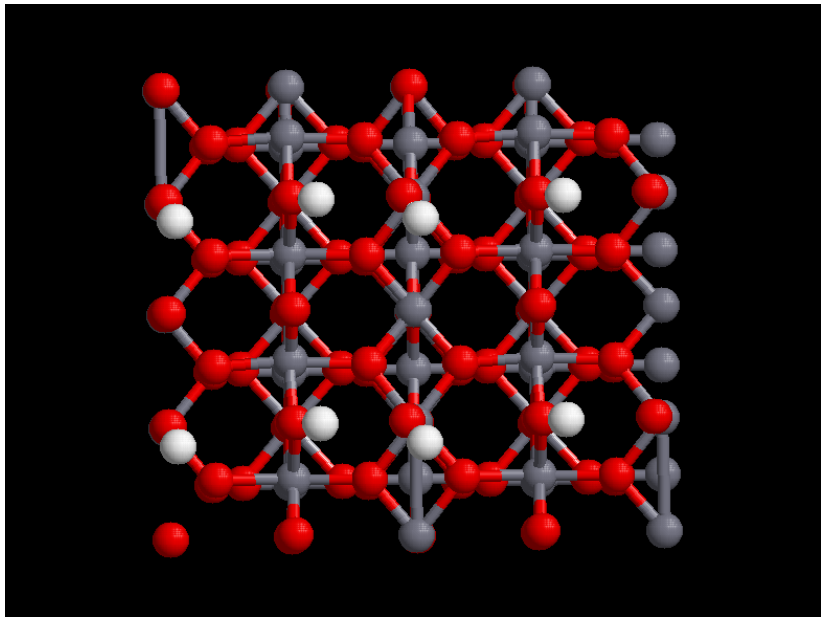

OH on hollow site (NaCl surface)
OH on hollow site (MgO surface)
OH on top site (TiO_2 surface)
H_2O on top site (NaCl surface)
H_2O on top site (MgO surface)
H_2O on top site (TiO_2 surface)
Na atom
Cl atom
Mg atom
O atom
Ti atom
H atom

Surface adsorption – H_2O



For H_2O adsorption on NaCl, MgO, TiO_2, graphene, Si, Al surfaces,
GGA predicts an correct adsorption energy.





PHYSICAL REVIEW B **86**, 045411 (2012)

Water does partially dissociate on the perfect TiO2 (110) surface: A quantitative structure determination

D. A. Duncan,1 F. Allegretti,1,2 and D. P. Woodruff1,*
1 *Physics Department, University of Warwick, Coventry CV4 7AL, United Kingdom*
2 *Physik Department E20, Technische Universita¨t Mu¨nchen, James-Franck Strasse 1, Mu¨nchen D-85748, Germany*
(Received 23 January 2012; revised manuscript received 22 June 2012; published 9 July 2012)

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  - ✓ ***O, OH & H_2O adsorption on surfaces***
  - ✓ ***CO adsorption on late TM (111) surfaces***

The CO/Pt(111) Puzzle†

Times Cited: **285**

Peter J. Feibelman,*,‡ B. Hammer,§ J. K. Nørskov,∥ F. Wagner,⊥ M. Scheffler,⊥ R. Stumpf,# R. Watwe,⊗ and J. Dumesic⊗

Sandia National Laboratories, Albuquerque, New Mexico 87185-1413, Institute of Physics and Astronomy, Aarhus University, DK-8000 Aarhus C, Denmark, Center for Atomic-Scale Materials Physics, Department of Physics, Technical University of Denmark, DK-2800 Lyngby, Denmark, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, D-14195 Berlin-Dahlem, Germany, Motorola Corporation, Computational Materials Group, Sandia National Laboratories, Albuquerque, New Mexico 87185-1415, and Department of Chemical Engineering, University of Wisconsin, Madison, Wisconsin 53706

TABLE 3: Binding Energy at *fcc*- Relative to Atop-Site for Low-Coverage CO/Pt(111)

supercell	θ(ML)	method	XC	ΔBE (eV)
$3 \times 2\sqrt{3}$	1/12	VASP, USP	PW91	0.25
2×2	1/4	Dacapo, USP	PW91	0.23
2×2	1/4	Dacapo, USP	PBE	0.24
2×2	1/4	Dacapo, USP	RPBE	0.16
2×2	1/4	Dacapo, USP	LDA	0.45
$c(4 \times 2)$	1/4	VASP, USP	LDA	0.41
$c(4 \times 2)$	1/4	Dacapo, USP	PW91	0.23
$c(4 \times 2)$	1/4	VASP, USP	PW91	0.18
$c(4 \times 2)$	1/4	VASP, PAW	PW91	0.13
$\sqrt{3} \times \sqrt{3}$-*R*30°	1/3	Dacapo, USP	PW91	0.23
$\sqrt{3} \times \sqrt{3}$-*R*30°	1/3	FP-LAPW	PW91	0.10

atomic conf.	4d 5s⁻	4d 5s⁻	4d⁻	4d⁻ 5s⁻	5d 6s⁻	5d 6s⁻	5d 6s⁻
n_d	6.6	7.6	8.7	9.6	6.2	7.2	8.3

atomic conf.	4d 5s	4d 5s	4d	4d 5s	5d 6s	5d 6s	5d 6s
n_d	6.6	7.6	8.7	9.6	6.2	7.2	8.3

1. LDA & GGA results : FCC site
2. DFT with hybrid functionals :
TOP site is slightly favor than FCC site (ΔE~50 meV)

Experimental result :
88% top site
12% bridge site

[ref] Blackman, G. S. et al. Phys. Rev. Lett. 1988, 61, 2352

CO @ TM (111) surface – DFT-RPA

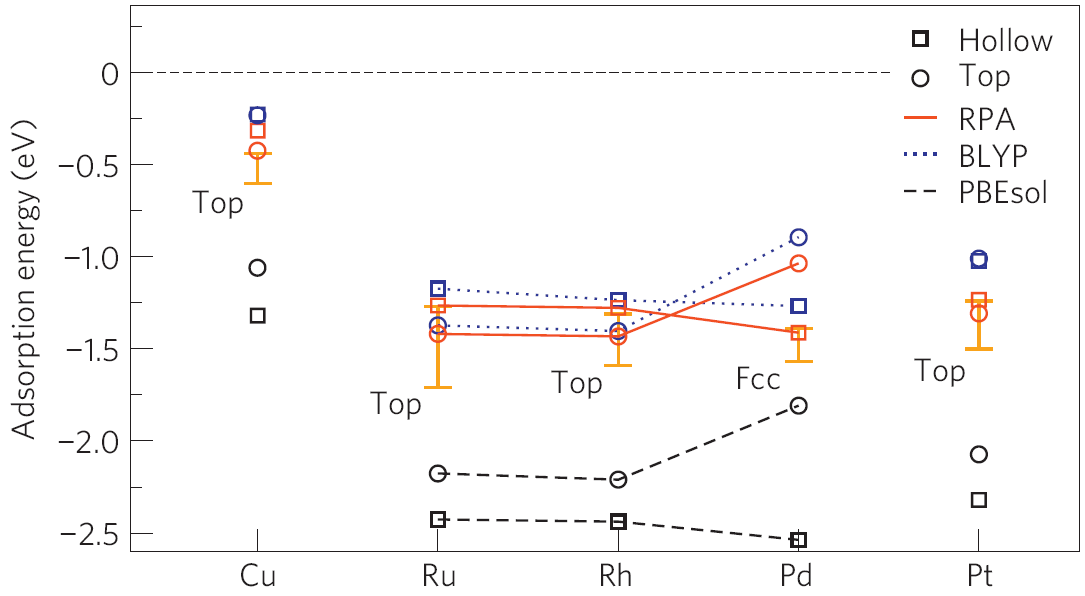
nature materials

LETTERS

PUBLISHED ONLINE: 25 JULY 2010 | DOI: 10.1038/NMAT2806

Accurate surface and adsorption energies from many-body perturbation theory

L. Schimka[1]*, J. Harl[1], A. Stroppa[2†], A. Grüneis[1], M. Marsman[1], F. Mittendorfer[1] and G. Kresse[1]



site adsorption by 350 and 550 meV, respectively. The three most critical cases are Cu, Pt and Rh, where most DFT functionals predict the wrong site order. The RPA restores the correct site order in all cases: −0.42 eV (Cu top) < −0.32 (Cu face-centred cubic (fcc)), −1.31 eV (Pt top) < −1.23 (Pt fcc) and −1.43 eV (Rh top) < −1.28 (Rh hcp).

Except on Pd(111), CO adsorbs at Top site, but LDA & PBE predict wrong sites!

Figure 3 | Surface energies, lattice constants and adsorption energies.

CO @ Pt & Au (111) surface - DMC

DMC input :
1. supercell : $2\sqrt{3}\times 2\sqrt{3}$ (θ(ML)=1/3)
2. time step = 0.01
3. number of moves = 30,000

CO @ Pt(111) – 400 electrons

DMC result : atop site
Ead (fcc) = -0.73(6) eV
Ead (bri) = -1.18(6) eV
Ead (atop) = -1.57(6) eV

Exp. result : atop site ~ -1.5eV

CO @ Au(111) – 436 electrons

DMC result : atop site
Ead (fcc) = -0.23(7) eV
Ead (atop) = -0.43(8) eV

Exp. result : atop site ~ -0.4eV

Diffusion Monte Carlo can predict
a correct adsorption site and adsorption energy.
But if there exists any simple reason for DFT
to predict a wrong adsorption site?

Summary and Conclusion

1. Both LDA and GGA predict an overbinding effect for many "*atom and molecule*" adsorption on graphene and Al(100) surface.
2. DMC predicts the surface energy of C(100), Si(100), Ge(100), NaCl, MgO, CaO, TiO_2 …… such that $\Delta S(DMC) > \Delta S(LDA) > \Delta S(PBE)$.
3. DMC results indicate that for O an OH adsorption on Al(100), C(100), NaCl, MgO, TiO_2 surfaces, both LDA and GGA predict an overbinding effect; however, GGA predict a correct adsorption energy for H_2O.
4. DMC results indicate that for CO adsorption on late TM (111) surfaces, except for Top-site, DFT (LDA or GGA) predict over binding effect for all the other sites and thus led to wrong site prediction.

It is about time
to do materials simulations
using Quantum Monte-Carlo

Take home message:

Please be sure the Exchange-Correlation Approximation used is correct enough to give the reliable results

⇔

using Quantum Monte-Carlo