Quantum Monte Carlo in the Apuan Alps IX
International Workshop, 26th July to 2nd August 2014
The Apuan Alps Centre for Physics @ TTI, Vallico Sotto, Tuscany, Italy

Binding energy of 2D materials using Quantum Monte Carlo

Ching-Ming Wei

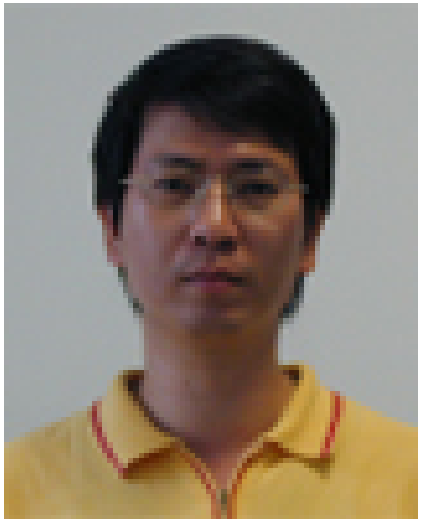
Institute of Atomic & Molecular Sciences,
Academia Sinica, *TAIWAN*

Support: MoST, Academia Sinica

Quantum Monte Carlo Group at Taiwan

Cheng-Rong Hsing (IAMS, 2002)

Cheng Ching (NCKU, 2007)



Chun-Ming Chang (NDHU, 2008)

Ching-Ming Wei (IAMS, 2006)

Collaborators: Neil Drummond, Pablo Lopez Rıos, Richard Needs

魏金明 *Wei, Ching-Ming*

禾 *standing grain*

鬼 *ghost*

金 *gold*

女 *woman*

sun 日月 *moon*

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)

DFT + AIRSS will become one powerful tool to find structure minimums

Too many functionals!

DFT community does need a lot of benchmark results where QMC can contribute and help!

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

QMC can provide help !

Good strategy for "poor" people (extremely CPU source limited) and "no interest" (actually no ability) in the development of QMC method and theory is to tackle the subjects related to material simulations with "big" difference when using different ExC functionals.

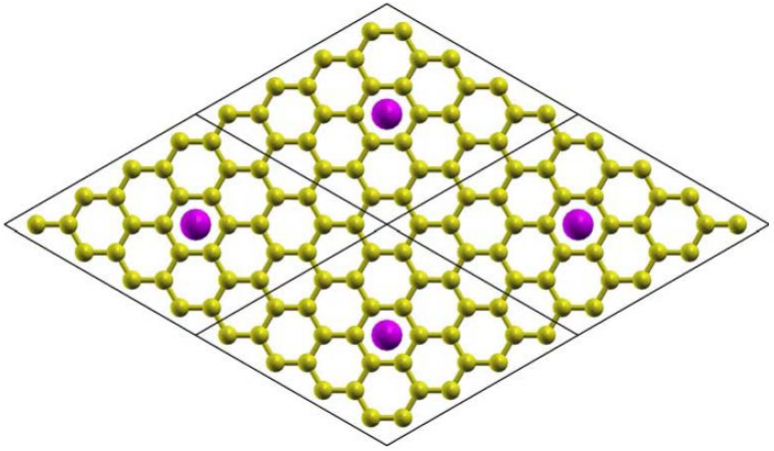
PHYSICAL REVIEW B 77, 235430 (2008)

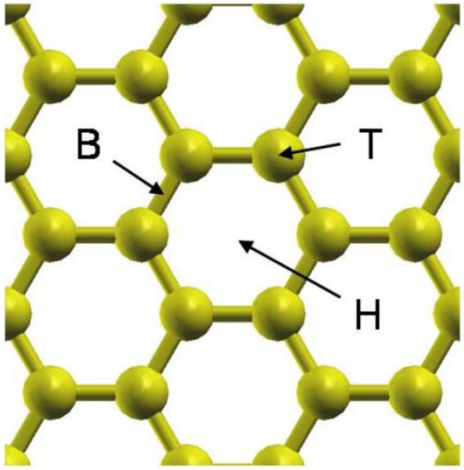
First-principles study of metal adatom adsorption on graphene

Kevin T. Chan,[1,2] J. B. Neaton,[3] and Marvin L. Cohen[1,2]
[1]*Department of Physics, University of California, Berkeley, California 94720, USA*
[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

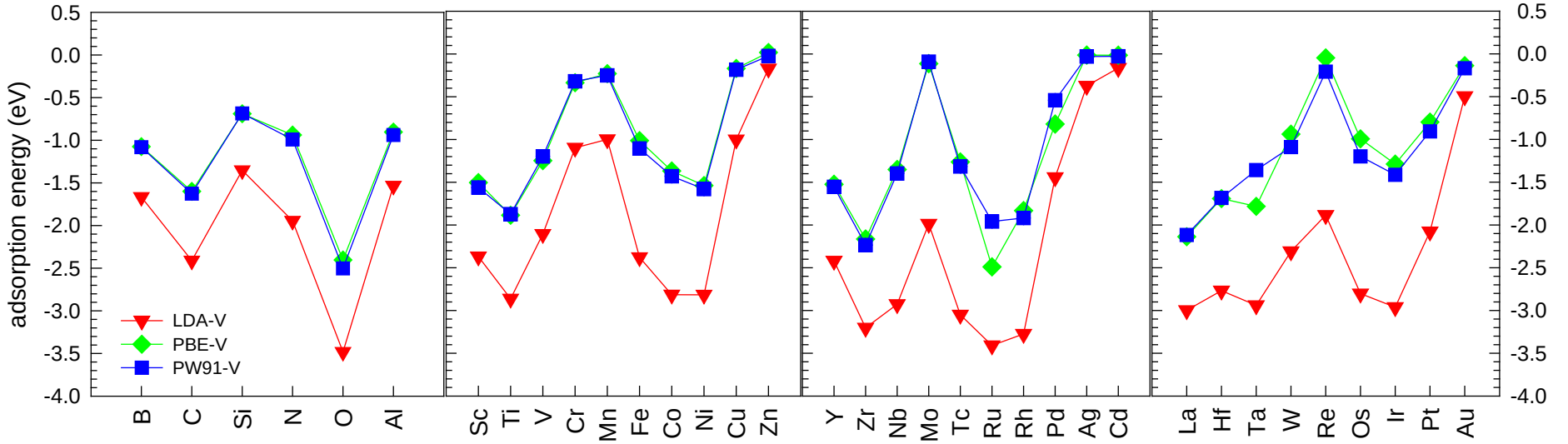
Li, Na, K, Ca, Al, Ga, In, Sn, Ti, Fe, Pd, Au





How about results from othe functional suchas LDA?

Single atom @ graphene

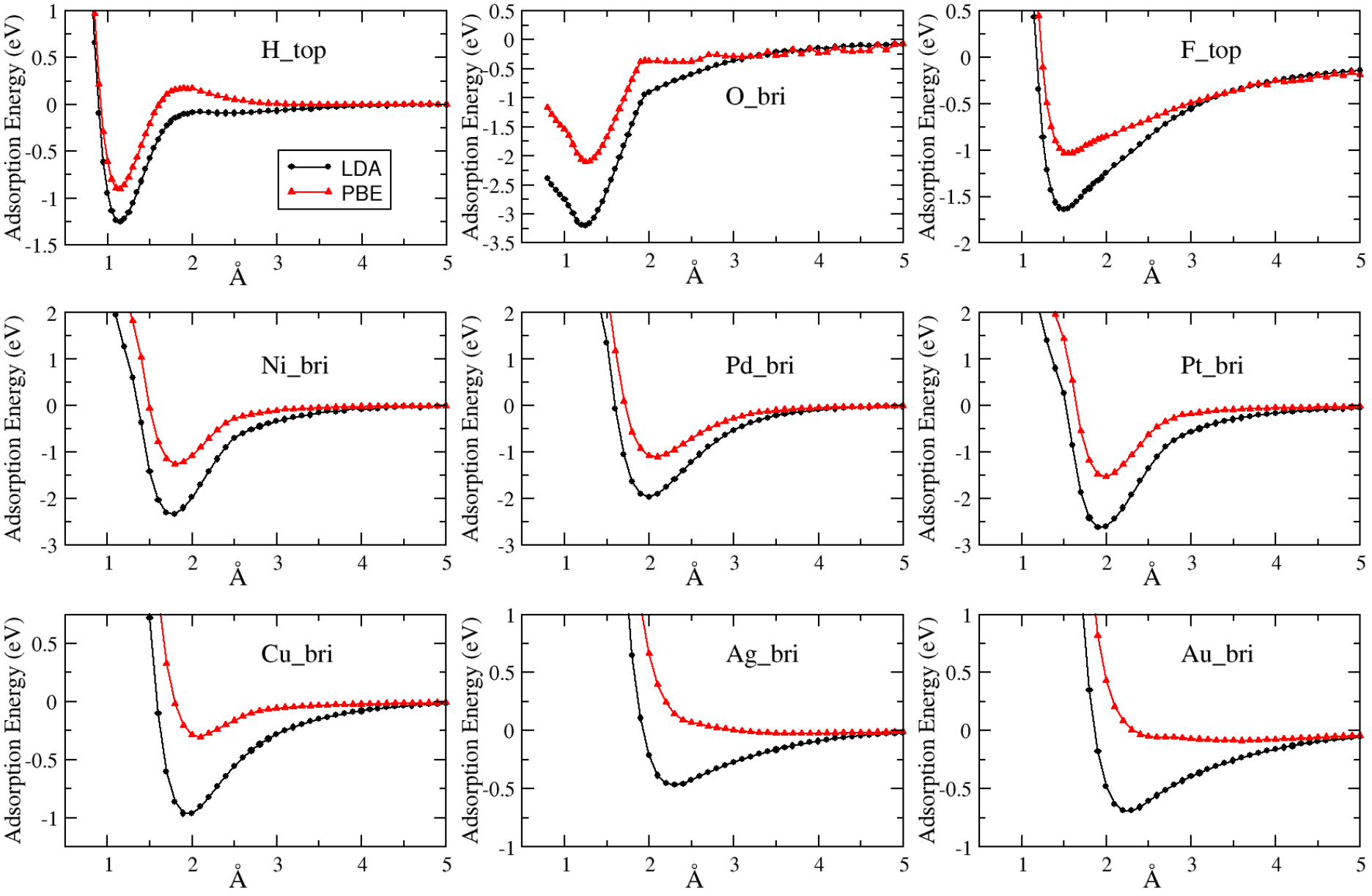


LDA & GGA predict different adsorption energy at preferred adsorption site!

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)

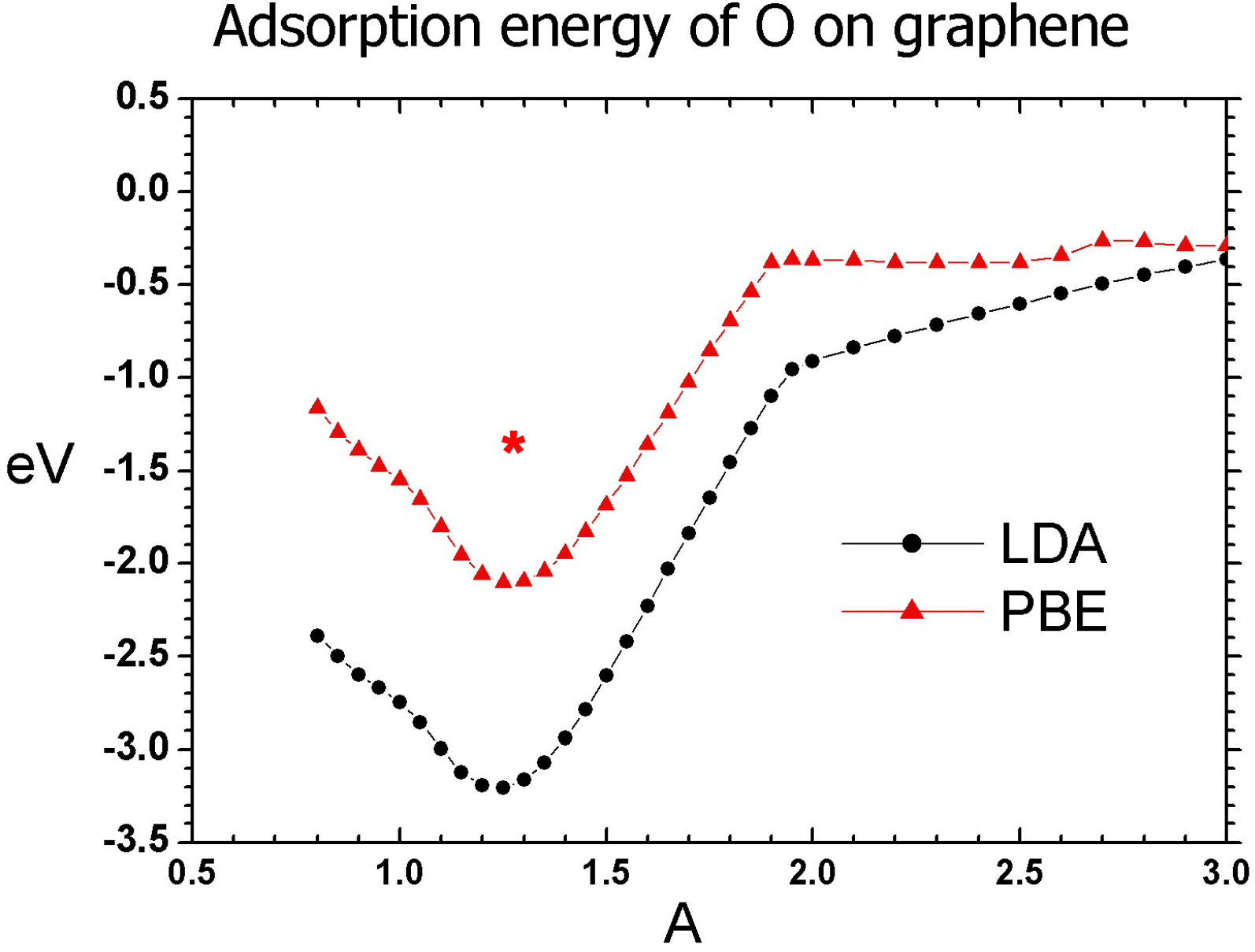


Need more accurate methods? QMC

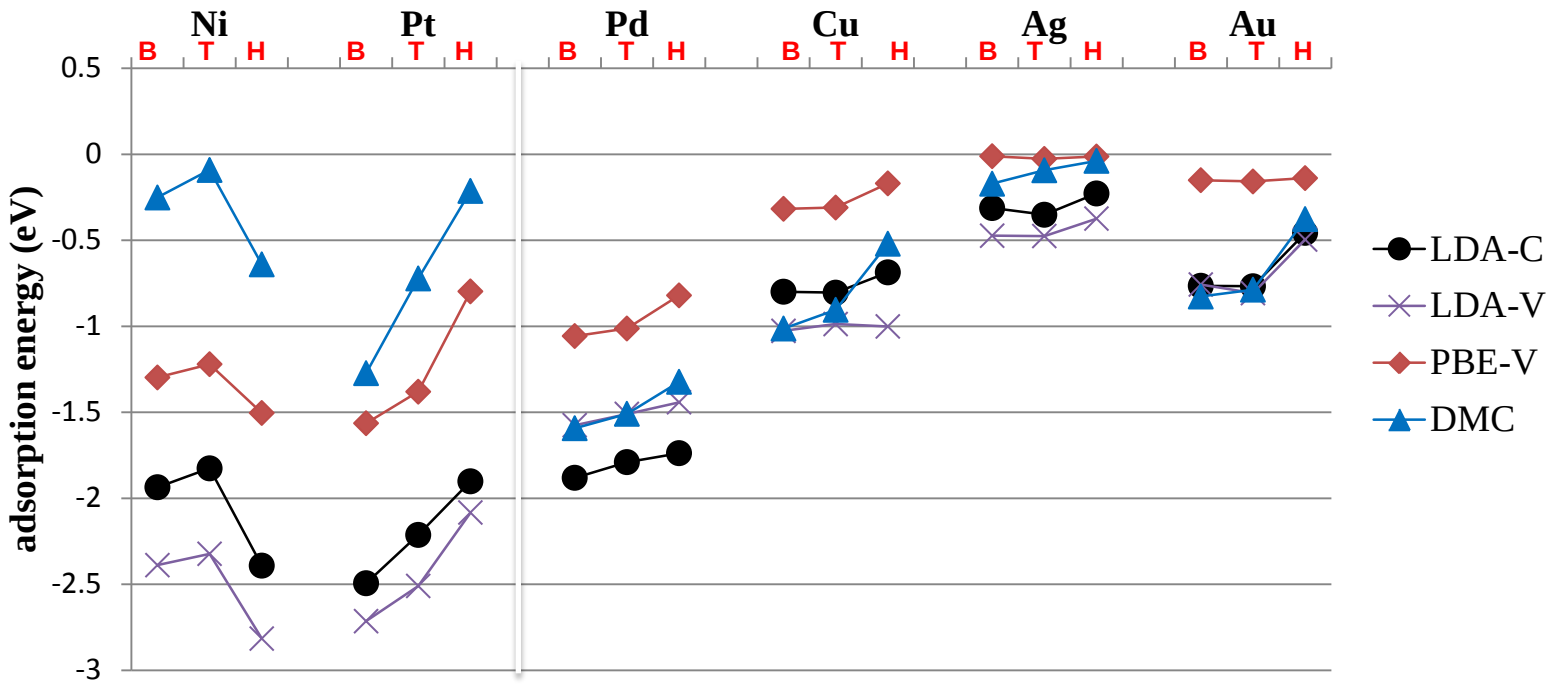
CASINO code : QMC Methods

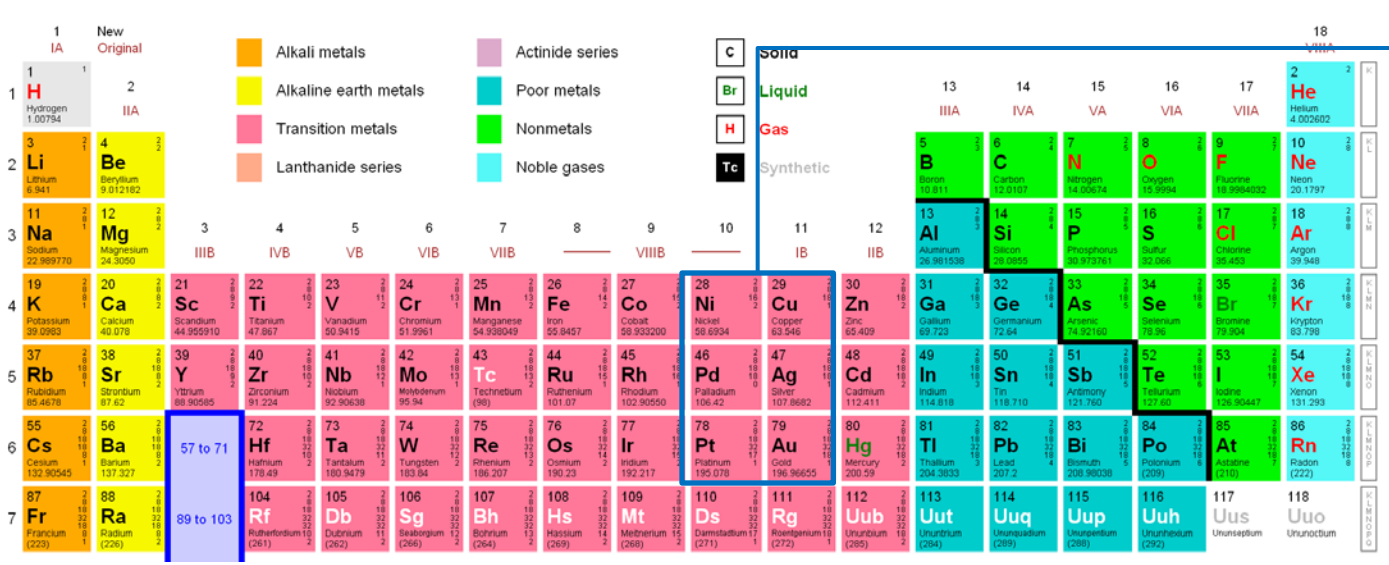
http://www.tcm.phy.cam.ac.uk/~mdt26/casino2.html

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


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

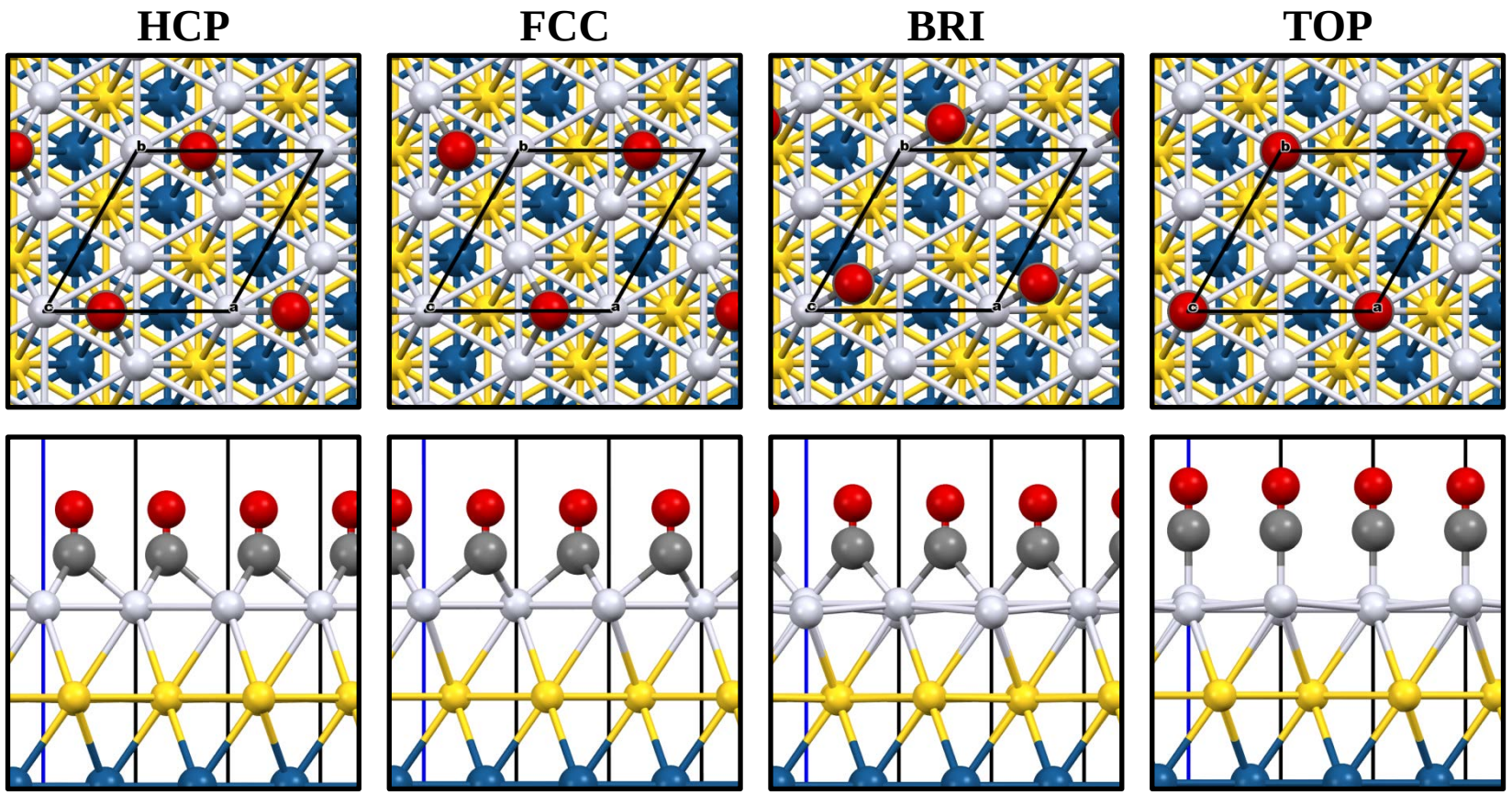
Single atom @ graphene

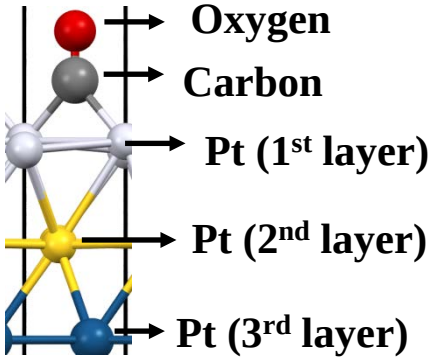




$3d^8$ $4s^2$	$3d^{10}$ $4s$
$4d^{10}$	$4d^{10}$ $5s$
$5d^9$ $6s$	$5d^{10}$ $6s$

CO adsorption on Pt(111) surface





If DFT will give a good description for the CO adsorption on late transition metal (111) surfaces?

The CO/Pt(111) Puzzle†

Times Cited: > 350

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

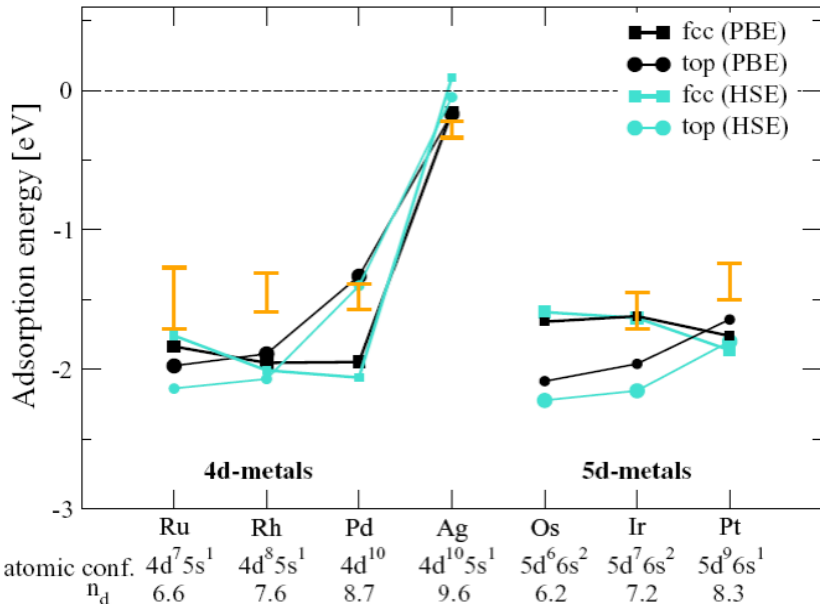
atomic conf.	4d 5s	4d 5s	4d	4d 5s	5d 6s	5d 6s	5d 6s
n_d	6.6	7.6	8.7	9.6	6.2	7.2	8.3

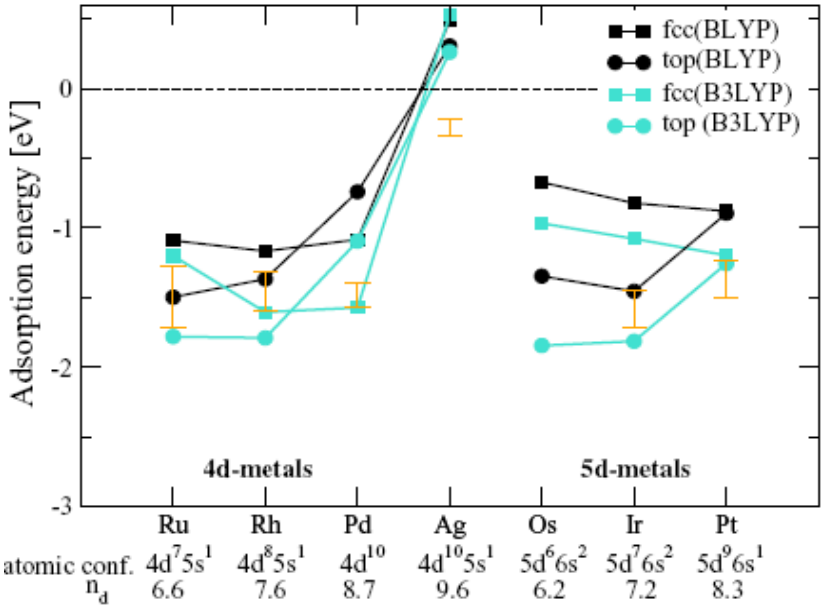
atomic conf. 4d 5s 4d 5s 4d 4d 5s 5d 6s 5d 6s 5d 6s
n_d 6.6 7.6 8.7 9.6 6.2 7.2 8.3

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





A Stroppa[1] and G Kresse

Faculty of Physics, University of Vienna, and Center for Computational Materials Science, Sensengasse 8/12, A-1090 Vienna, Austria

E-mail: alessandro.stroppa@univie.ac.at

New Journal of Physics **10** (2008) 063020 (17pp)

Received 1 April 2008

Published 19 June 2008

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

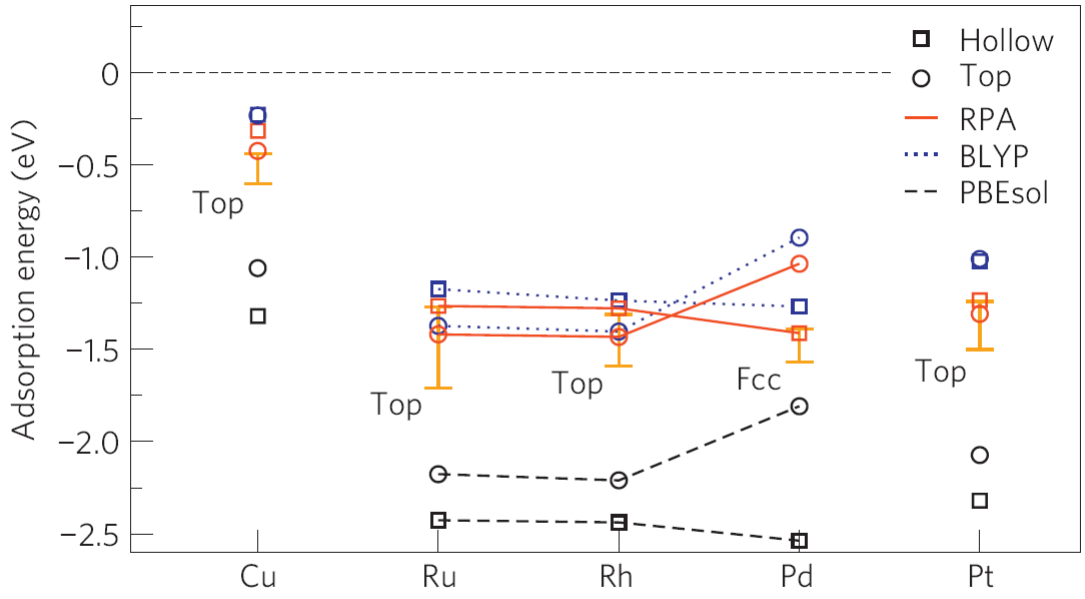
nature materials

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

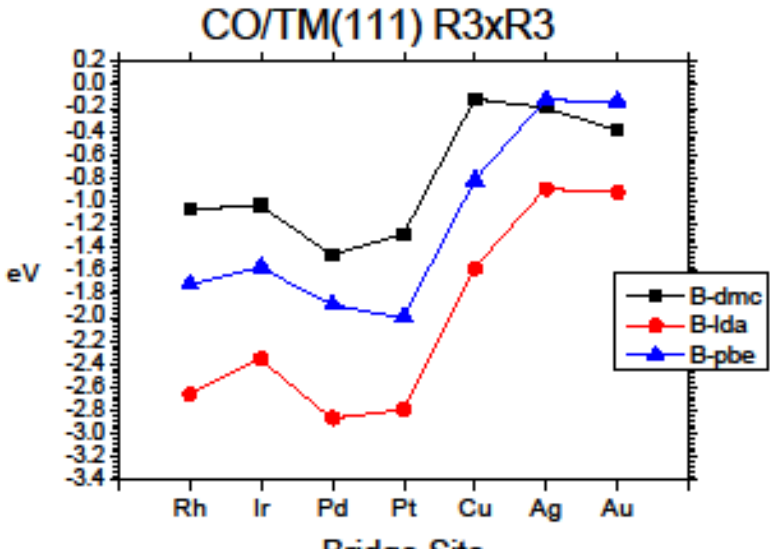
CO @ Pt(111) – 400 electrons

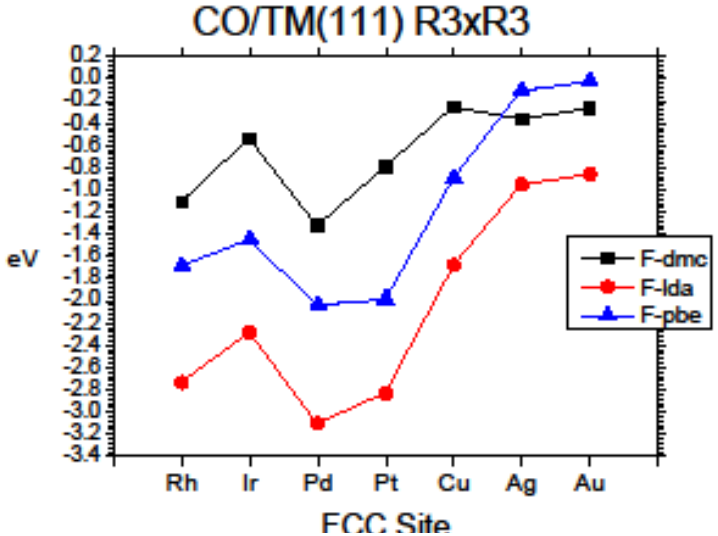
DMC result : atop site
Ead (fcc) = -0.73(6) eV
Ead (bri) = -1.18(6) eV
Ead (atop) = -1.57(6) eV
Exp. result : atop site ~ -1.5eV

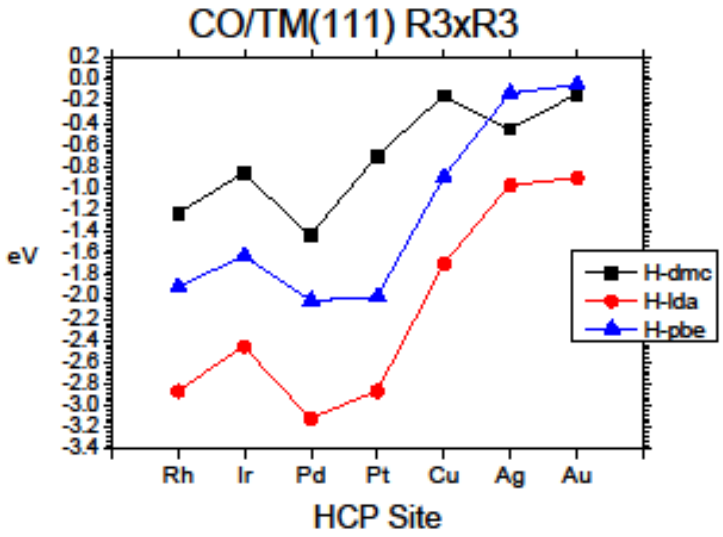
CO @ Au(111) – 436 electrons

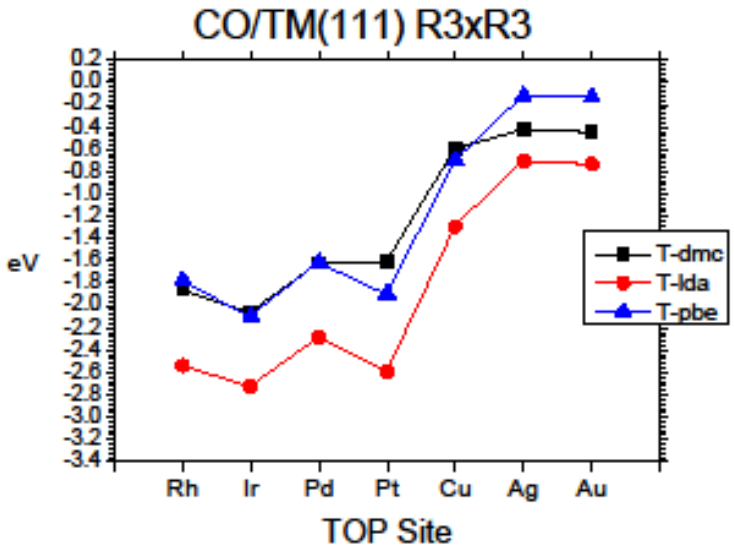
DMC result : atop site
Ead (fcc) = -0.23(7) eV
Ead (bri) = -0.36(7) eV
Ead (atop) = -0.43(8) eV
Exp. result : atop site ~ -0.4eV

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?





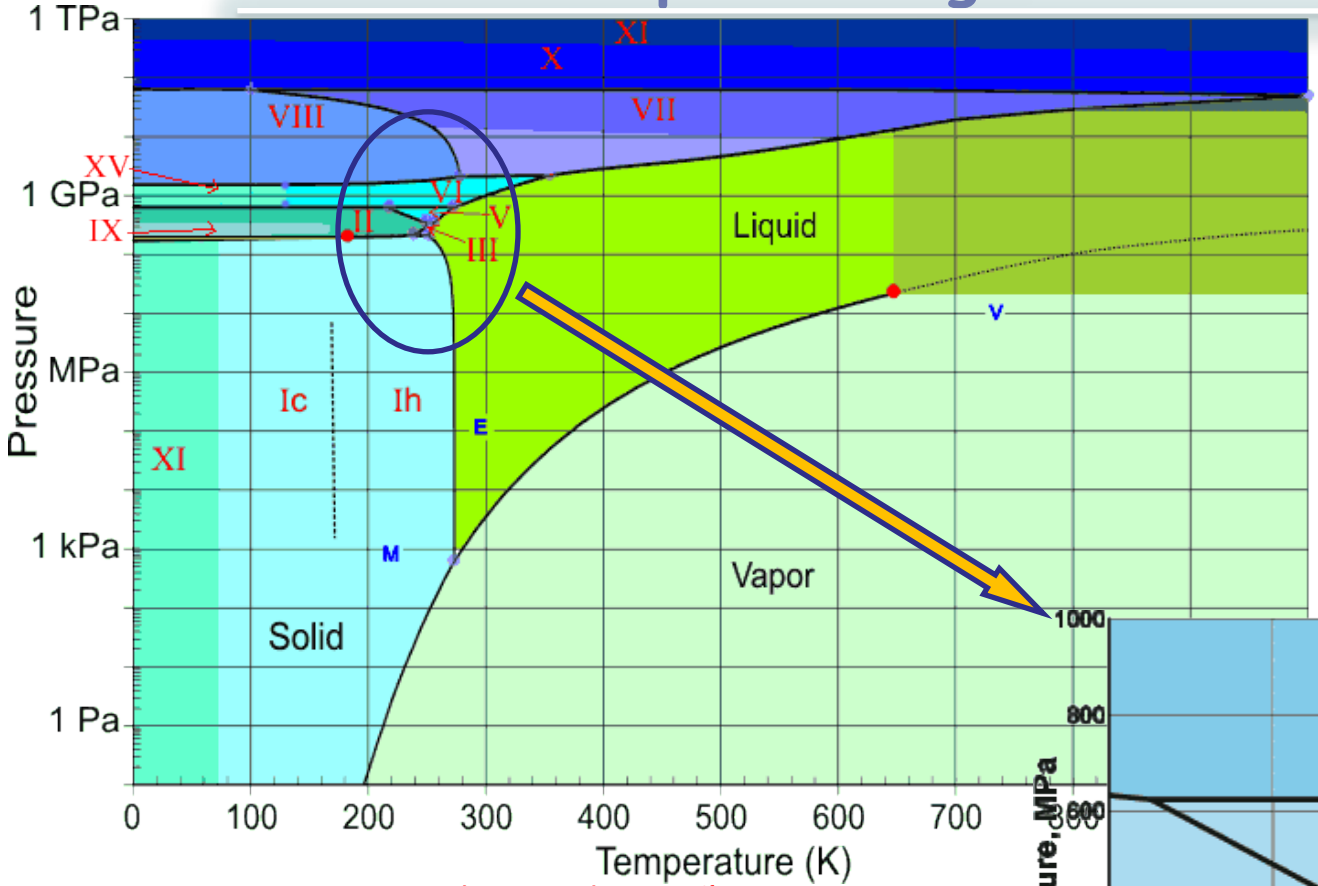


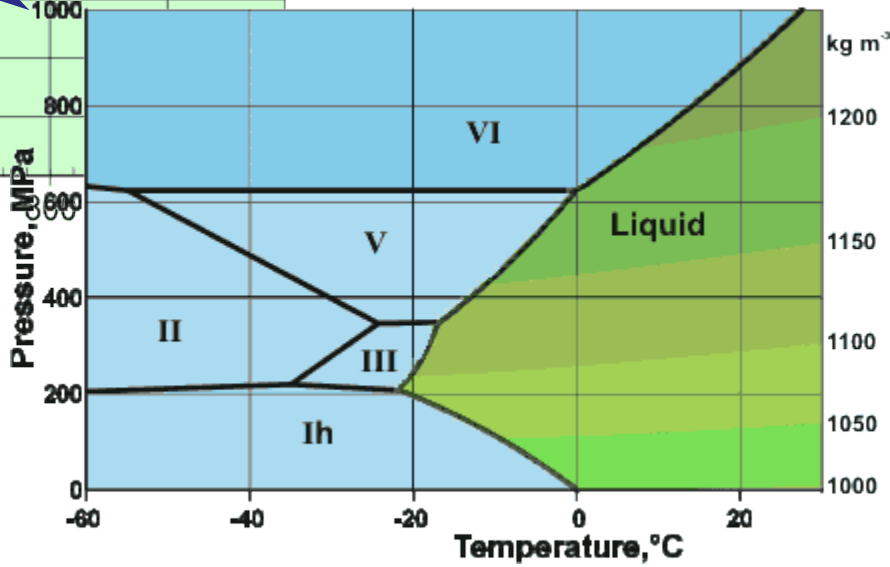


Over-binding effect does not appear on Top-site, but showed on other sites, and led to wrong site prediction!

(In preparation)

The phase diagram of water



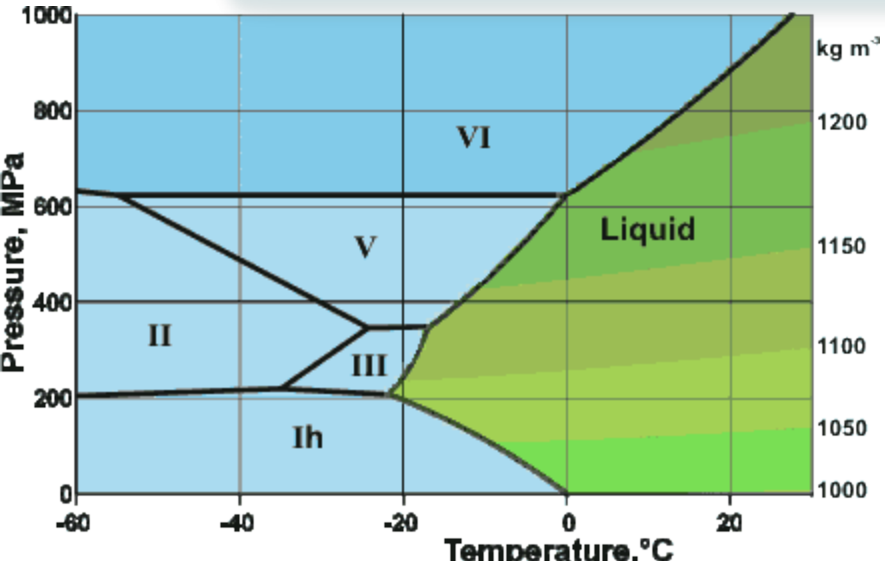


One may ask: Why a"poor" guy like you jumping into so expensive project which needs one meV/H_2O accuracy?

At that time, we are too stupid to know……

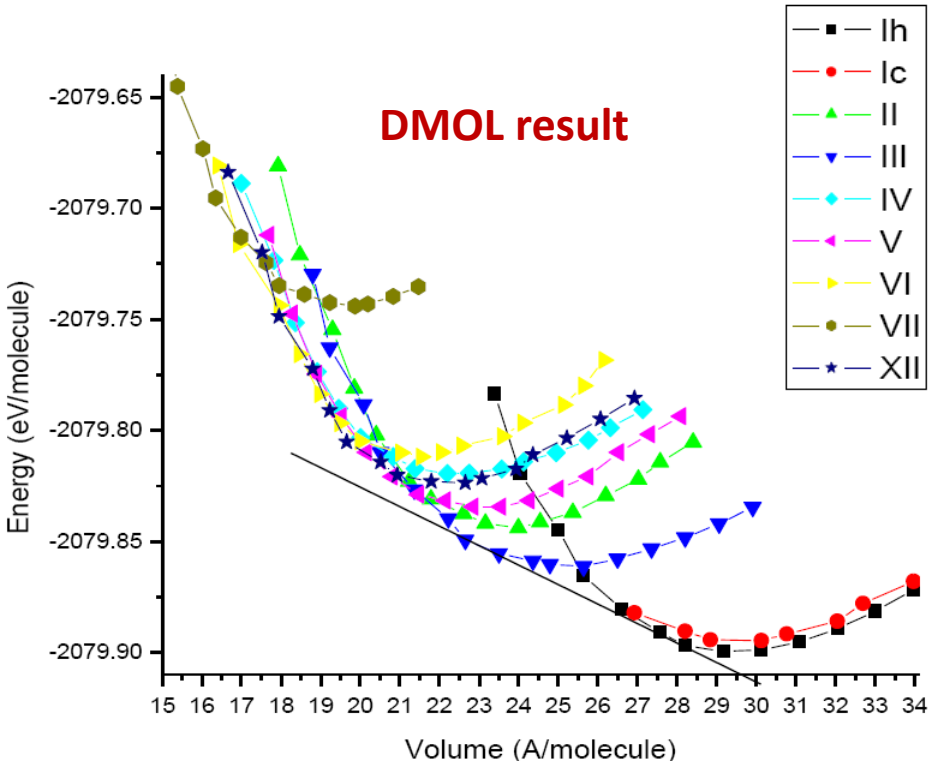
http://www1.lsbu.ac.uk/water/phase.html

DFT calculation of Ice

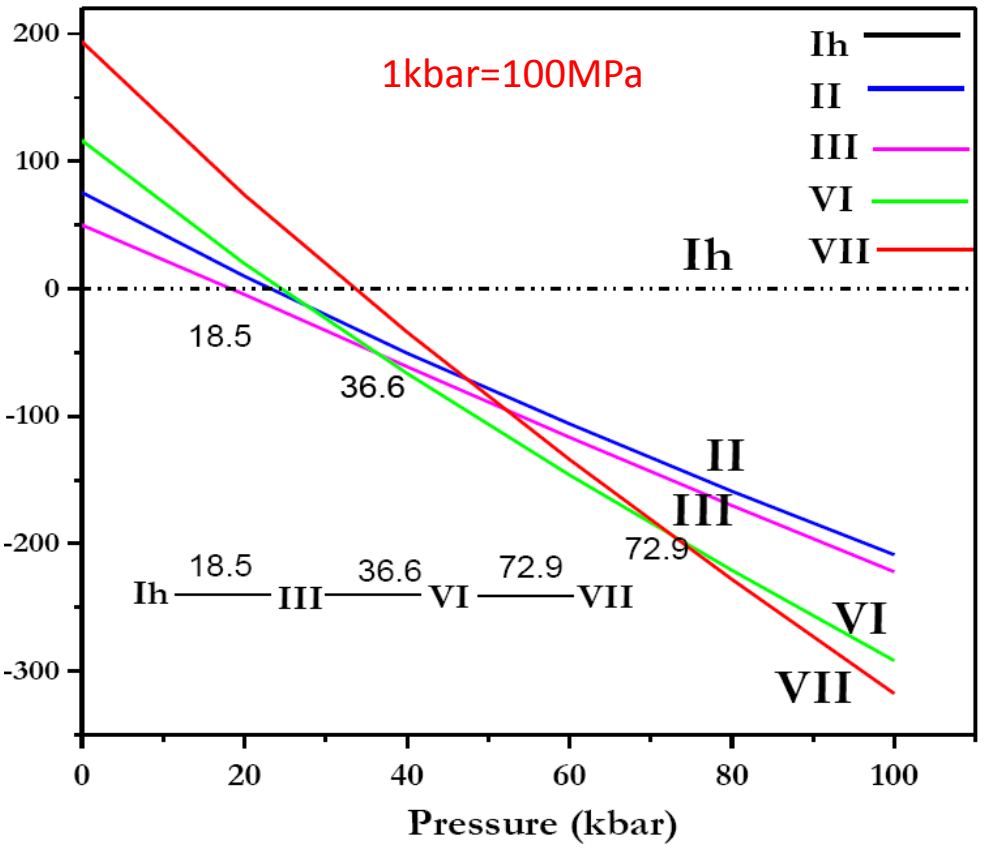


Prof. J-L Kuo's results

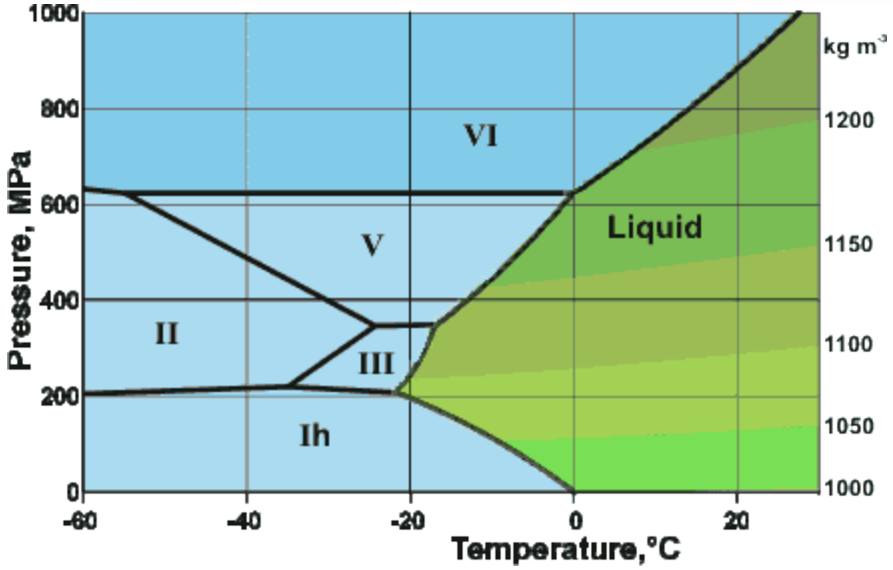
1. phase transition : Ih to III??
2. transition pressure is 10 times larger

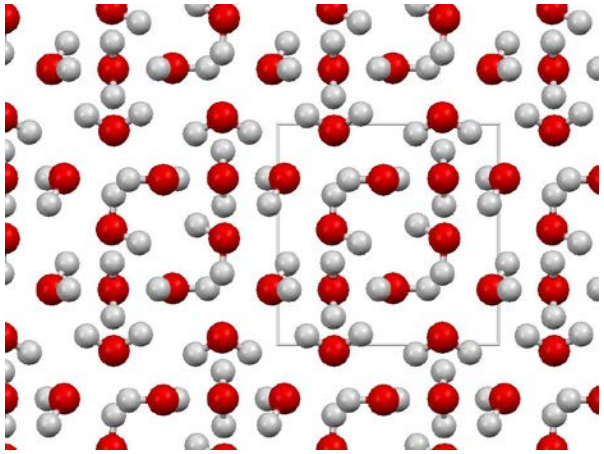


VASP-PBE result in 0 K



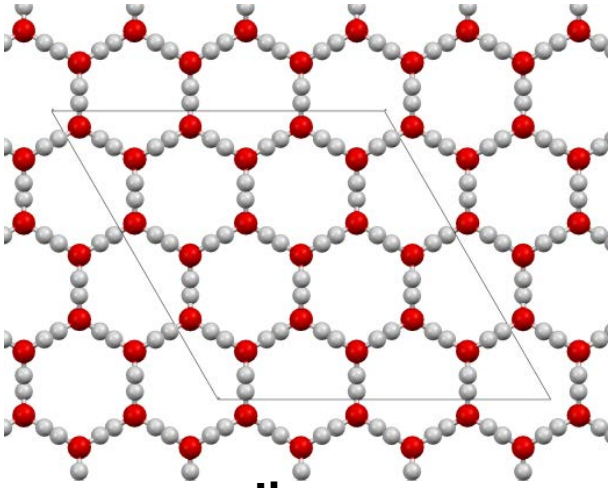
Structure of Ice





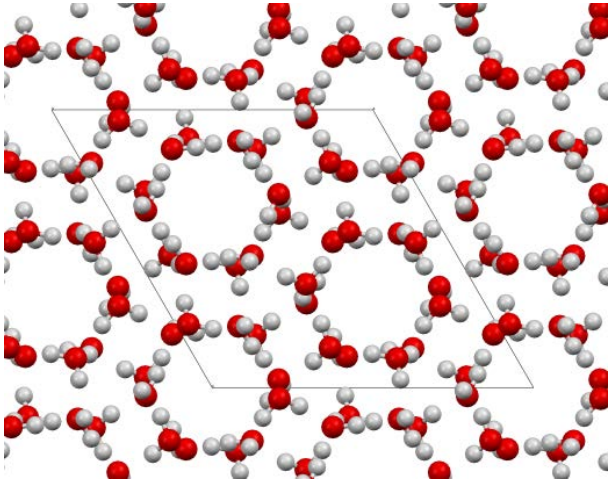
VI

tetragonal crystals
(Space group P42/nmc)



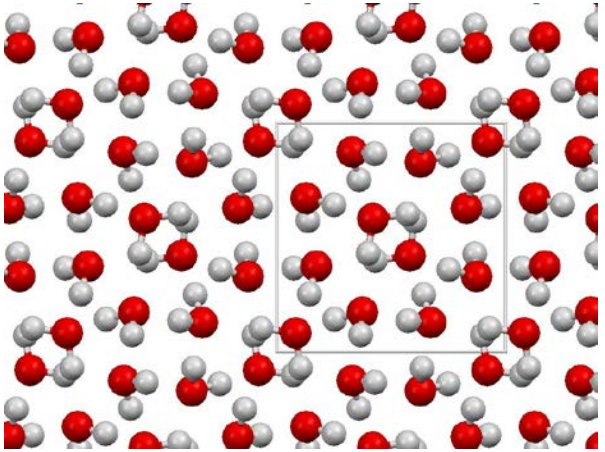
Ih

hexagonal ice
($P6_3/mmc$, symmetry D_{6h})



II-112.82

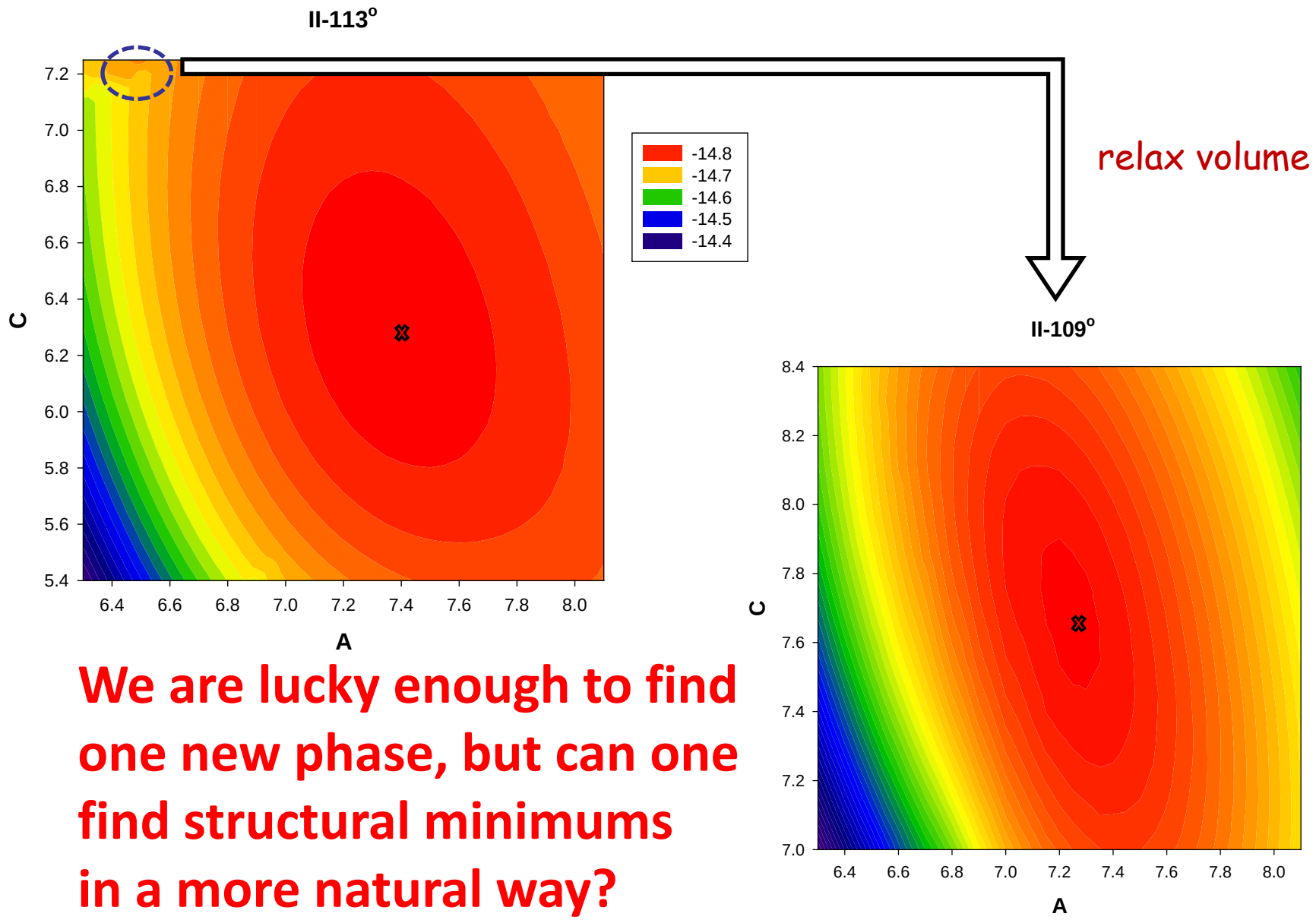
rhombohedral crystals
($R(-3)C$, symmetry S_6)



III

tetragonal crystals
(Space group P 4_1 2_1 2)

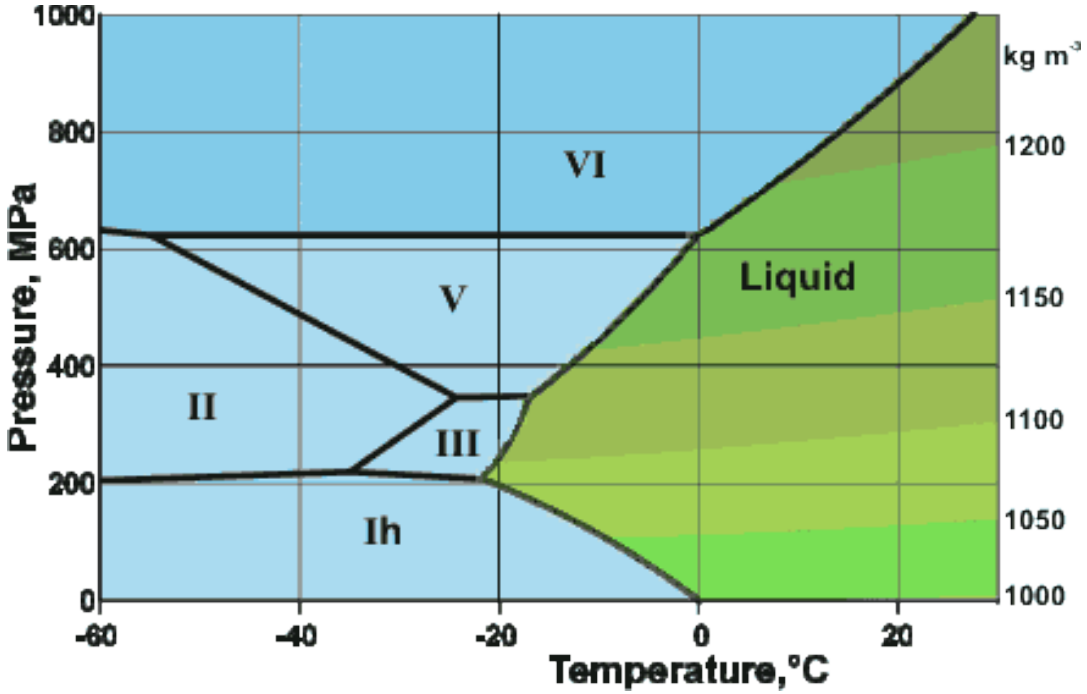
PES of Ice II

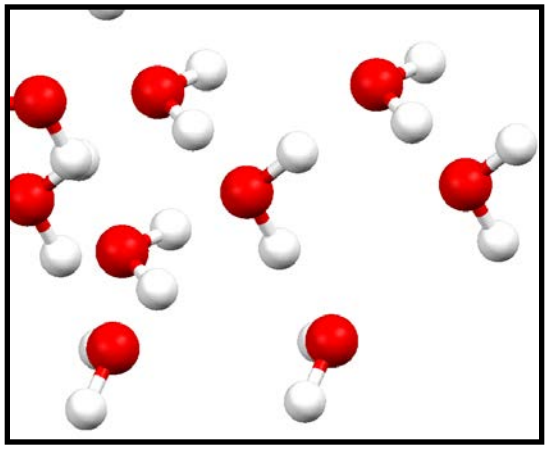


We are lucky enough to find one new phase, but can one find structural minimums in a more natural way?

AIRSS Application

Bulk system : ICE II



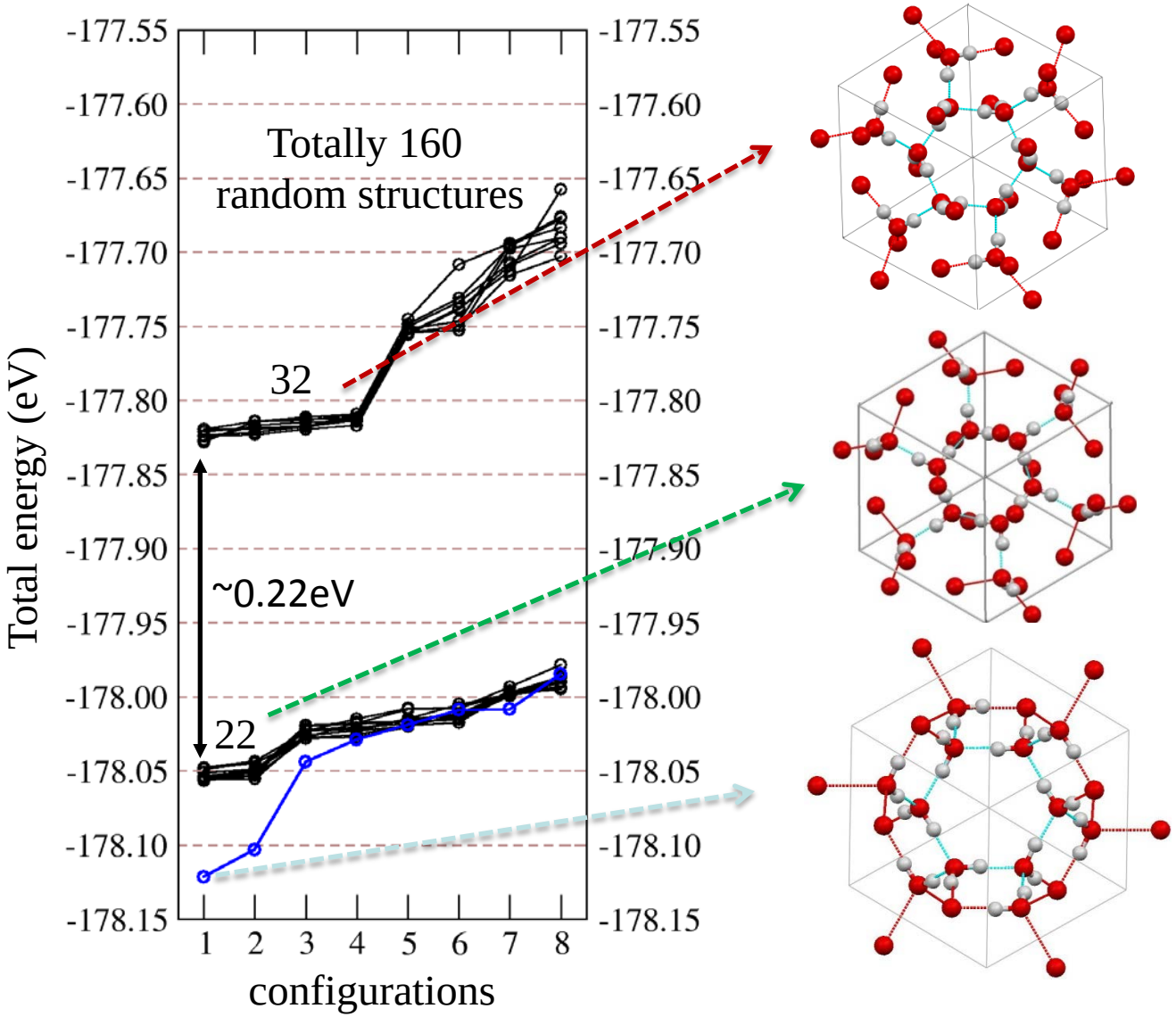


AIRSS Process

- Random generation of O atom positions and put constraints :
  - specific symmetry
  - Ice rule
  - the distance between oxygen atoms is sensible.
- Random generation of H atom positions and put constraints :
  - Ice rule
  - the distance between O and H atoms is sensible
- DFT calculation

AIRSS Application

Bulk system : ICE-II

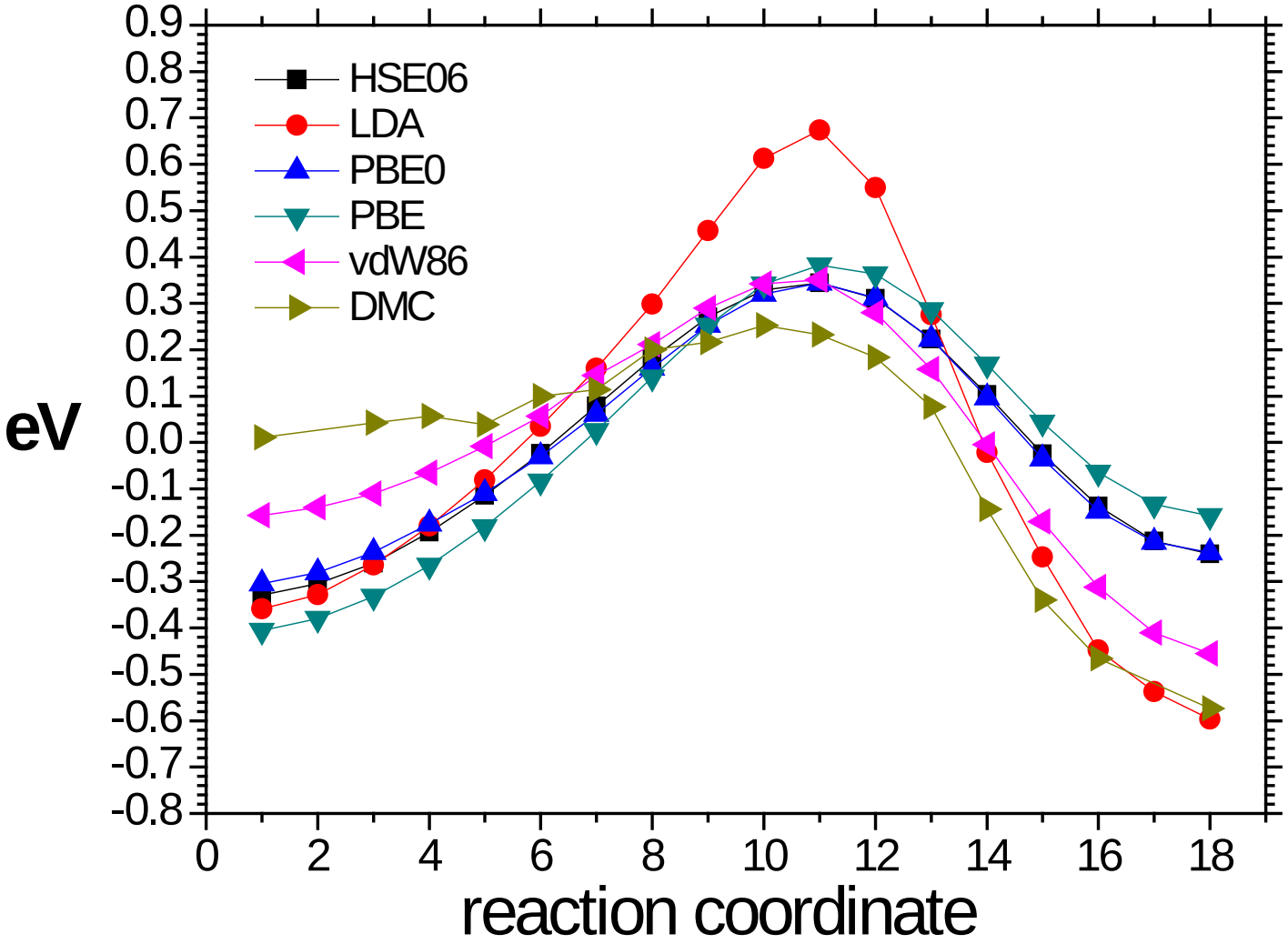


Exp. Structure
II-112.82
rhombohedral crystals
(R(-3)C, symmetry S_6)

New BCC
Structure
(bcc1)

New BCC
Structure
(bcc2)

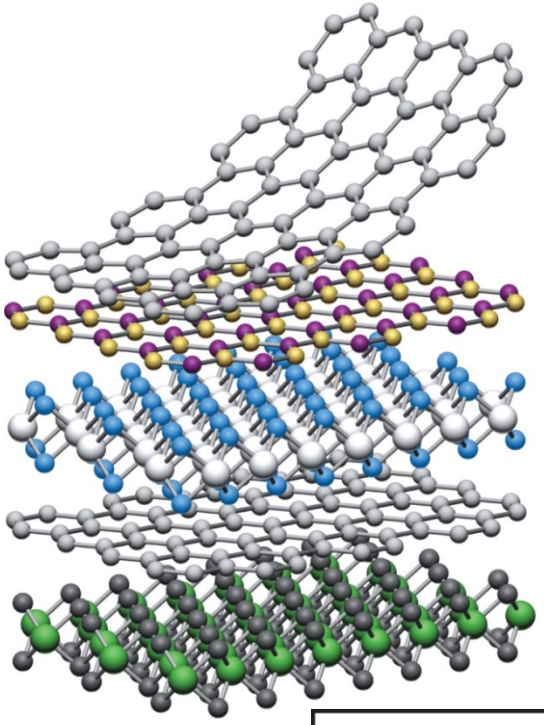
ICE II to bcc phase transition barrier

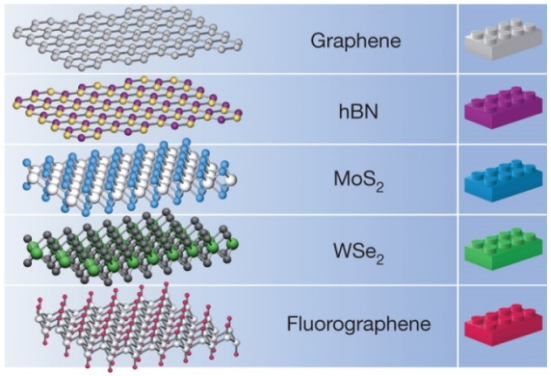


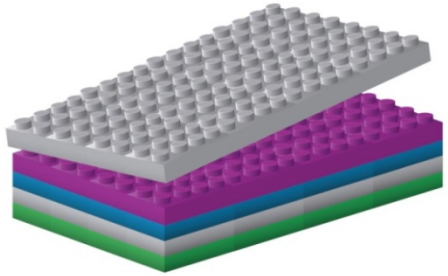
Finite size effect of QMC needs to be checked !

(In preparation)

van der Waals heterostructures





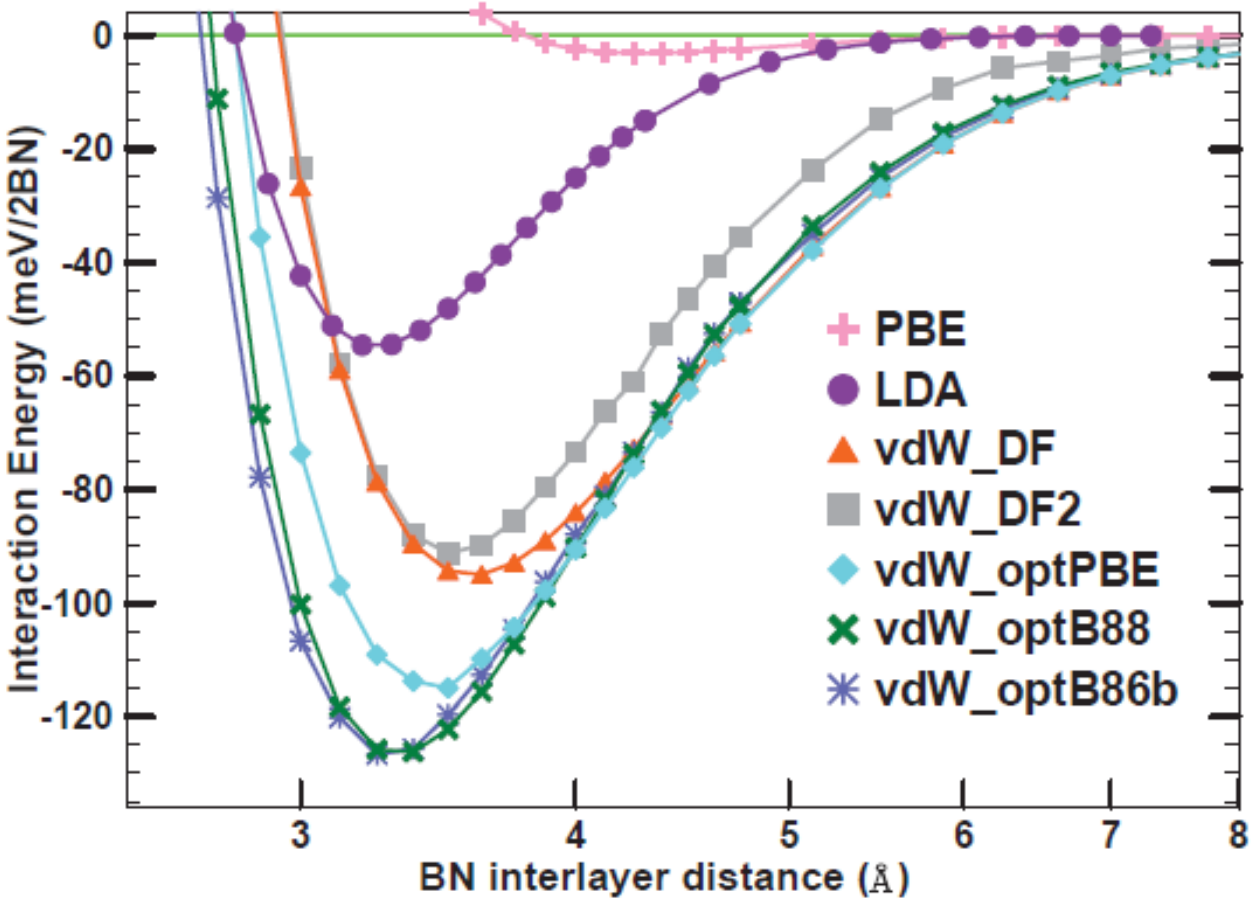


nature

AK Geim & IV Grigorieva
Nature **499**, 419-425 (2013)
doi:10.1038/nature12385

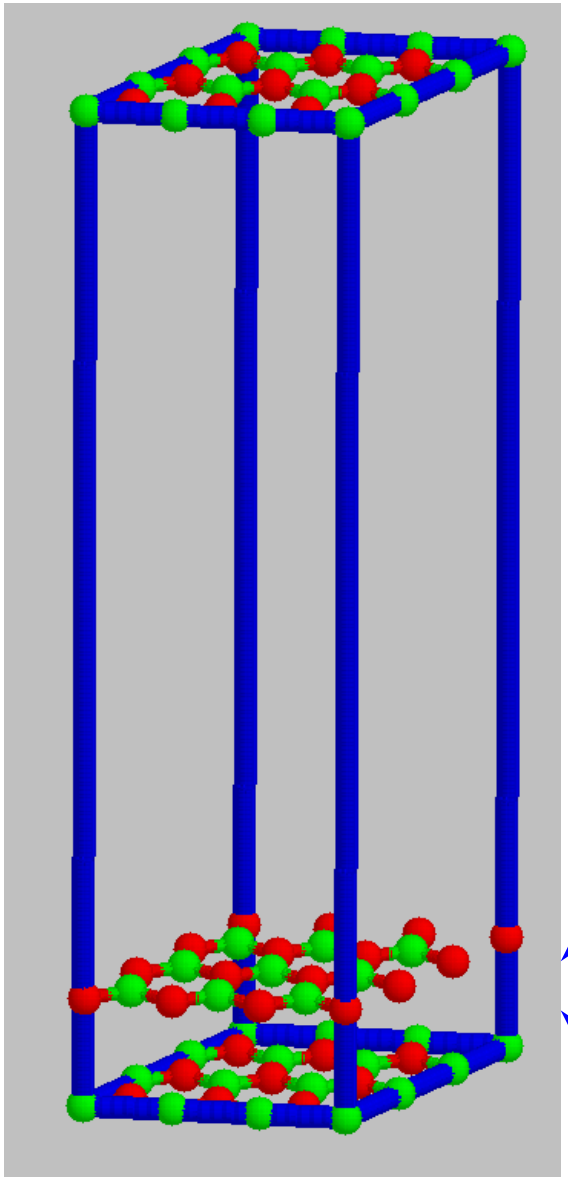
Graphene family	Graphene	hBN 'white graphene'	BCN	Fluorographene	Graphene oxide
2D chalcogenIdes	MoS_2, WS_2, $MoSe_2$, WSe_2	Semiconducting dichalcogenides: $MoTe_2$, WTe_2, ZrS_2, $ZrSe_2$ and so on		Metallic dichalcogenides: $NbSe_2$, NbS_2, TaS_2, TiS_2, $NiSe_2$ and so on	
				Layered semiconductors: GaSe, GaTe, InSe, Bi_2Se_3 and so on	
2D oxides	Micas, BSCCO	MoO_3, WO_3	Perovskite-type: $LaNb_2O_7$, $(Ca,Sr)_2Nb_3O_{10}$, $Bi_4Ti_3O_{12}$, $Ca_2Ta_2TiO_{10}$ and so on	Hydroxides: $Ni(OH)_2$, $Eu(OH)_2$ and so on	
	Layered Cu oxides	TiO_2, MnO_2, V_2O_5, TaO_3, RuO_2 and so on		Others	

The interaction energy of two BN films



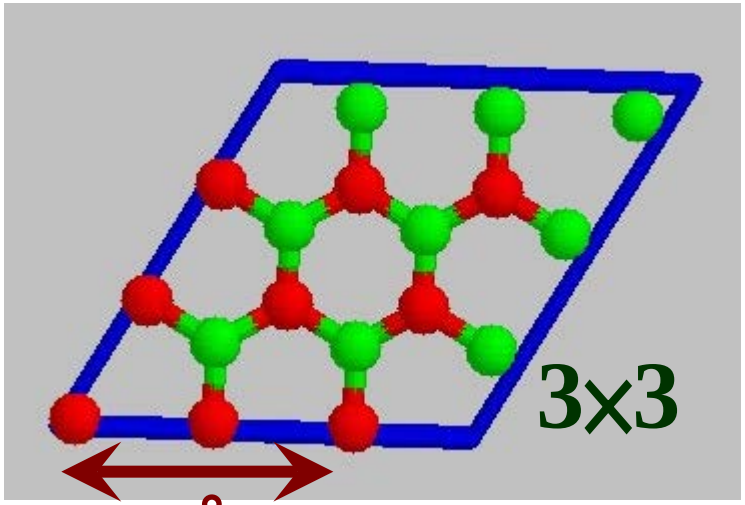
More reliable method is needed: QMC

BN bilayer : supercell structure



AA' stacking

Lateral : 3x3, 4x4

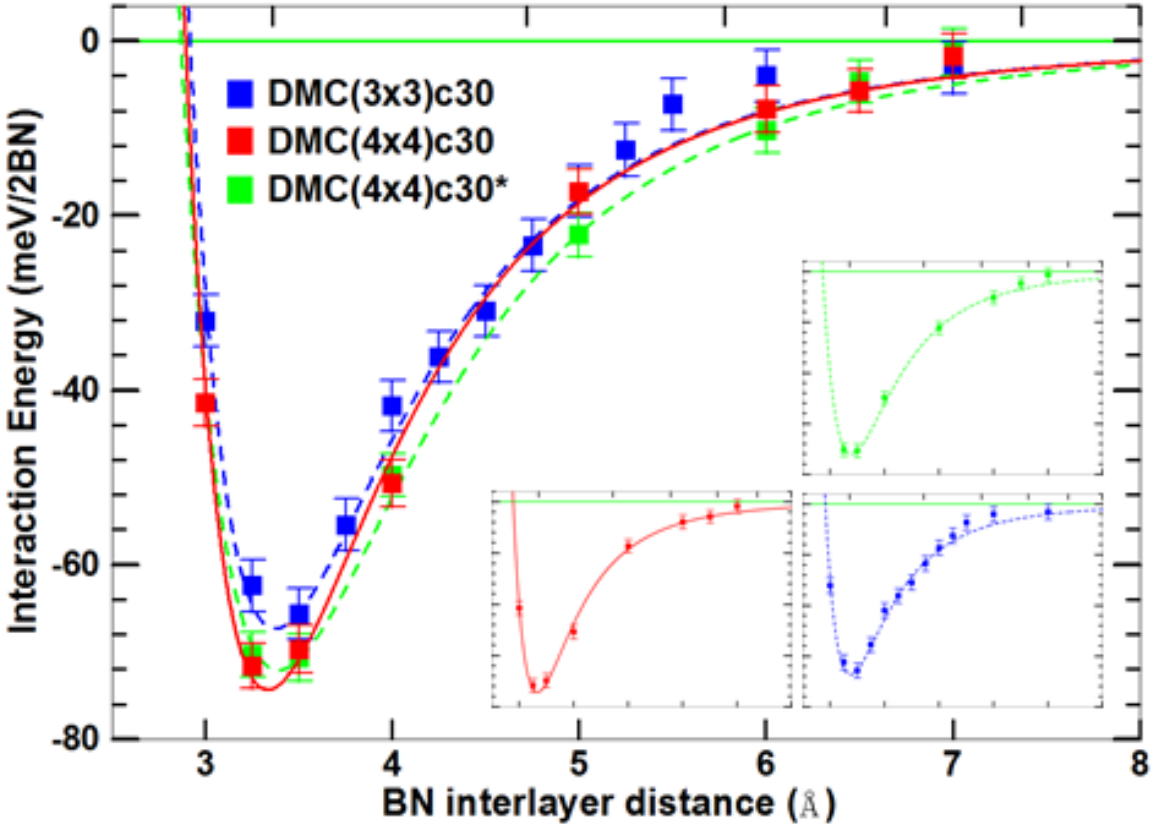


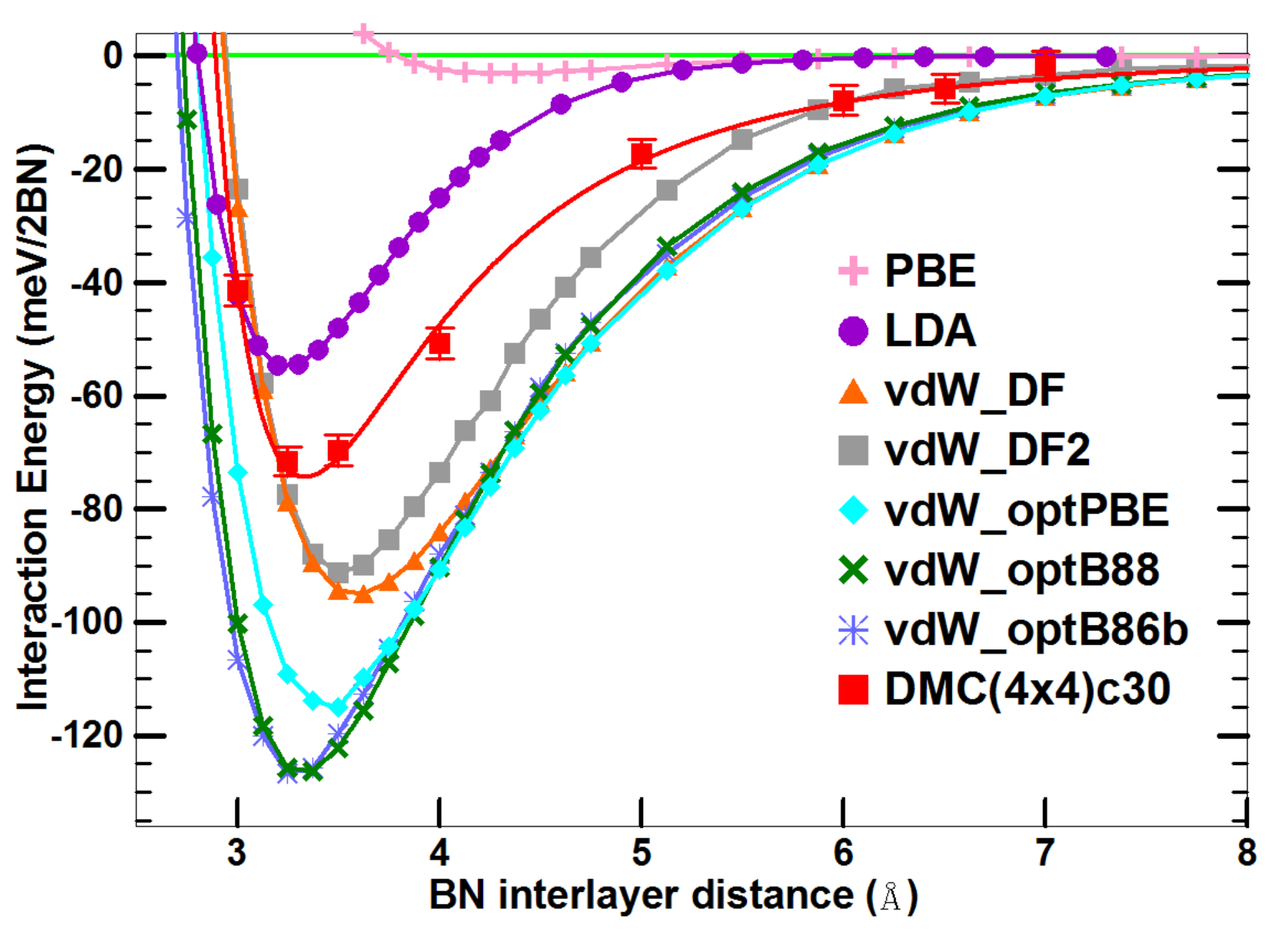
Interaction curve: DMC

σ < 2.5 meV/2BN

(total E ~ -700 eV/2BN)

CPU > 5 million core-hours

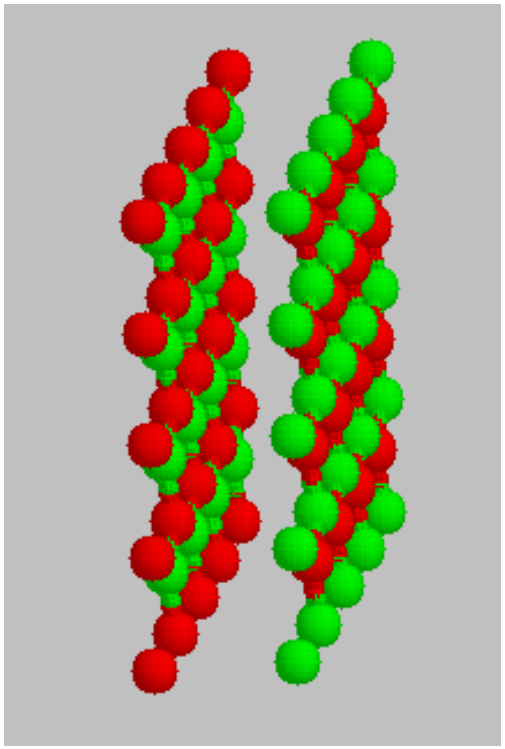



Interaction Energy (meV/2BN)
0
-20
-40
-60
-80
-100
-120
3
4
5
6
7
8
BN interlayer distance (Å)
PBE
LDA
vdW_DF
vdW_DF2
vdW_optPBE
vdW_optB88
vdW_optB86b
DMC(4x4)c30

2D systems

$$E_{vdW} \approx -\frac{C_6}{r^6}$$ for finite objects

$$E_{vdW} \approx -\frac{C_4}{r^4}$$ for infinite parallel insulating sheets



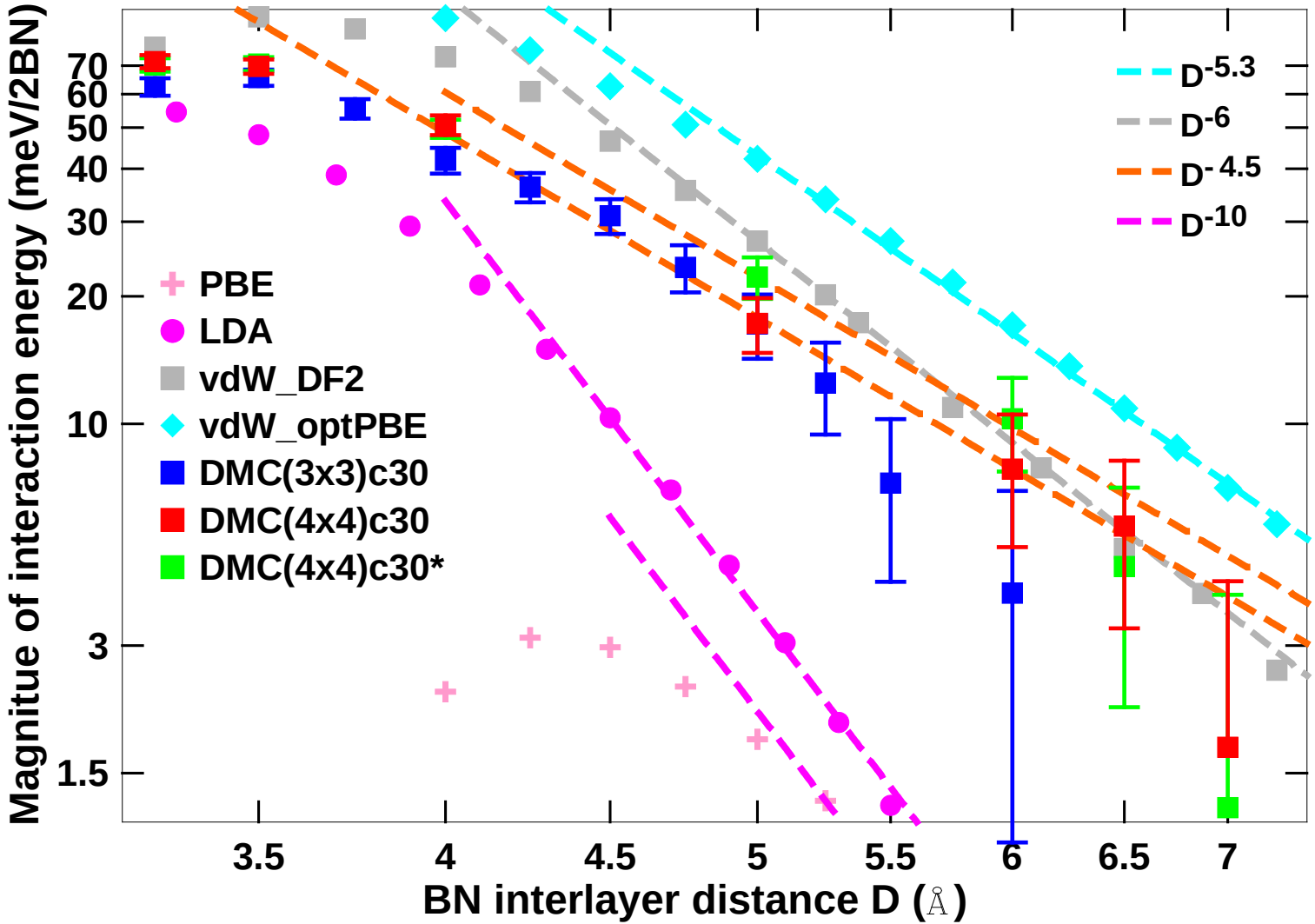
$$\int_{-\infty}^{+\infty} \frac{dxdy}{\left(\sqrt{x^2+y^2+d^2}\right)^6}$$

$$= \int_{-\infty}^{+\infty} \frac{rdrd\theta}{\left(r^2+d^2\right)^3} = \frac{1}{d^4}$$

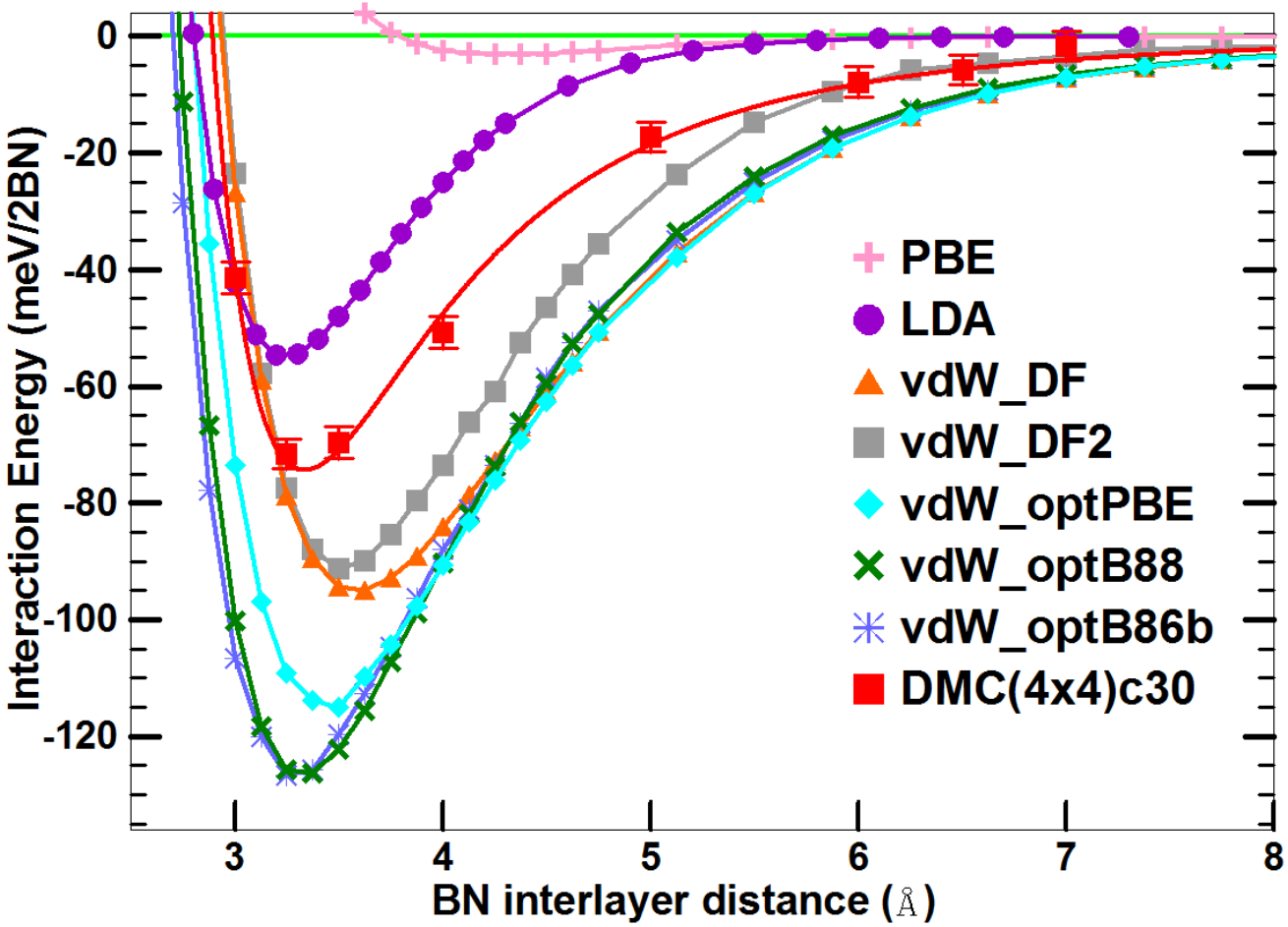
Long-Range behavior : $D^{-4.5}$

$D^{-5.3}$ vdW_optPBE **$D^{-4.5}$ DMC** **D^{-10} LDA**

D^{-6} vdW_DF2 **D^{-10} PBE**

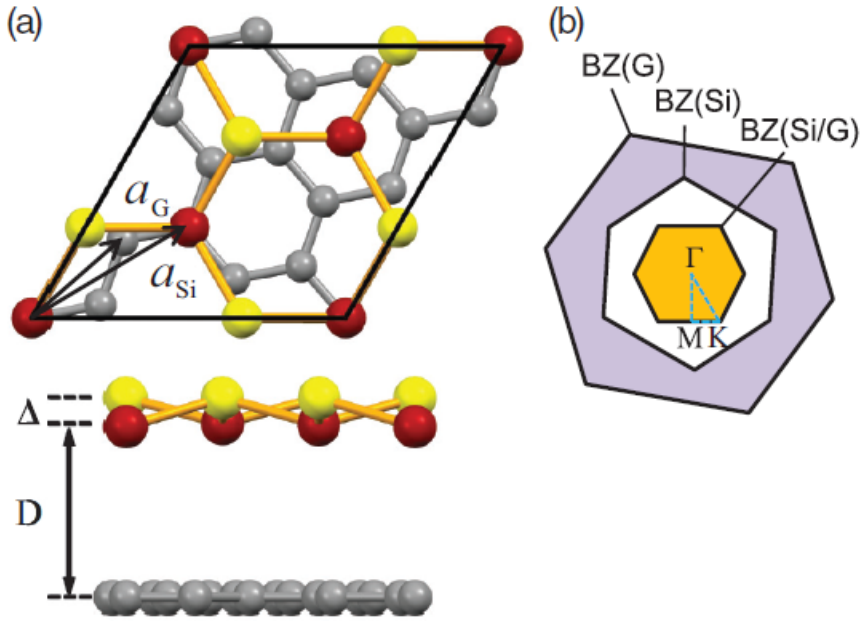


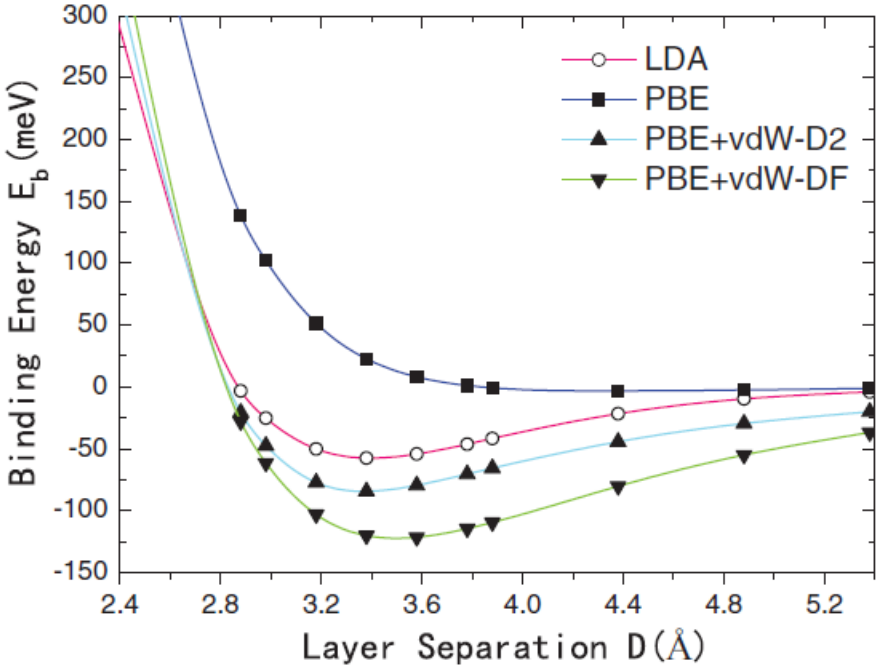
The interaction energy of two BN films



Can Van der Waals functionals accounts for Binding Energy of 2D Layer Materials such as graphene, BN flim, Silicene, MoS_2?

The binding energy of silicene and graphene





Consider Morie Patterns with small lattice mismatch of hetero bilayer structures !

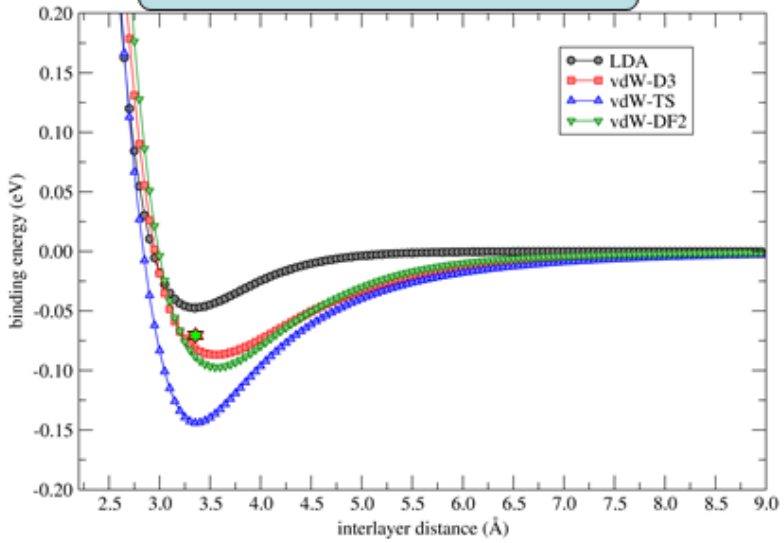
Silicene(√3x√3) / Graphene(√7x√7)

DMC (# of lines to discard)

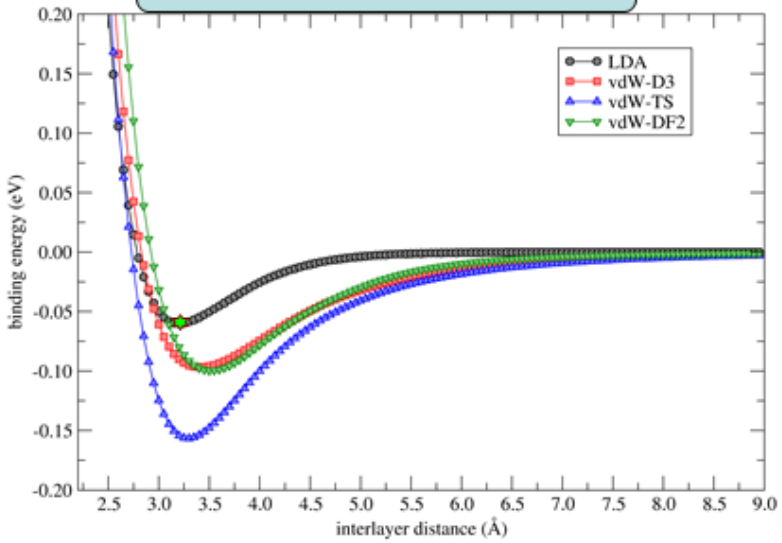
binding energy (meV)	20000	30000	40000	50000	60000	70000
Gra / Gra K441	66	66	67	67	69	71
BN / Gra K441 (B-Top)	61	61	61	62	63	61
Si(√3) / Gra(√7) S221	343	334	337	346	343	342
Si(√3) / BN(√7) S221	286	289	291	289	302	297
MoS_2 / MoS_2 S331	68	67	71	73	72	72
MoS_2(√7) / Gra(√12)	831	849	912	911	989	982
$MoSe_2$(√7) / BN(√12)	663	674	700	724	698	706

DFT-LDA optimized geometry is used in DMC calculation

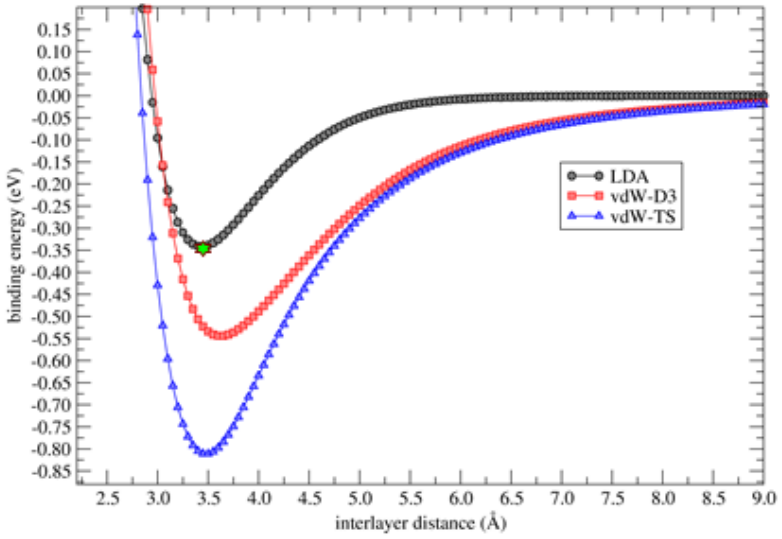
Graphene/Graphene



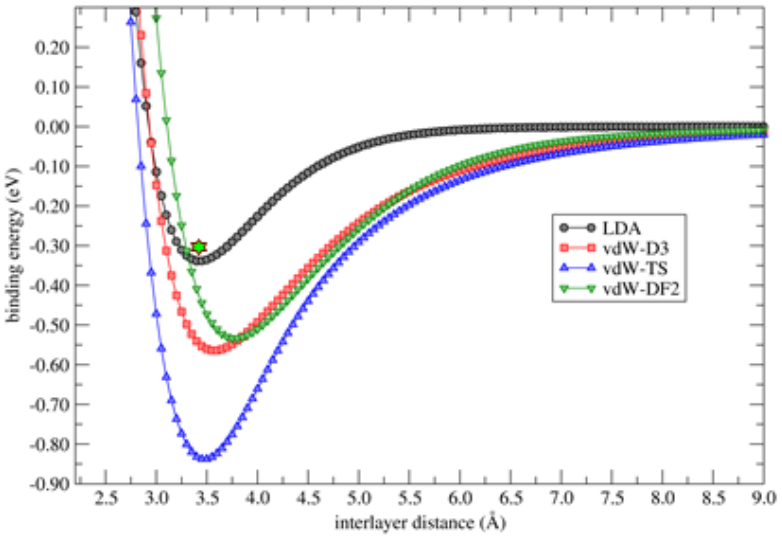
BN/Graphene



Silicene/Graphene



Silicene/BN



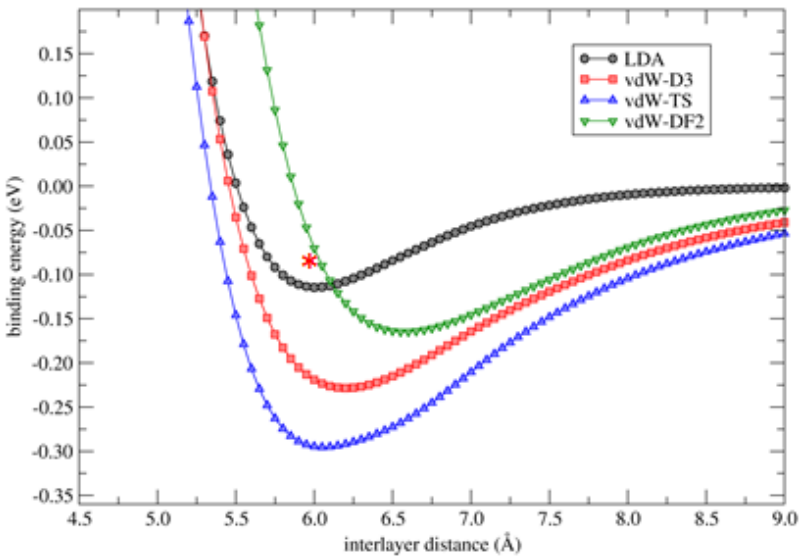
binding energy (meV)	VASP (LDA)	VASP (vdW_DF)	VASP (vdW_DF2)	VASP (vdW_optB86b)	CASTEP (LDA)	DMC 70000
Gra / Gra K441	47	97	95	127	53	71
BN / BN K441	55	95	91	127	49	71
BN / Gra K441 (B-Top)	60	99	98	136	60	61
Si(√3) / Gra(√7) S221	344	543	547	748	339	342
Si(√3) / BN(√7) S221	339	537	529	735	334	297

S221 means using Monkhorst-Pack 2x2x1 kpoint grids
K441 means using Gamma centered 4x4x1 kpoint grids

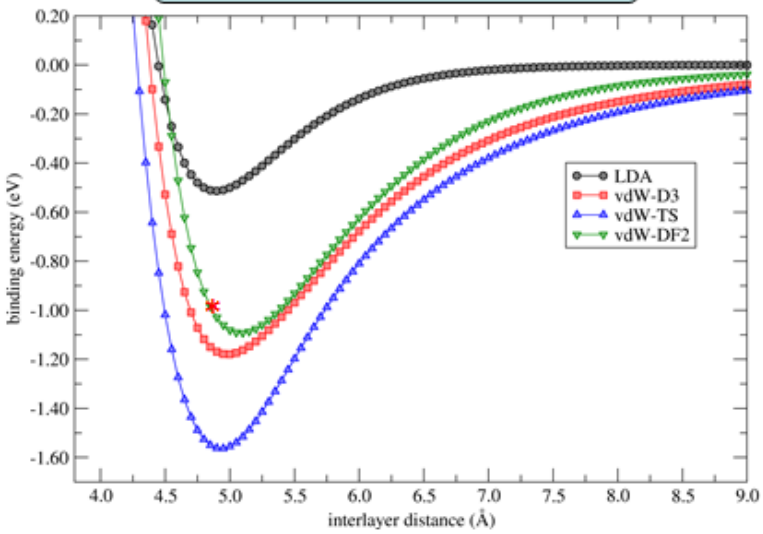
DFT-LDA optimized geometry is used in DMC calculation

1. *DMC shows a little trend that LDA might have done a reasonable job !*
2. *Currently available Van der Waals functionals might not account for Binding Energy of 2D Layer Materials !*
3. *Doing a curve for each system is perhaps necessary !*

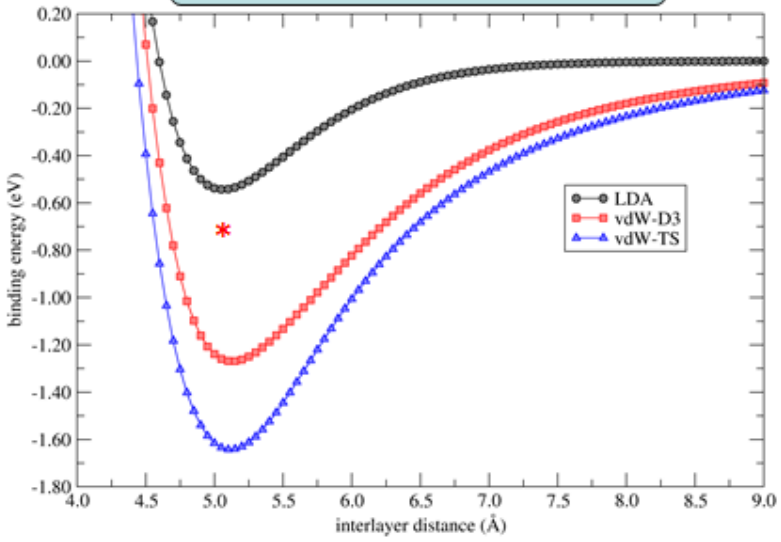
MoS_2/MoS_2



$MoS_2/Grapene$



$MoSe_2/BN$



After burning out more than one million core hours, the only thing that we learn is we need at least ten million core hours to gain a little more understanding! It is too early to say…… !

Quantum Monte Carlo in the Apuan Alps XI
International Workshop, 23th July to 30th July 2016
The Apuan Alps Centre for Physics @ TTI, Vallico Sotto, Tuscany, Italy

Binding energy of 2D materials using Quantum Monte Carlo

Ching-Ming Wei

Institute of Atomic & Molecular Sciences,

Academia Sinica, *TAIWAN*

See you in two years!

Support: MoST, Academia Sinica