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 Rios, Richard Needs
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


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.
First-principles study of metal adatom adsorption on graphene

Kevin T. Chan, J. B. Neaton, and Marvin L. Cohen

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**VASP-PBE**

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

*How about results from other functional such as 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 results)

Need more accurate methods? QMC
CASINO code: QMC Methods
http://www.tcm.phy.cam.ac.uk/~mdt26/casino2.html

<table>
<thead>
<tr>
<th>Adsorption Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
</tr>
<tr>
<td>B</td>
</tr>
</tbody>
</table>

- LDA-C
- LDA-V
- PBE-V
- DMC

Single atom @ graphene

- Alkali metals
- Alkaline earth metals
- Transition metals
- Nonmetals
- Noble gases
- Lanthanide series
- Actinide series

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

- Ni
- Pt
- Pd
- Cu
- Ag
- Au
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

Peter J. Feibelman,*‡ B. Hammer,§ J. K. Norskov,‖ 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

Experimental result:

88% top site
12% bridge site


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

<table>
<thead>
<tr>
<th>supercell</th>
<th>( \theta (\text{ML}) )</th>
<th>method</th>
<th>XC</th>
<th>( \Delta \text{BE} \text{ (eV)} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 3 \times 2 \sqrt{3} )</td>
<td>1/12</td>
<td>VASP, USP</td>
<td>PW91</td>
<td>0.25</td>
</tr>
<tr>
<td>( 2 \times 2 )</td>
<td>1/4</td>
<td>Dacapo, USP</td>
<td>PW91</td>
<td>0.23</td>
</tr>
<tr>
<td>( 2 \times 2 )</td>
<td>1/4</td>
<td>Dacapo, USP</td>
<td>PBE</td>
<td>0.24</td>
</tr>
<tr>
<td>( 2 \times 2 )</td>
<td>1/4</td>
<td>Dacapo, USP</td>
<td>RPBE</td>
<td>0.16</td>
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<tr>
<td>( 2 \times 2 )</td>
<td>1/4</td>
<td>Dacapo, USP</td>
<td>LDA</td>
<td>0.45</td>
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<tr>
<td>c(4 \times 2)</td>
<td>1/4</td>
<td>VASP, USP</td>
<td>LDA</td>
<td>0.41</td>
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<tr>
<td>c(4 \times 2)</td>
<td>1/4</td>
<td>Dacapo, USP</td>
<td>PW91</td>
<td>0.23</td>
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<tr>
<td>c(4 \times 2)</td>
<td>1/4</td>
<td>VASP, USP</td>
<td>PW91</td>
<td>0.18</td>
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<tr>
<td>c(4 \times 2)</td>
<td>1/4</td>
<td>VASP, PAW</td>
<td>PW91</td>
<td>0.13</td>
</tr>
<tr>
<td>( \sqrt{3} \times \sqrt{3} )-R30°</td>
<td>1/3</td>
<td>Dacapo, USP</td>
<td>PW91</td>
<td>0.23</td>
</tr>
<tr>
<td>( \sqrt{3} \times \sqrt{3} )-R30°</td>
<td>1/3</td>
<td>FP-LAPW</td>
<td>PW91</td>
<td>0.10</td>
</tr>
</tbody>
</table>

atomic conf. 4d, 5s | \( n_d = 6 \) | 4d, 5s | 7.6 | 8.7 | 9.6 | 6.2 | 7.2 | 8.3 | atomic conf. 4d, 5s | \( n_d = 6 \) | 4d, 5s | 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 (\( \Delta E \sim 50 \text{ meV} \))
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

Accurate surface and adsorption energies from many-body perturbation theory

L. Schimka\textsuperscript{1*}, J. Harl\textsuperscript{1}, A. Stroppa\textsuperscript{2†}, A. Grüneis\textsuperscript{1}, M. Marsman\textsuperscript{1}, F. Mittendorfer\textsuperscript{1} and G. Kresse\textsuperscript{1}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure3.png}
\caption{Surface energies, lattice constants and adsorption energies.}
\end{figure}

Except on Pd(111), CO adsorbs at Top site, but LDA & PBE predict wrong sites!
CO @ Pt(1 1 1) – 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 ~ -1.5 eV

DMC input:
1. supercell: \(2\sqrt{3} \times 2\sqrt{3}\) (9(ML)=1/3)
2. time step = 0.01
3. number of moves = 30,000

CO @ Au(1 1 1) – 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 ~ -0.4 eV

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)
One may ask: Why a "poor" guy like you jumping into so expensive project which needs one meV/H₂O accuracy? At that time, we are too stupid to know.....
DFT calculation of Ice

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

Prof. J-L Kuo’s results

1kbar = 100 MPa
Structure of Ice

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 P42/nmc)

VI

tetragonal crystals
(Space group P42/nmc)

II

Pressure, MPa

Temperature, °C

kg m$^3$

Liquid
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**
Totally 160 random structures

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

New BCC Structure (bcc1)

New BCC Structure (bcc2)

AIRSS Application
Bulk system : ICE-II

Total energy (eV)

configurations

-177.55
-177.60
-177.65
-177.70
-177.75
-177.80
-177.85
-177.90
-177.95
-178.00
-178.05
-178.10
-178.15

-177.55
-177.60
-177.65
-177.70
-177.75
-177.80
-177.85
-177.90
-177.95
-178.00
-178.05
-178.10
-178.15

-0.22 eV
Finite size effect of QMC needs to be checked!

(In preparation)
van der Waals heterostructures

AK Geim & IV Grigorieva
doi:10.1038/nature12385

<table>
<thead>
<tr>
<th>Graphene family</th>
<th>Graphene</th>
<th>hBN ‘white graphene’</th>
<th>BCN</th>
<th>Fluorographene</th>
<th>Graphene oxide</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>2D chalcogenides</strong></td>
<td>MoS$_2$, WS$_2$, MoSe$_2$, WSe$_2$</td>
<td>Semi-conducting dichalcogenides: MoTe$_2$, WTe$_2$, ZrS$_2$, ZrSe$_2$ and so on</td>
<td>Metallic dichalcogenides: NbSe$_2$, NbS$_2$, TaS$_2$, TiS$_2$, NiSe$_2$ and so on</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>2D oxides</strong></td>
<td>Micas, BSCCO</td>
<td>MoO$_3$, WO$_3$</td>
<td></td>
<td>Layered semiconductors: GaSe, GaTe, InSe, Bi$_2$Se$_3$ and so on</td>
<td>Hydroxides: Ni(OH)$_2$, Eu(OH)$_2$ and so on</td>
</tr>
<tr>
<td></td>
<td>Layered Cu oxides</td>
<td>TiO$_2$, MnO$_2$, V$_2$O$_5$, TaO$_3$, RuO$_2$ and so on</td>
<td>Perovskite-type: LaNb$_2$O$_7$, (Ca,Sr)$_2$Nb$<em>3$O$</em>{10}$, Bi$_4$Ti$<em>3$O$</em>{12}$, Ca$_2$Ta$<em>2$TiO$</em>{10}$ and so on</td>
<td></td>
<td>Others</td>
</tr>
</tbody>
</table>
The interaction energy of two BN films

More reliable method is needed: QMC
BN bilayer: supercell structure

$\text{c} = 30 \text{Å}$

AA’ stacking
Lateral: 3x3, 4x4

$d : \text{bilayer distance}$

$5 \text{Å}$

3x3
Interaction curve: DMC

\[ \sigma < 2.5 \text{ meV/2BN} \]

(total \[ E \approx -700 \text{ eV/2BN} \])

CPU > 5 million core-hours
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

\[
\int_{-\infty}^{+\infty} \frac{dxdy}{(\sqrt{x^2 + y^2 + d^2})^6} = \int_{-\infty}^{+\infty} \frac{rdrd\theta}{(r^2 + d^2)^3} = \frac{1}{d^4}
\]
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

![Graph showing magnitude of interaction energy vs BN interlayer distance](chart.png)
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($\sqrt{3}\times\sqrt{3}$) / Graphene($\sqrt{7}\times\sqrt{7}$)
DFT-LDA optimized geometry is used in DMC calculation

<table>
<thead>
<tr>
<th>binding energy (meV)</th>
<th>20000</th>
<th>30000</th>
<th>40000</th>
<th>50000</th>
<th>60000</th>
<th>70000</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gra / Gra</td>
<td>66</td>
<td>66</td>
<td>67</td>
<td>67</td>
<td>69</td>
<td>71</td>
</tr>
<tr>
<td>K441 (B-Top)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BN / Gra K441</td>
<td>61</td>
<td>61</td>
<td>61</td>
<td>62</td>
<td>63</td>
<td>61</td>
</tr>
<tr>
<td>BN K441 (B-Top)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si(√3) / Gra(√7)</td>
<td>343</td>
<td>334</td>
<td>337</td>
<td>346</td>
<td>343</td>
<td>342</td>
</tr>
<tr>
<td>S221</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si(√3) / BN(√7)</td>
<td>286</td>
<td>289</td>
<td>291</td>
<td>289</td>
<td>302</td>
<td>297</td>
</tr>
<tr>
<td>S221</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MoS₂ / MoS₂</td>
<td>68</td>
<td>67</td>
<td>71</td>
<td>73</td>
<td>72</td>
<td>72</td>
</tr>
<tr>
<td>S331</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MoS₂(√7) / Gra(√12)</td>
<td>831</td>
<td>849</td>
<td>912</td>
<td>911</td>
<td>989</td>
<td>982</td>
</tr>
<tr>
<td>MoSe₂(√7) / BN(√12)</td>
<td>663</td>
<td>674</td>
<td>700</td>
<td>724</td>
<td>698</td>
<td>706</td>
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</tbody>
</table>
DMC shows a little trend that LDA might have done a reasonable job!

Currently available Van der Waals functionals might not account for Binding Energy of 2D Layer Materials!

Doing a curve for each system is perhaps necessary!

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

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!
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……!
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