Weak interactions
treated by DMC

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Collaborators

- Dr. Nguyen Thanh Cuong
  JAIST --&gt; 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

$E_G(d)$
Background


**FMO-QMC** applied several years ago, but (Glycine Trimer) it doesn’t work well

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

\[
= \sum_{I=1}^{N} E_{IJ} - (N - 2) \sum_{I=1}^{N} E_{I}
\]

(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)
Stacking energy (kcal/mol)
Distance between two A-T Base layers (Å)

Stacking energy = \( E(R) - E(R_0=8) \)
Results - All electron

Distance between two A-T Base layers (Å)

Stacking energy = E(R) - E(R₀=8)
QMC/LDA trial nodes
TZ and DZ
QMC/GGA trial nodes
LDA & GGA

DNA ATAT stacking

Energy difference (kcal/mol) vs Distance (angstrom)
CO on Cu(111) surface

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

DFT fails to predict correct adsorption site for several transition and noble metal surfaces.
Discrepancies

<table>
<thead>
<tr>
<th>Co</th>
<th>Ni</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rh</td>
<td>Pd</td>
<td>Ag</td>
</tr>
<tr>
<td>Ir</td>
<td>Pt</td>
<td>Au</td>
</tr>
</tbody>
</table>

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

\[ E_F \]

\( 2\pi^* \)
\( 5\sigma \)
\( 1\pi \)
\( 4\sigma \)
\( 3\sigma \)

Free CO ; clean Cu surface

\( \pi^* \rightarrow d_{\text{planar}} \); strong / prefers HOLLOW

\( \sigma \rightarrow d_{(z^2)} \); weak, long-ranged / prefers TOP

M. Gajdos et al., Condens. Matter 16 (2004) 1141
**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 $2\pi$ is most favoured with the PW91 functional -> a fcc site most stable one.

HOMO/LUMO GAP underestimated in LDA

$\rightarrow [\pi^*-d]$ 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

atop
bridge
hcp-hollow
fcc-hollow
# Results so far

Energy (hartree/UnitCell)

<table>
<thead>
<tr>
<th>Structure</th>
<th>PBE-GGA</th>
<th>DMC (10k for stats.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ATOP</td>
<td>-1817.8330</td>
<td>-1806.25(1)</td>
</tr>
<tr>
<td>BRIDGE</td>
<td>-1817.8335</td>
<td>-1806.24(1)</td>
</tr>
<tr>
<td>HOLLOW (HCP)</td>
<td>-1817.8341</td>
<td>-1806.23(1)</td>
</tr>
<tr>
<td>HOLLOW (FCC)</td>
<td><strong>-1817.8345</strong></td>
<td>-1806.20(1)</td>
</tr>
</tbody>
</table>
DFT for QMC trial WF

DFT with PWSCF code

- A slab model: Cu(111) - \( (\sqrt{3} \times \sqrt{3}) - R30 \)
  with 4-layers (12 Cu atoms)
- PBE functional
- Trail-Needs small core pseudo potential
  KB ghost --> s-local for Cu
d-local for other
- \( E_{\text{cutoff}} = 250 \) Ry
- 2x2x1 \( k \)-mesh (shifted into L-pt)
  --> 816 electrons for QMC
## Trail-Needs PP

**Large Core for Cu: 11 electrons**

<table>
<thead>
<tr>
<th>$E_{\text{cutoff}}$ (Ry)</th>
<th>$E_{\text{total}}$ (Ry)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>-1020.85296106</td>
</tr>
<tr>
<td>200</td>
<td>-1205.79813236</td>
</tr>
<tr>
<td>300</td>
<td>-1250.80554480</td>
</tr>
<tr>
<td>400</td>
<td>-1260.09948666</td>
</tr>
<tr>
<td>500</td>
<td>-1261.43336365</td>
</tr>
<tr>
<td>600</td>
<td>-1261.50965834</td>
</tr>
<tr>
<td>700</td>
<td>-1261.51931978</td>
</tr>
<tr>
<td>800</td>
<td>-1261.54014445</td>
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**Small Core for Cu: 17 electrons**

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<tr>
<td>100</td>
<td>-3569.17561370</td>
</tr>
<tr>
<td>200</td>
<td>-3592.34897908</td>
</tr>
<tr>
<td>300</td>
<td>-3592.39104215</td>
</tr>
<tr>
<td>400</td>
<td>-3592.40725712</td>
</tr>
<tr>
<td>500</td>
<td>-3592.40804109</td>
</tr>
<tr>
<td>600</td>
<td>-3592.40821798</td>
</tr>
<tr>
<td>700</td>
<td>-3592.40834096</td>
</tr>
<tr>
<td>800</td>
<td>-3592.40844810</td>
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Reducing Cutoff

500 Ryd. required for DFT to converge

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

Less than 300 Ryd. is feasible

- $E_{\text{cutoff}} = 250$ Ry

- $2\times2\times1$ $k$-mesh (shifted into L-pt)

--> 816 electrons for QMC
Reducing Cutoff

GaN442 case

![Graph showing energy difference vs PW cutoff (Ryd.) for different methods: SCF, HPVNC, VNC, and LNC.](image)
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

...walkers dying off

with T-move

w/o T-move
## Results so far

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Energy (hartree/UnitCell)
HPCF setup

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

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

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

- 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.)

<table>
<thead>
<tr>
<th>label</th>
<th>CPU time</th>
<th>real time</th>
</tr>
</thead>
<tbody>
<tr>
<td>4/T/F</td>
<td>7236.7598</td>
<td>7237.3755</td>
</tr>
<tr>
<td>32/T/F</td>
<td>37691.1875</td>
<td>46593.4492</td>
</tr>
</tbody>
</table>

(100Ryd.)

Another test with 300 Ryd.

<table>
<thead>
<tr>
<th>label</th>
<th>CPU time</th>
<th>real time</th>
</tr>
</thead>
<tbody>
<tr>
<td>4/F/T</td>
<td>1625.4000</td>
<td>1674.2101</td>
</tr>
<tr>
<td>4/T/T</td>
<td>1775.5400</td>
<td>1822.2231</td>
</tr>
</tbody>
</table>

- 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) - \( (\sqrt{3} \times \sqrt{3}) \) - R30 with 4-layers (12 Cu atoms)

- PBE functional

- PAW pseudopotential

- \( E_{\text{cutoff}} = 150 \text{ Ry} \)

- \( 14 \times 14 \times 1 \) \( k \)-mesh
PAW-DFT results

Adsorption energy (eV)

\[ E_{\text{adsorption}} = E_{\text{CO-Cu(111)}} - \left( E_{\text{CO}} + E_{\text{Cu(111)}} \right) \]

<table>
<thead>
<tr>
<th></th>
<th>atop</th>
<th>bridge</th>
<th>hcp-hollow</th>
<th>fcc-hollow</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(111) 4-Layers</td>
<td>-0.583 eV</td>
<td>-0.637 eV</td>
<td>-0.711 eV</td>
<td>-0.714 eV</td>
</tr>
<tr>
<td>7-Layers</td>
<td>-0.618 eV</td>
<td>-0.670 eV</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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

- 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