Quantum Monte Carlo applications to noncovalent interactions in cyclohexasilane dimers

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collaborating with Prof. Ryo Maezono

Outline of this talk

- *p*-DIB polymorphism
  - progress from my previous talk
- Noncovalent interactions in cyclohexasilane
  - for industrial applications
  - for simulations of liquid structure & wettability
- Metallic hydrogen at high pressure
  - some preliminary results (in progress)

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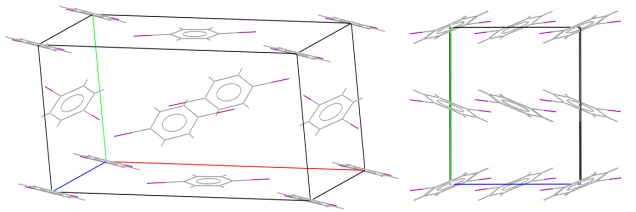
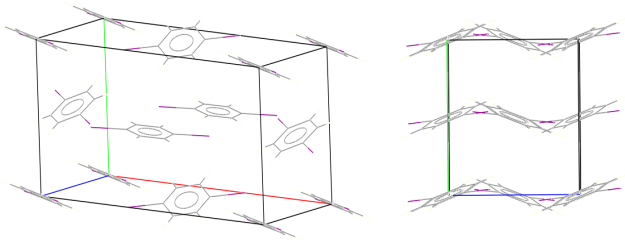
DMC results for the polymorphism of *p*-DIB

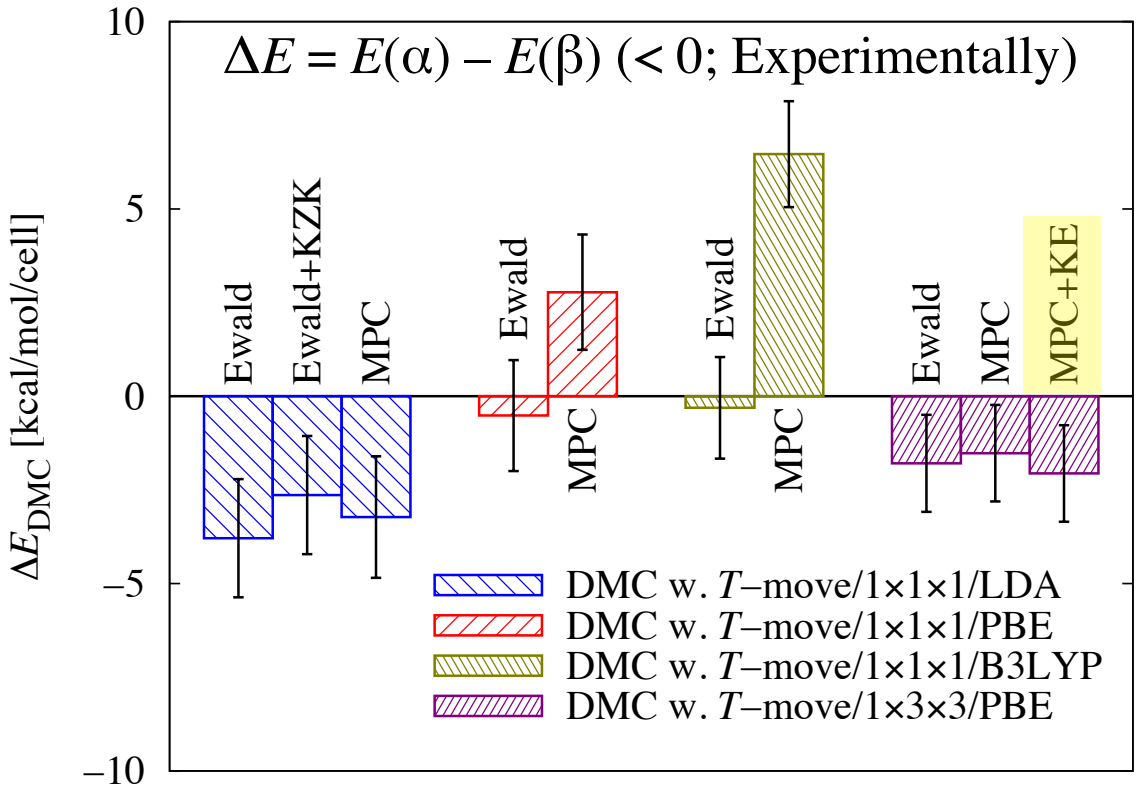
K. Hongo, M.A. Watson, T. Iitaka, A. Asupru-Guzik, R. Maezono, submitted to JCTC

β-phase (*Pccn*)





α-phase (*Pbca*)



Finite size errors in DMC/1x3x3

(kcal/mol/cell)

ΔE_1 : one-body FSE estimated from DFT

ΔT_2 : kinetic energy correction by CCMH

ΔU_2 : MPC correction

	α	β	$\Delta(\alpha-\beta)$
ΔE_1	0.1	0.0	0.1
ΔT_2	4.4	4.9	-0.5
ΔU_2	10(1)	10(1)	0(2)

The two-body FSEs for each phase are larger than the energy difference (ca. -2 kcal/mol/cell).

Summary & Future work

- The two-body FSEs are larger than the energy difference in 1x3x3 – we could not say any definitive conclusion, though the sign of the energy difference is consistent with experiment.
- Nodal surface dependence within 1x3x3 is still an open question.

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Cyclosilane (Si_nH_{2n})

as source materials for Si films by liquid process

significant reduction in the complexity of required equipment and the cost involved,
→ good for the environment

Prof. Tatsuya Shimoda Group from JAIST

Ref; Nature 440, 783 (2006).

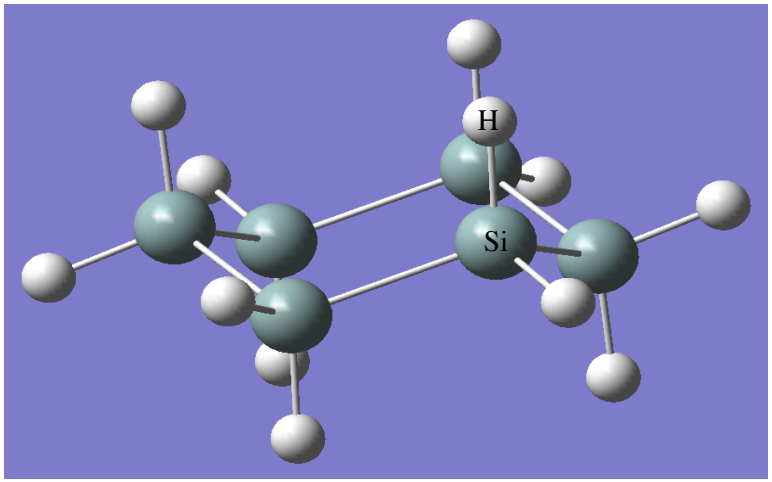
Microscopic liquid structures;

classical/ab initio molecular dynamics (MD)

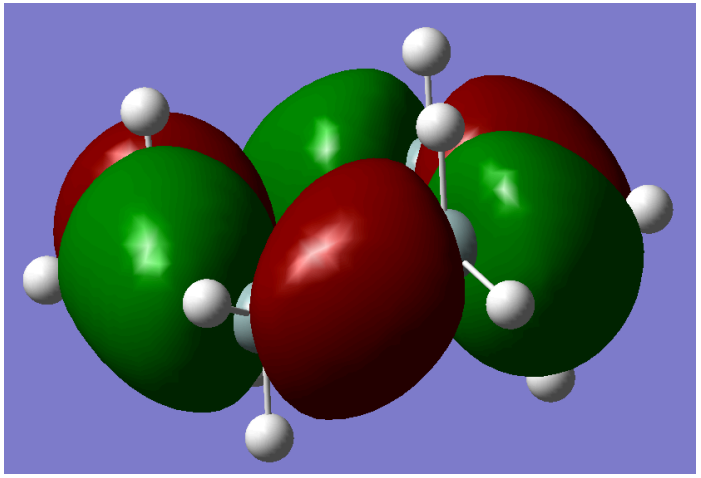
Molecular interactions;

→ appropriate force fields/DFT functionals are unknown…

Molecular interactions of Cyclohexasilane (CHS; Si_6H_{12})



monomer geometry; ring, chair



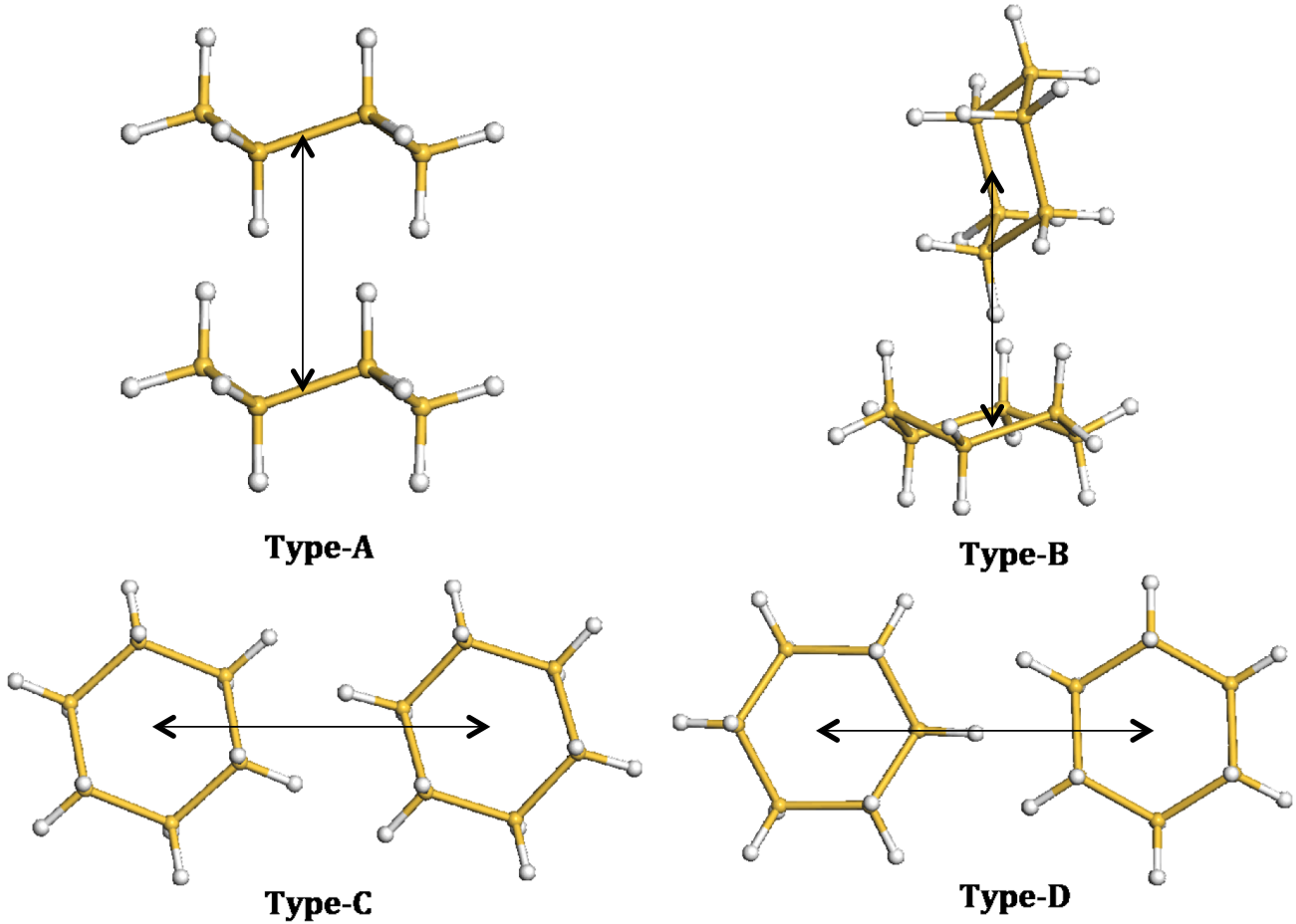
HOMO level; σ bond

H saturated systems; all the π orbitals of Si_6H_6 bind with 6 H's

Si_6H_{12} dimer: Non-π stacking → aliphatic-aliphatic interactions

no previous theoretical work

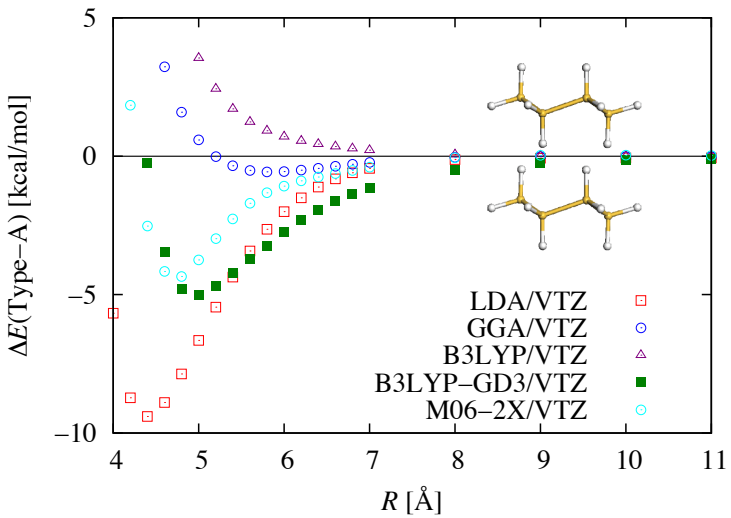
Typical dimer configurations

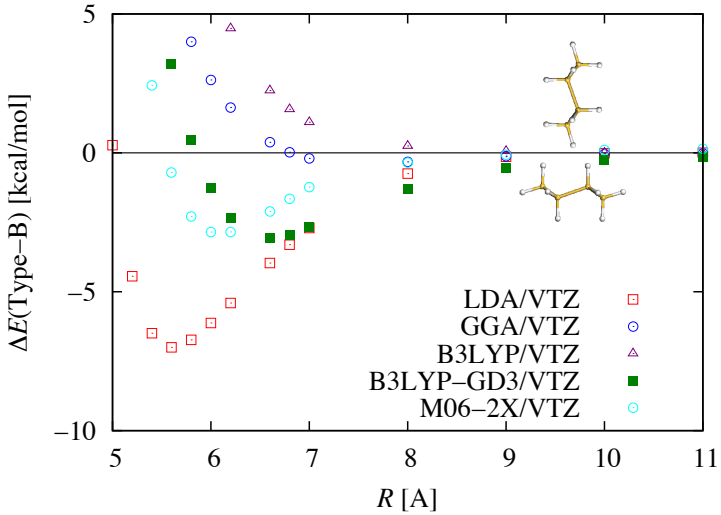


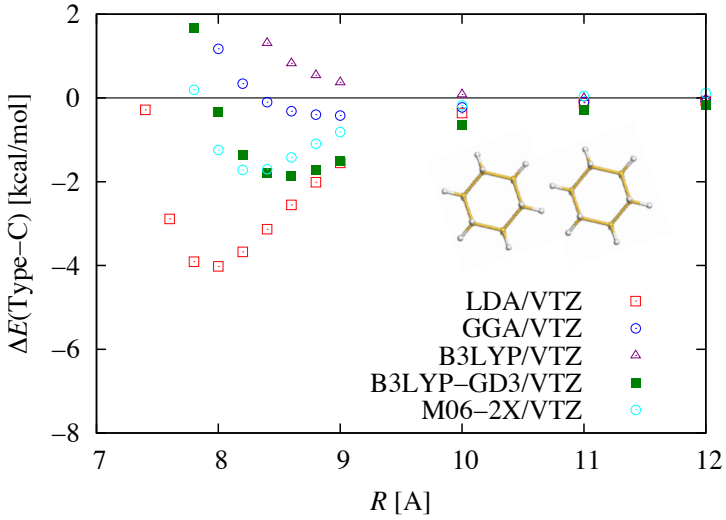
DFT methods using G09

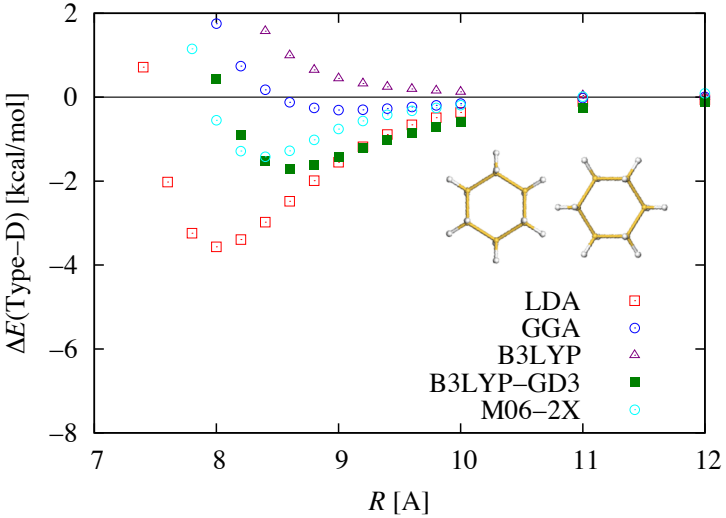
- Basis set superposition error (BSSE) correction
- Conventional functionals
  - Local & semi-local: SVWN, PBE
  - Hybrid: B3LYP
- Recently developed functionals
  - Hybrid meta-GGA: M06-2X
  - DFT-D: B3LYP-GD3
- Pseudopotential/Basis function
  - Burkatzki-Filipi-Dolg/VTZ level (same as QMC)

DFT PES results









B3LYP-GD3 vs. M06-2X → reference data needed!

MP2/CCSD(T)/QMC

MP2 calculations using G09

- Basis sets
  - VTZ level with Burkatzki-Filipi-Dolg PP
  - cc-pVDZ(DZ)/cc-pVTZ(TZ)
  - aug-cc-pVDZ(aDZ)/aug-cc-pVTZ(aTZ)
  - Complete basis set (CBS) (by Truhlar's scheme)

$$\Delta E_{\mathrm{MP2}}^{\mathrm{CBS}} = \Delta E_{\mathrm{HF}}^{\mathrm{CBS}} + \Delta E_{\mathrm{correlation}}^{\mathrm{CBS}}$$

$$\begin{cases} \Delta E_{\mathrm{HF}}^{\mathrm{CBS}} = \dfrac{3^{\alpha}}{3^{\alpha}-2^{\alpha}}\Delta E_{\mathrm{HF}}^{3} - \dfrac{2^{\alpha}}{3^{\alpha}-2^{\alpha}}\Delta E_{\mathrm{HF}}^{2};\ \alpha = 3.4 \\ \Delta E_{\mathrm{correlation}}^{\mathrm{CBS}} = \dfrac{3^{\beta}}{3^{\beta}-2^{\beta}}\Delta E_{\mathrm{correlation}}^{3} - \dfrac{2^{\beta}}{3^{\beta}-2^{\beta}}\Delta E_{\mathrm{correlation}}^{2};\ \beta_{\mathrm{MP2}} = 2.2 \end{cases}$$

Cardinal numbers 2/3 correspond to DZ/TZ or aDZ/aTZ.

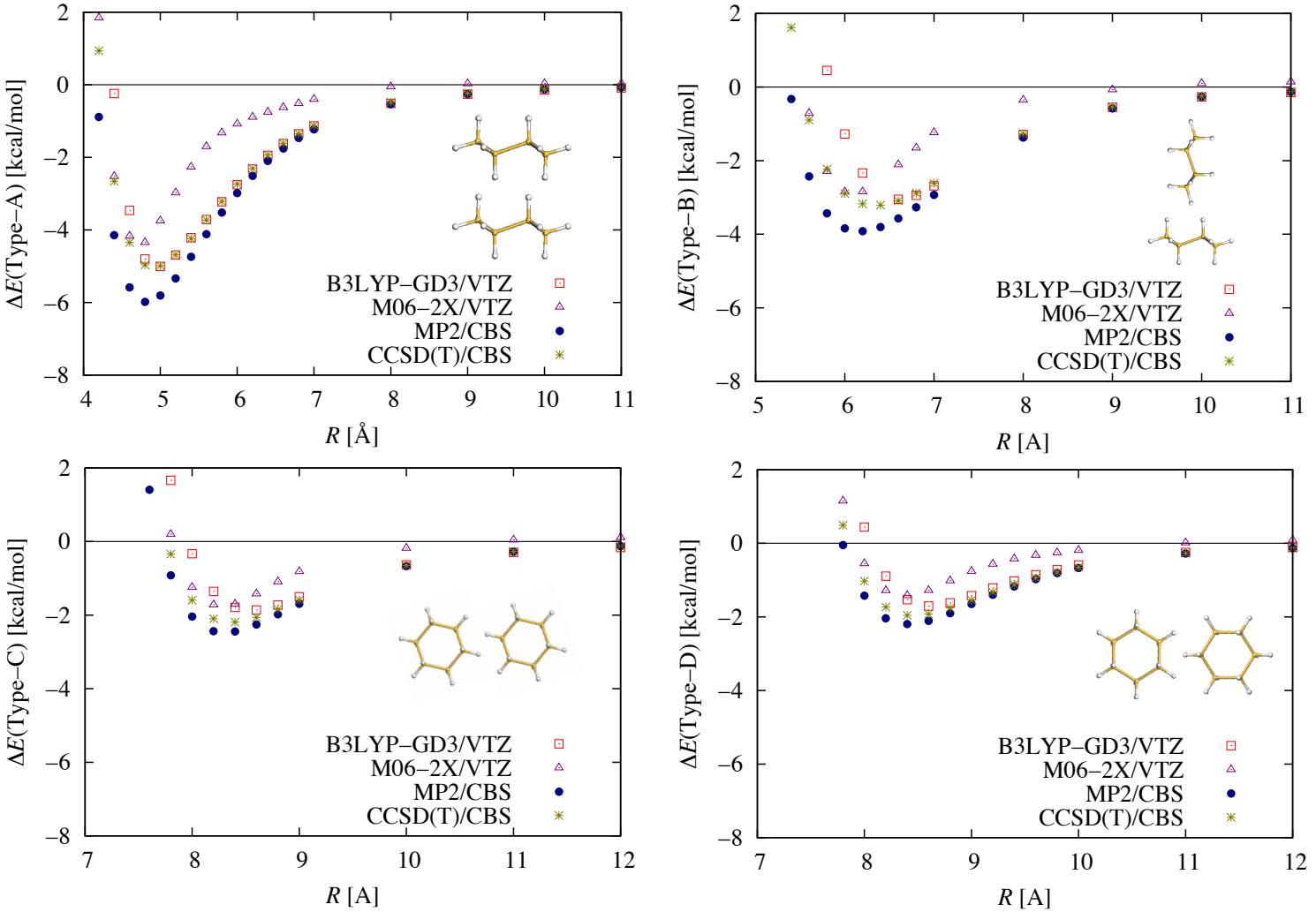
CCSD(T) calcultions using G09

- Basis sets
  - only cc-pVDZ (DZ)
    - did not run with BFD, TZ, aDZ, aTZ, …
  - CBS extrapolation (by Hobza's scheme)

$$\Delta E^{\mathrm{CBS}}_{\mathrm{CCSD(T)}} = \Delta E^{\mathrm{CBS}}_{\mathrm{MP2}} + \left(\Delta E^{\mathrm{DZ}}_{\mathrm{CCSD(T)}} - \Delta E^{\mathrm{DZ}}_{\mathrm{MP2}} \right)$$

assuming that $\left(\Delta E^{\mathrm{DZ}}_{\mathrm{CCSD(T)}} - \Delta E^{\mathrm{DZ}}_{\mathrm{MP2}} \right)$ exhibits only a small basis set dependence.

Comparison with correlated methods

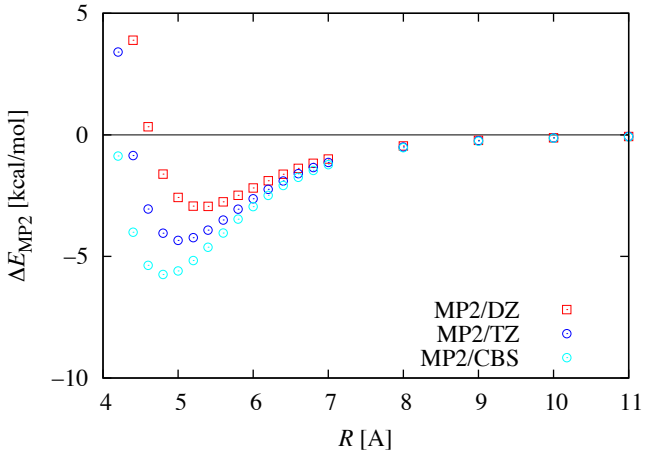


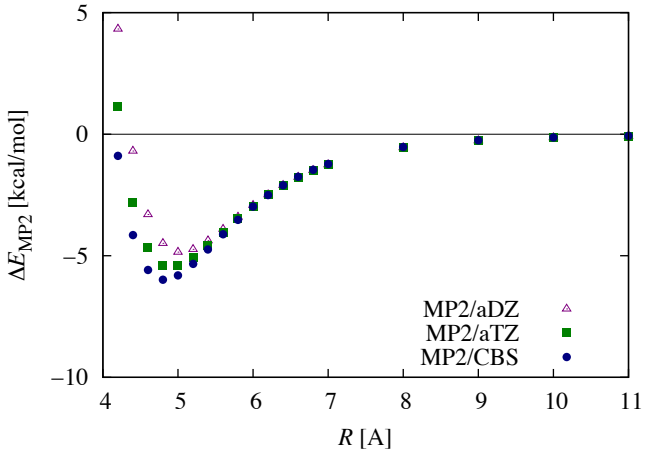
B3LYP-GD3 seems closer to CCSD(T)/CBS than M06-2X…

Basis set issues (CBS extrapolation)

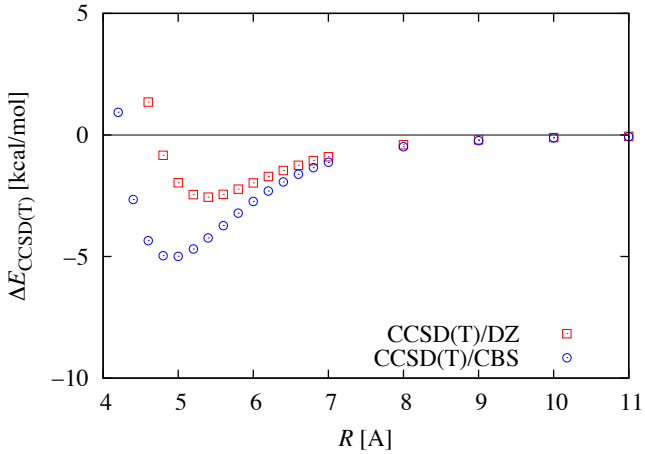
$$\Delta E_{\mathrm{MP2}}^{\mathrm{CBS}} = \Delta E_{\mathrm{HF}}^{\mathrm{CBS}} + \Delta E_{\mathrm{correlation}}^{\mathrm{CBS}}$$

$$\Delta E_{\mathrm{HF}}^{\mathrm{CBS}} = \frac{3^{\alpha}}{3^{\alpha}-2^{\alpha}}\Delta E_{\mathrm{HF}}^{3} - \frac{2^{\alpha}}{3^{\alpha}-2^{\alpha}}\Delta E_{\mathrm{HF}}^{2};\ \alpha = 3.4 \qquad \Delta E_{\mathrm{correlation}}^{\mathrm{CBS}} = \frac{3^{\beta}}{3^{\beta}-2^{\beta}}\Delta E_{\mathrm{correlation}}^{3} - \frac{2^{\beta}}{3^{\beta}-2^{\beta}}\Delta E_{\mathrm{correlation}}^{2};\ \beta_{\mathrm{MP2}} = 2.2$$





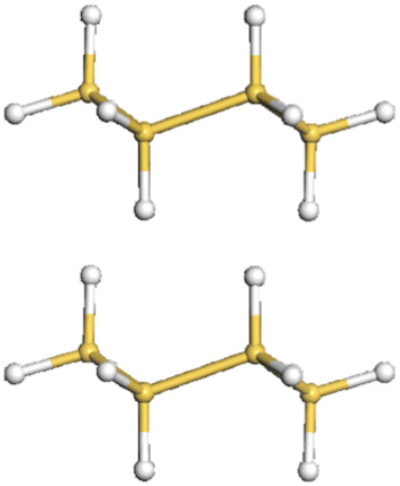
$$\Delta E_{\mathrm{CCSD(T)}}^{\mathrm{CBS}} = \Delta E_{\mathrm{MP2}}^{\mathrm{CBS}} + \left(\Delta E_{\mathrm{CCSD(T)}}^{\mathrm{DZ}} - \Delta E_{\mathrm{MP2}}^{\mathrm{DZ}}\right)$$



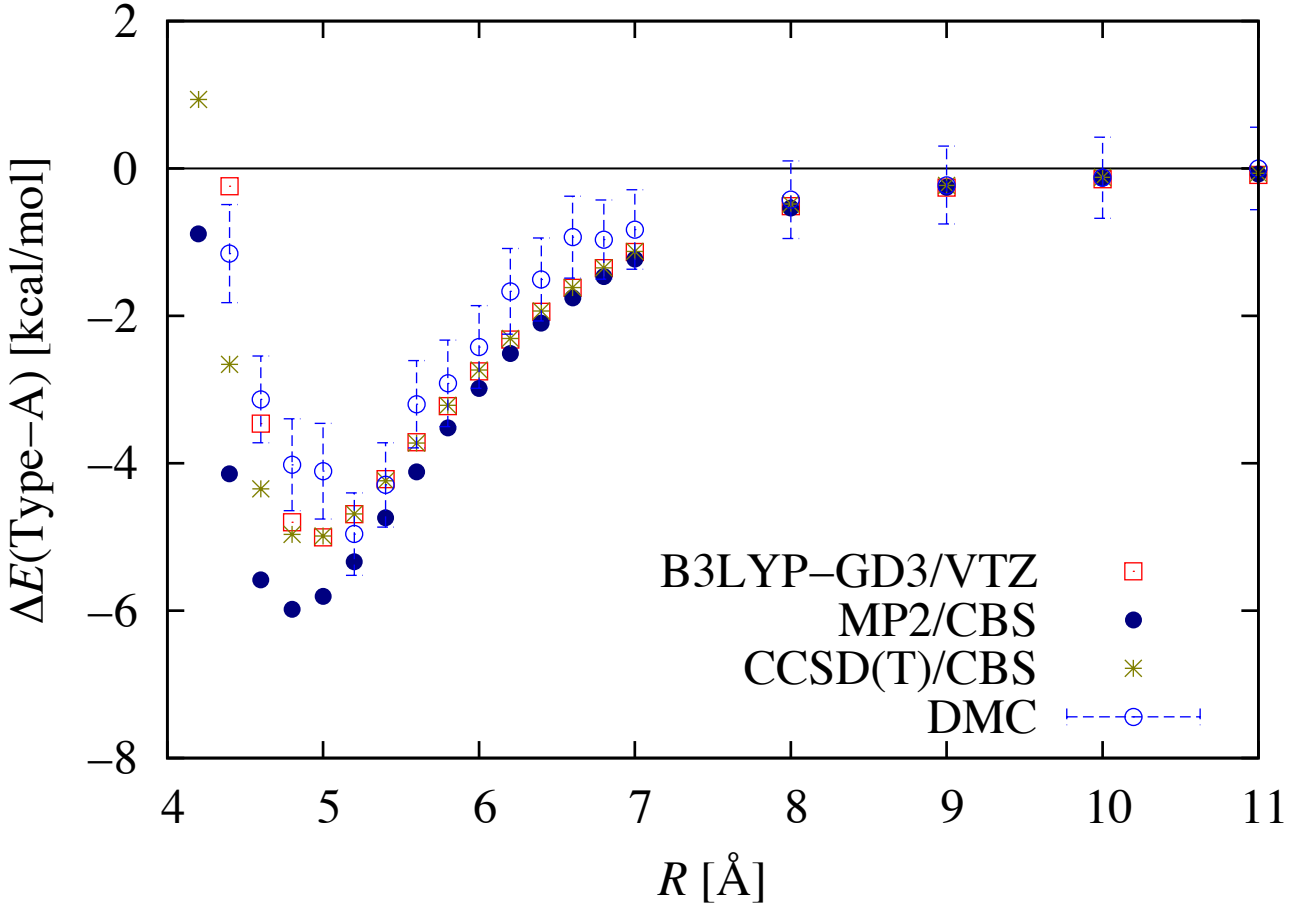
QMC calculations

- DMC calculations using CASINO
- Burkatzki-Fillippi-Dolg PPs with associated basis sets
  - VTZ basis set
  - CHS dimer; 36 atoms & 72 electrons
- Trial wavefunction = Slater-Jastrow type
  - B3LYP trial nodes (generated by Gaussian 09)
  - Jastrow factor: one-, two-, and three-body terms (up to 8the poly.)
- computational conditions of DMC
  - # of walkers = 1024, # of MC steps = 8×10^4

QMC results for Type-A (preliminarily)



Type-A



Summary & Future work

Aliphatic-aliphatic interactions of the Si_6H_{12} dimer for four dimer configurations were studied using DMC, MP2, CCSD(T), and various DFT methods.

- ✓ Popular DFT methods fail to describe the interactions.
- ✓ M06-2X gives an equilibrium distance and binding energy, which is consistent with CCSD(T), but its potential energy curve differs.
- ✓ The DMC result for Type-A is in good agreement with CCSD(T) and B3LYP-GD3.

More statistical accumulation is necessary for Type-A.

DMC simulations for Type-B/C/D are now running.

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Metallic hydrogen at high pressure (590 GPa)

- Collaborators
  - Prof. Tastuki Oda (Kanazawa University)
  - Dr. Takahiro Ishikawa (Osaka University)

Phase with Anomalous Crystal Structure Fluctuation in Dense Solid Atomic Hydrogen

Takahiro Ishikawa,[1,*] Hitose Nagara,[2] Tatsuki Oda,[3] Naoshi Suzuki,[4] and Katsuya Shimizu[1]

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[2]*Department of Applied Mathematics and Physics, Tottori University, 4-104 Koyama-cho-minami, Tottori, Tottori 680-8552, Japan*
[3]*Institute of Science and Engineering, Kanazawa University, Kakuma, Kanazawa, Ishikawa 920-1192, Japan*
[4]*Department of Pure and Applied Physics, Faculty of Engineering Science, Kansai University, 3-3-35 Yamate, Suita, Osaka 564-8680, Japan*

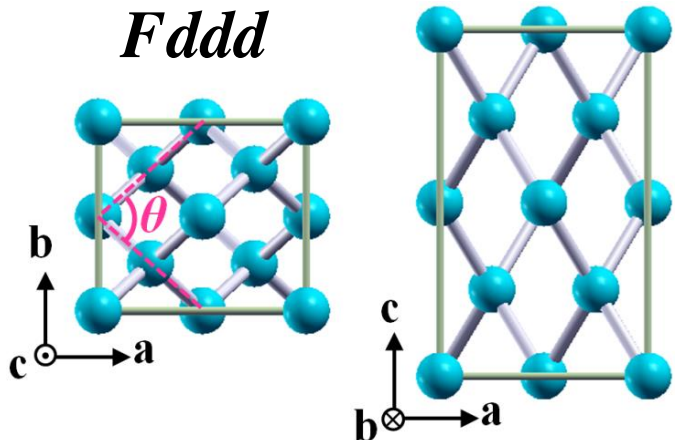
(Dated: May 18, 2013)

A phase with a frequent structural fluctuation within an orthorhombic $F222$ space group has been predicted in solid atomic hydrogen above 600 GPa via *ab-initio* genetic algorithm and molecular dynamics techniques. Its crystal structure is of a slight monoclinic distortion of the tetragonal $I4_1/amd$ earlier predicted by *ab-initio* studies. The molecular dynamics simulations have clarified that the phase shows a fluctuation among the $I4_1/amd$ and $F222$ structures in the pressure range of 600-2250 GPa at 100 K where the thermal fluctuation is assumed to become influential.

Reviewer's comment on their paper

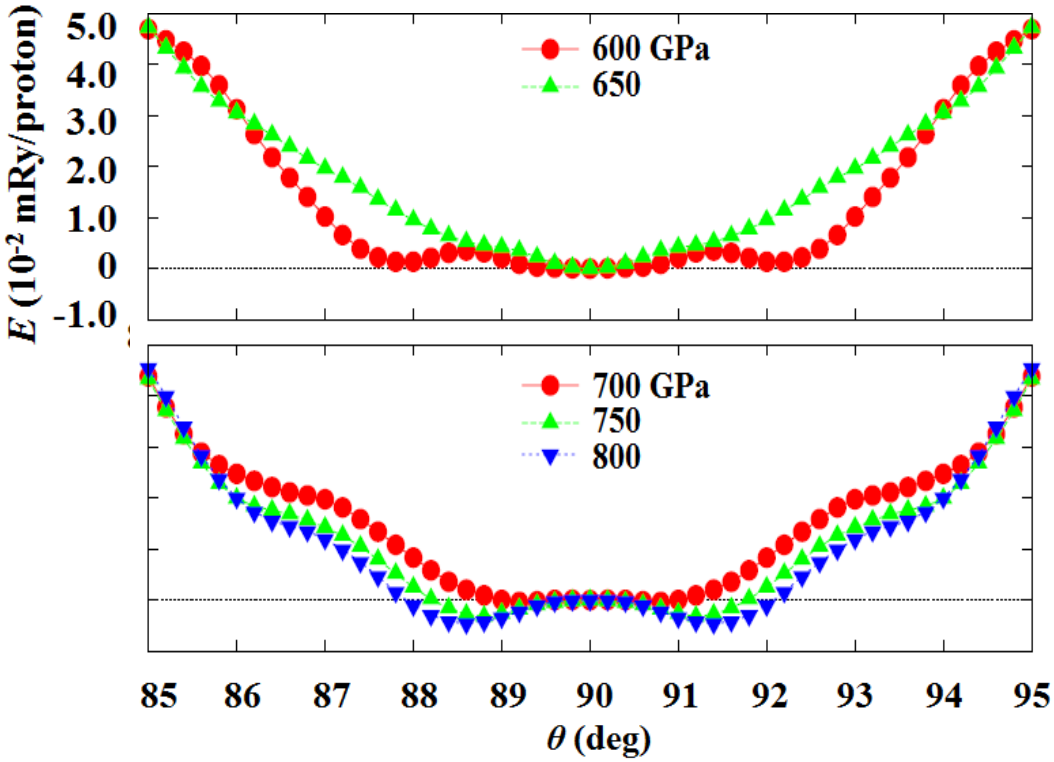
In summary, this work is still in a premature state. Their re-discovered Fddd structure is not new, and the claimed structure fluctuation is not convincing. There are still many works that should be done before the authors can reach a reliable conclusion. I recommend the authors ①using more accurate DMC calculations to check the numeric accuracy of their results, ②including zero point motion contribution in their analysis to give reliable physical pictures, and ③using large enough supercells to validate their conclusion in the thermodynamic limit. Only after these improvements have been done, then we can finally say whether they observed some unusual behavior of dense hydrogen or not.

Within DFT

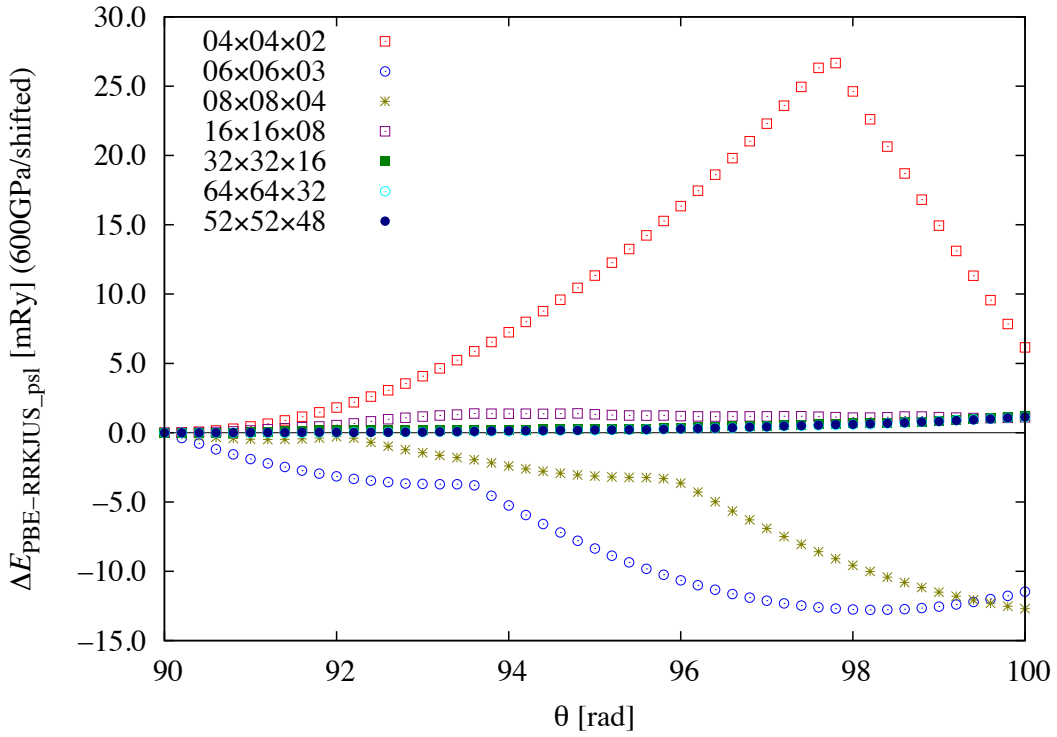


$\theta = 90°$ => Cs-IV ($I4_1/amd$)

PES: GGA/USPP/160 Ry/52x52x48



k-mesh dependence within DFT (600GPa)

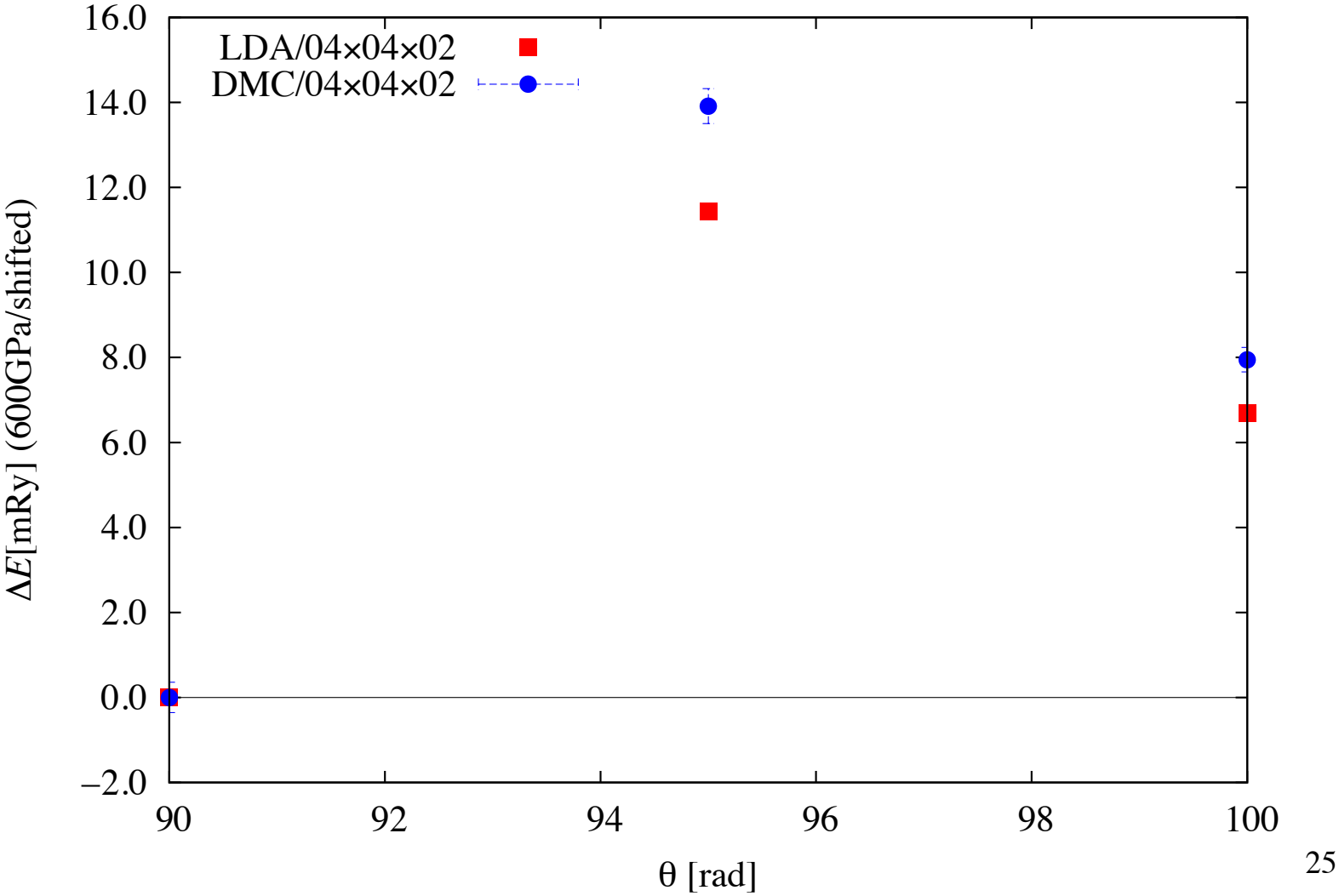


# of electrons: 4x4x2 => 128, 6x6x3 => 432,
8x8x4 => 1024, 10x10x5 => 2000…

a quite severe system for QMC

DMC/4x4x2 at 600GPa

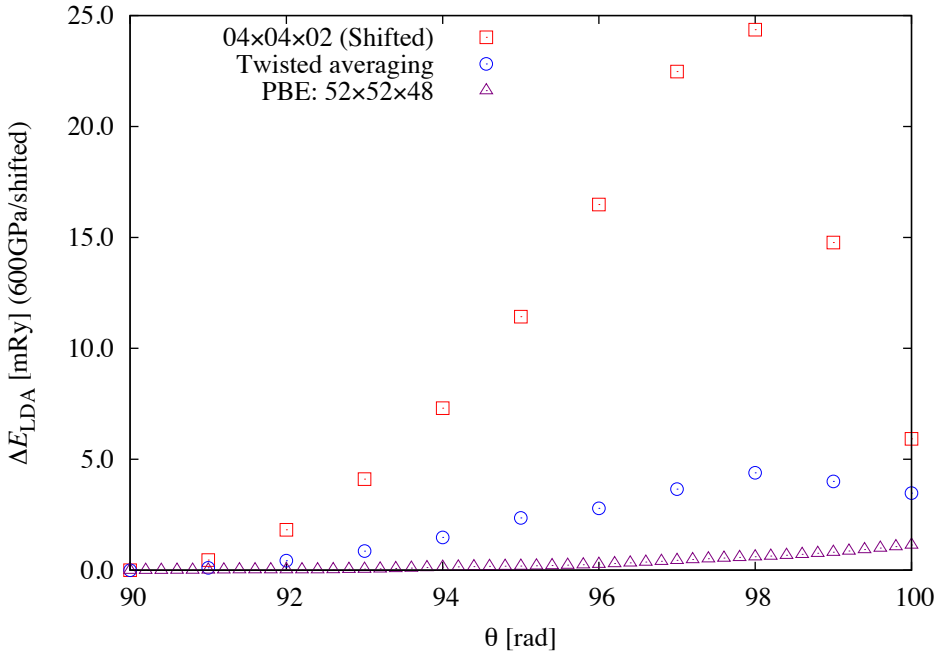
LDA-PZ/NC-TN/150 Ry



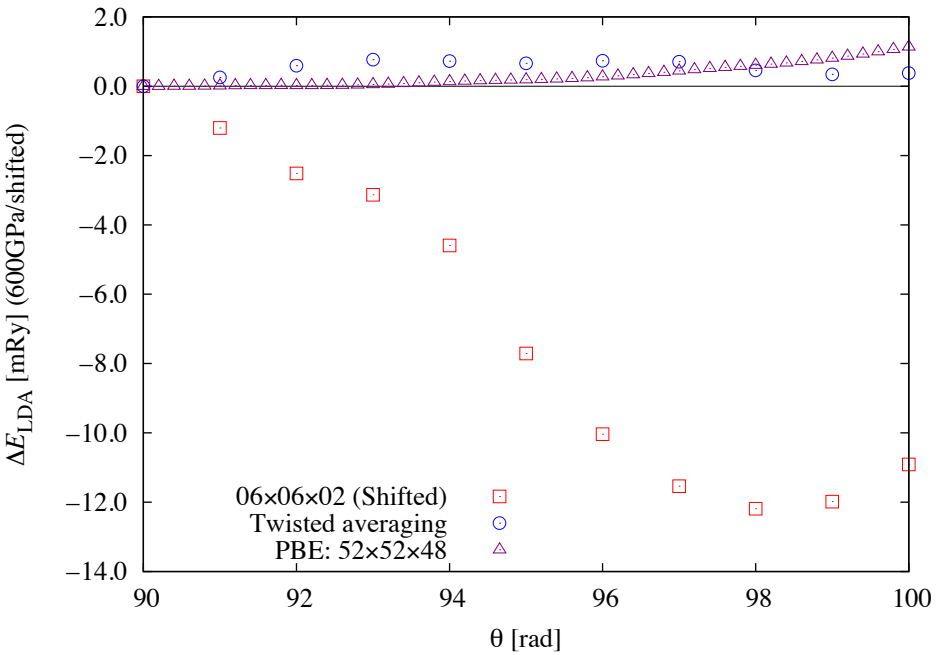
Twist averaging within DFT

LDA-PZ/NC-TN/150

04x04x02/12 twists



06x06x03/12 twists



More twists leads to more accurate results??

Future work

- XC functionals/Pseudopotential dependence
- varing the number of twists
- twist averaging DMC for 4x4x2 and 6x6x3

Thank you !