Quantum Monte Carlo in the Apuan Alps VIII @ TTI, Vallico Sotto, Tuscany, Italy, 08/02/2013

Finite-size effects in diffusion Monte Carlo simulations of *para*-diiodobenzene

Kenta Hongo

kenta_hongo@mac.com

Assistant Professor,
School of Information Science, JAIST
(Prof. Ryo Maezono's group)

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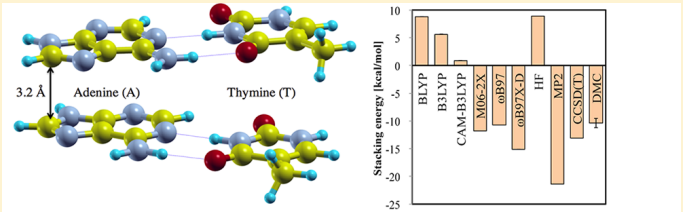
The Importance of Electron Correlation on Stacking Interaction of Adenine-Thymine Base-Pair Step in B-DNA: A Quantum Monte Carlo Study

Kenta Hongo,*,† Nguyen Thanh Cuong,‡ and Ryo Maezono†

†School of Information Science, JAIST, Asahidai 1-1, Nomi, Ishikawa 923-1292, Japan

‡Nanosystem Research Institute (NRI), National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba 305-8568, Japan

ABSTRACT: We report fixed-node diffusion Monte Carlo (DMC) calculations of stacking interaction energy between two adenine(A)−thymine(T) base pairs in B-DNA (AA:TT), for which reference data are available, obtained from a complete basis set estimate of CCSD(T) (coupled-cluster with singles, doubles, and perturbative triples). We consider four sets of nodal surfaces obtained from self-consistent field calculations and examine how the different nodal surfaces affect the DMC potential energy curves of the AA:TT molecule and the resulting stacking energies. We find that the DMC potential energy curves using the different nodes look similar to each other as a whole. We also benchmark the performance of various quantum chemistry methods, including Hartree−Fock (HF) theory, second-order Møller−Plesset perturbation theory (MP2), and density functional theory (DFT). The DMC and recently developed DFT results of the stacking energy reasonably agree with the reference, while the HF, MP2, and conventional DFT methods give unsatisfactory results.



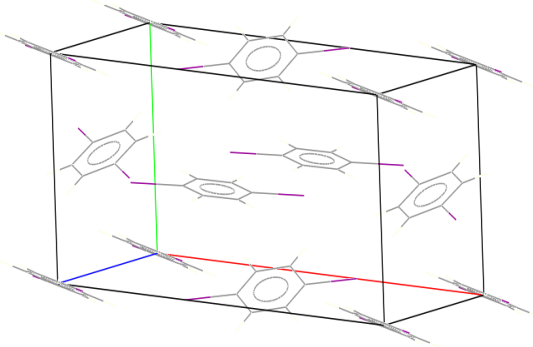
The importance of electron correlation on stacking interaction of adenine:thymine base-pair step in B-DNA: A quantum Monte Carlo study

J. Chem. Theory Comput. 2013, 9, 1081-1086.

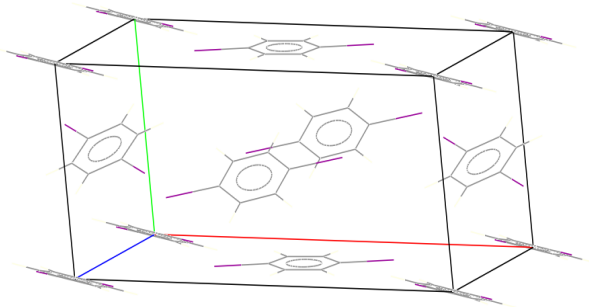
Polymorphism in *p*-DIB

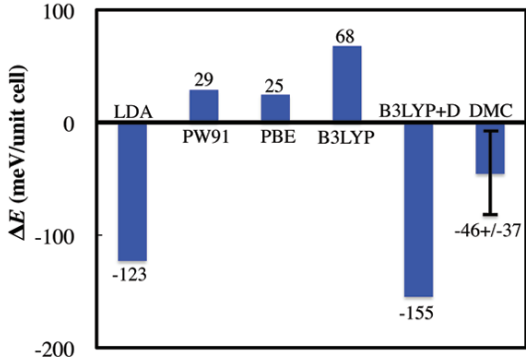
Transition from α- to β-phase occurs at 326 K

α-phase (*Pbca*)



β-phase (*Pccn*)





The first application of QMC to molecular crystal systems:
K. Hongo, M. A. Watson, R. S. Sánchez-Carrera, T. Iitaka, A. Aspruru-Guzik,
J. Phys. Chem. Lett. 1, 1789 (2010).

Motivation

- Previous study
  - First application of QMC to molecular crystals
  - Only 1x1x1 simulation cell size
  - Finite size effects: correction by Kwee, Zhang, Krakauer
    - *a posteriori* scheme
- Present study
  - investigate FSEs *a priori* with larger cell size (1x3x3)

Finite-size effects

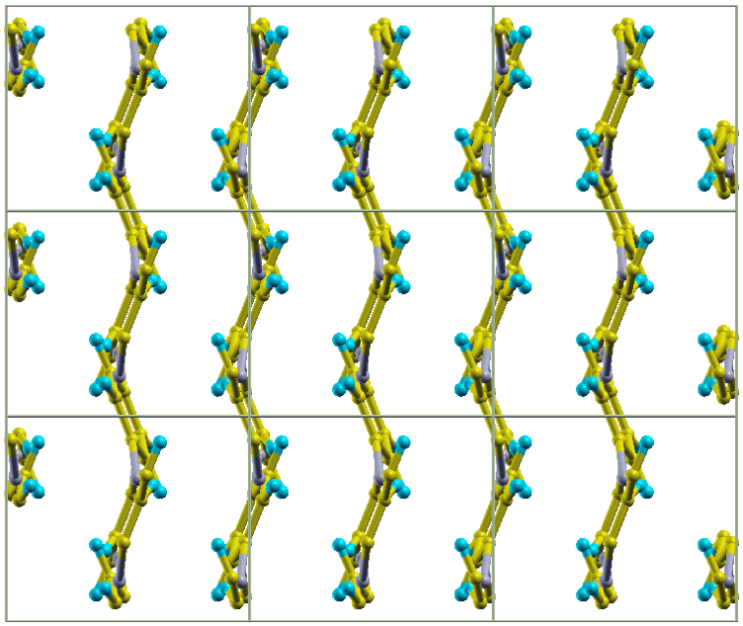
- Periodicity of solid
  - Extrapolation to infinite size
- Finite size effects [1]
  - One-body
    - Twisted-averaging scheme (for metallic systems) [2]
  - Two-body
    - Model periodic coulomb (MPC) interaction [3]
    - Chiesa, Ceperley, Martin, Holzmann (CCMH) scheme [4]
    - Kwee, Zhang, Krakauer (KZK) scheme (LDA only) [5]

References:
[1] Phys. Rev. B 78, 125106 (2008).
[2] Phys. Rev. E 64, 016702 (2001).
[3] Phys. Rev. B 53, 1814 (1996), Phys. Rev. B 55, R4851 (1997).
[4] Phys. Rev. Lett. 97, 076404 (2006).
[5] Phys. Rev. Lett. 100, 126404 (2008).

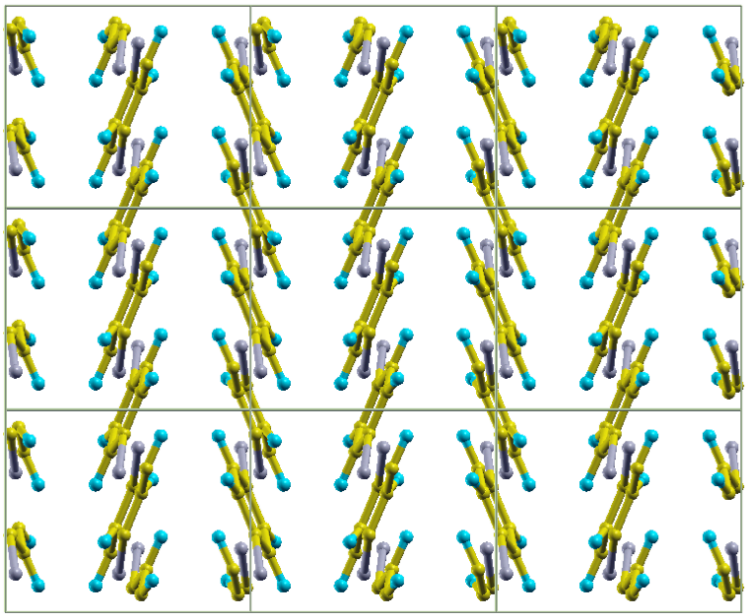
Simulation cell size

previous: 1x1x1 (168 electrons)

present: 1x3x3 (1,512 electrons)
→ costs 729 (= 9^3) times more…



α-phase



β-phase

K computer

from: http://www.fujitsu.com/global/about/tech/k/

2048-core parallel computing for 1x3x3

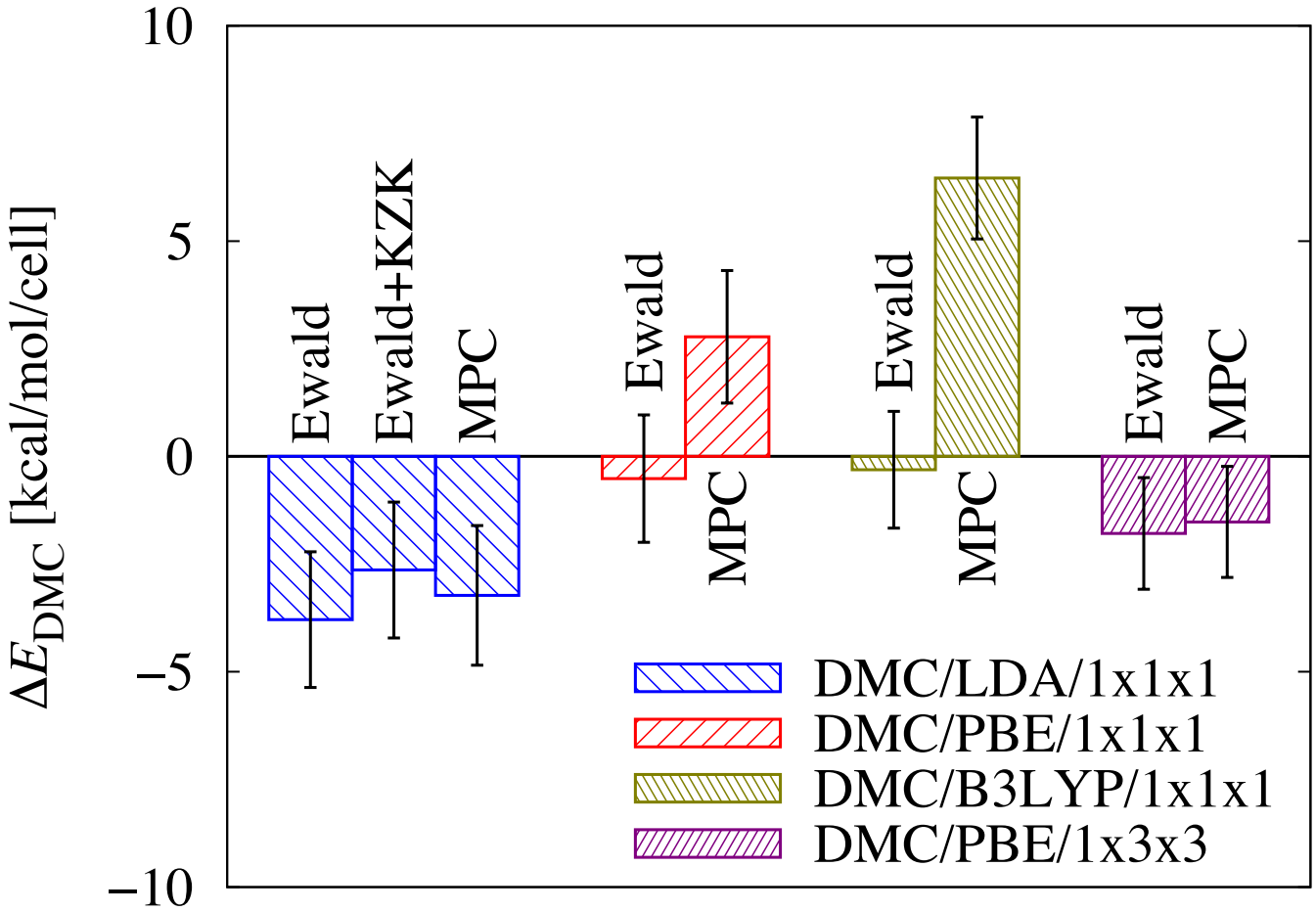
took about 400,000 core-hour (8 days)…

DMC with CASINO

- Pseudo potential = Trail-Needs type (CASINO library)
  - *T*-move scheme
- Trial nodal surface
  - LDA/GGA-PBE/B3LYP for 1x1x1 (40 Hartree cut off energy)
  - GGA-PBE for 1x3x3 (40 Hartree cut off energy)
  - One- & two-body Jastrow (24 & 12 parameters; varmin-linjas opt)
- computational conditions of DMC
  - 1x1x1: target population # = 1,280, # of MC steps = 1×10^5
  - 1x3x3: target population # = 20,480, # of MC steps = 7×10^3
  - time step = 0.01 – (check time-step bias only for 1x1x1)

Relative stability of polymorphs

$\Delta E = E(\alpha) - E(\beta)$ (< 0; Experimentally)



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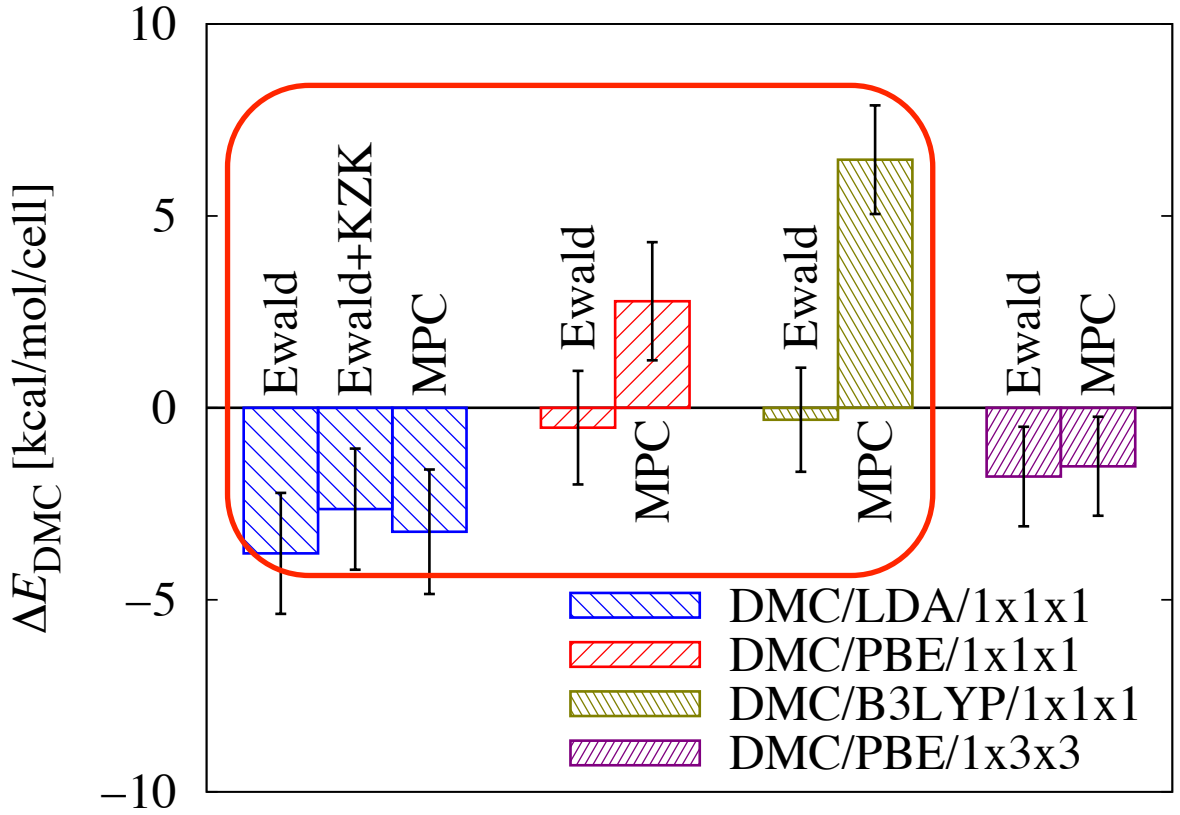
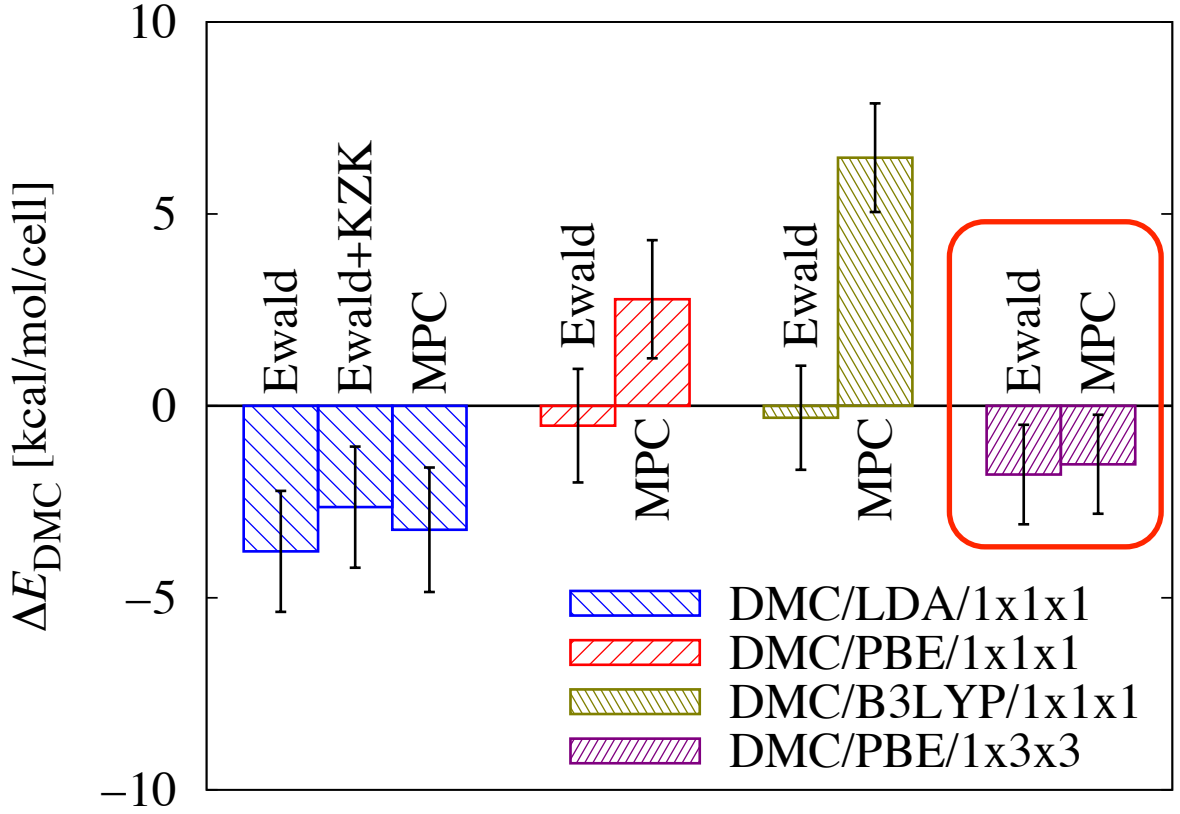


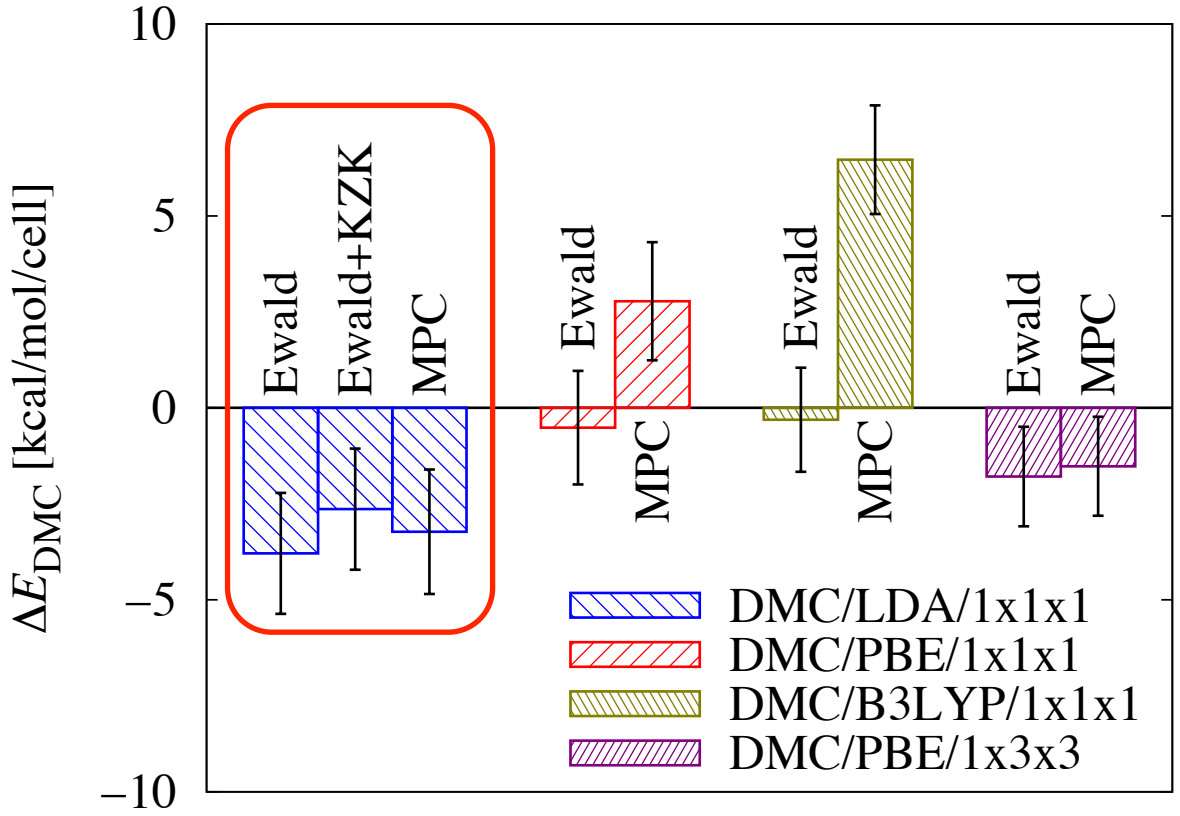
- Strong dependence of FSEs on nodal surfaces (1x1x1)
  - unreliable results within 1x1x1
  - previous LDA case was lucky case

cont'd (2)



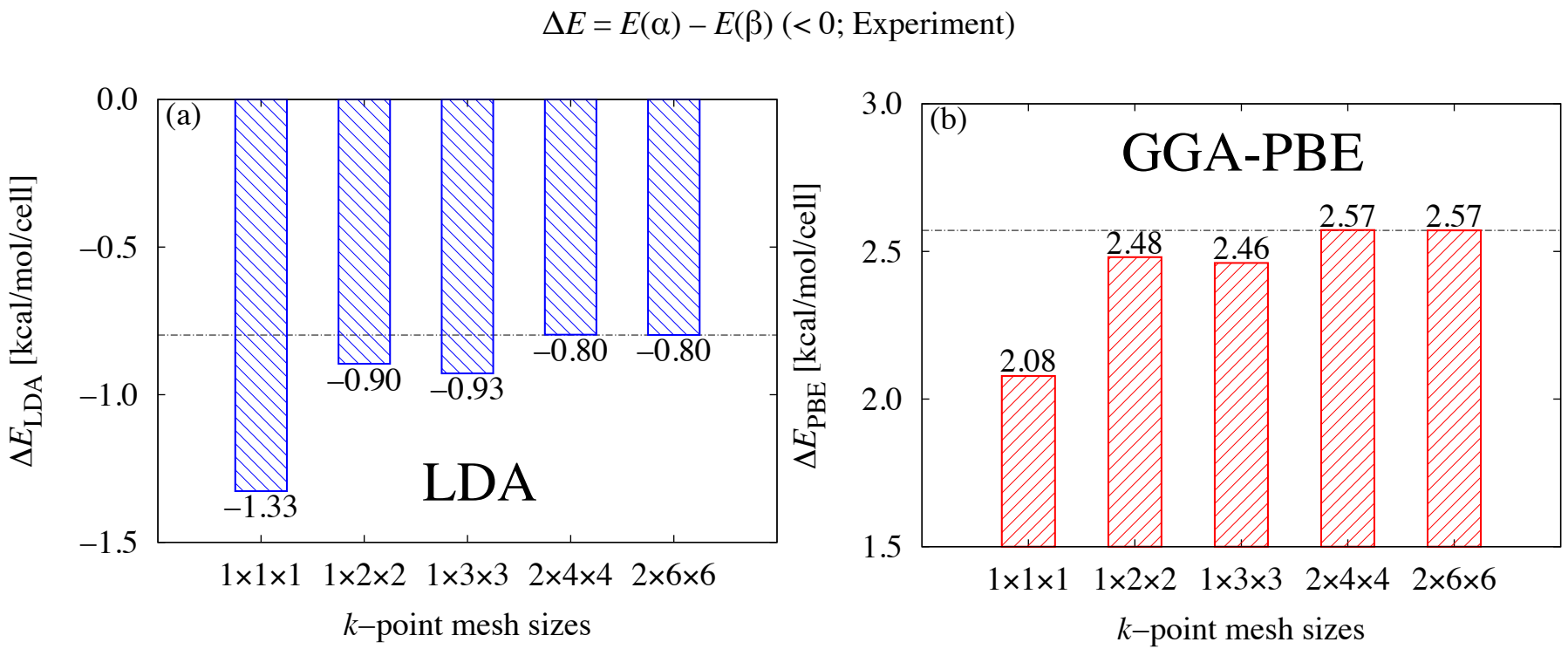
- Agreement between Ewald and MPC estimates (1x3x3)
  - 1x3x3 is necessary for a reliable prediction of the polymorphism

cont'd (3)



- KZK correction to LDA works well (like MPC)

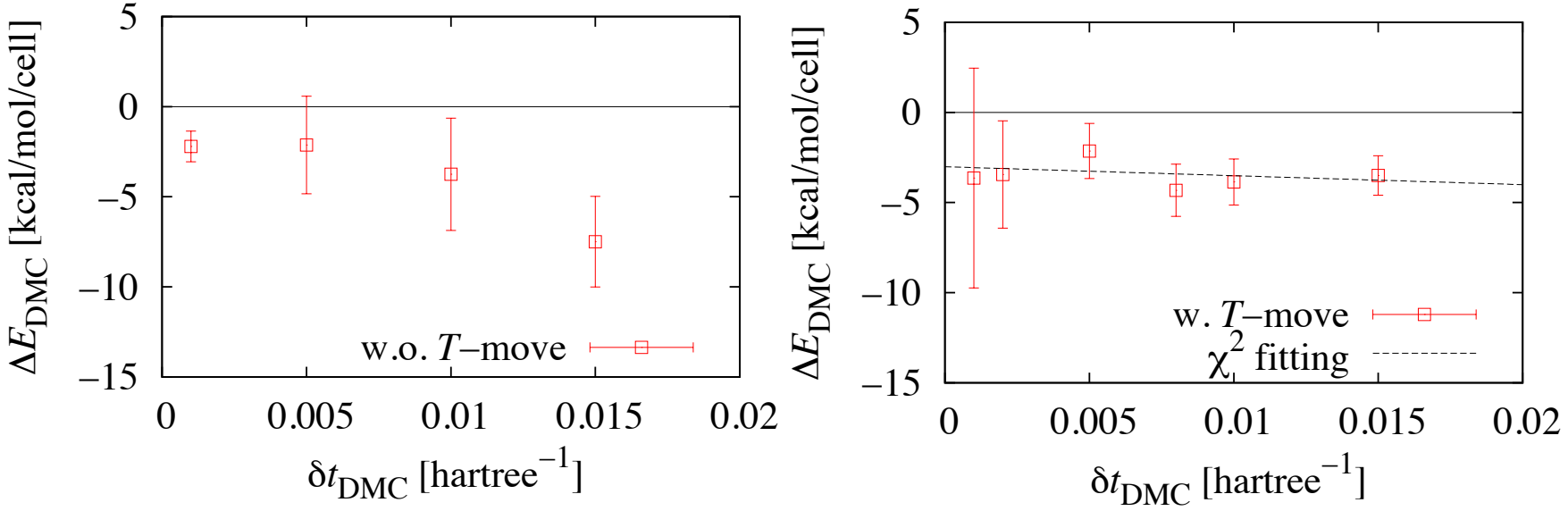
Within DFT framework



- 1x3x3 is large enough to remove one-body FSE for QMC nodes
- LDA/1x1x1 evaluation of ΔE is a not bad approximation.

T-move scheme & Time-step bias

DMC-Ewald/LDA/1x1x1



- Strong time-step dependence when without using *T*-move
- *T*-move is important to perform simulations efficiently

Summary

- We have investigated FSEs in DMC simulations of p-DIB polymorphism using a larger cell (1x3x3) than before (1x1x1).
- Remarkable dependence of FSEs on the trial nodal surface (within 1x1x1)
  - success in our previous work was found to be “lucky”.
- 1x3x3 cell size is large enough to get a reliable result of energy difference (from a comparison of Ewald & MPC).
- KZK turns out to work similar to MPC.
- *T*-move scheme was necessary for stable population control behaviors and small time-step bias.

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Thank you !