

Quantum Monte Carlo Study of Molecular Crystals

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Ab-initio Electronic structure calculations

•The Schrodinger equation for many-electron systems

$$\left[-\sum_j \nabla_j^2 + V(\vec{r}_1, \dots, \vec{r}_N)\right] \cdot \Psi(\vec{r}_1, \dots, \vec{r}_N) = E \cdot \Psi(\vec{r}_1, \dots, \vec{r}_N)$$

•Ab-initio methods

Solid state physics;  
 $\frac{\delta E[\rho(\vec{r})]}{\delta \rho} = 0$

Quantum chemistry;  
 $\frac{\delta E[\Psi(\vec{r}_1, \dots, \vec{r}_N)]}{\delta \Psi} = 0$

Density functional theory (DFT)  
a variational problem of minimizing the energy with respect to the electron density

a variational problem of minimizing the energy with respect to the many-electron wavefunction

Molecular orbital (MO) methods (HF, CI, CC, etc.)

Quantum Monte Carlo Methods

physical quantity : an expectation value of an operator

$$\langle \hat{O} \rangle = \frac{\int d\vec{R} \cdot \Phi^*(\vec{R}) \cdot \hat{O} \Phi(\vec{R})}{\int d\vec{R} \cdot \Phi^*(\vec{R}) \Phi(\vec{R})} = \frac{\int d\vec{R} \cdot |\Phi|^2 \cdot [\Phi^*(\vec{R}) \cdot \hat{O} \Phi(\vec{R})]}{\int d\vec{R} \cdot |\Phi|^2} = \langle \Phi^*(\vec{R}) \cdot \hat{O} \Phi(\vec{R}) \rangle$$

Monte Carlo sampling according to 3N dimensional distribution  $|\Phi|^2$

However,  $\Phi$  is unknown....

Variational Monte Carlo (VMC);  $\Phi(\vec{R}) = \Psi_T(\vec{R})$  a choice of trial wavefunction

Accuracy of results strongly depends on the trial wavefunction adopted.

Diffusion Monte Carlo (DMC);

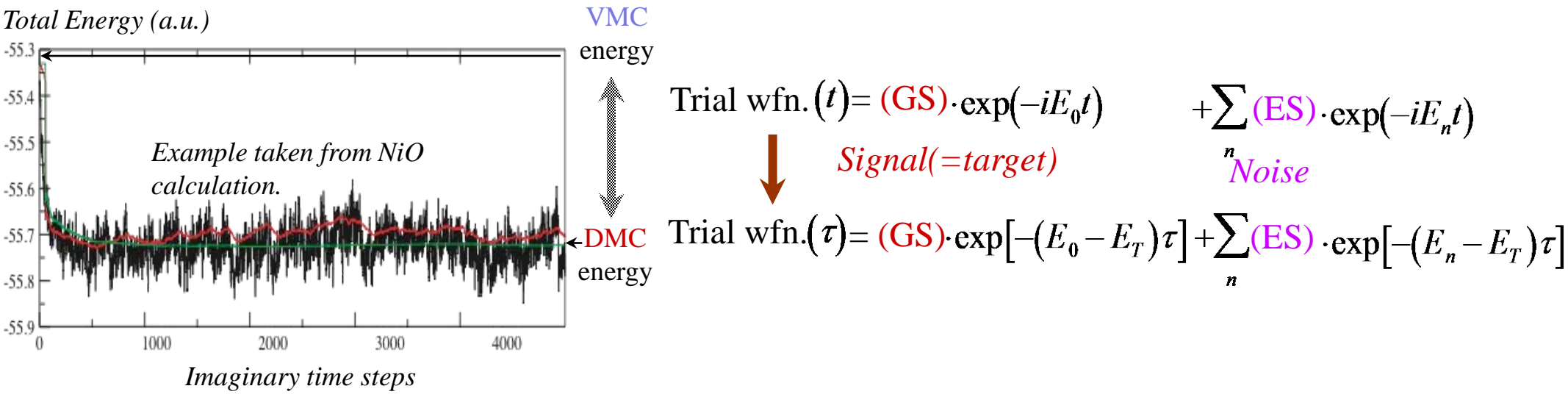
$$\Phi = \Phi(\vec{R}, \tau)$$

an imaginary time-dependent trial wavefunction that converges to the exact wavefunction after a long enough interval  $\tau$

$$\Phi(\vec{R}, 0) = \Psi_T(\vec{R}) \xrightarrow[\substack{\tau \rightarrow \infty \\ |\Phi\rangle = \exp[-tH] \cdot |\Psi_{init}\rangle}]{\tau \rightarrow \infty} \Phi(\vec{R}, \tau) \rightarrow \Phi_{Exact}(\vec{R})$$

Iterative operation of the imaginary-time evolution operator

Basic idea of DMC: “Purification” of the trial wavefunction



•Current topics in electronic structure calculations

A variety of materials are investigated in experiment: transition metal oxides, and

Molecular Crystals

Aspirin

P. Veshweshwar, et al, J.Am. Chem. Soc. 127, 16802 (2005)

DNTT

R. S. Sánchez-Carrera, et al, J. Phys. Chem. C 114, 2334 (2010).

Picene

R. Mitsuhashi, et al, Nature 464, 76 (2010).

Polymorphism in Molecular Crystals

- the existence of more than one form of a compound

Each polymorph has different physical and chemical properties

e.g. effects of polymorphism on charge transport in organic semiconductors

Fluorinated 5,11-bis(triethylsilyl)ethynyl)antradihiophene (diF TES ADT)

O. D. Jurchescu, et al, Phys. Rev. B 80, 085201 (2009).

para-diiodobenzene (p-DIB)

A semiconductor with high mobility as (opt)electronic devices

Room-temperature hole mobility = 12 cm<sup>2</sup>/(V s)

L. M. Schwartz and J. F. Horning, Mol. Cryst. 2, 379 (1967).  
R. S. Sánchez-Carrera, et al. Chem. Mater. 20, 5832 (2008).

Typical  $\pi$ -conjugated organic semiconductors have a room-temperature charge-carrier mobility  $\approx 1$  cm<sup>2</sup>/(V s)

Polymorphism in p-DIB

$\alpha$ -phase (*Pbca*)      $\beta$ -phase (*Pccn*)

Transition from  $\alpha$ - to  $\beta$ -phase occurs at 326 K

(The  $\alpha$ -phase is more stable than the  $\beta$ -phase at zero temperature)

Previous DFT calculations [A. Brillante, et al, J. Cam. Chem. Soc 127, 3038, (2005)]:

Exchange-correlation functional = BLYP functional + Pseudopotential = Troullier-Martins

The  $\alpha$ -phase is less stable by  $\approx 0.002$  eV/atom than the  $\beta$ -phase at 0 K.

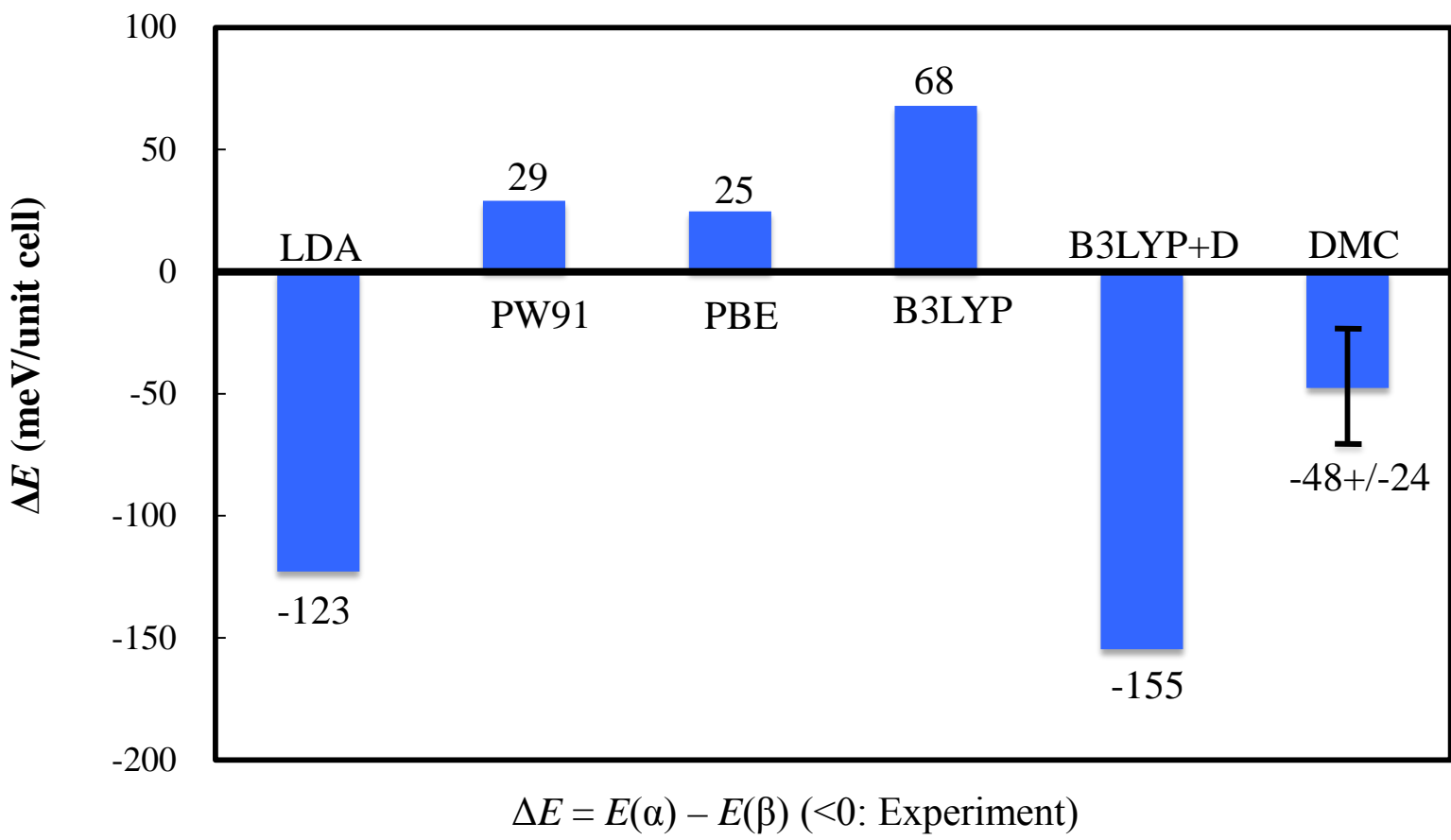
Contrary to experimental results!

Present Study

- DIB is a challenging benchmark system for ab initio methods.
- DMC is one of the most promising candidates in light of accuracy and cost.
- Purpose of our study
  - To investigate the relativities of two DIB polymorphs using DMC and DFT (DFT approximations: LDA, PW91, PBE, B3LYP, B3LYP+D)

Results and Discussion

Energies at the experimental geometries: relative stability



- The DMC result is consistent with experiment, i.e., a negative  $\Delta E$ .
  - The DMC value = - 48 +/- 24 meV
  - The probability that the DMC value of  $\Delta E$  has a positive sign is about 4 %.
- GGAs and B3LYP predict a positive  $\Delta E$ .
- LDA and B3LYP+D correctly give the sign, but strongly overestimate  $|\Delta E|$ , compared to DMC.
  - It is well-known that LDA frequently overbinds.
  - The Grimme semiempirical dispersion correction is important.

Summary and Perspective

- We studied the relative stabilities of two polymorphs of DIB using DMC and DFT.
- The DFT results were inconsistent with experiment.
- The DMC results correctly predicts that the  $\alpha$  phase is more stable than the  $\beta$  one.
- My goal is to exploit molecular crystals for highly-efficient clean energy materials
  - DMC studies of other molecular crystals are in progress.

Acknowledgement

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