Quantum Monte Carlo Study of Molecular Crystals

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Ab-initio Electronic structure calculations

·The Schrodinger equation for many-electron systems

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

·Ab-initio methods

Solid state physics; $\dfrac{\delta E[n(\vec{r})]}{\delta n} = 0$ **Density functional theory (DFT)** a **variational problem** of minimizing the energy with respect to **the electron density**

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

$$\langle \hat{O} \rangle = \frac{\int d\vec{R} \cdot \Phi^*(\vec{R}) \cdot \hat{O}\Phi(\vec{R})}{\int d\vec{R} \cdot \Phi^*(\vec{R})\Phi(\vec{R})} = \frac{\int d\vec{R} \cdot |\Phi|^2 \cdot \left[\Phi^{-1}(\vec{R}) \cdot \hat{O}\Phi(\vec{R}) \right]}{\int d\vec{R} \cdot |\Phi|^2} = \langle \Phi^{-1}(\vec{R}) \cdot \hat{O}\Phi(\vec{R}) \rangle$$

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

However, Φ 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 wavefuntion adopted.
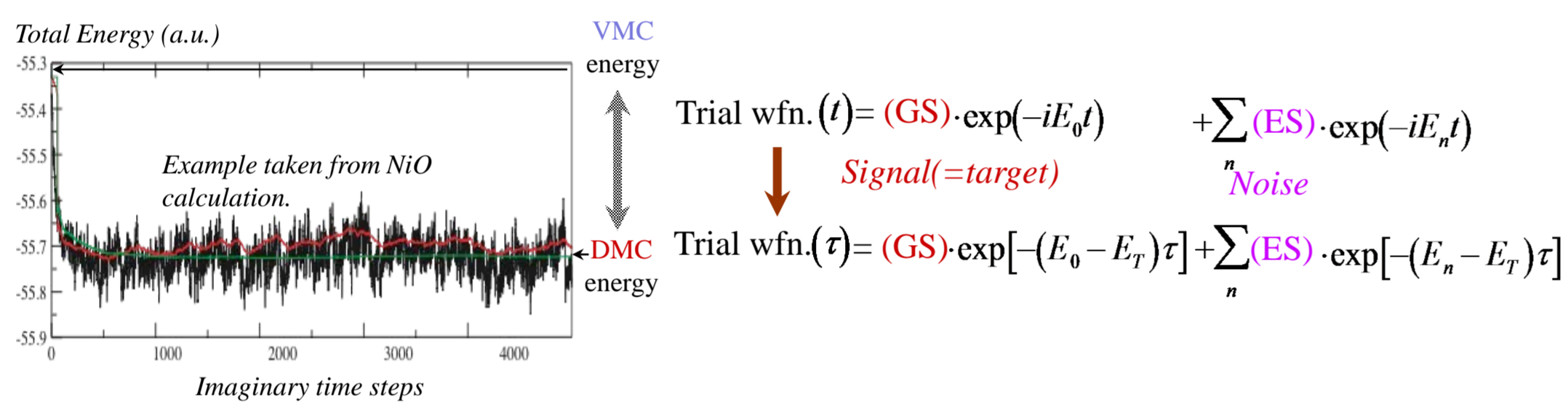
Diffusion Monte Carlo (DMC);

$\Phi = \Phi(\vec{R}, \tau)$ an imaginary time-dependent trial wavefunction that converges to the exact wavefunction after a long enough interval τ

$$\Phi(\vec{R}, 0) = \Psi_T(\vec{R}) \xrightarrow{\tau \to \infty} \Phi(\vec{R}, \tau) \to \Phi_{Exact}(\vec{R})$$

$$|\Phi\rangle = \exp[-\tau H] \cdot |\Psi_{init}\rangle$$

Iterative operation of the imaginary-time evolution operator

⟹ Basic idea of DMC: "*Purification*" of the trial wavefunction

Total Energy (a.u.)

Example taken from NiO calculation.

Imaginary time steps

VMC energy

DMC energy

Trial wfn.$(t) = $ (GS)$\cdot \exp(-iE_0 t) + \sum_n$ (ES)$\cdot \exp(-iE_n t)$

Signal(=target)   *Noise*

Trial wfn.$(\tau) = $ (GS)$\cdot \exp[-(E_0 - E_T)\tau] + \sum_n$ (ES)$\cdot \exp[-(E_n - E_T)\tau]$

·Current topics in electronic structure calculations

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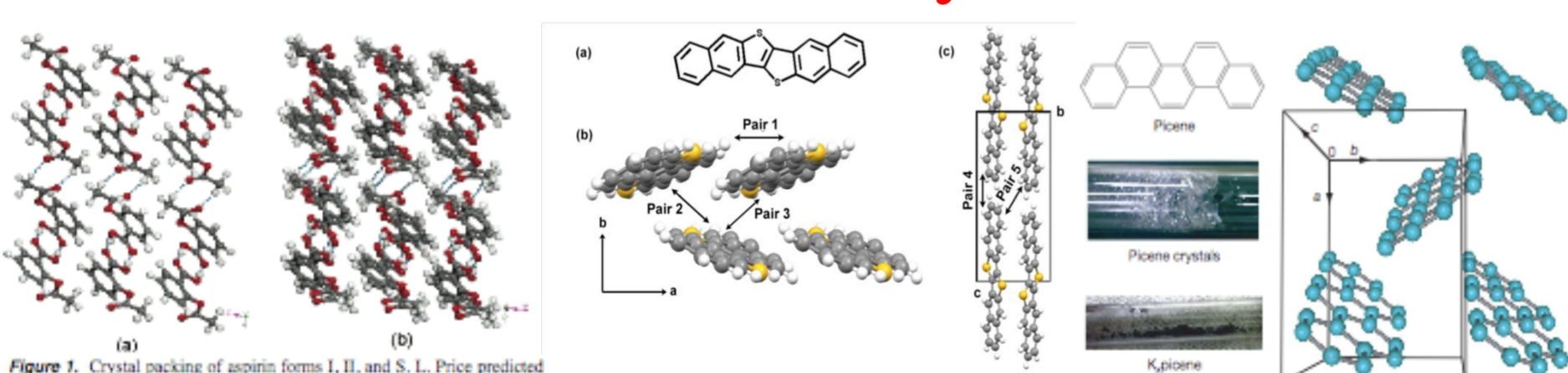
Molecular Crystals

Figure 1. (a) Crystal packing of aspirin forms I, II, and S. L. Price predicted form II. (a) Form I: 1D chains sustained by alternating carboxylic acid and acetyl group centrosymmetric dimers. (b) Form II: acid dimers are connected via catemeric methyl C–H⋯O and phenyl C–H⋯O (not shown) hydrogen bonds. (c) Acetyl group C–H⋯O dimers in form I and catemers

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

Figure 1. (a) Chemical structure of DNTT. (b) Crystal structure of DNTT in the all-plane. (c) Crystal structure of DNTT in the *b*c-plane (a=6.187, b=7.662, c=16.21 Å, β=92.49). Labels correspond to the DNTT molecular pairs used in the calculation of transfer integrals.

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

Figure 1 Molecular structure, crystal structure and physical appearance of picene. Photographs show perylene picene (taps white) and K_picene (bottom; black).

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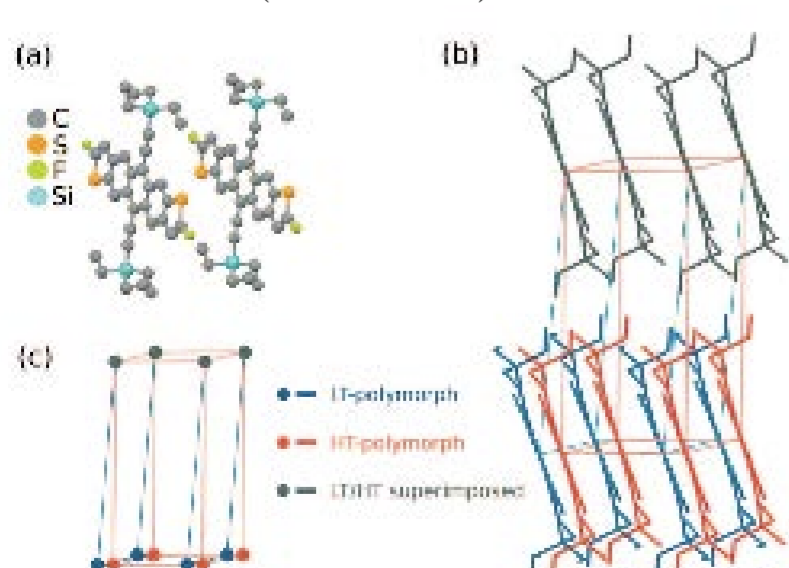R. Mitsuhashi, et al, Nature 464, 76 (2010).

Polymorphism in Molecular Crystals

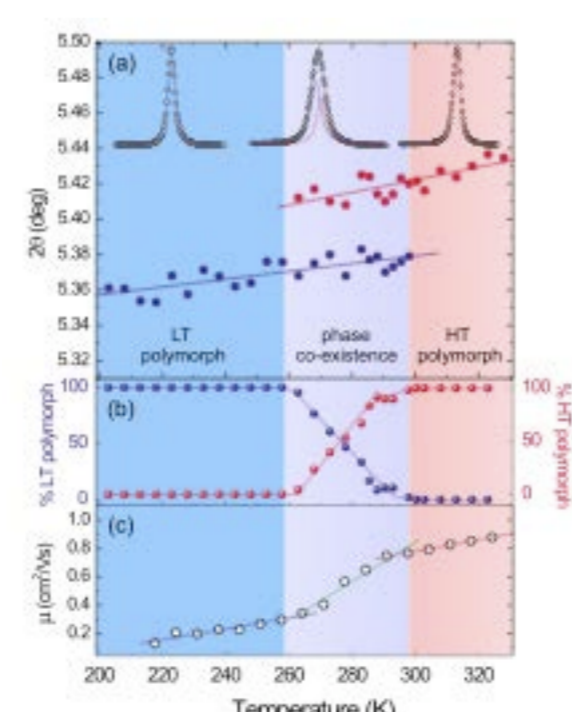- the existence of more than one form of a compound

Each polymorph has different physical and chemical properties

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

Fluorinated 5,11-bis(triethylsilylethynyl)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 cm²/(V s)

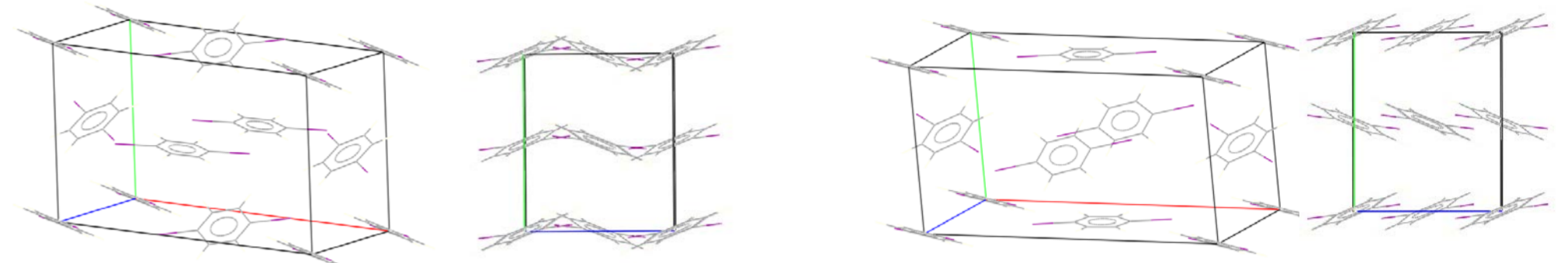L. M. Schwartz and J. F. Horning, Mol. Cryst. 2, 379 (1967).
R. S. Sánchez-Carrera, et al. Chem. Mater. 20, 5832 (2008).

Typical π-conjugated organic semiconductors have a room-temperature charge-carrier mobility ≈ 1 cm²/(V s)

Polymorphism in *p*-DIB

α-phase (*Pbca*)   β-phase (*Pccn*)

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

(The α-phase is more stable than the β-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 α-phase is less stable by ≈0.002 eV/atom than the β-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
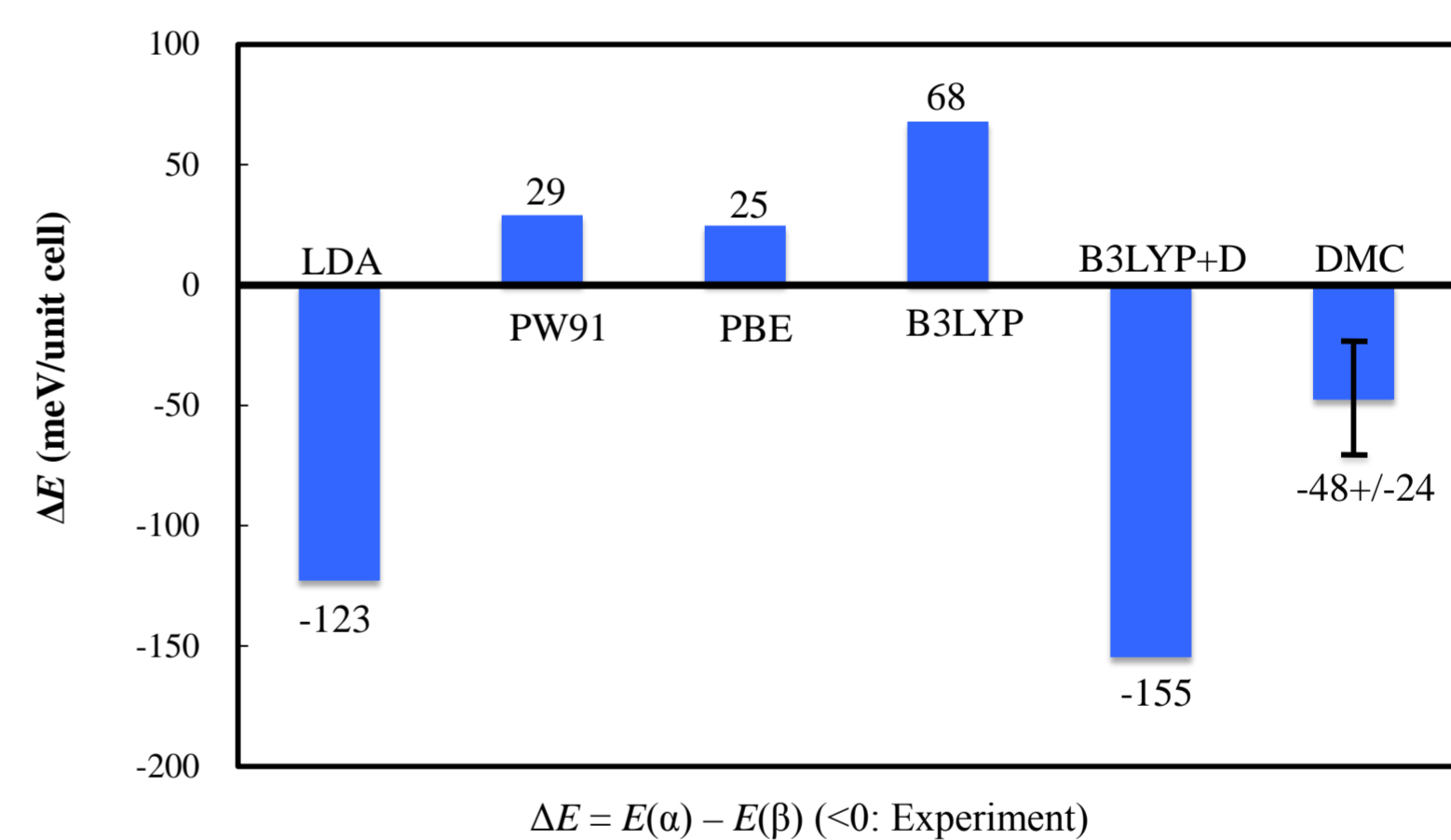
$\Delta E = E(\alpha) - E(\beta)$ (<0: Experiment)

- The DMC result is consistent with experiment, i.e., a negative ΔE.
  - The DMC value = - 48 +/- 24 meV
  - The probability that the DMC value of ΔE has a positive sign is about 4 %.
- GGAs and B3LYP predict a positive ΔE.
- 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 α phase is more stable than the β one.
- My goal is to exploit molecular crystals for highly-efficient clean energy materials
  – DMC studies of other molecular crystals are in progress.

Acknowledgement

大学共同利用機関法人 情報・システム研究機構
統計数理研究所

The Institute of Statistical Mathematics