Fundamental Understanding of Materials Properties Based on the Exact Solution of Many Body Coulombic System by Diffusion Quantum Monte Carlo Method

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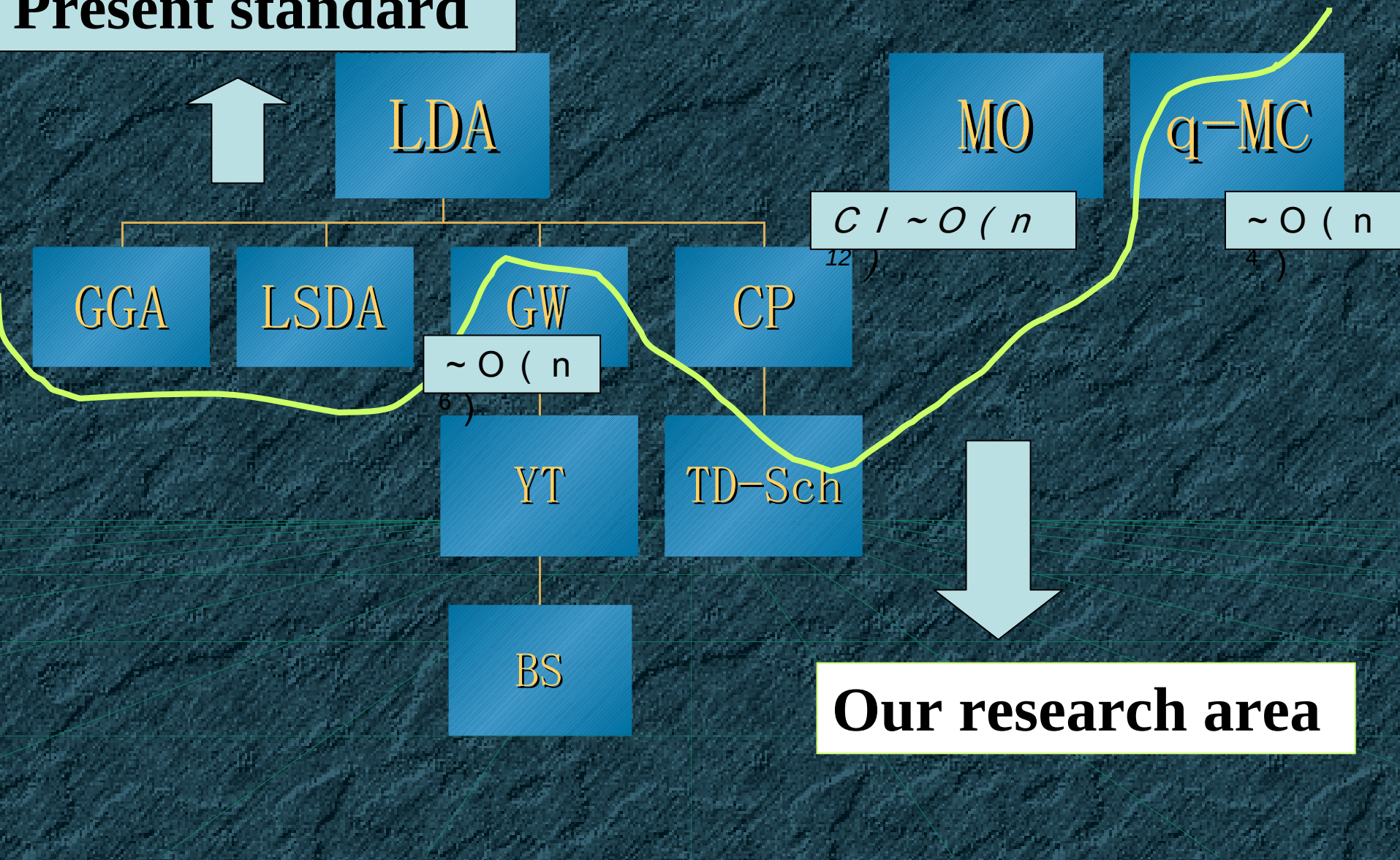
Why *ab initio* simulation can predict new materials?

- **Objects of the materials research are many body system via Coulomb interaction**
  - **Si, steel, DNA all the same !**
- **Described by Schroedinger equation (Dirac eq.)**
- **More than 50 years ago, Dirac already said that "All necessary equations are known, only to solve them!"**

- **But!!! Many body problem is too much time consuming… difficult to be solved … approximations have applied up to the present!**
- **And, many misunderstandings happened!!!**

Ab initio calculation has no experimental parameters but a lot of approximations included!

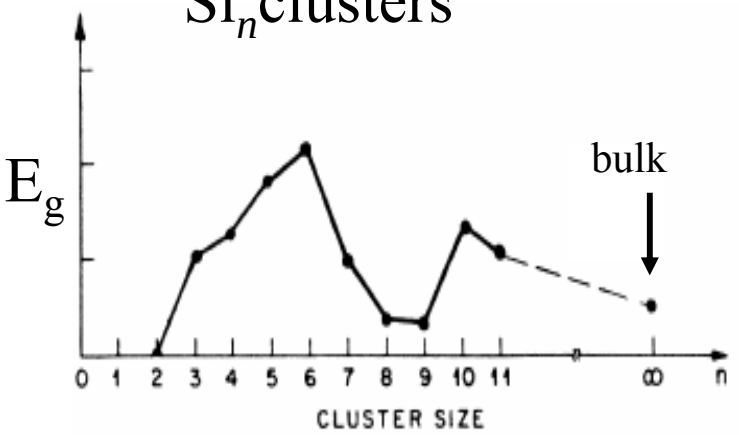
Present standard



Our research area

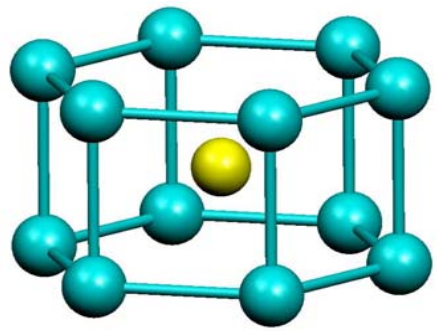
Is LDA good enough?

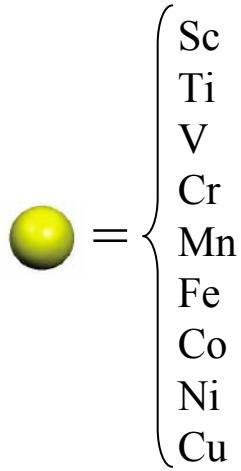
Si_nclusters



Size dependence

$TM@Si_n$ clusters





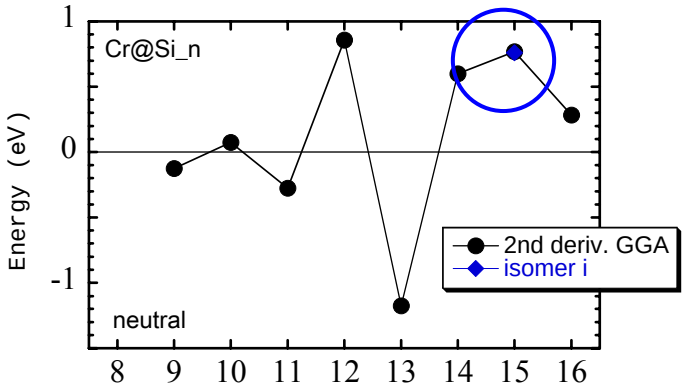
structure

Computer simulation

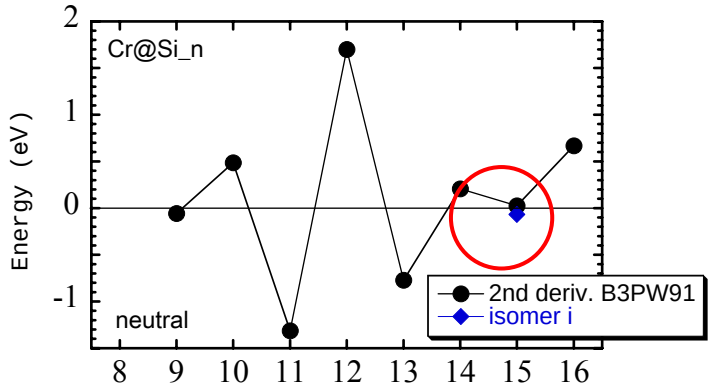
Normally within LDA → good enough?

Cr@Si$_n$ clusters

GGA



B3PW91



※positive energy→ stable

・ n=12 cluster

GGA and B3PW91→max stable

・ n=15(structural isomers)

GGA and B3PW91 give fundamentally different r

→more accurate method is necessary !

Exact solution of quantum mechanical equation for Coulombic many body system

- Complete solution with electron exchange-correlation → quantum Monte Carlo method
- No restriction for functions
  → diffusion QMC : completely numerical solution ; no restrictions

- Virial theorem：T and V are not independent!

  General rule for all states in Coulombic system

  Coulomb force is the result of geometry；three dim. space！

  Necessary condition for exact theory

$$2T+V=0 \Rightarrow E=-T=V/2$$

T：kinetic energy of electrons

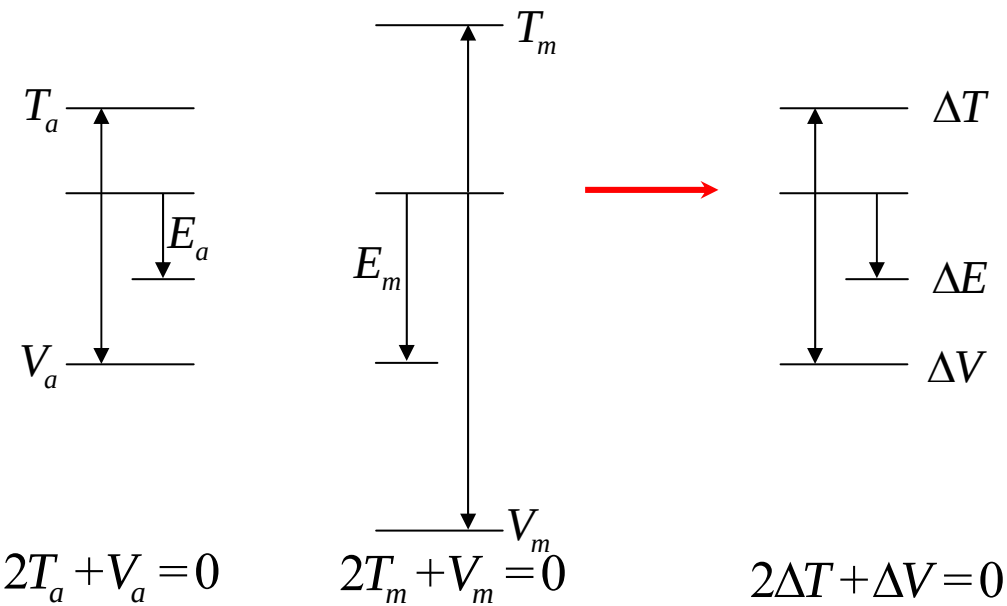
V：sum of $V_{ee}+V_{eN}+V_{NN}$

- Forming of molecule: nucleus-electron interaction is only attarctive

2 independent atoms H + H

molecule H_2

energy difference (molecule-2 atoms)



$2T_a+V_a=0$ $2T_m+V_m=0$ $2\Delta T+\Delta V=0$

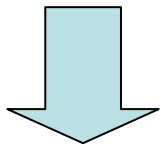
condition for molecular stability

$$\Delta E<0$$

$$\Delta T>0$$
$$\Delta V<0$$
$$-\Delta V/\Delta T=2$$

Origin of molecular stability?

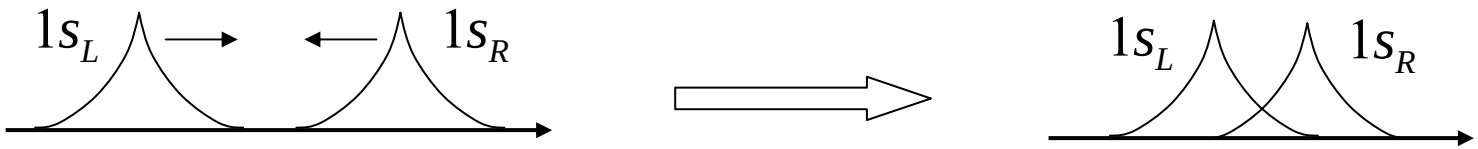
- Electron clouds overlaps?... No!!
- e-e interaction V_{ee} is repulsive!... Not possible!



- Most important interaction to make molecules stable is nucleus-electron V_{Ne} attractive force!

Ex.1 How H_2 molecule formed from 2H atoms?

Two models for H_2 molecular state
HL and MO



Two H atoms

Molecular state

Heitler-London(HL)model

$$\Psi_{HL}(1,2) \propto 1s_L(1)1s_R(2) + 1s_L(2)1s_R(1)$$

Independent states

Minimum orbitals MO

$$\Psi_{MO}(1,2) \propto (1s_L(1) + 1s_R(1))(1s_L(2) + 1s_R(2))$$

Molecular state expressed by
1s orbitals only

biding energy	Expl.	HL	MO
$-\Delta E$ / eV	4.74	2.48	2.88

Based on the 1s H atom orbitals only

→ Molecular orbitals are not the linear combination of atomic orbitals !

Stability condition fulfilled?

HL and MO give reversed values

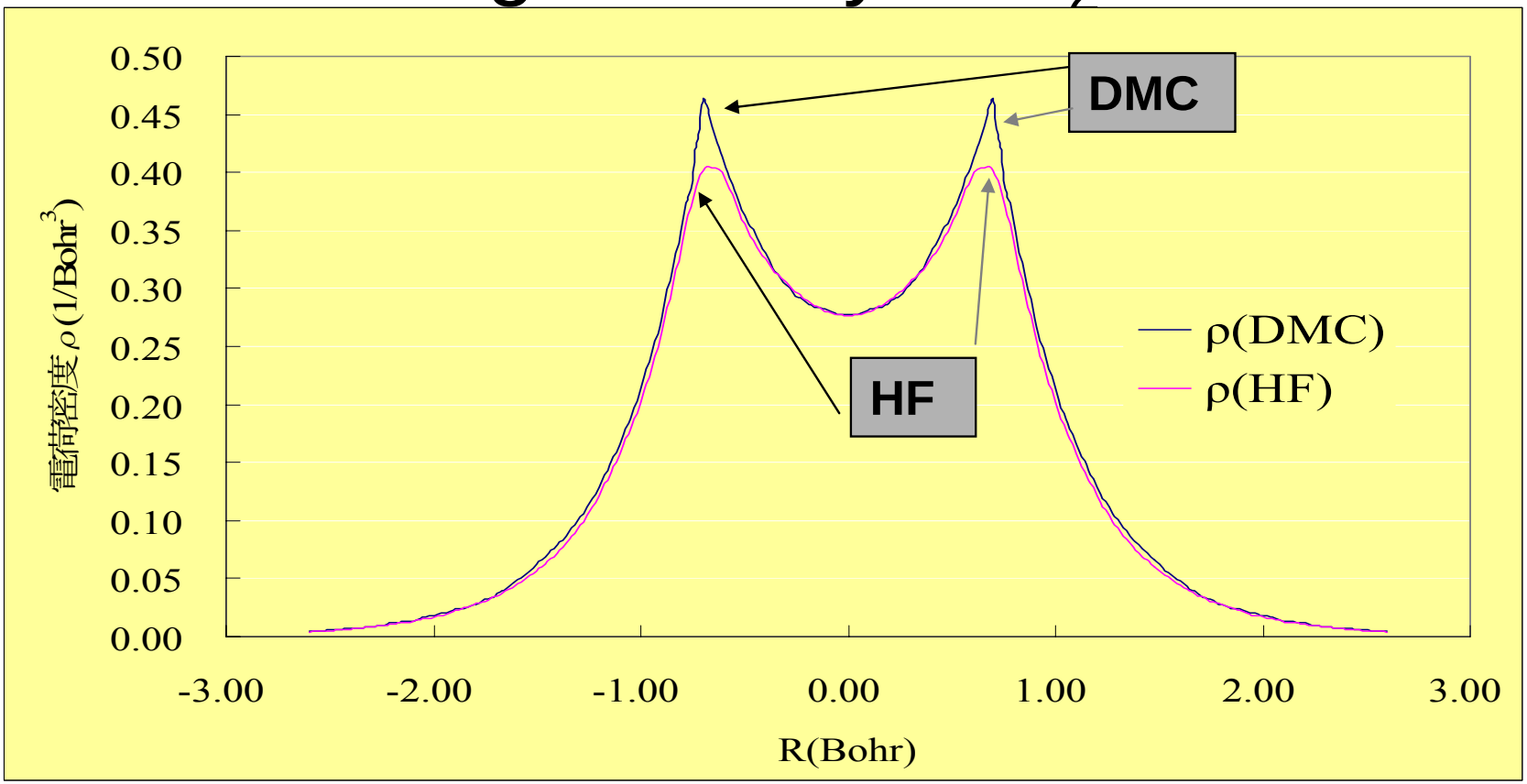
(eV)	condition	HL	MO	HF	DMC	Expl.
ΔE	negative	-2.48	-2.88	-3.63	-4.75	-4.75
ΔT	positive	-5.01	-4.22	3.63	4.8(1)	
ΔV	negative	2.53	1.33	-7.27	-9.6(1)	
$-\Delta V/\Delta T$	2	0.5	0.3	2.0	2.0(1)	

absolutely

Only by the 1s orbitals, it is not possible to explain the stability of H_2 molecule. Contradict to virial theorem.

Stability of materials should be realized by nucleus-electron int.

Why molecule is stabilized: Charge density in H_2

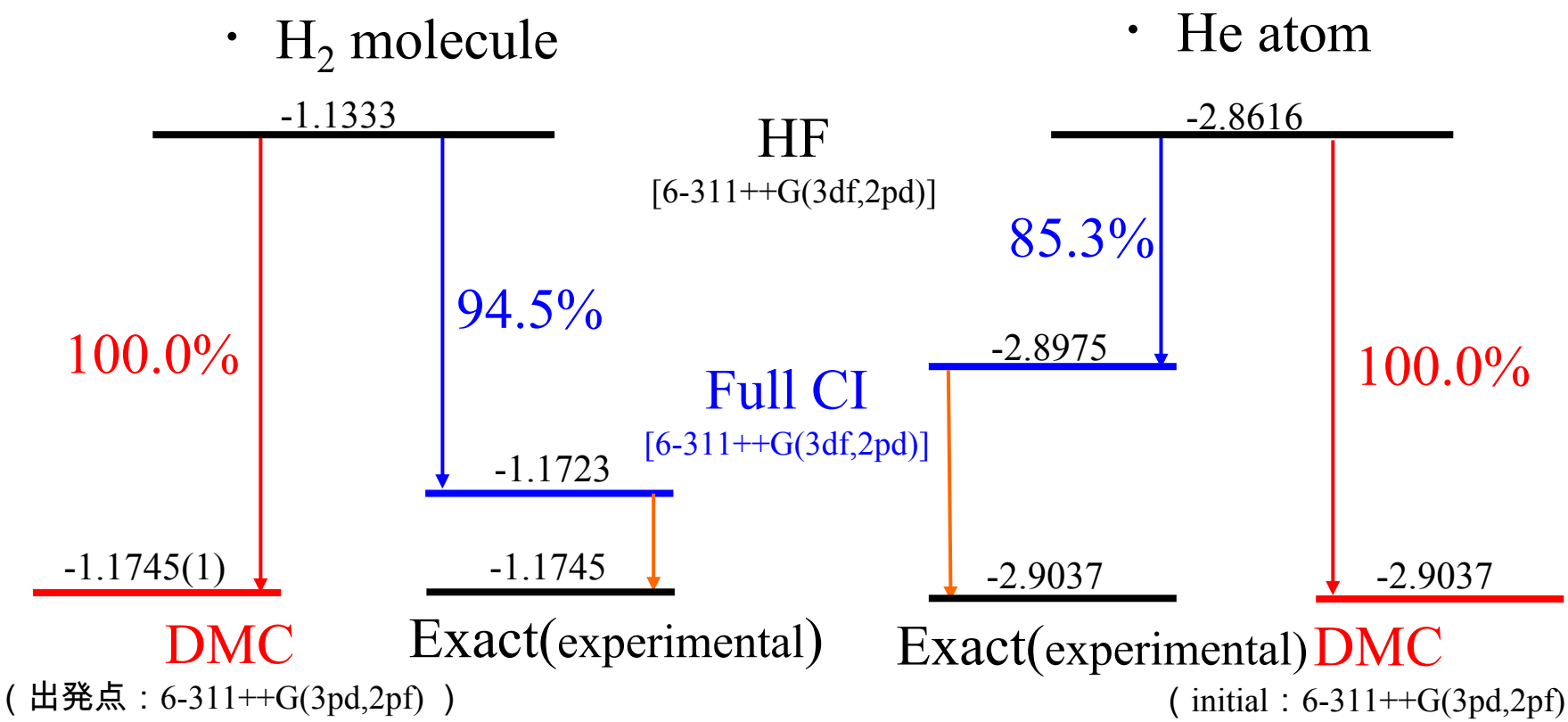


Heitler-London theory (LCAO with 1s atomic orbital) fails!

Virial theorem (2T+V=0) should be satisfied!

DMC: kinetic energy increases and potential energy more decreases!

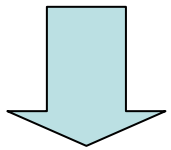
Correlation energy in electron system



Self healing of amplitude by imaginary time evolution
→ Exact numerical solutions

Correct explanation of Hund's multiplicity rule

- Electron exchange interaction?
- At that time, researchers were astonished and tried to explain all of quantum mechanical phenomena by e-exchange.
- Magnetism = Heisenberg model? … No!!



- Exact numerical calculation including all interactions V_{ee} and V_{eN}!

Diffusion Quantum Monte Carlo (DQMC) method

Imaginary-time evolution projector method

Identical with solving ***the 'exact' many-body Schrödinger equation***

Electron correlation can be fully taken into account !

Example 1:
New interpretation of ***Hund's multiplicity rule*** for carbon atom

DMC	E_{total}	V_{ee}	V_{en}	V_{total}	*Vrial ratio*
Triplet	-37.8280(7)	12.595(6)	**-88.253(27)**	-75.658(27)	1.99996
Singlet	-37.8107(5)	12.430(4)	-88.053(18)	-75.622(18)	1.99997

V_{ee} for triplet is larger

V_{en} contributes mostly

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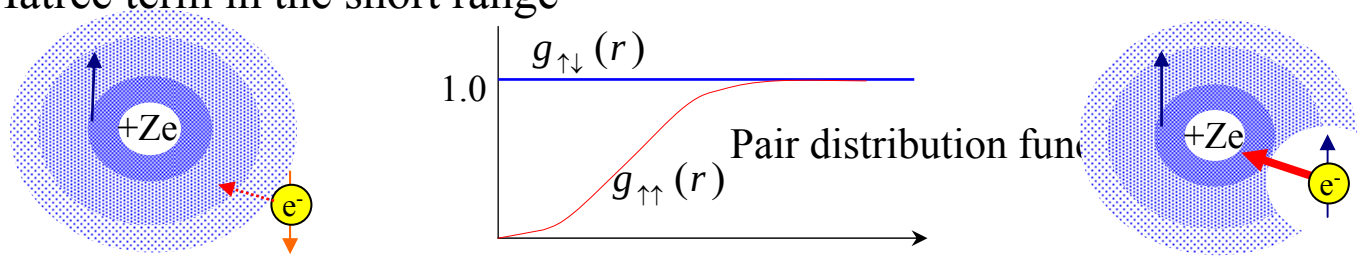
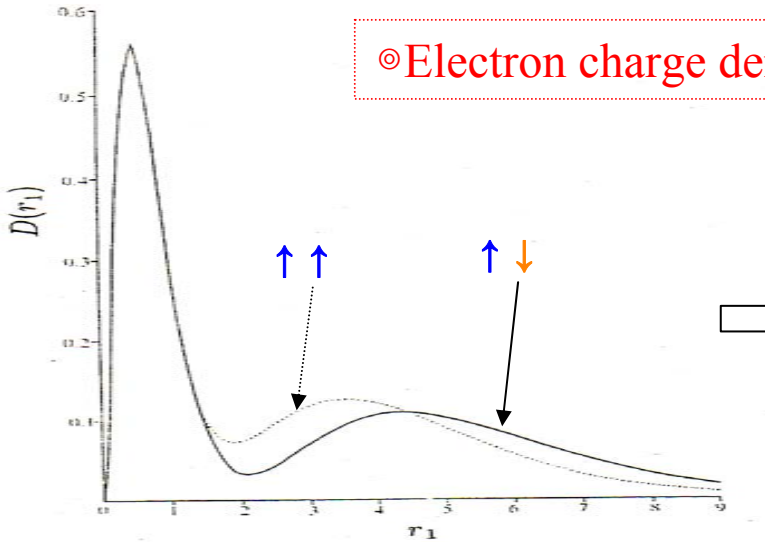
Correct explanation of Hund's multiplicity rule

①Selfconsistent Hartree-Fock Approximation

Exchange term in HF equation weakens the nuleus shielding
by Hatree term in the short range



Electronic states having more parallel spins feel more attraction from nuleus



◎Electron charge density contracts around nucleus

$$V_{ne}(\uparrow\uparrow) < V_{ne}(\uparrow\downarrow)$$

$$V_{ee}(\uparrow\uparrow) > V_{ee}(\uparrow\downarrow)$$

$$T(\uparrow\uparrow) > T(\uparrow\downarrow)$$

Absolute value estimation of other physical quantities

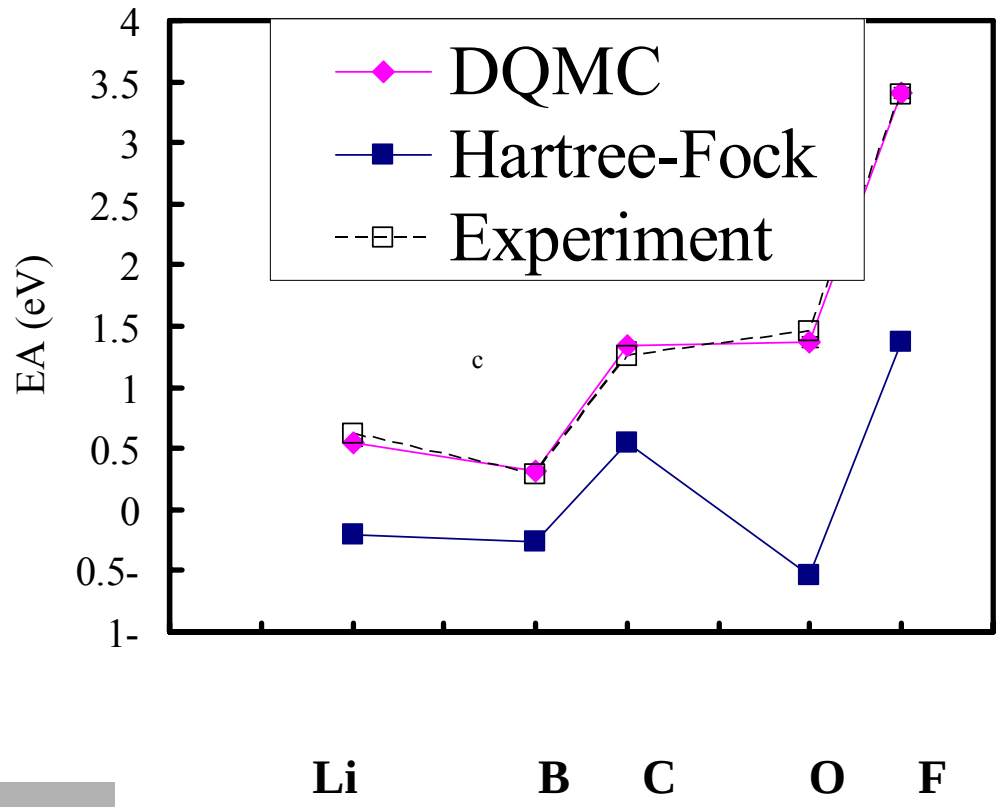
- Electron affinity
- Ionization potential
- HOMO-LUMO gap

- Completed for 3p systems. Computing for transition metals.
- Extension to crystals

Exact Computation of Electron Affinity by Diffusion QMC Method

Electron affinities of light atoms

The electron correlation plays an important role in ***EAs !***



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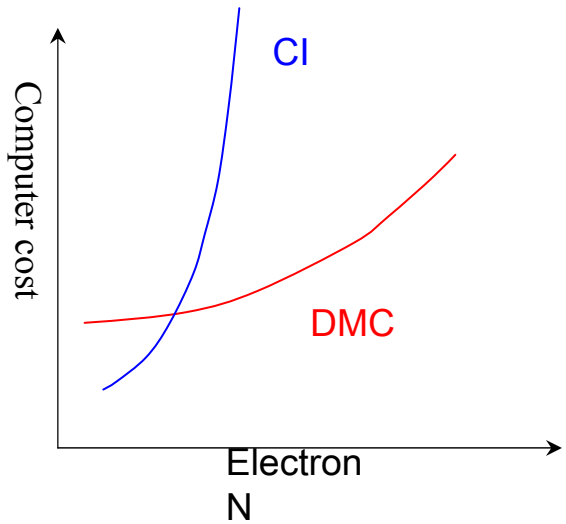
computing cost for *ab initio* methods

	quantitative	Computer cost
DFT	△	N^3
→complete numerical calculation needed!		
Quantum chemistry	○	$N^6 \sim N!$
Diffusion quantum MC	○	$N^3 \sim N^4$



Ab initio DMS seems to be a better method in future

Collaborators

- V. Kumar, M. Sluiter, J.-Z. Yu, H. Mizuseki, Q. Sun, T. M. Briere, T. Nishimatsu, R. V. Belosludov, A.A. Farajian, J.-T. Wang, Z. Zong, S. Ishii, A. Jain, Q. Wang, G. Zhou, Murgan, C. Majumder, K. Ohno, W. Kohn, S. Louie, H. Yasuhara, B.-L. Gu, P. Jena, Dong, M. Radney, K. Esfarjani, L. Wille, K. Parlinski, S. Tse, S. T. Chui, D.-S. Wang, R.-B. Tao, Z.-Q. Li, Y. Guo, L. Zhou, J. Wu, V. R. Belosludov, Y. C. Bae, A. Taneda, Y. Maruyama, R. Sahara, H.-P. Wang, Z. Tang, T. Ikeshoji, H. Chen, K. Shida, T. Morisato, K. Hongo, H. Kawamura, Khazaei, etc.
- + Experimentalists: M. Kawasaki, T. Oku, T. Hashizume, T. Kondow, S. Tanemura, K. Sumiyama, T. Sakurai, T. Fukuda, etc.
- +Companies: Hitachi, Seiko-Epson, NEC-Tokin, New Japan Steel, Codec, Tore-Dawconing, IBM, etc.