

A New Variational Approach to Strongly
Correlated Electrons:
From 1D Hubbard Model
to the First-Principles Hamiltonian

Shinji Tsuneyuki

Department of Physics, The University of Tokyo.

Collaborators:

Naoto Umezawa (NIMS, Tsukuba)

Rei Sakuma (AIST, Tsukuba)

Keitaro Sodeyama (U. Tokyo)

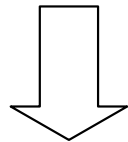
Contents

- Introduction: Problems of DFT and WFT
- **Basic Idea of the Transcorrelated Method**
- **Application to Hubbard Model**
- **Application to Electron Gas**
- **Application to Semiconductors**
- Conclusion

To establish a new method of electronic structure calculation applicable to a variety of electronic systems from 1D Hubbard model to the first-principles Hamiltonian.

Problems of the present DFT *in Its Application to Solids*

- Kohn-Sham **band gap** is too small.
- **Mott insulator** is not realized.
- **Cohesive energy** is not so accurate, especially for **van der Waals interaction**.
- **Systematic improvement is difficult.**



Let us revisit Wave Function Theory!

Wave Function Theory for Solids

- Hartree-Fock
 - Anomaly at ε_F in metals
 - Koopmans' theorem gives too large band gap ($E_g^{\text{HF}}(\text{Si}) > 6\text{eV}$, $E_g^{\text{EXP}}(\text{Si}) = 1.17\text{eV}$)
- MP2, CC, CI
 - Too heavy for solids
- VMC with Slater-Jastrow-type wave function
 - HF/LDA orbitals are not accurate
- DMC
 - Fixed-node approximation
 - Only the ground state
- Transcorrelated Method

Transcorrelated Method

S.F. Boys and N.C. Handy, Proc. R. Soc. (1969)

N.C. Handy, Mol. Phys. (1971)

S. Ten-no, Chem. Phys. Lett. (2000)

O. Hino, Y. Tanimura, and S. Ten-no, J. Chem. Phys. (2001)

N. Umezawa and S. Tsuneyuki, J. Chem. Phys. (2003), (2004).

Phys. Rev. B (2004). ← Electron gas

R. Sakuma and S. Tsuneyuki,

J. Phys. Soc. Jpn. 75, 103705 (2006).

↑ The first application to real solids!

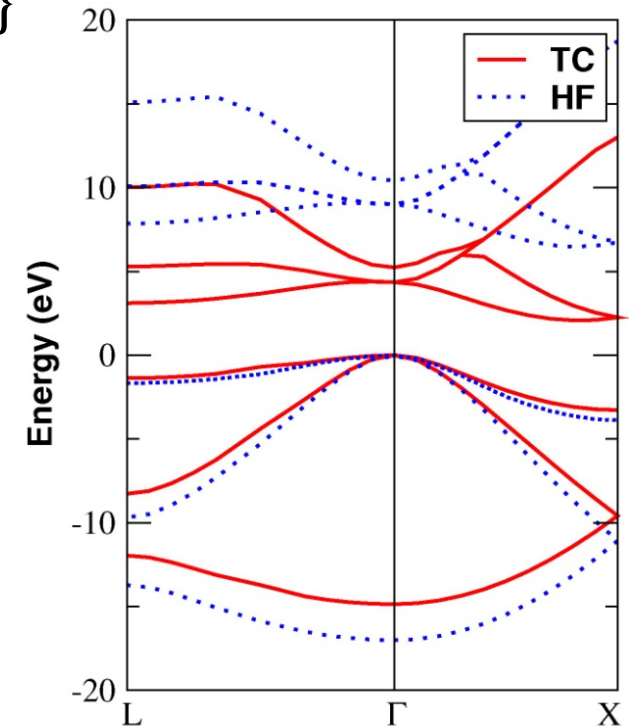
Transcorrelated Method: Summary

- A wave function theory with a Slater-Jastrow-type **explicitly correlated wave function**

$$\Psi = \exp \left[- \sum_{i>j} u_{ij}(r_{ij}) \right] \det \{ \varphi_1, \varphi_2, \dots \}$$

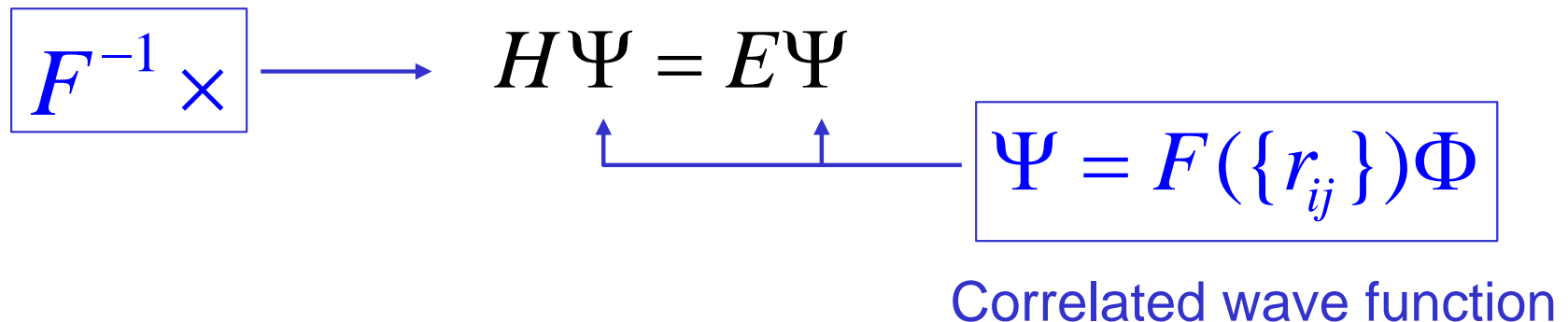
- No Monte Carlo Sampling
- Total energy + Orbital energy

➔ Band Structure



Basic Idea of the Transcorrelated Method

S.F. Boys and N.C. Handy (1969)



F : Jastrow factor.

$$H_{\text{TC}} \equiv F^{-1} H F \quad \text{Transcorrelated Hamiltonian}$$
$$H_{\text{TC}} \Phi = E \Phi \quad \text{Similarity Transformation}$$

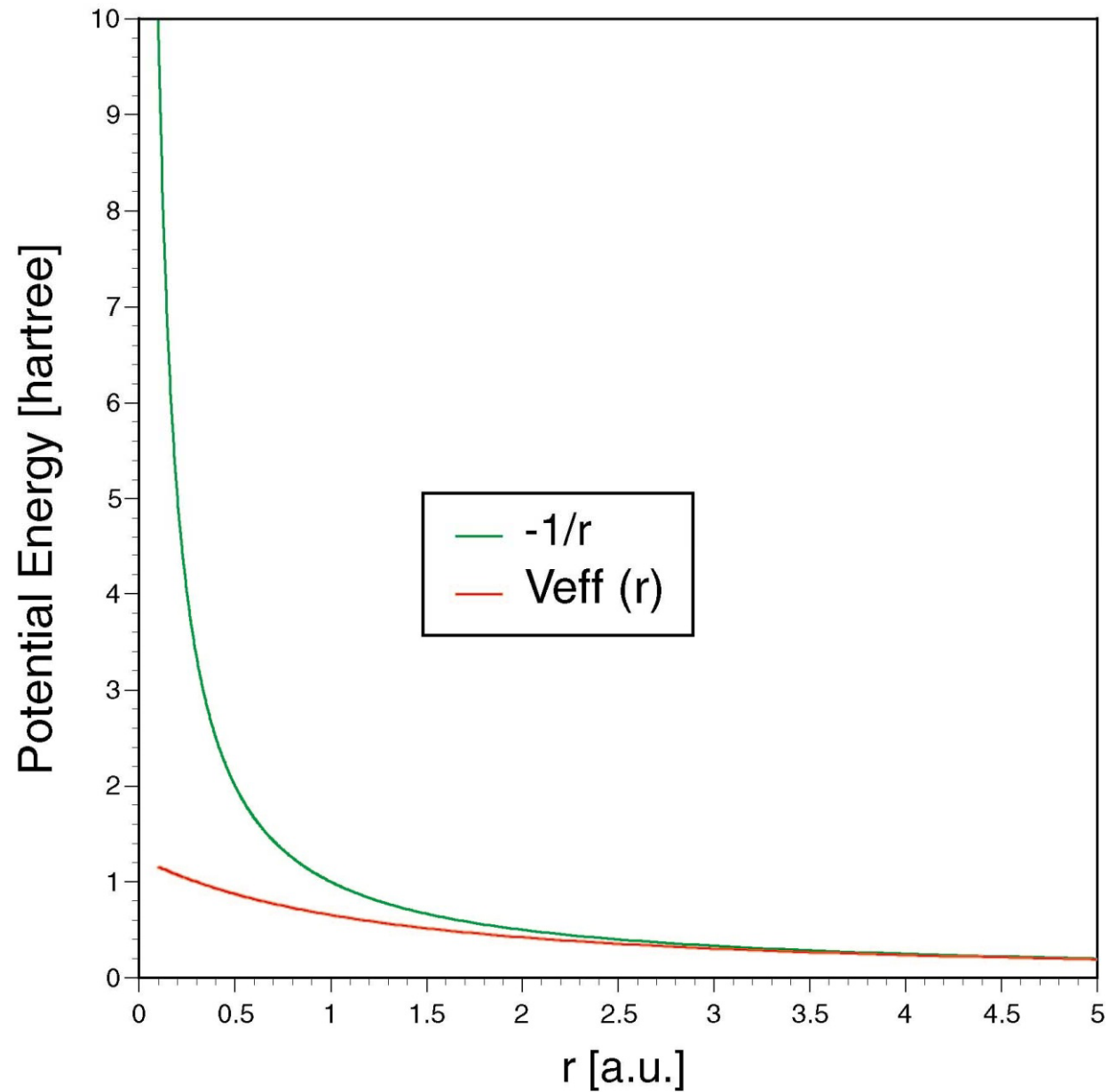
Hartree-Fock Approx. $\Phi = \det\{\varphi_1, \varphi_2, \dots\}$

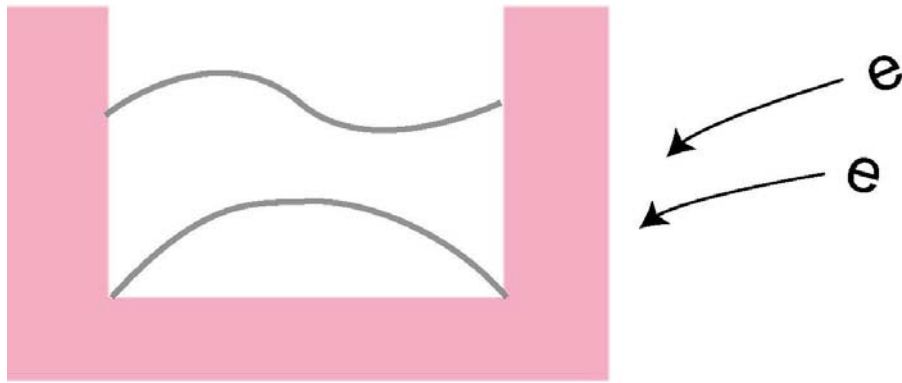
Transcorrelated Hamiltonian H_{TC}

$$F = e^U = \exp\left(-\sum_{i>j} u_{\sigma_i\sigma_j}(r_{ij})\right)$$

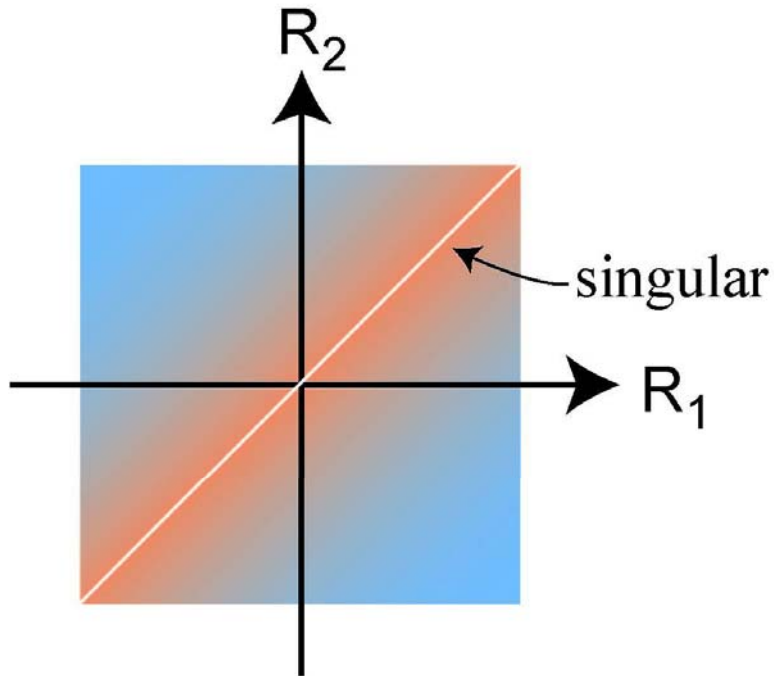
$$\begin{aligned} H_{\text{TC}} &= F^{-1} H F \\ &= \sum_i \left\{ -\frac{1}{2} \nabla_i^2 + v_{\text{ext}}(\mathbf{r}_i) \right\} + \frac{1}{2} \sum_i \sum_{j \neq i} \frac{e^2}{r_{ij}} \\ &\quad + \frac{1}{2} \sum_i \sum_{j \neq i} \left[\nabla_i^2 u_{ij} - (\nabla_i u_{ij})^2 + 2 \nabla_i u_{ij} \cdot \nabla_i \right] \\ &\quad - \frac{1}{2} \sum_i \sum_{j \neq i} \sum_{k \neq i, j} \nabla_i u_{ij} \cdot \nabla_i u_{ik} \end{aligned}$$

Effective Two-Body Interaction in H_{TC}



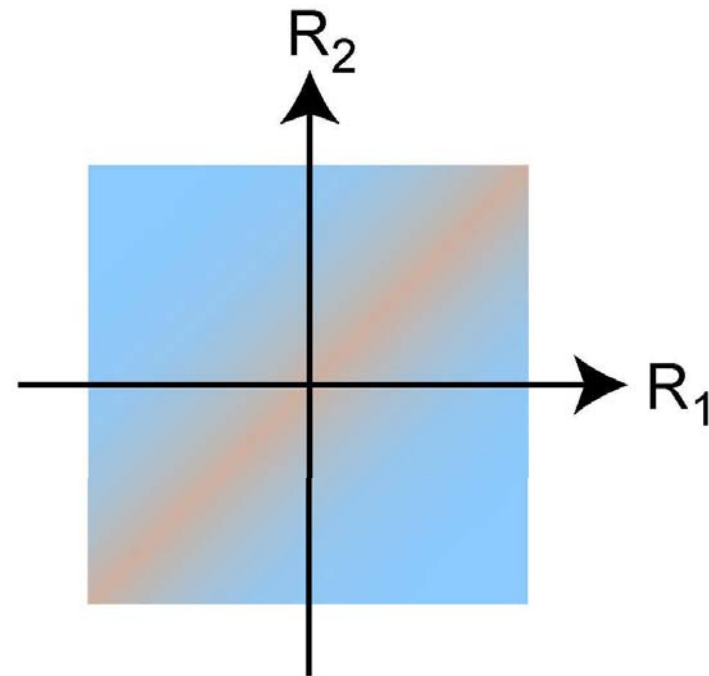


2 electrons in a
1D potential well



Bare Coulomb Potential

$$\Psi(1, 2) \neq \psi(1)\psi(2) \times (\text{spin})$$



Transcorrelated Potential

$$\Psi(1, 2) : \psi(1)\psi(2) \times (\text{spin})$$

A Merit of the Similarity Transformation

If we use so-called correlated wave functions, to calculate the total energy, we have to evaluate *many-body integrals*.

$$E = \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle} = \frac{\langle \Phi | F H F | \Phi \rangle}{\langle \Phi | F^2 | \Phi \rangle}$$

$$\Psi = F(\{r_{ij}\})\Phi$$
$$\Phi = \det\{\varphi_k(\mathbf{x})\}.$$

In the *Transcorrelated Method*, we need *at most three-body integrals* to calculate the total energy.

$$E_{\text{TC}} = \frac{\langle \Phi | H_{\text{TC}} | \Phi \rangle}{\langle \Phi | \Phi \rangle} = \frac{\langle \Phi | H + V_2 + V_3 | \Phi \rangle}{\langle \Phi | \Phi \rangle}$$

TC-SCF Equation

$$H_{\text{TC}}\Phi = E\Phi \quad \Longleftrightarrow \quad \langle \delta\Phi | H_{\text{TC}} | \Phi \rangle = E \langle \delta\Phi | \Phi \rangle$$

- If we adopt a Slater determinant for Φ , we get a **Hartree-Fock-like SCF equation** with three-body potentials to obtain one-electron orbitals.

$$\left(-\frac{1}{2}\Delta + v_{\text{ext}} + v_{\text{H}} + v_{\text{x}} + v_{\text{TC}}^{(2)} + v_{\text{TC}}^{(3)} \right) \varphi_i = \sum_j \varepsilon_{ji} \varphi_j$$

- **Koopmans' theorem** for the orbital energy ε_i .
- **Bloch states and band structure** for periodic systems.

TC-SCF equations (Bi-orthogonal Formalism)

$$\begin{aligned} H_{\text{TC}} |R\rangle &= E |R\rangle, \\ \langle L| H_{\text{TC}} &= E \langle L|. \end{aligned} \iff \boxed{\delta E_{\text{pseudo}} = \delta \frac{\langle L| H_{\text{TC}} |R\rangle}{\langle L|R\rangle} = 0}$$

Hartree-Fock-like SCF equations
for 1-electron orbitals

- **Up-to-three-body** potentials.
- **Koopmans' theorem** for the orbital energy ε_i .
- **Bloch states** and **band structure** for periodic systems.

How to Optimize the Jastrow Function F ?

Since H_{TC} is *not* a Hermitian, the total energy

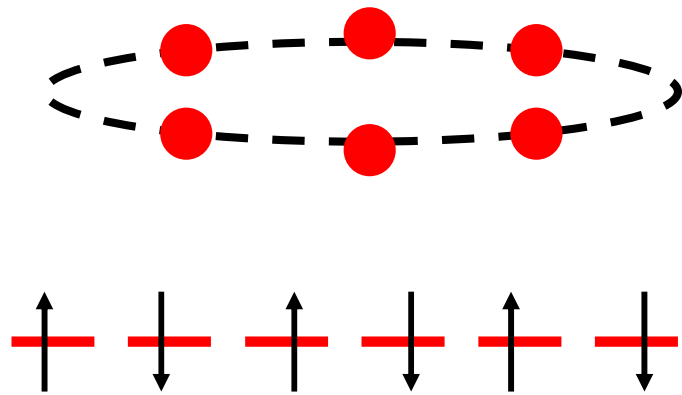
$$E = \langle \Phi | H_{\text{TC}} | \Phi \rangle / \langle \Phi | \Phi \rangle$$

no longer has the lower bound. So we minimize the variance.

$$\text{Variance: } \sigma_{\text{TC}}^2 = \frac{\int |E\Phi - H_{\text{TC}}\Phi|^2 d^{3N}x}{\int |\Phi|^2 d^{3N}x}.$$

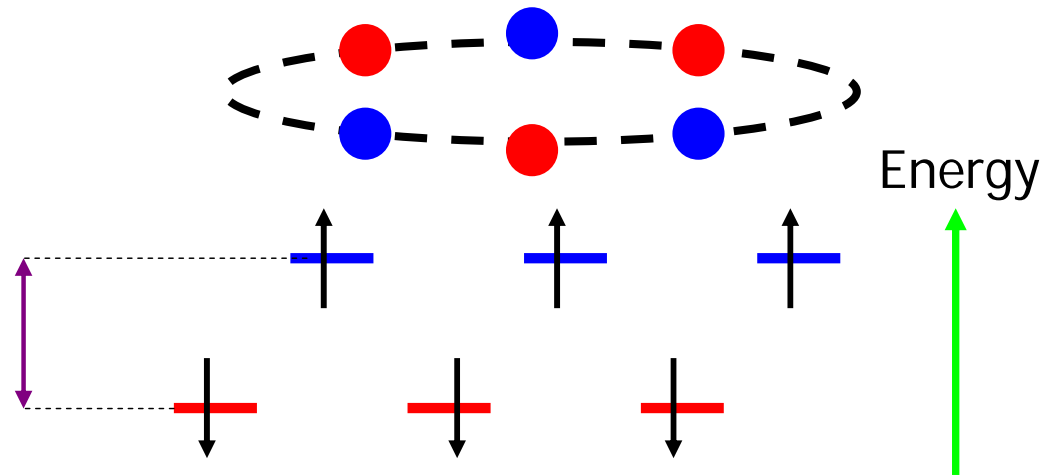
Variance minimization on F needs 5-body integrals, and so we use conventional **VMC** for first-principles calculation in first-principles calculation. Otherwise we use **RPA** Jastrow function at present.

Model Hamiltonian



$$H = \sum_{ij\sigma} t_{ij} a_{i\sigma}^\dagger a_{j\sigma} + U \sum_i n_{i\uparrow} n_{i\downarrow}$$

Hubbard Model



$$H = \sum_i \varepsilon_i (n_{i\uparrow} + n_{i\downarrow}) + \sum_{ij\sigma} t_{ij} a_{i\sigma}^\dagger a_{j\sigma} + U \sum_i n_{i\uparrow} n_{i\downarrow}$$

Ionic Hubbard Model

Transcorrelated Hamiltonian H_{TC} (2)

$$H = \sum_{i,j,\sigma} t_{ij} a_{i\sigma}^\dagger a_{j\sigma} + U \sum_i n_{i\uparrow} n_{i\downarrow}, \quad \boxed{H_{\text{TC}} = F^{-1} H F}$$

$$F = \prod_i g^{n_{i\uparrow} n_{i\downarrow}} = \prod_i \left[1 - (1-g) n_{i\uparrow} n_{i\downarrow} \right] \quad \text{Gutzwiller Function}$$

$$F^{-1} = \prod_i g^{-n_{i\uparrow} n_{i\downarrow}} = \prod_i \left[1 - \left(1 - \frac{1}{g}\right) n_{i\uparrow} n_{i\downarrow} \right]$$

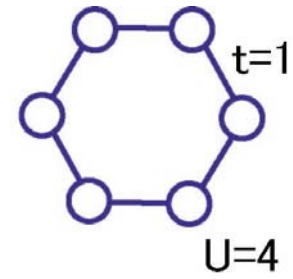
$$\boxed{H_{\text{TC}} = \sum_{i,j,\sigma} t_{ij} \left[1 - \left(1 - \frac{1}{g}\right) n_{i\bar{\sigma}} \right] \left[1 - (1-g) n_{j\bar{\sigma}} \right] a_{i\sigma}^\dagger a_{j\sigma} + U \sum_i n_{i\uparrow} n_{i\downarrow}}$$

How to Optimize the Gutzwiller Function

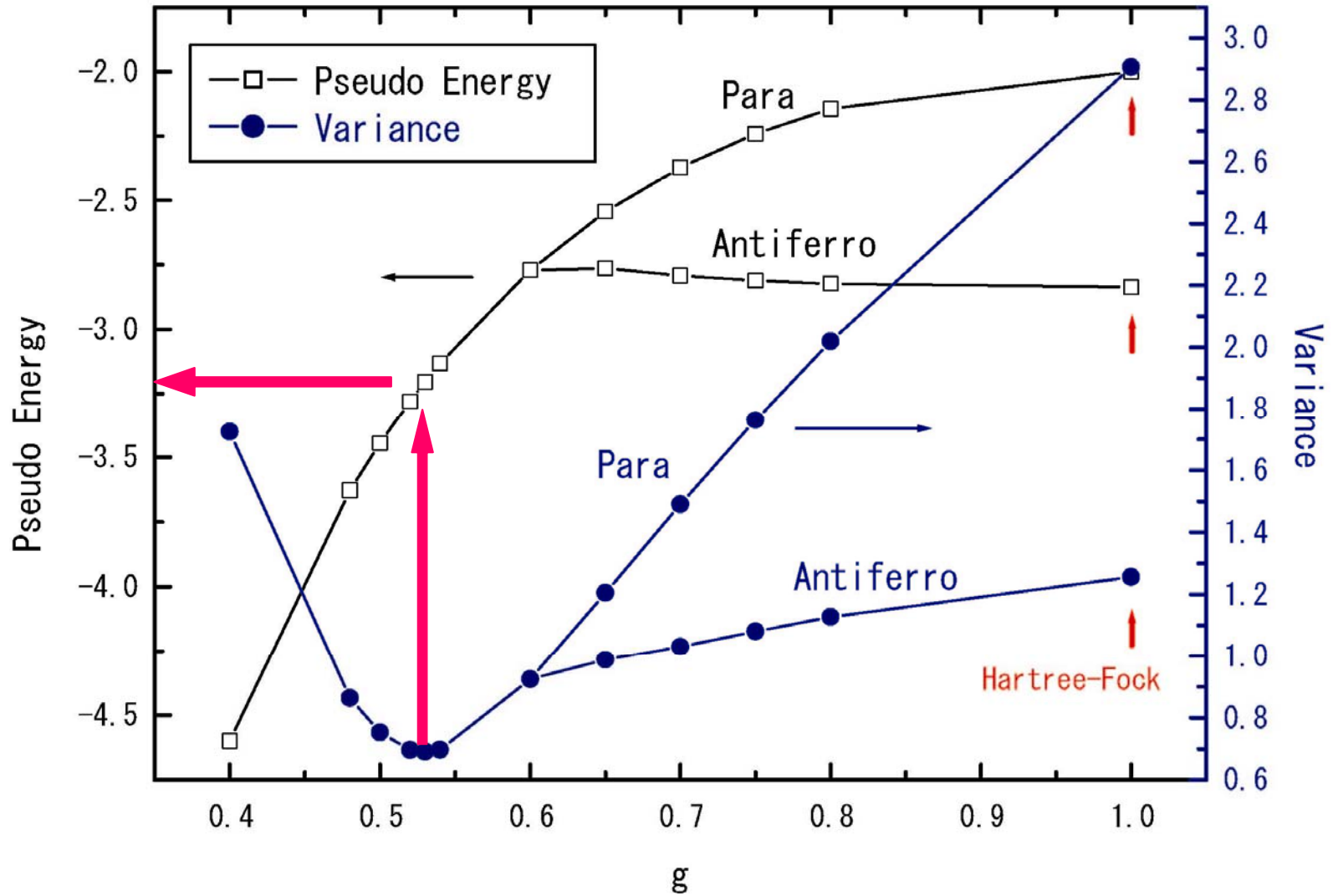
Gutzwiller factor g is optimized so that the **energy variance** defined below is minimized:

$$\begin{aligned}\sigma_R^2 &\equiv \frac{\langle R | (H_{\text{TC}}^\dagger - E)(H_{\text{TC}} - E) | R \rangle}{\langle R | R \rangle} \\ &= \frac{\sum_{i,j} \langle R | (H_{\text{TC}}^\dagger - E) | L^i \rangle \langle R^i | R^j \rangle \langle L^j | (H_{\text{TC}} - E) | R \rangle}{\langle R | R \rangle}\end{aligned}$$

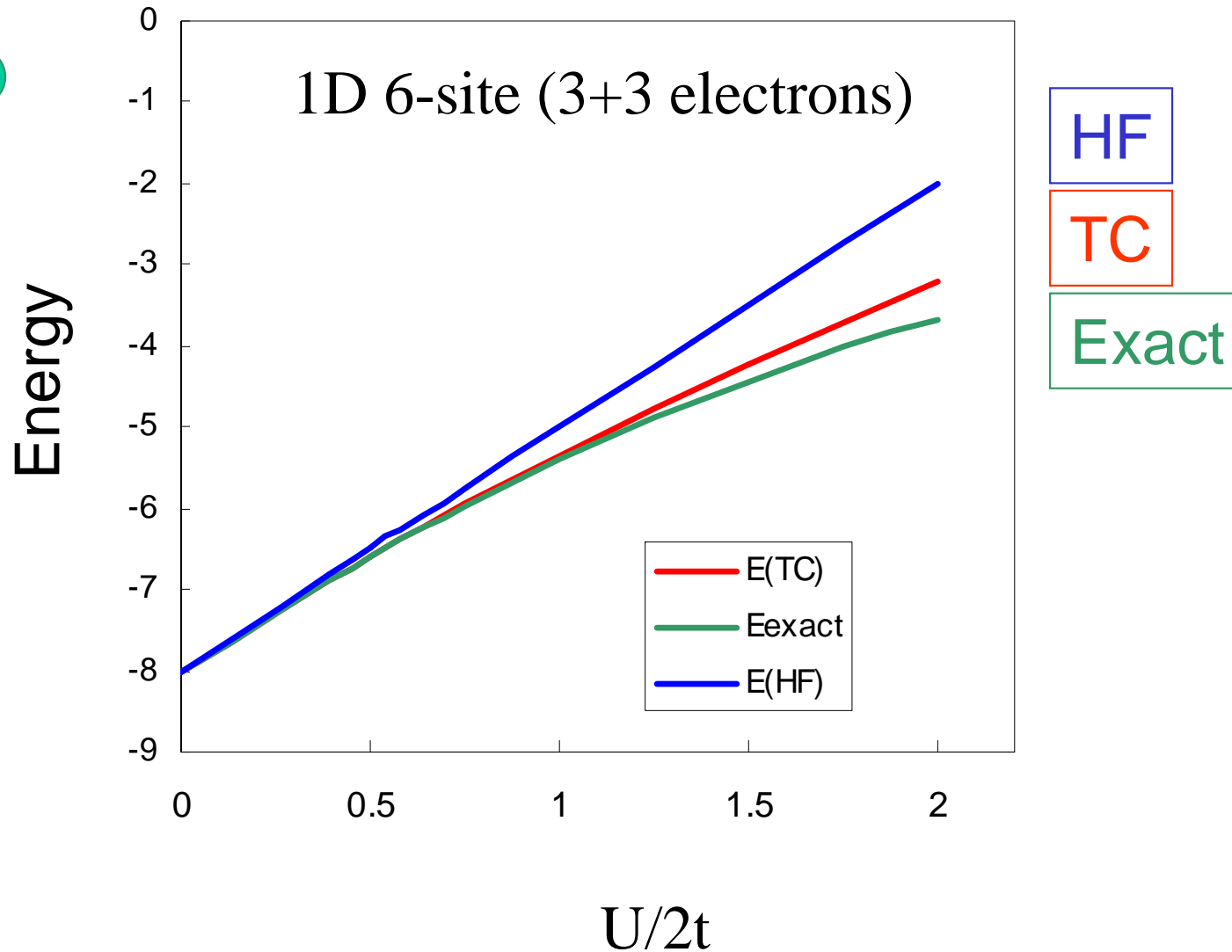
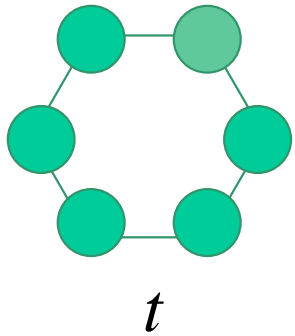
1D 6-site Hubbard Model



6-site ring, 3+3 electrons, $U=4$



Ground State Energy of the Hubbard Model



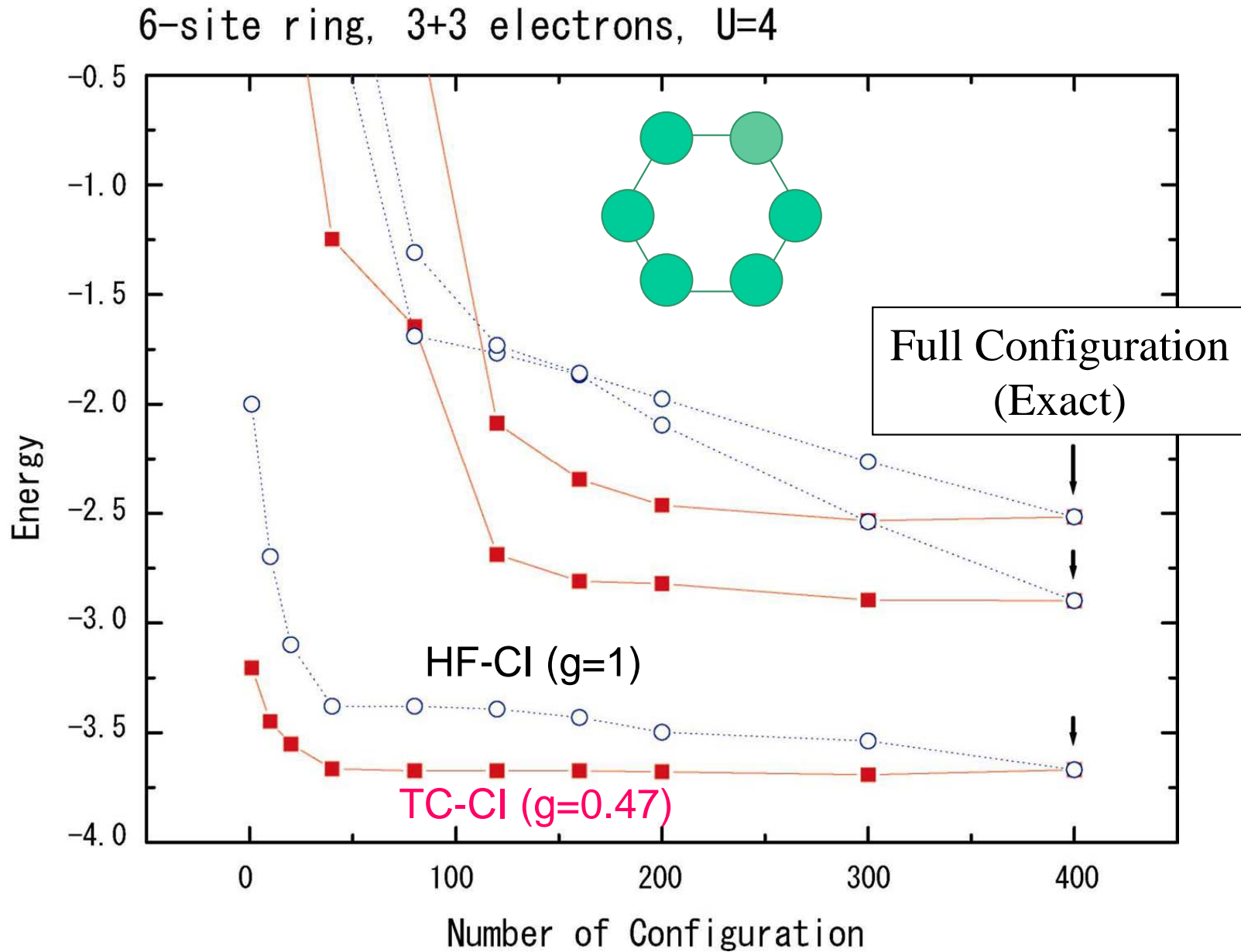
Configuration Interaction (CI)

$$\begin{aligned}H_{\text{TC}} |R\rangle &= E |R\rangle, & \langle L | H_{\text{TC}} &= E \langle L |, \\ |R\rangle &= \sum c_i |R_i\rangle, & \langle L | &= \sum c_i^* \langle L_i |, \\ |R_i\rangle &= \prod_k^{\text{occ.}} a_{k(i)}^{R\dagger} |0\rangle, & |L_i\rangle &= \langle 0 | \prod_k^{\text{occ.}} a_{k(i)}^L\end{aligned}$$

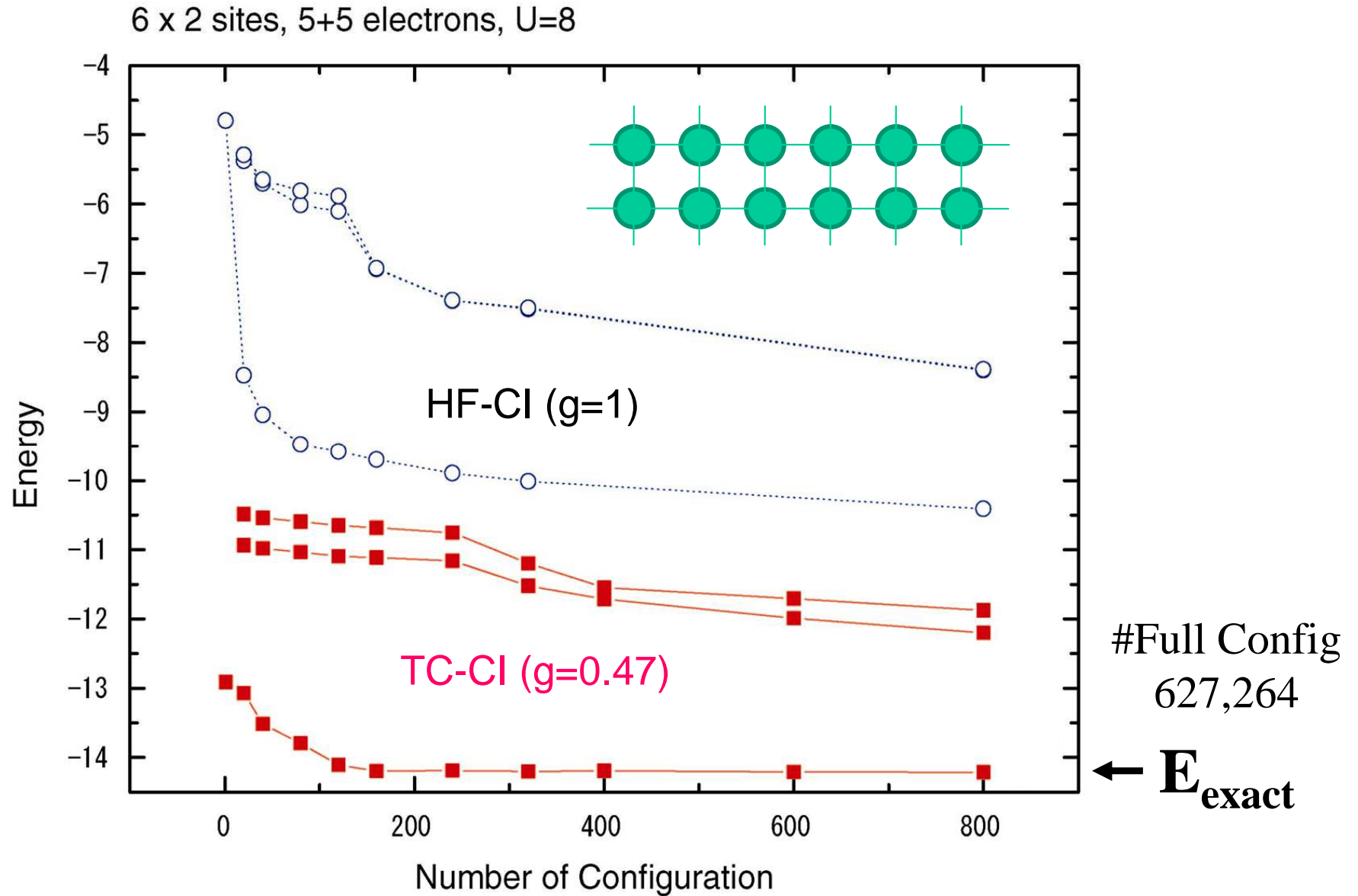
Matrix elements for CI

$$(H_{\text{TC}})_{ij} = \langle L_i | H_{\text{TC}} | R_j \rangle$$

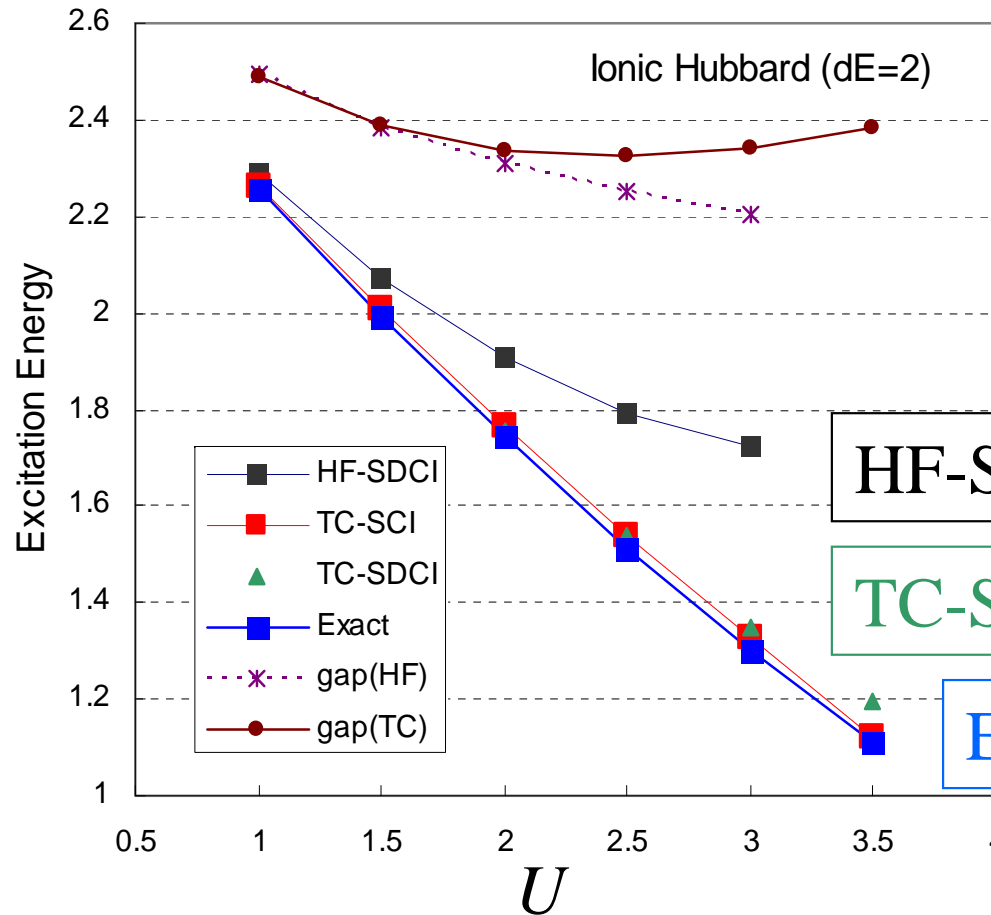
Configuration Interaction (CI)



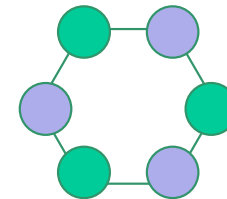
Configuration Interaction (CI)



1st Excitation Energy by SCI, SDCI



Ionic Hubbard Model
6 sites, half-filled

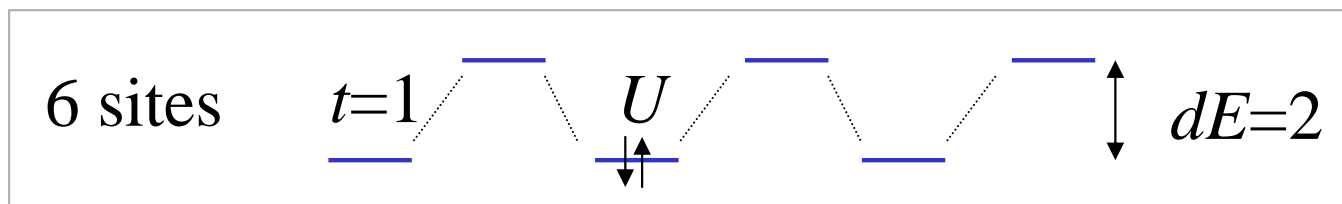


HF-SDCI

TC-SDCI

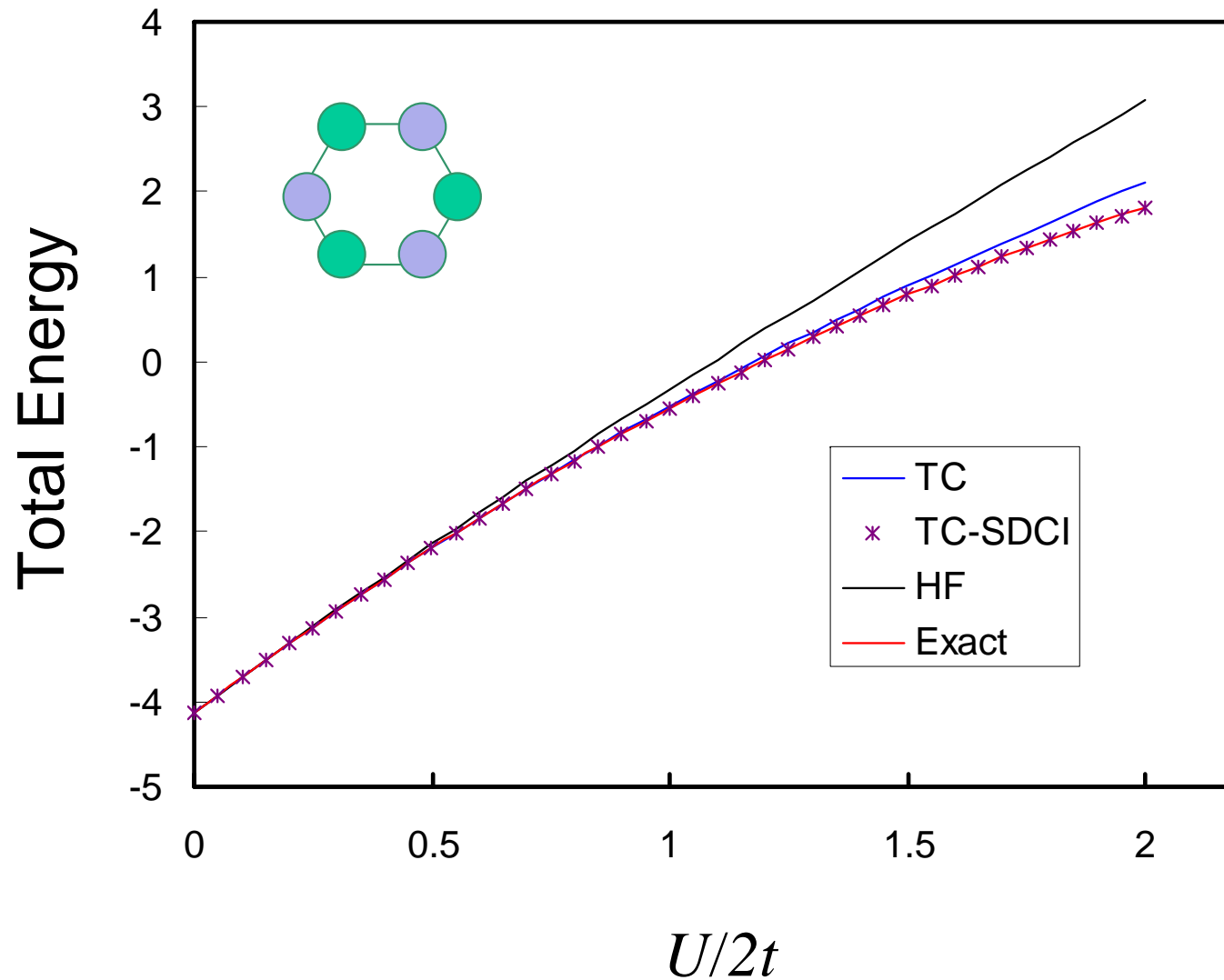
TC-SCI

Exact

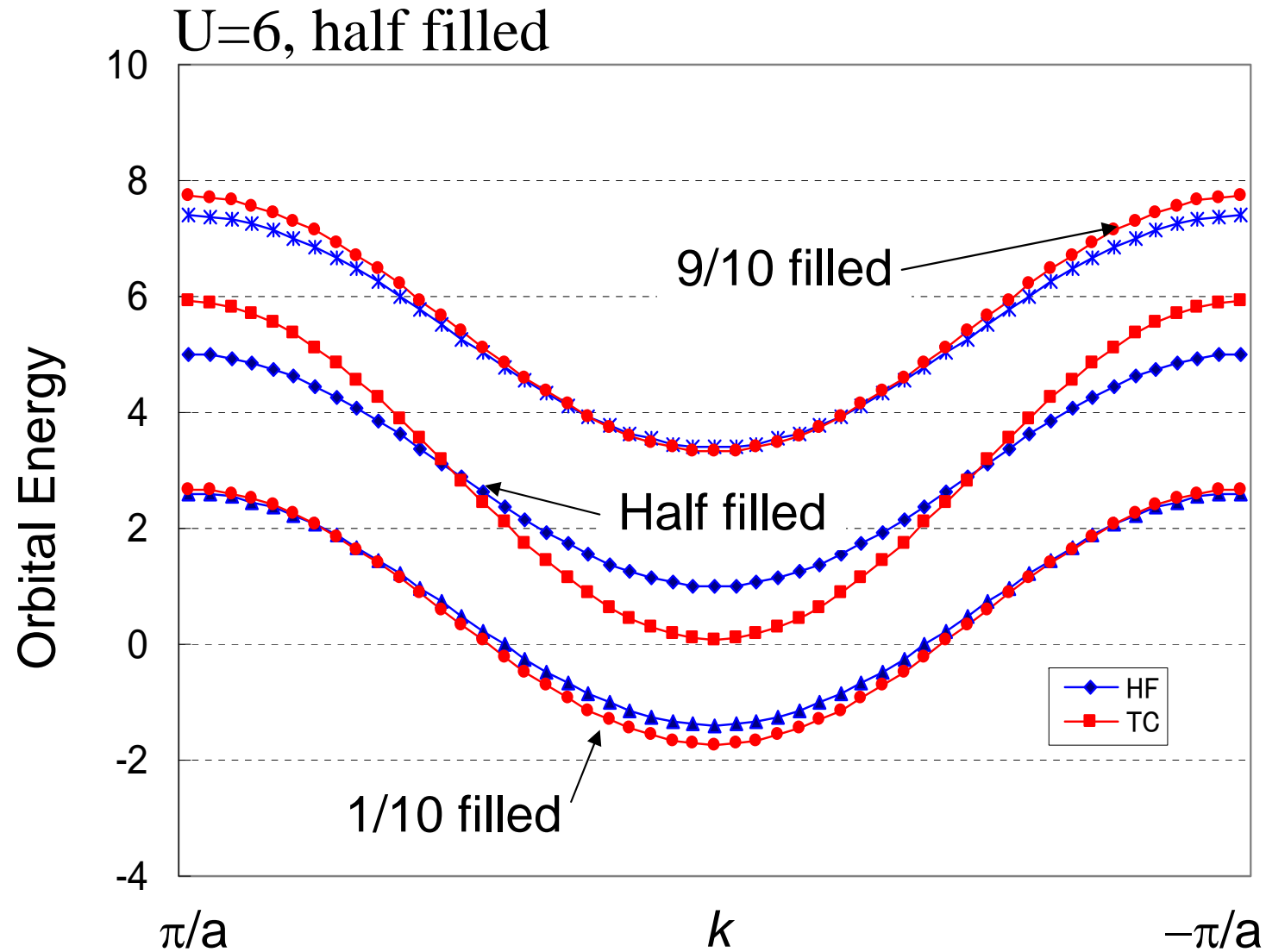


Total Energy by TC-SDCI

1D ionic 6-site (3+3 electrons)



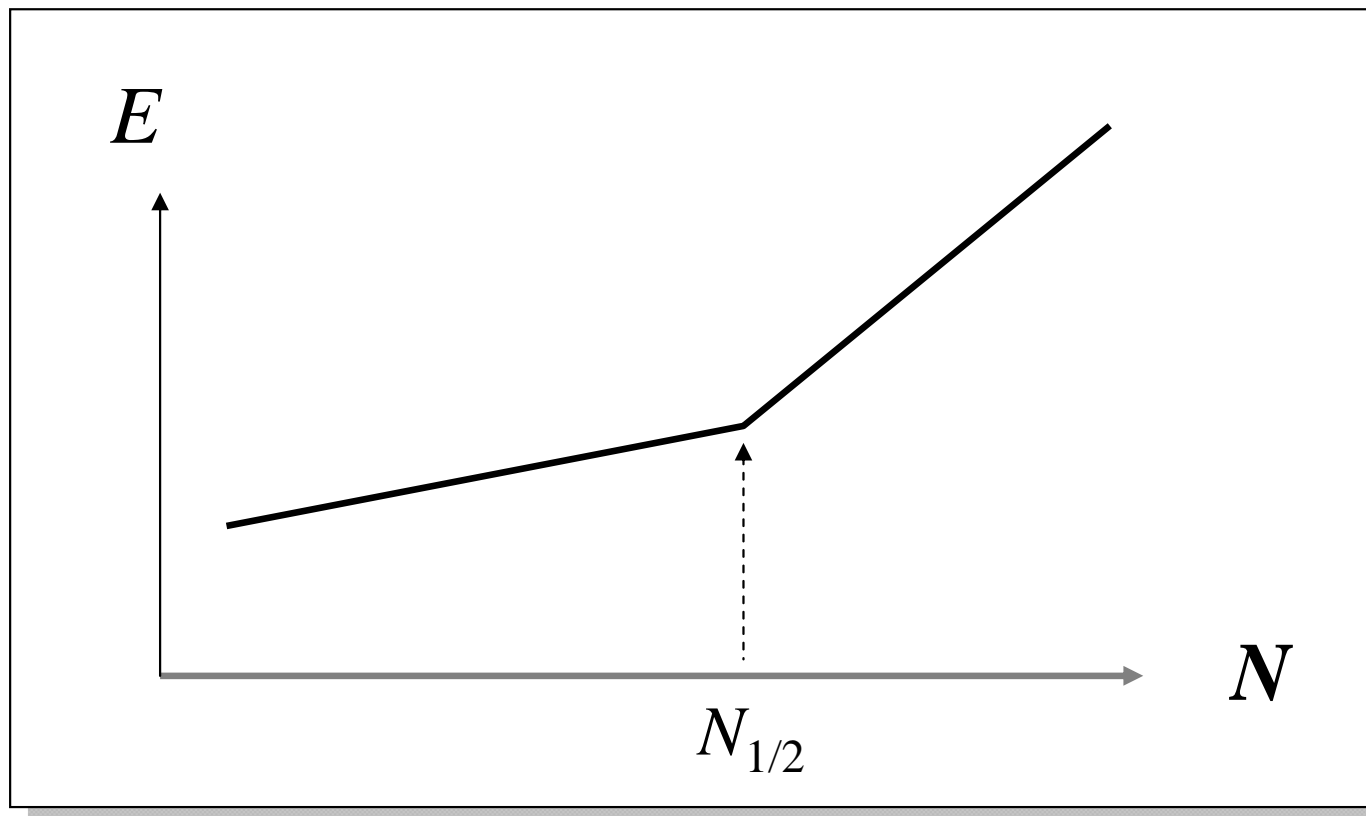
1D Periodic Hubbard Model



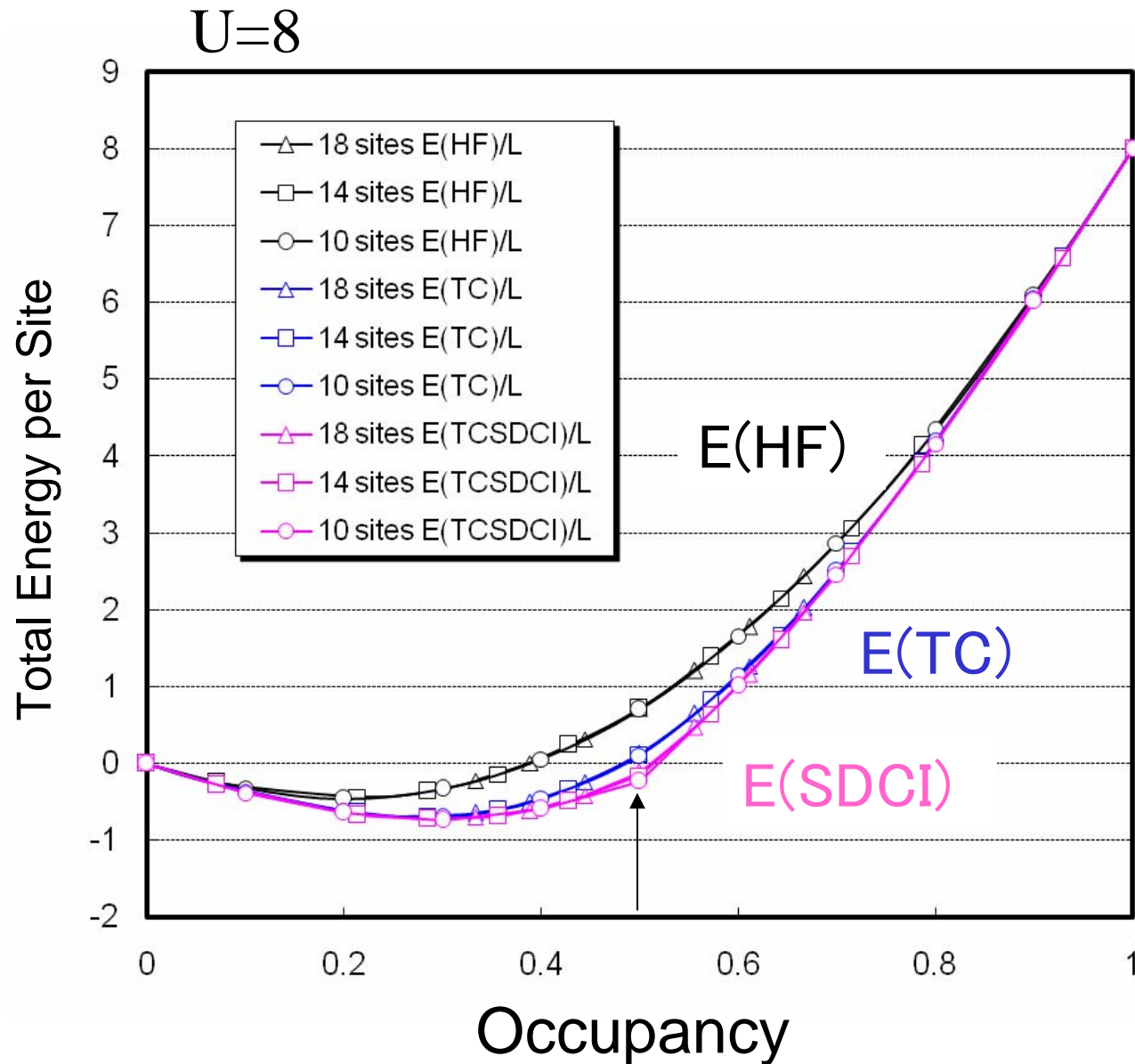
Can we describe Mott-Hubbard insulators?

Definition of the gap

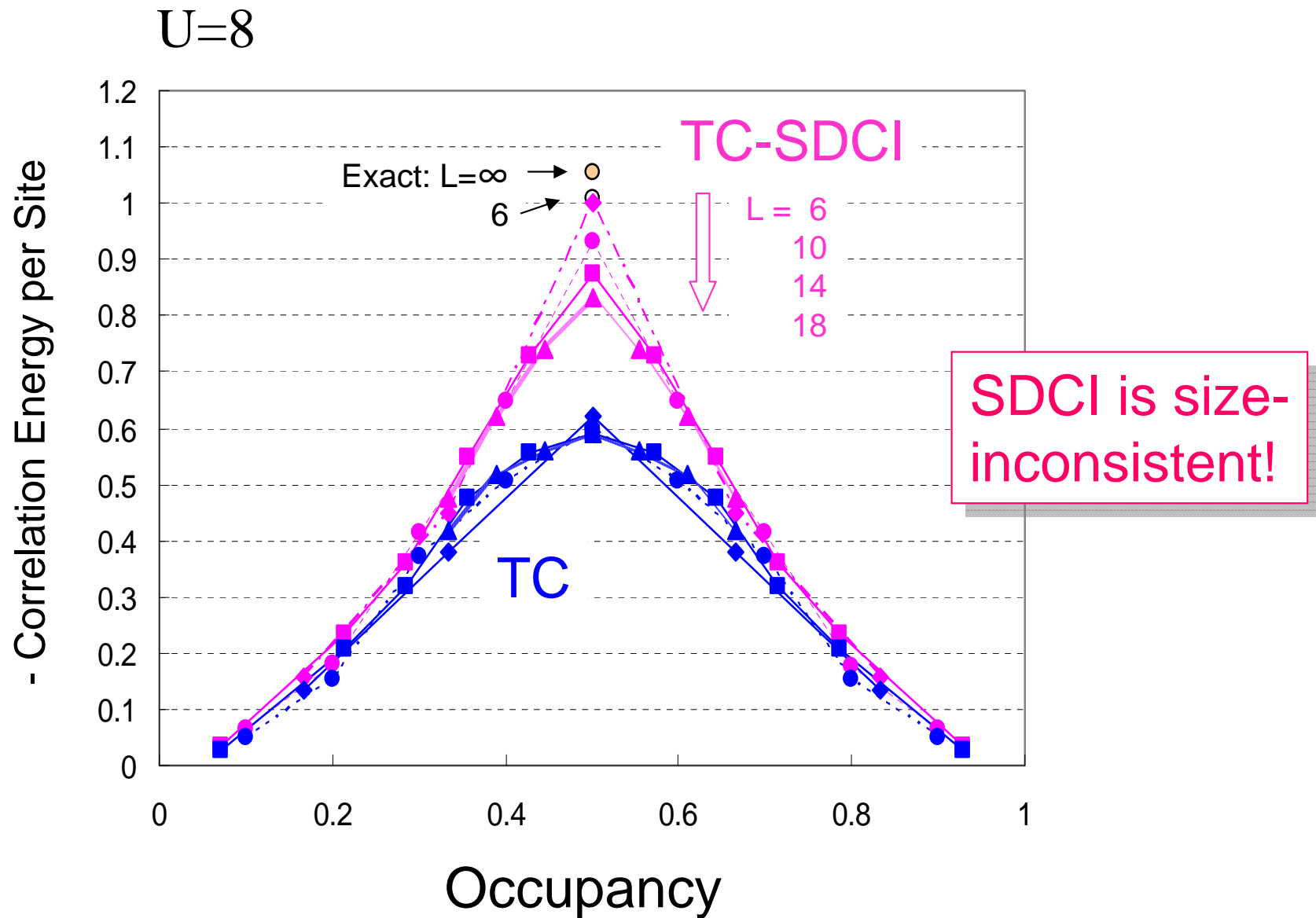
$$E_{\text{gap}} = \{E(N+1) - E(N)\} - \{E(N) - E(N-1)\}$$



Total Energy per Site



Correlation Energy per Site



Jastrow Function for Solids

In the present work, we use the simplest F that satisfies the **cusp condition** at small r and reproduces the **RPA correlation function** at large r .

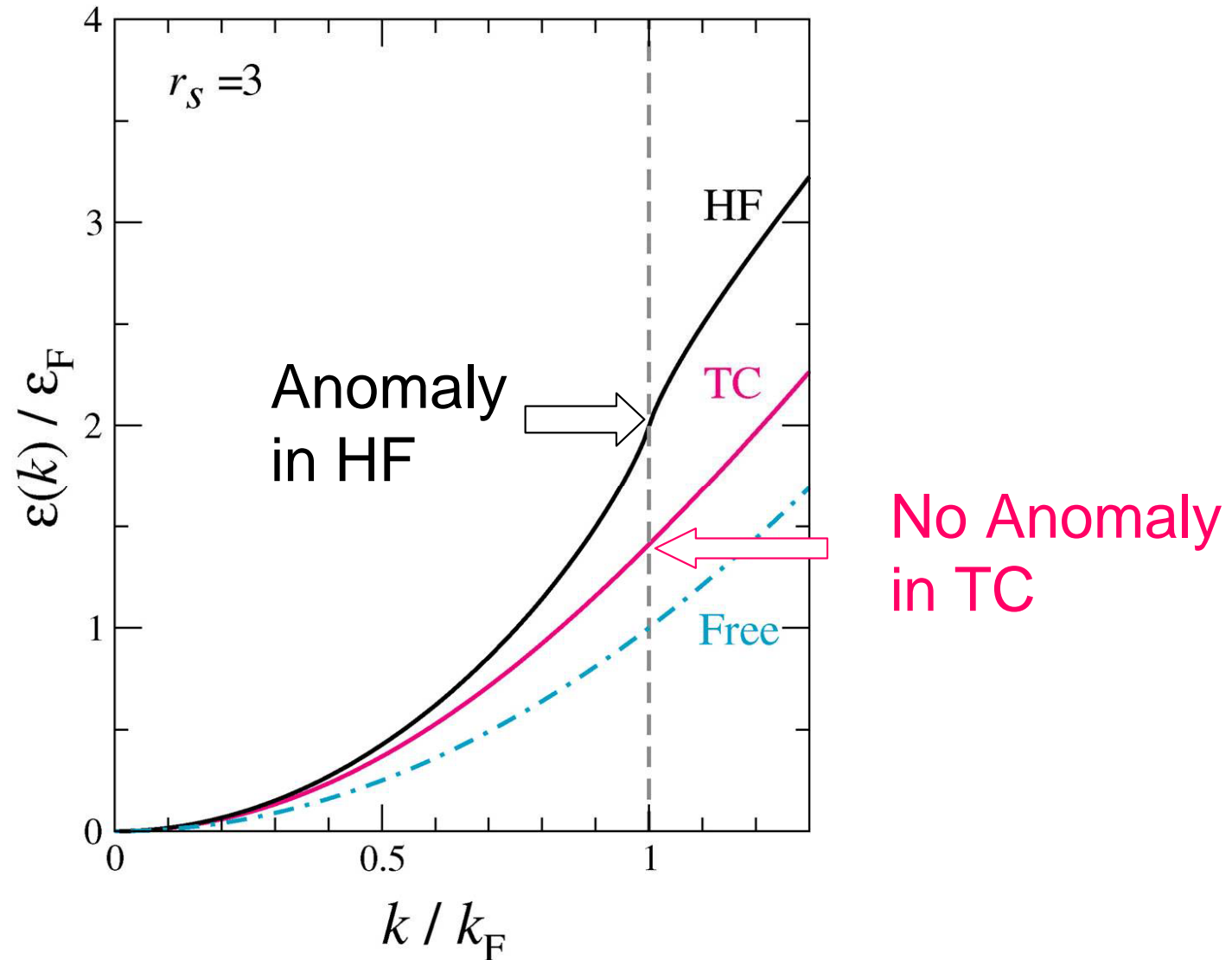
$$F = \exp \left(- \sum_{i>j} \frac{A_{\sigma\sigma'}}{r_{ij}} \left(1 - e^{-r_{ij}/F_{\sigma\sigma'}} \right) \right),$$

$$\frac{A_{\sigma\sigma'}}{2F_{\sigma\sigma'}^2} = \alpha_{\sigma\sigma'} \quad (\alpha_{\uparrow\uparrow} = \frac{1}{4}, \alpha_{\uparrow\downarrow} = \frac{1}{2}),$$

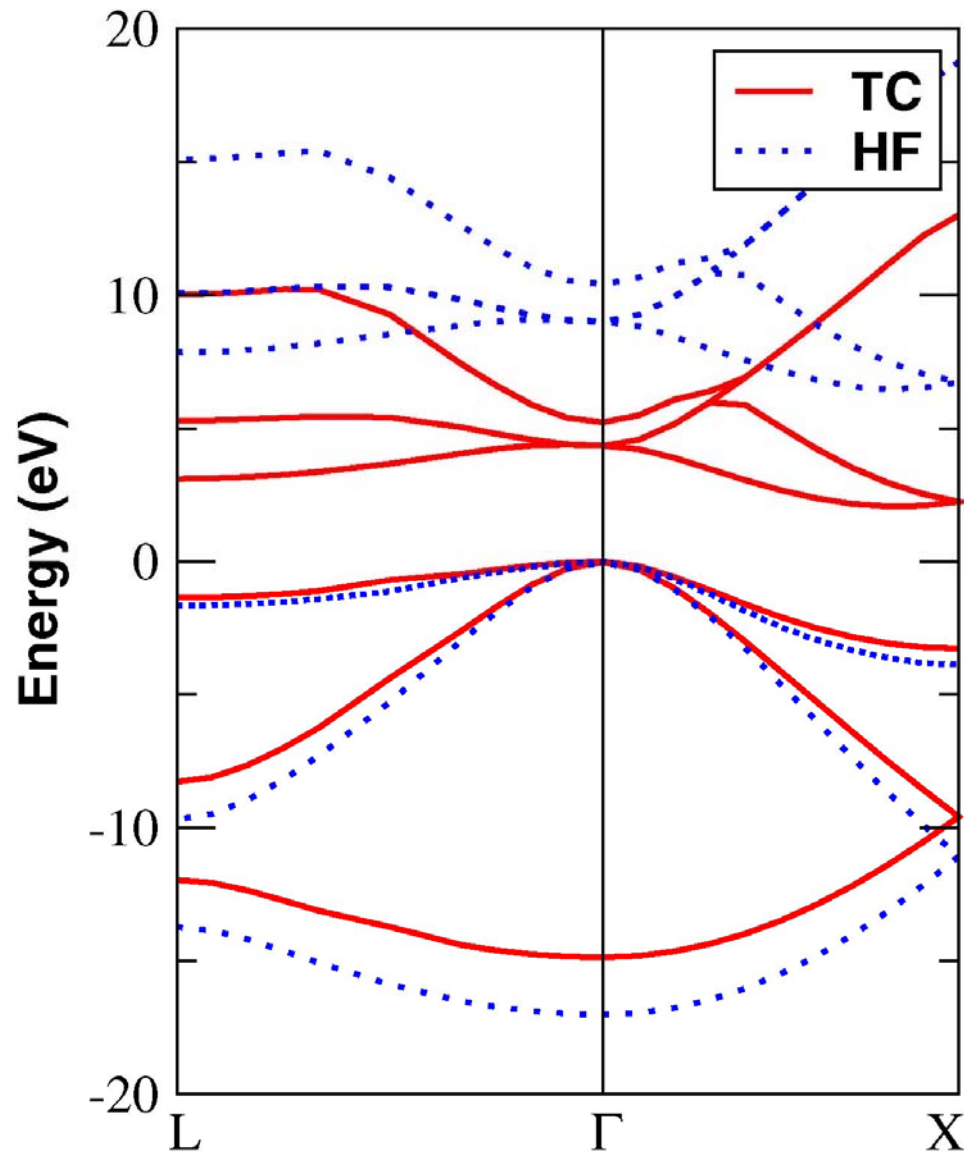
$$A_{\uparrow\uparrow} = A_{\uparrow\downarrow} = \frac{1}{\omega_p} = \frac{1}{\sqrt{4\pi n}}.$$

No need of optimization!

Electron Gas: Single-Particle Energy Dispersion



Band Structure of Si

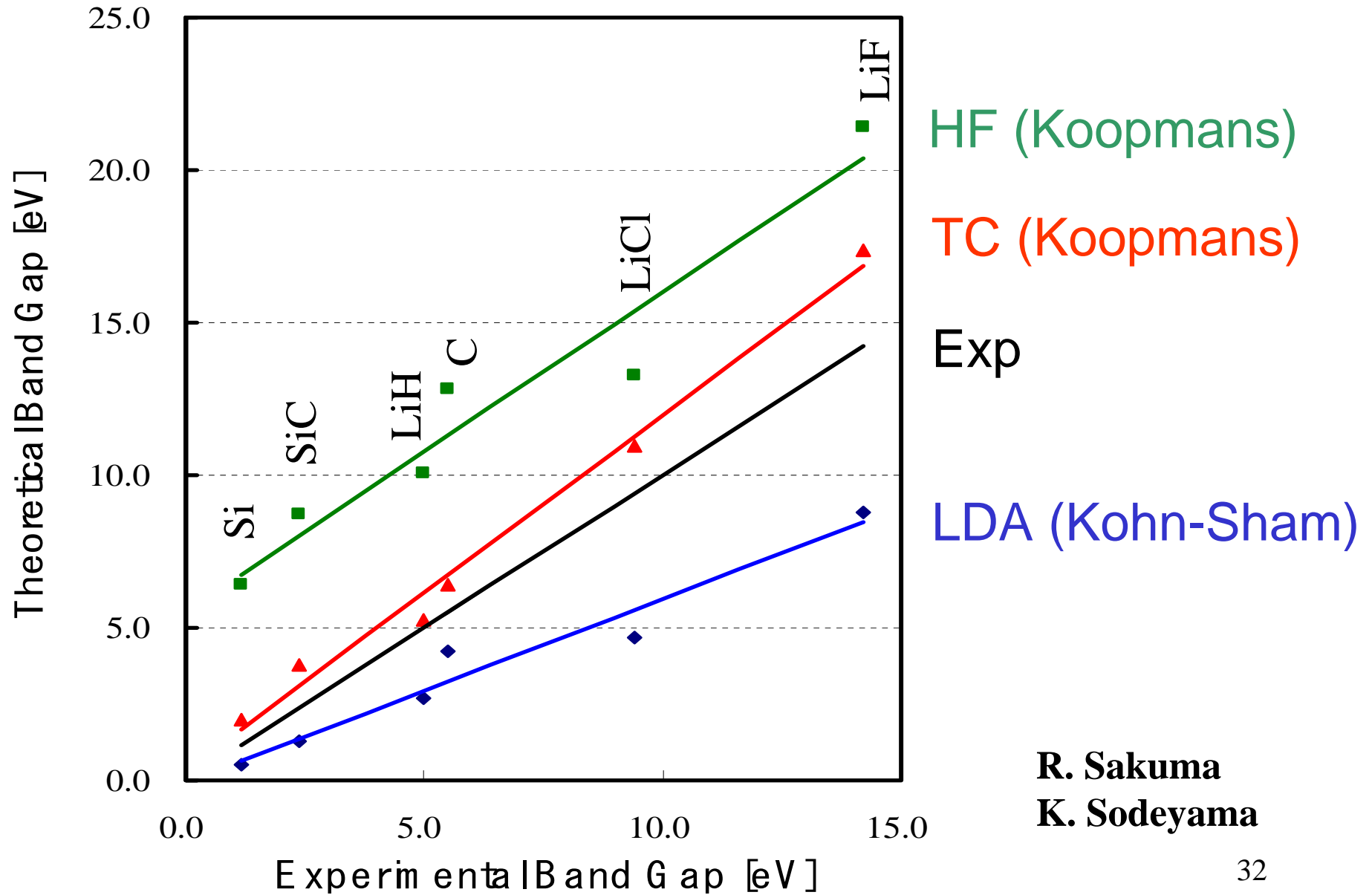


	E_g (in eV)
Exp.	1.17
HF(PP)	6.2
TC(PP)	2.0
scGW(PP)	1.91-2.23
scGW(AE)	1.02-1.14
LDA	0.5

PP: Pseudo-Potential
AE: All Electron

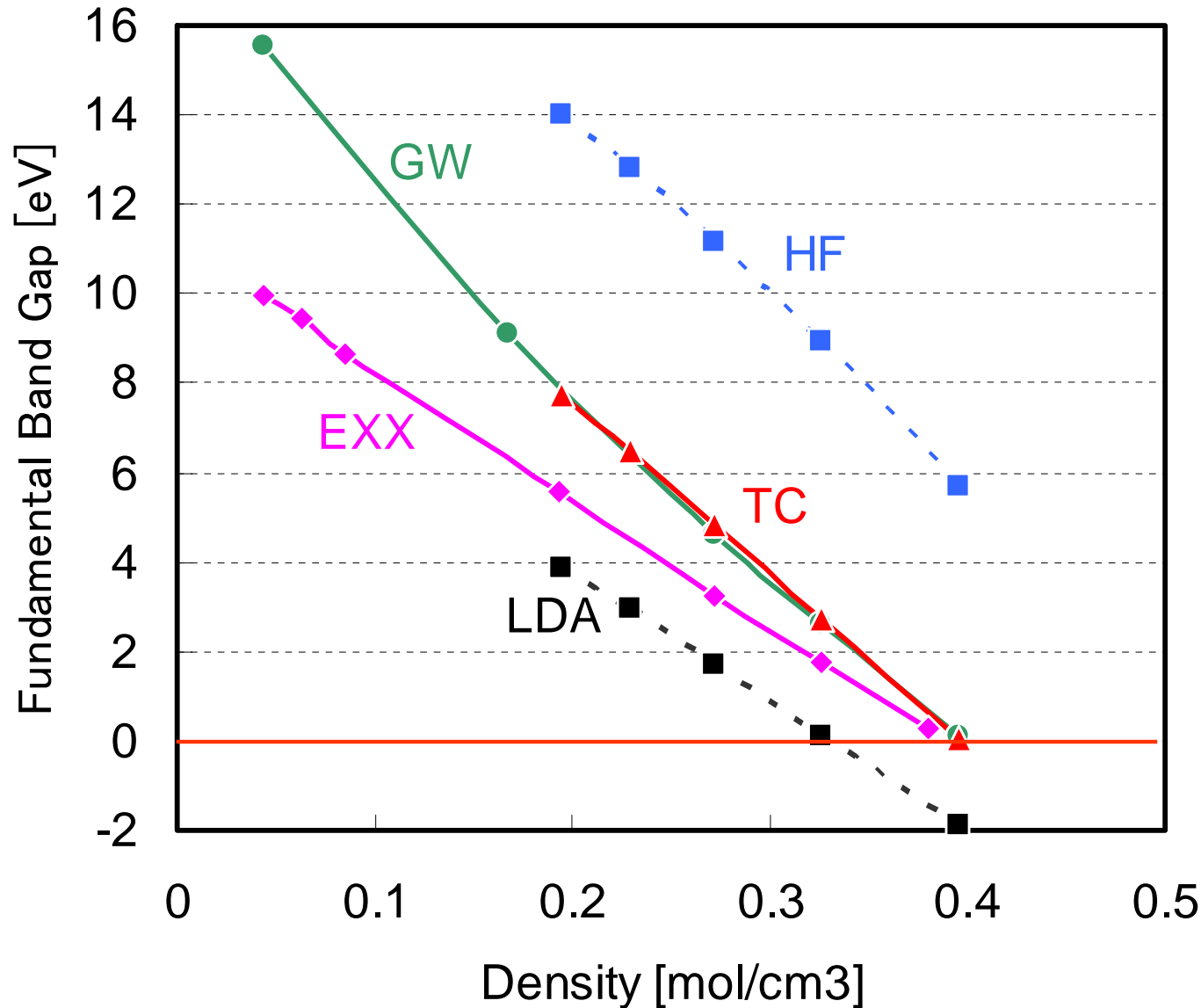
R. Sakuma and S. Tsuneyuki,
J. Phys. Soc. Jpn. 75, 103705 (2006).
31

Band Gap: Summary



R. Sakuma
K. Sodeyama

Band Gap of Solid H₂ (mhcp)



GW (one shot):

H. Chacham and S. G. Louie,
Phys. Rev. Lett. 66, 64 (1991);
H. Chacham, X. Zhu, and S. G. Louie,
Phys. Rev. B 46, 6688 (1992).

EXX:

M. Städele and R.M. Martin,
Phys. Rev. Lett. 84, 6070(2000).

HF, TC:

unpublished

Total Energy of Diamond (Carbon)

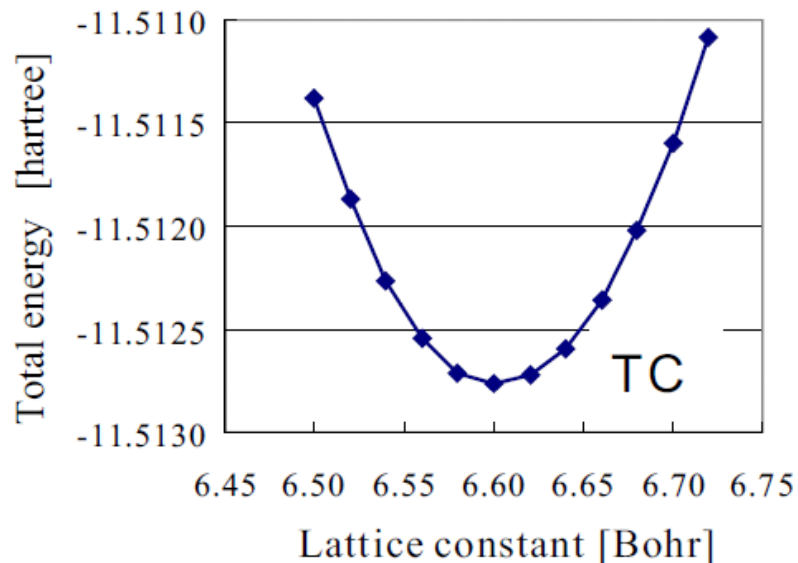
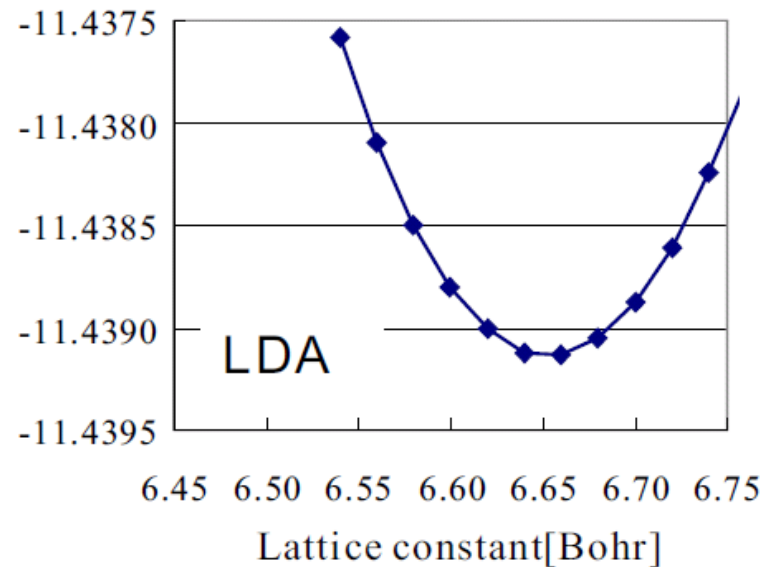
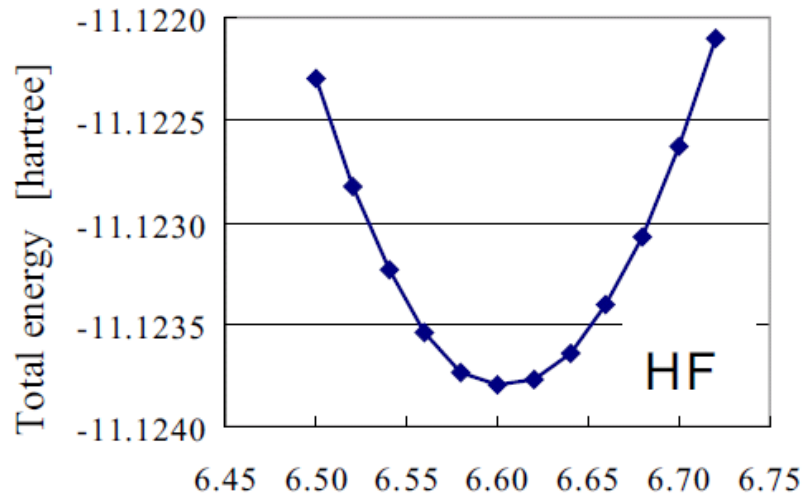


Table 4. Calculated lattice constants a_0 and bulk moduli B_0 in diamond

	a_0 [Bohr]	B_0 [GPa]
LDA	6.65	467
HF	6.60	524
TC	6.60	501
Expt.	6.74	443

Conclusion

- We propose to use the transcorrelated method for describing strongly correlated electrons in solids.
- A merit of the TC method is that it reconciles one-electron picture with many-body wave function beyond Hartree-Fock approximation. **Koopmans' theorem** holds for the orbital energy of the TC-SCF equation, with which **band structure** is available.
- To describe Mott transition in the Hubbard model, SDCI with Gutzwiller-Slater-type wave function does not seem to be sufficient. We perhaps need long-range correlation function.

FAQ

Q: How much is the computational cost?

Is it reasonable compared with other methods?

A: The SCF equation is similar to the Hartree-Fock equation but needs three-body integrals. *In case of the plane wave basis set, it scales as*

$$\text{CPU time} \propto N_{\text{band}}^4 \times N_k^3 \times N_{\text{PW}} \ln N_{\text{PW}}.$$