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)
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 \textit{in Its Application to Solids}

- Kohn-Sham \textit{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 $\epsilon_F$ in metals
  - Koopmans’ theorem gives too large band gap ($E_g^{HF}(Si) > 6eV$, $E_g^{EXP}(Si) = 1.17eV$)
- 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


Electron gas

R. Sakuma and S. Tsuneyuki,

The first application to real solids!
Transcorrelated Method: Summary

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

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

- No Monte Carlo Sampling

- Total energy + Orbital energy

→ Band Structure
Basic Idea of the Transcorrelated Method

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

\[ F^{-1} \times H \Psi = E \Psi \]

\[ \Psi = F(\{r_{ij}\})\Phi \]

Correlated wave function

\[ F \text{: Jastrow factor.} \]

\[ H_{\text{TC}} \equiv F^{-1}HF \]

\[ H_{\text{TC}} \Phi = E\Phi \]

Transcorrelated Hamiltonian

Similarity Transformation

Hartree-Fock Approx. \[ \Phi = \det \{\varphi_1, \varphi_2, \ldots\} \]
Transcorrelated Hamiltonian $H_{TC}$

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

$$H_{TC} = F^{-1} HF$$

$$= \sum_i \left\{ -\frac{1}{2} \nabla_i^2 + v_{\text{ext}}(r_i) \right\} + \frac{1}{2} \sum_i \sum_{j \neq i} \frac{e^2}{r_{ij}}$$

$$+ \frac{1}{2} \sum_i \sum_{j \neq i} \left[ \nabla_i^2 u_{ij} - (\nabla_i u_{ij})^2 + 2 \nabla_i u_{ij} \cdot \nabla_i \right]$$

$$- \frac{1}{2} \sum_i \sum_{j \neq i} \sum_{k \neq i, j} \nabla_i u_{ij} \cdot \nabla_i u_{ik}$$
Effective Two-Body Interaction in $H_{TC}$

![Graph showing potential energy vs. distance in H_Tc](image)
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 Smilarity Transformation

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

\[ E = \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle} = \frac{\langle \Phi | FHF | \Phi \rangle}{\langle \Phi | F^2 | \Phi \rangle} \]

\[ \Psi = F(\{r_{ij}\})\Phi \]

\[ \Phi = \det\{\varphi_k(x)\}. \]

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

\[ E_{TC} = \frac{\langle \Phi | H_{TC} | \Phi \rangle}{\langle \Phi | \Phi \rangle} = \frac{\langle \Phi | H + V_2 + V_3 | \Phi \rangle}{\langle \Phi | \Phi \rangle} \]
TC-SCF Equation

\[ H_{TC} \Phi = E \Phi \quad \iff \quad \langle \delta \Phi \big| H_{TC} \big| \Phi \rangle = E \langle \delta \Phi \big| \Phi \rangle \]

- If we adopt a Slater determinant for \( \Phi \), 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 \( \varepsilon_i \).
- Bloch states and band structure for periodic systems.
TC-SCF equations (Bi-orthogonal Formalism)

\[ H_{TC} \left| R \right\rangle = E \left| R \right\rangle, \]
\[ \left\langle L \right| H_{TC} = E \left\langle L \right| . \]

\[ \delta E_{\text{pseudo}} = \delta \frac{\left\langle L \right| H_{TC} \left| R \right\rangle}{\left\langle L \right| R \right\rangle} = 0 \]

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

- Up-to-three-body potentials.
- Koopmans’ theorem for the orbital energy \( \epsilon_i \).
- 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

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

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

Variance:

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

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)

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

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

Gutzwiller Function

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

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

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

$$\sigma_R^2 \equiv \frac{\langle R\left|\left(H_{TC}^\dagger - E\right)\left(H_{TC} - E\right)\right| R \rangle}{\langle R | R \rangle}$$

$$= \sum_{i,j} \frac{\langle R\left|\left(H_{TC}^\dagger - E\right)|L^i\rangle\langle R^i | R^j \rangle\langle L^j |\left(H_{TC} - E\right)| R \rangle}{\langle R | R \rangle}$$
Ground State Energy of the Hubbard Model

1D 6-site (3+3 electrons)

Energy vs. $U/2t$

- $E_{\text{TC}}$
- $E_{\text{exact}}$
- $E_{\text{HF}}$

HF
TC
Exact
Configuration Interaction (CI)

\[ H_{TC} |R\rangle = E |R\rangle, \]
\[ |R\rangle = \sum c_i |R_i\rangle, \]
\[ |R_i\rangle = \prod_{k} a_{k(i)}^{R\dagger} |0\rangle, \]
\[ \langle L | H_{TC} = E \langle L |, \]
\[ \langle L | = \sum c_i^* \langle L_i |, \]
\[ |L_i\rangle = \langle 0 | \prod_{k} a_{k(i)}^{L} \]

Matrix elements for CI

\[ (H_{TC})_{ij} = \langle L_i | H_{TC} | R_j \rangle \]
Configuration Interaction (CI)

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

Full Configuration (Exact)

HF-CI (g=1)

TC-CI (g=0.47)
Configuration Interaction (CI)

6 x 2 sites, 5+5 electrons, U=8

- Energy vs. Number of Configuration
- HF-CI (g=1)
- TC-CI (g=0.47)

#Full Config 627,264

$E_{\text{exact}}$
$1^{st}$ Excitation Energy by SCI, SDCI

Ionic Hubbard Model
6 sites, half-filled

$U$

Excitation Energy

HF-SDCI
TC-SCI
TC-SDCI
Exact

$U$

6 sites

$t=1$

$dE=2$
Total Energy by TC-SDCI

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

![Graph showing total energy vs. $U/2t$ for different methods including TC, TC-SDCI, HF, and Exact.](image)

- TC
- TC-SDCI
- HF
- Exact
1D Periodic Hubbard Model

U=6, half filled

Orbital Energy

π/a  k  −π/a

9/10 filled

Half filled

1/10 filled

HF
TC
Can we describe Mott-Hubbard insulators?

Definition of the gap

\[ E_{\text{gap}} = \left\{ E(N+1) - E(N) \right\} - \left\{ E(N) - E(N-1) \right\} \]
Total Energy per Site

U=8

E(HF)
E(TC)
E(SDCI)
Correlation Energy per Site

U=8

- Correlation Energy per Site

Occupancy

TC-SDCI

SDCI is size-inconsistent!

Exact: L=∞ → 6 → L = 6
10
14
18

TC
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

<table>
<thead>
<tr>
<th>Method</th>
<th>Eg (in eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exp.</td>
<td>1.17</td>
</tr>
<tr>
<td>HF(PP)</td>
<td>6.2</td>
</tr>
<tr>
<td>TC(PP)</td>
<td>2.0</td>
</tr>
<tr>
<td>scGW(PP)</td>
<td>1.91-2.23</td>
</tr>
<tr>
<td>scGW(AE)</td>
<td>1.02-1.14</td>
</tr>
<tr>
<td>LDA</td>
<td>0.5</td>
</tr>
</tbody>
</table>

PP: Pseudo-Potential
AE: All Electron

Band Gap: Summary

Theoretical Band Gap [eV]

HF (Koopmans)
TC (Koopmans)
Exp
LDA (Kohn-Sham)

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);

EXX:

HF, TC:
unpublished
Total Energy of Diamond (Carbon)

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

<table>
<thead>
<tr>
<th></th>
<th>$a_0$ [Bohr]</th>
<th>$B_0$ [GPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>LDA</td>
<td>6.65</td>
<td>467</td>
</tr>
<tr>
<td>HF</td>
<td>6.60</td>
<td>524</td>
</tr>
<tr>
<td>TC</td>
<td>6.60</td>
<td>501</td>
</tr>
<tr>
<td>Expt.</td>
<td>6.74</td>
<td>443</td>
</tr>
</tbody>
</table>

K. Sodeyama, R. Sakuma and ST (FADFT, P05)
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.
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*

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