Outline

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Introduction

Schrödinger equation

\[ \hat{H}\psi(r_1, r_2, \cdots, r_N) = E\psi(r_1, r_2, \cdots, r_N), \]

\[ \hat{H} = -\frac{1}{2} \sum_i \nabla_i^2 + \sum_i v_{\text{ext}}(r_i) + \sum_{i<j} \frac{1}{|r_i - r_j|}. \]

Hartree-Fock approximation

Rank-1 tensor product (Single determinant) approximation

Conventional description of electron correlations

- Configuration expansions (MBPT, CI, CC, etc.),
- "Best rank-K" (MCSCF).

Slow convergence.
Jastrow ansatz for electron correlation

\[ \psi(R) = e^{\tau(R)}\phi(R), \quad R = (r_1, r_2, \cdots, r_N), \]

where \( \tau(R) \) is a function with permutational symmetry, and \( \phi \) is a single (or multi) determinant reference wave function.

**Motivations for Jastrow ansatz**

- Compact description of electron correlation,
- Speed up the configuration basis-set convergence (R12, F12, etc.),
- Platform for new numerical techniques (Wavelets, sparse grids, tensor products, etc.).
Available equations for Jastrow ansatz

- Linked-cluster expansion,
- Fermi hyper-netted-chain equations (FHNC),
- Random phase approximations (RPA).

Too complicated for implementation.

Desire: simple and efficient equations.
Variational ground state energy

\[ E_0 = \min_{\tau \in T, \Phi \in F} \frac{\langle \Phi | e^{\tau \hat{H}} e^{-\tau} | \Phi \rangle}{\langle \Phi | e^{2\tau} | \Phi \rangle}, \]

\( T \): spanned by a set of basis functions \( \tau(R) = \sum_{\alpha} c_{\alpha} U_{\alpha}(R) \),

\( F \): defined by a given primitive orbital basis set and the rank of \( \Phi \).

Practical equations

\[
\begin{cases}
\langle \Phi | U_{\alpha} e^{\tau} (\hat{H} - E_{\text{var}}[\Phi]) e^{-\tau} | \Phi \rangle = 0, \quad (V.1) \\
\min_{\Phi \in F} E_{\text{var}}[\Phi] = \min_{\Phi \in F} \frac{\langle \Phi | e^{\tau \hat{H}} e^{-\tau} | \Phi \rangle}{\langle \Phi | e^{2\tau} | \Phi \rangle}. \quad (V.2)
\end{cases}
\]

Can only be used by QMC.
Transcorrelated equation of Boys and Handy

\[
\begin{aligned}
\langle \Phi | U_\alpha e^{-\tau (\hat{H} - E_{TC})} e^\tau | \Phi \rangle & \geq 0, \quad (TC-C) \\
\langle \frac{\partial \Phi}{\partial C_{i\mu}} | e^{-\tau (\hat{H} - E_{TC})} e^\tau | \Phi \rangle & \geq 0, \quad (TC-O)
\end{aligned}
\]

\(\Phi\): single determinant wave function with the orbitals been spanned by a primitive basis set \(\{\chi_\mu\}\)

\[
\phi_i(r) = \sum_\mu C_{i\mu} \chi_\mu(r).
\]

The similarity transformation is used to remove the exponential factor

\[
e^{-\tau} \hat{H} e^{\tau} = \hat{H} + [\hat{H}, \tau] - \frac{1}{2} \sum_i (\nabla_i \tau)^2,
\]

which gives rise to a non-Hermitian term \([\hat{H}, \tau]\), and leads to lose of variational bound.
\[ < \Phi | U_\alpha e^\tau (\hat{H} - E_{\text{var}}) e^\tau | \Phi > = 0, \]

\[ < \Phi | U_\alpha e^{-\tau} (\hat{H} - E_{\text{TC}}) e^\tau | \Phi > = 0, \]

**Variational features of the TC-C equation**

- In the limiting case when \( \mathcal{T} = \{ U_\alpha \} \) forms a complete basis set for functions with permutation symmetry, the TC-C equation is equivalent to the variational equation (V.1).

- In case of small basis sets with only up to two-body correlation terms, the TC-C equation still serves as a good approximation of equation (V.1), as long as \( \Phi \) is not much worse than \( \Phi_{HF} \).

Transcorrelated and variational correlation energies. The variational energies are calculated with VMC for both TC (\( \tau_{TC} \)) and energy optimised correlation functions (\( \tau_{opt} \)). The single determinant reference function \( \Phi \) is fixed as the Hartree-Fock wave function. (H. Luo, W. Hackbusch and H.-J. Flad, Mol. Phys., 108(2010)425.)

<table>
<thead>
<tr>
<th>Term (( \mathcal{T} ))</th>
<th>8</th>
<th>17</th>
<th>92</th>
<th>103</th>
<th>125</th>
</tr>
</thead>
<tbody>
<tr>
<td>TC</td>
<td>-0.3370(4)</td>
<td>-0.3431(4)</td>
<td>-0.3567(3)</td>
<td>-0.3290(5)</td>
<td>-0.2634(3)</td>
</tr>
<tr>
<td>VMC (( \tau_{TC} ))</td>
<td>-0.3367(5)</td>
<td>-0.3446(3)</td>
<td>-0.3581(2)</td>
<td>-0.3310(4)</td>
<td>-0.2657(2)</td>
</tr>
<tr>
<td>VMC (( \tau_{opt} ))</td>
<td>-0.3369(5)</td>
<td>-0.3458(4)</td>
<td>-0.3599(5)</td>
<td>-0.331(1)</td>
<td>-0.2678(5)</td>
</tr>
</tbody>
</table>
Variational transcorrelated method

Replace (V.1) with TC-C in the variational equation, we get the variational transcorrelated equation

\[
\begin{align*}
< \Phi | U_\alpha (\hat{H} + [\hat{H}, \tau]) - \frac{1}{2} \sum_i (\nabla_i \tau)^2 - E_{TC} | \Phi > &= 0, \quad (TC-C) \\
\min_{\Phi \in F} E_{TC} &= \min_{\Phi \in F} < \Phi | \hat{H} - \frac{1}{2} \sum_i (\nabla_i \tau)^2 | \Phi >, \quad (VTC-\Phi)
\end{align*}
\]

where the non-Hermitian term \([\hat{H}, \tau]\) simply drops out from equation (VTC-\(\Phi\)) since \(< \Phi | [\hat{H}, \tau] | \Phi > = 0\).

The variational transcorrelated equation can be applied to a single determinant Jastrow ansatz as well as to a multi-determinant one.
Suppose $\mathbf{T}$ contains only up to two body terms

$$\tau = \frac{1}{2} \sum_{ij} u(r_i, r_j).$$

The effective Hamiltonian $\tilde{H} = \hat{H} - \frac{1}{2} \sum_i (\nabla_i \tau)^2$ contains then only up to three body operators

$$\tilde{H} = \hat{H} + K + L,$$

$$K = -\frac{1}{2} \sum_{pqrs} \langle pq | (\nabla_1 u(r_1, r_2))^2 | rs \rangle a_p^\dagger a_q^\dagger a_s a_r,$$

$$L = -\frac{1}{2} \sum_{pqrstu} \langle pqr | \nabla_1 u(r_1, r_2) \cdot \nabla_1 u(r_1, r_3) | stu \rangle a_p^\dagger a_q^\dagger a_r^\dagger a_u a_t a_s,$$
Hartree-Fock type orbital equation

\[
\sum_{\nu} \tilde{F}_{\mu\nu} C_{i\nu} = \epsilon_i \sum_{\nu} S_{\mu\nu} C_{i\nu},
\]

\[
\tilde{F}_{\mu\nu} = \frac{1}{2} \frac{\partial^2}{\partial C_{i\mu} \partial C_{i\nu}} \langle \Phi | \tilde{H} | \Phi \rangle.
\]

Those three-body terms of \(\tilde{F}_{\mu\nu}\) have a special structure

\[
\langle \mu jk | L_{123} | \nu j'k' \rangle = - \int d^3 x \chi_\mu(x) \chi_\nu(x) \tilde{T}_{jj'}(x) \cdot \tilde{T}_{kk'}(x),
\]

\[
\tilde{T}_{ij}(x_1) = \int d^3 x_2 \nabla_1 u(x_1, x_2) \phi_i(x_2) \phi_j(x_2).
\]
A simple (but not efficient) algorithm

- Slater type primitive orbital basis,
- Polynomial basis for the correlation factor

\[ u_{lmn,AB}(\mathbf{r}_i, \mathbf{r}_j) = \bar{r}_i^l \bar{r}_j^m \bar{r}_ij^n, \quad \bar{r} = r/(1 + r), \]

- QMC calculation of the TC-C matrix elements,
- Gaussian package for Fork operators (fit STO by GTO basis),
- Numerical integration for effective potentials \((L, K)\).

Transcorrelated and variational ground state energies calculated for \(C_2\).

<table>
<thead>
<tr>
<th></th>
<th>(E_{HF})</th>
<th>(E_{TC-C})</th>
<th>(E_{VTC})</th>
<th>(E_{\text{Var}[\Psi_{TC}]})</th>
<th>(E_{\text{VMC}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>VTC-O</td>
<td>-75.406</td>
<td>-75.807(1)</td>
<td>-75.814(1)</td>
<td>-75.813(1)</td>
<td>-75.8069(5)</td>
</tr>
</tbody>
</table>

\(a\): J. Toulouse and C. J. Umrigar, J. Chem. Phys. 126(2007)084102, where slightly different bases for orbitals and \(\tau\) were used.
Motivations for multi-configuration methods

Multi-configuration wave functions are necessary for

- systems with quasi-degenerate ground states (with low lying excited states),
- dealing with chemical reactions (transition structures, reactive intermediates, excited electronic states, etc.)

Multi-configuration self consistent field (MCSCF) method:

- Optimize both orbitals and CSF coefficients (a combination of HF and CI methods).
- Not efficient for the description of dynamic correlation.

Variational transcorrelated method could be a potential candidate for a new MCSCF approach!
A transcorrelated CI approach

As a preliminary test of the variational transcorrelated method on multi-configuration Jastrow ansatz, we try to solve a CI type transcorrelated equation

$$\psi = \sum_i c_i \Phi_i, \quad \sum_j < \psi_i | \tilde{H} | \psi_j > = c_j = E_{\psi_i},$$

where the matrix elements are (for the moment) calculated by QMC.

Transcorrelated and variational ground state energies calculated for $C_2$, where a 7 determinants (CAS(8.5)) reference is used.

<table>
<thead>
<tr>
<th></th>
<th>$E_{HF}$</th>
<th>$E_{TC-C}$</th>
<th>$E_{VTC}$</th>
<th>$E_{\text{var}[\Psi_{TC}]}$</th>
<th>$E_{\text{VMC}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>VTC-CI</td>
<td>-75.477</td>
<td>-75.829(1)</td>
<td>-75.832(1)</td>
<td>-75.832(1)</td>
<td>-75.8094(5)$^a$, -75.8374(5)$^b$</td>
</tr>
</tbody>
</table>

$a, b$: J. Toulouse and C. J. Umrigar, J. Chem. Phys. 126(2007)084102, where (a) is a CI type result and (b) is essentially a MCSCF result.
Conclusion

We propose a new transcorrelated method for the calculation of electron correlation, which can be applied to a single determinant Jastrow ansatz as well as a multi-determinant one. For the single determinant ansatz, we obtain a Hartree-Fock type self-consistent equation for the optimization of orbitals, and for the multi-determinant ansatz we have tested a CI type equation. We apply the new equations to $C_2$ molecule, and the results are in very good agreements with those of variational quantum Monte Carlo.

Future works

- Extend to variational transcorrelated MCSCF method.
- Generate a complete Gaussian package of the VTC method.
- Incorporate tensor product technique in VTC.