Variational transcorrelated method

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Introduction

Schrödinger equation

$$\hat{H}\Psi(\mathbf{r}_1, \mathbf{r}_2, \cdots, \mathbf{r}_N) = E\Psi(\mathbf{r}_1, \mathbf{r}_2, \cdots, \mathbf{r}_N),$$

$$\hat{H} = -\frac{1}{2}\sum_i \nabla_i^2 + \sum_i v_{ext}(\mathbf{r}_i) + \sum_{i<j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}.$$

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

$$\Psi(\mathbf{R}) = e^{\tau(\mathbf{R})}\Phi(\mathbf{R}), \quad \mathbf{R} = (\mathbf{r}_1, \mathbf{r}_2, \cdots, \mathbf{r}_N),$$

where $\tau(\mathbf{R})$ is a function with permutational symmetry, and Φ 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.).

Introduction
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VTC method
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VTC ORB
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MC-VTC
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Conclusion
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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 transcorrelated method

Variational equations

Variational ground state energy

$$E_0 = \min_{\tau \in \mathbb{T}, \Phi \in \mathbb{F}} \frac{< \Phi | e^\tau \hat{H} e^\tau | \Phi >}{< \Phi | e^{2\tau} | \Phi >},$$

$\mathbb{T}$: spanned by a set of basis functions $\tau(R) = \sum_\alpha c_\alpha U_\alpha(R)$,
$\mathbb{F}$: defined by a given primitive orbital basis set and the rank of Φ.

Practical equations

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

Can only be used by QMC.

Transcorrelated equation of Boys and Handy

$$\begin{cases} < \Phi|U_\alpha e^{-\tau}(\hat{H} - E_{\mathsf{TC}})e^{\tau}|\Phi >= 0, & \text{(TC-C)} \\\\ < \frac{\partial \Phi}{\partial C_{i_\mu}}|e^{-\tau}(\hat{H} - E_{\mathsf{TC}})e^{\tau}|\Phi >= 0, & \text{(TC-O)} \end{cases}$$

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

$$\phi_i(\mathbf{r}) = \sum_\mu C_{i\mu}\chi_\mu(\mathbf{r}).$$

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.

V1:Variational equation for τ

$$< \Phi|U_\alpha e^\tau(\hat{H} - E_{var})e^\tau|\Phi >= 0,$$

TC-C:TC equation for τ

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

Variational features of the TC-C equation

- In the limiting case when $\mathbb{T} = \{U_\alpha\}$ 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 Φ is not much worse than Φ_{HF}.

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

	Ne			H_2O	CH_4
$N_{term}(\mathbb{T})$	8	17	92	103	125
TC	-0.3370(4)	-0.3431(4)	-0.3567(3)	-0.3290(5)	-0.2634(3)
VMC(τ_{TC})	-0.3367(5)	-0.3446(3)	-0.3581(2)	-0.3310(4)	-0.2657(2)
VMC(τ_{opt})	-0.3369(5)	-0.3458(4)	-0.3599(5)	-0.331(1)	-0.2678(5)

Variational transcorrelated equation

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

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

where the non-Hermitian term $[\hat{H}, \tau]$ simply drops out from equation (VTC-Φ) 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.

Hongjun Luo   **Variational transcorrelated method**

Variational transcorrelated orbital equation

Effective VTC Hamiltonian

Suppose $\mathbb{T}$ contains only up to two body terms

$$\tau = \frac{1}{2} \sum_{ij} u(\mathbf{r}_i, \mathbf{r}_j).$$

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

$$
\begin{aligned}
\tilde{H} &= \hat{H} + K + L, \\
K &= -\frac{1}{2} \sum_{pqrs} < pq|(\nabla_1 u(\mathbf{r}_1, \mathbf{r}_2))^2|rs > a_p^\dagger a_q^\dagger a_s a_r, \\
L &= -\frac{1}{2} \sum_{pqrstu} < pqr|\nabla_1 u(\mathbf{r}_1, \mathbf{r}_2) \cdot \nabla_1 u(\mathbf{r}_1, \mathbf{r}_3)|stu > a_p^\dagger a_q^\dagger a_r^\dagger a_u a_t a_s,
\end{aligned}
$$

Hartree-Fock type orbital equation

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

$$\tilde{F}_{\mu\nu} = \frac{1}{2} \frac{\partial^2}{\partial C_{i\mu} \partial C_{i\nu}} <\Phi|\tilde{H}|\Phi>.$$

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

$$<\mu j k|L_{123}|\nu j' k'> = -\int d^3 x \chi_\mu(x)\chi_\nu(x)\vec{T}_{jj'}(x) \cdot \vec{T}_{kk'}(x),$$

$$\vec{T}_{ij}(x_1) = \int d^3 x_2 \nabla_1 u(x_1, x_2)\phi_i(x_2)\phi_j(x_2).$$

A simple (but not efficient) algorithm

- Slater type primitive orbital basis,

- Polynomial basis for the correlation factor

$$u_{lmn,AB}(\mathbf{r}_i, \mathbf{r}_j) = \bar{r}_{iA}^l \bar{r}_{jB}^m \bar{r}_{ij}^n, \quad \bar{r} = r/(1 + r),$$

- 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.

	E_{HF}	E_{TC-C}	E_{VTC}	$E_{var}[\Psi_{TC}]$	E_{VMC}
VTC-O	-75.406	-75.807(1)	-75.814(1)	-75.813(1)	$-75.8069(5)^a$

a: J. Toulouse and C. J. Umrigar, J. Chem. Phys. 126(2007)084102, where slightly different bases for orbitals and τ were used.

Multi-configuration variational transcorrelated method

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 coeficients (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

$$\Psi = \sum_I c_I \Phi_I, \quad \sum_J <\Psi_I|\tilde{H}|\Psi_J> c_J = Ec_I,$$

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.

	E_{HF}	E_{TC-C}	E_{VTC}	$E_{var}[\Psi_{TC}]$	E_{VMC}
VTC-CI	-75.477	-75.829(1)	-75.832(1)	-75.832(1)	$-75.8094(5)^a$, $-75.8374(5)^b$

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.

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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-consistant 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.