Density Matrix Renormalization Group Tailored Coupled Cluster (DMRG-TCC)

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Overview

i) Coupled cluster struggles with strong correlated systems[1]
ii) Multi reference coupled cluster does not have a closed theory[1]
iii) Full-CI is a numerically expensive scheme[2]
iv) DMRG is an approximation to the FCI solution with a complexity comparable to CCSDT[2]

Subsequently, we use the DMRG to approximate the FCI solution and 'tailor' the single reference coupled-cluster method with this approximation.[3]

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[1] Lyakh, D. I., Musiał, M., Lotrich, V. F. and Bartlett, R. J. (2011). Multireference nature of chemistry: The coupled-cluster view. *Chemical reviews*, 112(1), 182-243

[2] Szalay, S., Pfeffer, M., Murg, V., Barcza, G., Verstraete, F., Schneider, R., & Legeza, Ö. (2015).Tensor product methods and entanglement optimization for ab initio quantum chemistry. *International Journal of Quantum Chemistry*, 115(19), 1342-1391.

[3] Veis, L., Antalik, A., Brabec, J., Neese, F., Legeza, Ö., & Pittner, J. (2016). Coupled cluster method with single and double excitations tailored by matrix product state wave functions. *The journal of physical chemistry letters*, 7(20), 4072-4078.

Electronic Schrödinger Equation

Rayleigh-Ritz variational principle:

$$E_0 = \min_{\substack{\psi \neq 0 \\ \psi \in \mathbb{V}}} \frac{\mathcal{A}(\psi,\psi)}{\langle \psi,\psi \rangle_{L^2}} \quad \text{and} \quad \psi_0 = \operatorname*{argmin}_{\substack{\psi \neq 0 \\ \psi \in \mathbb{V}}} \frac{\mathcal{A}(\psi,\psi)}{\langle \psi,\psi \rangle_{L^2}} \,, \tag{1}$$

with

$$\mathcal{A}(u,v) := \frac{1}{2}\langle \nabla u, \nabla v \rangle_{L^2} + \langle V u, v \rangle_{L^2}$$

and

$$\mathbb{V} := H^1\left(\left(\mathbb{R}^3 \times \left\{\pm\frac{1}{2}\right\}\right)^N\right) \cap \bigwedge_{i=1}^{N} L^2\left(\mathbb{R}^3 \times \left\{\pm\frac{1}{2}\right\}\right)$$

Approximation of $\mathbb{V}$

Spin orbitals: $\chi_i \in H^1(\mathbb{R}^3 \times \{\pm\frac{1}{2}\})$, $i \in \{1, ..., K\}$
Slater determinants (SD):
$\phi[\nu_1, ..., \nu_N](x_1, s_1; ...; x_N, s_N) = \frac{1}{\sqrt{N!}} \det(\chi_{\nu_i}(x_j, s_j))_{i,j=1}^N$
with $\nu_1 \leq ... \leq \nu_N$
FCI space $\mathcal{H}_K$: liner hull of all possible SDs
Reference State: W.l.o.g. $\phi_0 = \phi[1, ..., N]$
Excitation operator: $X_\mu : \mathcal{H}_K \to \mathcal{H}_K$ with $\mu = \binom{A_1, ..., A_k}{I_1, ..., I_k}$, where $o(\mu) = \{I_1, ..., I_k\} \subseteq \{1, ..., N\}$ and $\mathrm{v}(\mu) = \{A_1, ..., A_k\} \subseteq \{N+1, ..., K\}$ holds. k is called excitation rank and $\mathcal{J}$ the set of all possible excitation indices μ.
Wave characterization: Imposing $\langle \psi, \phi_0 \rangle_{L^2} = 1$

linear parametrization	$\psi = (I+S)\phi_0$, with $S = \sum_{\mu \in \mathcal{J}} c_\mu X_\mu$
exponential parametrization	$\psi = e^T \phi_0$, with $T = \sum_{\mu \in \mathcal{J}} t_\mu X_\mu$

Externally Corrected Coupled Cluster

Appealing ansatz[4]:

We approximate the different correlations by different methods.

- Choosing a small set of spin orbitals $\rightarrow$ static correlation
- The rest of the spin orbital basis $\rightarrow$ dynamic correlation

[4] Kinoshita, T., Hino, O., and Bartlett, R. J. (2005). Coupled-cluster method tailored by configuration interaction. *The Journal of chemical physics*, 123(7), 074106.

Splitting the Set of Spin Orbitals

Let $\{\chi_1, ..., \chi_K\} \subseteq H^1(\mathbb{R}^3 \times \{\pm\frac{1}{2}\})$ be a set of $L^2(\mathbb{R}^3 \times \{\pm\frac{1}{2}\})$-orthonormal spin orbitals with $K > N$ and ϕ_0 the considered reference Slater determinant. We define

$$\begin{aligned} \mathscr{B}_{CAS} &= \{\underbrace{\chi_1, ..., \chi_N}_{\text{occupied}}, \underbrace{\chi_{N+1}, ..., \chi_d}_{\text{unoccupied}}\} \ , \\ \mathscr{B}_{ext} &= \{\underbrace{\chi_{d+1}, ..., \chi_K}_{\text{external}}\} \ , \end{aligned} \tag{2}$$

the basis sets of the complete active space part $\mathscr{B}_{CAS}$ and of the external space part $\mathscr{B}_{ext}$. Using $\mathscr{B}_{CAS}$ we define $\mathcal{H}_{CAS}$.
Analogously, we split the set of excitation-indices $\mathcal{J}$ describing the set of possible excitations. We define

$$\mathcal{J}_{CAS} := \{\mu \in \mathcal{J} | X_\mu \phi_0 \in \mathcal{H}_{CAS}\} \tag{3}$$

and

$$\mathcal{J}_{ext} := \{\mu \in \mathcal{J} | X_\mu \phi_0 \notin \mathcal{H}_{CAS}\} \ . \tag{4}$$

TCC-Equations (Linked Formulation)

Given a DMRG solution $\phi_{CAS} = e^{T^{CAS}}\phi_0$, the linked DMRG-TCC-equations are:

$$\begin{cases} E_0^{(TCC)} = \left\langle \phi_0, e^{-T^{CAS}} e^{-T^{ext}} H e^{T^{ext}} e^{T^{CAS}} \phi_0 \right\rangle \\ \qquad\quad 0 = \left\langle \phi_\mu, e^{-T^{CAS}} e^{-T^{ext}} H e^{T^{ext}} e^{T^{CAS}} \phi_0 \right\rangle, \quad \mu \in \mathcal{J}_{ext} \end{cases}$$

TCC-Function

Let K, $N \in \mathbb{N}$ with $K > N$ be fixed, $\mathscr{B} = \{\chi_1, ..., \chi_K\}$ a set of $L^2(\mathbb{R}^3 \times \{\pm\frac{1}{2}\})$-orthonormal spin orbitals and ϕ_0 a reference state for an N-electron problem. Further, be $\mathscr{B}_{CAS}$ and $\mathscr{B}_{ext}$ a given partition of $\mathscr{B}$ and ϕ_{CAS} the DMRG solution on $\mathcal{H}_{CAS}$. We define

$$f : \mathbb{R}^{|\mathcal{J}_{ext}|} \to \mathbb{R}^{|\mathcal{J}_{ext}|};\ t \mapsto (f_\mu(t))_{\mu \in \mathcal{J}_{ext}} \ , \tag{5}$$

where

$$f_\mu(t) = \langle \phi_\mu, e^{-T^{CAS}} e^{-T} H e^{T} e^{T^{CAS}} \phi_0 \rangle_{L^2} \tag{6}$$

as the DMRG-TCC function. We call

$$\mathcal{V}_{ext} := \left\{ t \in \mathbb{R}^{|\mathcal{J}_{ext}|} \mid 1 = \langle \phi_0, exp(\sum_{\nu \in \mathcal{J}_{ext}} t_\nu X_\nu) \phi_{CAS} \rangle_{L^2} \right\} \tag{7}$$

the space of external cluster amplitudes. We further denote $\mathcal{H}_{ext} = \{T\,\phi_0 \mid t \in \mathcal{V}_{ext}\}$ the external space.

TCC-Equations (Linked Formulation) with TCC-Function

Using the DMRG-TCC function we can express the linked DMRG-TCC-equations as

$$\langle v, f(t) \rangle_2 = 0 \quad , \forall \; v \in \mathcal{V}_{ext} \; . \tag{8}$$

Local Version of Zarantonello's theorem

Let $f : X \to X'$ be a map between a Hilbert space $(X, \langle \cdot, \cdot \rangle, \| \cdot \|)$ and its dual X', and let $x_* \in B_\delta$ be a root, $f(x_*) = 0$, where B_δ is an open ball of radius δ around x_*.
Assume that f is Lipschitz continuous in B_δ, i.e., for all $x_1, x_2 \in B_\delta$ holds

$$\|f(x_1) - f(x_2)\|_{X'} \leq L\|x_1 - x_2\| \quad (9)$$

for a constant $L \geq 0$. Be further f locally strongly monotone in B_δ, i.e., for all $x_1, x_2 \in B_\delta$ holds

$$\langle f(x_1) - f(x_2), x_1 - x_2 \rangle \geq \gamma \|x_1 - x_2\|^2 \quad (10)$$

for some constant $\gamma > 0$. Then holds

i) The root x_* is unique in B_δ.

ii) Moreover, let $X_d \subset X$ be a closed subspace such that x_* can be approximated sufficiently well, i.e. the distance $d(x_*, X_d)$ is small. Then, the projected problem $f_d(x_d) = 0$ has a unique solution $x_d \in X_d \cap B_\delta$, and

$$\|x_* - x_d\| \leq \frac{L}{\gamma} d(x_*, X_d) \ . \quad (11)$$

Problematic

Note: In the regime of DMRG-TCC we have almost degenerate Eigenstates!

The assumption of a HOMO-LUMO gap, i.e., $\varepsilon_0 = \lambda_{N+1} - \lambda_N > 0$ is no longer justified.

However, as we use a basis splitting ansatz the assumption of a CAS-ext gap, i.e., $\varepsilon_0 = \lambda_{d+1} - \lambda_N > 0$ is reasonable.

Norm Estimates

Theorem

For $t \in \mathcal{V}_{ext}$ *there holds:* $\|t\|_{\mathcal{V}_{ext}} \sim \|T^{ext}\phi_{CAS}\|_{H^1}$

Theorem

For $t \in \mathcal{V}_{ext}$ *there holds:* $\|T\psi\|_{H^1} \leq C\|t\|_{\mathcal{V}_{ext}}\|\psi\|_{H^1}, \ \forall \psi \in \mathcal{H}_K.$
Moreover: $\|T\|_{\mathcal{B}(H^1)} \sim \|t\|_{\mathcal{V}_{ext}}$

Lipschitz Continuity

Theorem

The DMRG-TCC function is differentiable. Furthermore, the Fréchet derivative is Lipschitz continuous as well as all higher derivatives. In particular, for any neighborhood $U_R(0) \subseteq \mathcal{V}_{ext}$ with $f : U_R(0) \to \mathcal{V}_{ext}$ there exists a Lipschitz constant $L(R)$ such that

$$\|f(t) - f(t')\|_{\mathcal{V}_{ext}} \leq L(R)\|t_1 - t_2\|_{\mathcal{V}_{ext}} \tag{12}$$

for $\|t_1\|_{\mathcal{V}_{ext}}, \ \|t_2\|_{\mathcal{V}_{ext}} \leq R$.

Lipschitz Continuity (Proof)

The DMRG-TCC function's derivative is

$$(f'(t))_{\mu,\nu} = \langle \phi_\mu, e^{-T}[e^{-T_{\text{CAS}}} H e^{T_{\text{CAS}}}, X_\nu] e^{T} \phi_0 \rangle_{L^2} \ .$$

For given $s, u \in \mathcal{V}_{\text{ext}}$

$$|\langle f'(t)s, u\rangle_2| = |\langle U\phi_0, e^{-T}[e^{-T_{\text{CAS}}} H e^{T_{\text{CAS}}}, S] e^{T} \phi_0 \rangle_{L^2}| \leq C \|s\|_{\mathcal{V}_{\text{ext}}} \|u\|_{\mathcal{V}_{\text{ext}}} \ .$$

This shows the boundedness of $f'(t) : \mathcal{V}_{\text{ext}} \to \mathcal{V}_{\text{ext}}$. Hence, f is differentiable for all $t \in \mathcal{V}_{ext}$. Using the mean value theorem we obtain

$$\|f(t_2) - f(t_1)\|_{\mathcal{V}_{ext}} \leq \|f'(ct_1 + (1-c)t_2)\|_{\mathcal{B}(\mathcal{V}_{ext})} \|t_1 - t_2\|_{\mathcal{V}_{ext}} \ ,$$

where $t_1, \ t_2 \in \mathcal{V}_{ext}$ with $\|t_1\|_{\mathcal{V}_{ext}}, \ \|t_2\|_{\mathcal{V}_{ext}} \leq R$ for some $R > 0$ and $c \in (0,1)$. Hence, it follows the Lipschitz continuity of f.

Local Strong Monotonicity

We impose:

i)

$$\langle T\phi_0, (F - \Lambda_0)T\phi_0\rangle_{L^2} \geq \eta \|T\phi_0\|_{H^1}^2 \text{(Gårding estimate)}$$

ii) The operator

$$O : \mathcal{V}_{ext} \to H^1\left((\mathbb{R}^3 \times \{\pm\frac{1}{2}\})^N\right); t \mapsto e^{-T} e^{-T^{CAS}} W e^{T^{CAS}} e^{T} \phi_0 \ ,$$

where the fluctuation potential W, i.e., $W = H - F$, is Lipschitz continuous with a constant fulfilling

$$L < \frac{\eta}{C\|e^{T^{CAS}}\|_{\mathcal{B}(H^1)}^2 \|e^{-T^{CAS}}\|_{\mathcal{B}(H^1)}}$$

C is the constant s.t. $\|t\|_{\mathcal{V}_{ext}} \leq C\|T\phi_{CAS}\|_{H^1}$.

Local Strong Monotonicity (Proof)

We find

$$\langle f(t_1) - f(t_2), t_1 - t_2 \rangle_2 = \langle (T_1 - T_2)\phi_0, e^{-T_{\mathsf{CAS}}}(H_{t_1} - H_{t_2}) e^{T_{\mathsf{CAS}}}\phi_0 \rangle_{L^2}$$
$$= \langle (T_1 - T_2)\phi_0, e^{-T_{\mathsf{CAS}}}[F, T_1 - T_2] e^{T_{\mathsf{CAS}}}\phi_0 \rangle_{L^2} \tag{13}$$
$$+ \langle (T_1 - T_2)\phi_0, O(t_1) - O(t_2) \rangle_{L^2} \ ,$$

where $H_{t_i} = \exp(-T_i) H \exp(T_i)$. We define $[F, e^{T_{\mathsf{CAS}}}] = S$. As an excitation operator, S commutes with $e^{\pm T_{\mathsf{CAS}}}$ and $\Delta T = T_1 - T_2$. Therefore,

$$e^{-T_{\mathsf{CAS}}}[F, \Delta T] e^{T_{\mathsf{CAS}}} = F \Delta T - \Delta T F \ . \tag{14}$$

This yields

$$\langle f(t_1) - f(t_2), t_1 - t_2 \rangle_2 \geq \eta \|\Delta T \phi_0\|_{H^1}^2 - CL \|\Delta T \phi_0\|_{H^1} \|\Delta T \phi_{CAS}\|_{H^1}$$
$$\geq \gamma \|t_1 - t_2\|_{\mathcal{V}_{ext}}^2 \ , \tag{15}$$

with $\gamma > 0$.

DMRG-TCCSD

Theorem

Let $T_1^{ext} = 0$. *Then linked and unlinked DMRG-TCC equations are equivalent.*

Theorem

The solution of DMRG-TCCSD does not depend on T_k^{CAS} *for* $k > 3$.

Outlook

i) Explicit calculations for the involved constants

ii) Error estimate containing the DMRG error

iii) Error estimates for truncated DMRG-TCC

Thank you for your attention