Multi-Reference Coupled Cluster Method

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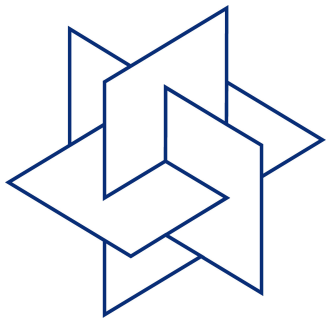

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Mathematics for key technologies

Overview:

I. Motivation

IIa. Coupled Cluster Method (TCCSD)

IIa. Complete Active Space Coupled Cluster Method (CAS-SS)

III. Bivariational Formulation

IV Theoretical Results and Conclusions

Motivation

Given the electronic Schrödinger equation

$$H\Psi = E\Psi$$

the wave function Ψ can be approximated

- by a possible nonlinear parametrization, e.g. as tensor network (matrix product) states $\Psi \in \mathcal{M} \Rightarrow$ DMRG
- or nonlinear parametrization, e.g. single reference coupled cluster CC $\Psi = e^T \Phi_0$, Φ_0 reference Slater determinant.
- multi-reference CC ansatz

$$\Psi \in \text{span}\{e^{T_j}\Phi_j \ : \ \Phi_j \in \mathscr{H}_{cas}, j = 0, \ldots, n-1\}$$

  where $\mathscr{H}_{cas}$ is a possibly not too large subspace generated by Slater determinants (Full CI Space)
- here we are interested in the first n Eigenfunctions for $E_0, \ldots, E_{n-1}$

Motivation - single reference Coupled Cluster (CC)

We try to replace $H : \mathscr{H} \to \mathscr{H}$ by a model operator $\overline{H}_0 : \mathscr{V} \to \mathscr{V}$ where $\mathscr{V} \subset \mathscr{H}$ is a suitable subspace of $\mathscr{H}$. We are searching a transformation $\varphi : \mathscr{H} \to \mathscr{H}$ and consider

$$\overline{H}_0 := P_0 \overline{H} P_0 =:= P_0 \varphi^{-1} \circ H \circ \varphi P_0 \ : \ \mathscr{V} \to \mathscr{V}$$

where $P_0 : \mathscr{H} \to \mathscr{V}$. For example the CC ansatz

$$\Psi = e^T \Phi \in \mathscr{H} \text{ where } \Phi \in \mathscr{V}$$

$$\overline{H} := \varphi^{-1} \circ H \circ \varphi = e^{-T} H e^T \ , \ \mathscr{H} \to \mathscr{H}$$

Notice that $\bar{H}$ is NOT Hermitean (or symmetric) !
Example: $\mathscr{V} := \text{span}\{\phi_0\}$ where ϕ_0 is a single Slater determinant e.g HF determinant: standard CC

$$\overline{H}_0 \phi_0 = E_{CC} \phi_0$$

State Universal CC with CASCC

Manifold of *oblique* n-dimensional projectors:

$$\mathscr{P}_n := \left\{ P = P^2 \mid TraceP = n \right\} \subset \mathscr{L}(\mathscr{H} \to \mathscr{H}) \ ,$$

$$P \in \mathscr{P}_n$$

if and only if there are *biorthogonal* sets $\tilde{B} = \{\tilde{\psi}_i\}_{i=1}^n \subset \mathscr{H}$ and $B = \{\psi_i\}_{i=1}^n \subset \mathscr{H}$ such that

$$u \mapsto Pu = \sum_{i=1}^{n} \psi_i \langle \tilde{\psi}_i, u \rangle \ , \ P = \sum_{i=1}^{n} |\psi_i\rangle\langle\tilde{\psi}_i| \ , \ \langle \tilde{\psi}_i, \psi_j \rangle = \delta_{i,j}$$

- For any pair of n-dimensional non-orthogonal subspaces $\mathscr{V} \subset \mathscr{H}$ and $\tilde{\mathscr{V}} \subset \mathscr{H}$, there is a unique projector P with these spaces as left/right ranges.
- P - density matrix

State Universal CC Bivariational principle

Consider the functional $S : \mathscr{P}_n \to \mathbb{C}$ given by

$$\boxed{S(P) = Tr(HP) = \sum_{i=1}^{n} \langle \tilde{\psi}_i, H\psi_i \rangle}$$

Problem: find $P_* \in \mathscr{P}_n$ such that $S'(P_*) = 0$ are stationary, is equivalent to the *two-sided Bloch equation*

$$\boxed{(I - P_*)HP_* = 0, \quad P_*H(I - P_*) = 0}$$

Equivalently, $\mathscr{V} = P_*\mathscr{H}$ is a *right invariant subspace* and $\tilde{\mathscr{V}} = P_*^\dagger \mathscr{H}$ is a *left invariant subspace*, simultaneously.
The projected *effective Hamiltonian* $H_{\text{eff}} = P_*HP_*$ has n exact eigenvalues E_i of H, and that $S(P_*) = \sum_{i=1}^{n} E_i$.

- In the literature, only the right Bloch equation is usually considered when developing SU-MRCC theories. This is a major component of the novelty here.
- The bivariational principle given here is a search for invariant spaces – not individual eigenvectors.

IIa

Single Reference Coupled Cluster - revisited

IIb

State Specific MR Coupled Cluster

L. Adamowicz, J.-P. Malrieu, and V. V. Ivanov, J. Chem. Phys. 112, 10075 (2000).

Second quantization - revisited

Second quantization: annihilation operators:

$$a_j \Psi[j, 1, \ldots, N] := \Psi[1, \ldots, N]$$

and $:= 0$ if j not apparent in $\Psi[\ldots]$.
The adjoint of a_b is a creation operator v

$$a_b^\dagger \Psi[1, \ldots, N] = \Psi[b, 1, \ldots, N] = (-1)^N \Psi[1, \ldots, N, b]$$

Theorem (Slater-Condon Rules)

$H : \mathscr{H} \to \mathscr{H}$ resp. $H : \mathscr{H}_{FCI} \to \mathscr{H}_{FCI}$ reads as (basis dependent)

$$\boxed{H = F + U = \sum_{p,q} f_r^p a_p^\dagger a_r + \sum_{p,q,r,s} u_{rs}^{pq} a_q^\dagger a_p^\dagger a_r a_s}$$

Excitation operators

Single excitation operator , Let $\Psi_0 = \Psi[1, \ldots, N]$ be a reference determinant then e.g.

$$\boxed{X_1^k \Psi_0 := a_k^\dagger a_1 \Psi_0}$$

$(-1)^{-p}\Psi_1^k = \Psi[k, 2, \ldots, N] = X_1^k \Psi_0 = X_j^k \Psi[1, \ldots, \ldots, N] = a_k^\dagger a_1 \Psi_0$

higher excitation operators

$$X_\mu := X_{l_1,\ldots,l_k}^{b_1,\ldots,b_k} = \prod_{i=1}^{k} X_{l_i}^{b_i} \quad , \quad 1 \leq l_i < l_{i+1} \leq N \ , \ N < b_i < b_{i+1} \ .$$

A CI solution $\Psi = c_0\Psi_0 + \sum_{\mu\in\mathcal{J}} c_\mu \Psi_\mu$ can be written by

$$\Psi = \left(c_0 + \sum_{\mu\in\mathcal{J}} c_\mu X_\mu \right) \Psi_0 \ , \ c_0, c_\mu \in \mathbb{R} \ .$$

Intermediate normalization: $c_0 := 1$ i.e. $\langle \Psi . \Psi_0 \rangle = 1$ and

$$[X_\mu, X_\nu] = 0$$

(Multi-Reference) Coupled-Cluster Ansatz

- One-particle basis, complete active space (CAS)

$$B_{cas} = \{\underbrace{\psi_1, \ldots, \psi_N}_{\text{occupied}}, \underbrace{\psi_{N+1}, \ldots, \psi_d}_{\text{CAS-unoccupied}}\},$$

$$B_K = \{\underbrace{\psi_1, \ldots, \psi_N, \psi_{N+1}, \ldots, \psi_d}_{\text{CAS}}, \underbrace{\psi_{d+1}, \ldots, \psi_K}_{\text{external}}\},$$

- Replacement of occupied by unoccupied orbitals in reference Ψ_0,

$$\Psi[1, \ldots, i_1, .., i_k, .., N] \xrightarrow{\text{“excitation”}} \Psi_\alpha = \Psi[1, ., \not{i}_1, .., \not{i}_k, .., a_1, .., a_k],$$

gives $$\mathbb{B}_K = \{\Psi_0\} \cup \{\Psi_\alpha \mid \alpha \in \mathcal{I}_K\}.$$

Indices: $i, j := 1, \ldots, N$ -occupied ; $a, b := N+1, \ldots, d$ - (unocc.) CAS ; $u, v = d+1, \ldots, K$ - external,

$z = K+1 \ldots, \infty$ virtual

Coupled-Cluster Ansatz

- Intermediate normalization $\langle \Psi, \Psi_0 \rangle := 1$, $\langle \Psi_0, \Psi_0 \rangle := 1$!!!
- Galerkin Full CI (CAS) solution Ψ is expressed by excitations,

$$\Psi = \Psi_0 + \Psi^* = \Psi_0 + \sum_{\mu \in J} s_\mu \Psi_\mu$$

- Coupled-Cluster-Ansatz:

Nonlinear Parametrisation for $\Psi = \Psi_0 + \Psi^*$:

cluster operator $T =: T(\mathbf{t}) = \sum_{\mu \in \mathcal{J}} t_\mu X_\mu$ such that

$$\Psi = e^{T(\mathbf{t})} \Psi_0,$$

$$\langle X_\mu \Psi_0, H e^{T(\mathbf{t})} \Psi_0 \rangle = E \langle X_\mu \Psi_0, e^{T(\mathbf{t})} \Psi_0 \rangle \quad \forall \ \mu \in \mathcal{J} \cup \{0\}.$$

Remark. The BCH expansion terminates and is computable!

Coupled-Cluster Ansatz

- Intermediate normalization $\langle \Psi, \Psi_0 \rangle := 1$, $\langle \Psi_0, \Psi_0 \rangle := 1$!!!
- Galerkin Full CI (CAS) solution Ψ is expressed by excitations,

$$\Psi = \Psi_0 + \Psi^* = \Psi_0 + \sum_{\mu \in J} s_\mu X_\mu \Psi_0 =: (I + S(s))\Psi_0$$

- Coupled-Cluster-Ansatz:

Nonlinear Parametrisation for $\Psi = \Psi_0 + \Psi^*$:

cluster operator $T =: T(\mathbf{t}) = \sum_{\mu \in \mathcal{J}} t_\mu X_\mu$ such that

$$\Psi = e^{T(\mathbf{t})}\Psi_0,$$

$$\boxed{\langle X_\mu \Psi_0, e^{-T(\mathbf{t})} H e^{T(\mathbf{t})} \Psi_0 \rangle = E \langle \Psi_\mu, \Psi_0 \rangle = \quad E\delta_{0,\mu} \ \forall \ \ \mu}$$

Remark. The BCH expansion terminates and is computable!

Coupled Cluster Method - Exponential-ansatz

Theorem (S. 06)

Let Φ_0 be a reference Slater determinant, e.g. $\Phi_0 = \Psi_{HF}$ and $\Psi \in \mathscr{H}_{FCI}$, $(\mathscr{H})$, satisfying

$$\langle \Psi, \Phi_0 \rangle = 1 \quad \textit{intermediate normalization} \ .$$

Then there exists an excitation operator
(T_1 - single-, T_2 - double- , ... excitation operators)

$$T = \sum_{i=1}^{N} T_i = \sum_{\mu \in \mathcal{J}} t_\mu X_\mu \quad \textit{such that}$$

$$\boxed{\Psi = e^T \Phi_0} = \Pi_\mu (I + t_\mu X_\mu) \Phi_0 \ .$$

Key observations: for analytic functions :

$$f(T) = \sum_{k=0}^{N} a_k T^k \text{ since } \ [X_\mu, X_\nu] = 0 \ , \ X_\mu^2 = 0 \ , \ T^N = 0 \ .$$

IIb

State Specific MR Coupled Cluster

L. Adamowicz, J.-P. Malrieu, and V. V. Ivanov, J. Chem. Phys. 112, 10075 (2000).

State Specific Multi-Reference Coupled Cluster Method

(Adamovicz, Piecuch et al. (2000) - A MR CC keeping all elegance of SR CC

Ansatz: Given FCI solution $\Psi_{cas}(\approx \Psi_{DMRG}$ for example)

$$\Psi = \Psi_K = e^{T^{ext}+T^{cas}}\Phi_0 := e^{T^{ext}}\Psi_{cas},$$

with allowed (external) excitations T^{ext} (only single /doubles)

$X_i^\alpha = a_\alpha^\dagger a_i$, $\alpha = N{+}1, \ldots K$ (unoccupied) , $i = 1, \ldots, N$ (occupied)

$$T^{ext} := T_1^{ext} + T_2^{ext}$$

$T_1^{ext} = \sum t_i^v X_i^v$, $v = d+1, \ldots, K$ external, T_2^{ext} contains only $\mu \notin \mathcal{I}_{cas}$, which are of form

$$X_\mu = X_{i,j}^{u,v} = X_i^u X_j^v, X_{i,j}^{a,v} = X_i^a X_j^v \quad \text{, i.e. } \Psi_\mu = X_{i,j}^{a,v}\Psi_0 \perp \mathscr{H}_{cas}$$

$$\boxed{\Psi := e^{T_1^{ext}+T_2^{ext}} e^{(T_1^{cas}+T_2^{cas}+T_3^{cas}+T_4^{cas}+\cdots)}\Psi_0 := e^{T_1^{ext}+T_2^{ext}}\Psi_{cas}}$$

State Specific (CAS) Coupled Cluster Method

We introduce the non symmetric CAS Hamiltonian $\overline{H}^{cas} = \overline{H}^{cas}(\mathbf{t})$ on the CAS space

$$\boxed{\overline{H}^{cas}(\mathbf{t}) = P_{\mathscr{H}_{cas}} e^{-T^{ext}(\mathbf{t})} H e^{T^{ext}(\mathbf{t})} P_{\mathscr{H}_{cas}}}$$

We us consider the linked (external) CC equations

$$0 = \mathbf{f}_{\mu}(\mathbf{t}) := \langle X_{\mu}\phi_0, e^{-T^{ext}(\mathbf{t})} H e^{T^{ext}(\mathbf{t})} \Phi_{cas} \rangle \quad , \quad \forall \mu \in \mathcal{I}_{ext}$$

together with

$$\overline{H}^{cas}(\mathbf{t})\Phi_{cas} = E\Phi_{cas}$$

Then the total (CC) energy $E \approx E_{cc}$ is an eigenvalue of $\overline{H}^{cas}$ with right eigenvector Φ_{cas} i.e.

$$\boxed{\overline{H}^{cas}\Phi_{cas} = E\Phi_{cas}}$$

$\overline{H}^{cas}$ is considered as our model operator acting on $\mathscr{H}_{cas}$

State Universal CC

We consider n first m (approximate) eigenstates (e.g. the (ground) state is degenerate), (with a positive spectral gap to the next)

$$H\Psi_i = E\Psi_i \ , \ i = 1, \ldots, n \ , \ E = E_0 \ , \ \langle \Psi_i, \Psi_j \rangle = \delta_{i,j}$$

Consider

$$\begin{aligned} \Psi_j &:= e^{T_j}\Phi_j \ , \ T_j = \sum_\mu (t_\mu)_j X_\mu \ , \ \mu \in \mathcal{I}_{ext} \ , \ \Lambda_j = \sum_\mu \lambda_{j,\mu} X_\mu \\ \tilde{\Psi}_j &:= e^{-T_j^\dagger}(\tilde{\Phi}_j + \Lambda_j \phi_0) \ , \ \tilde{\Phi}_j, \Phi_j \in \mathscr{H}_{cas} \end{aligned}$$

we impose (bi-) orthogonality

$$\langle \tilde{\Psi}_i, \Psi_j \rangle = \delta_{i,j}$$

$$\begin{aligned} \delta_{i,j} = \langle \tilde{\Psi}_i, \Psi_j \rangle &= \langle \tilde{\Phi}_i, e^{T_j - T_i}\Phi_j \rangle + \langle \Lambda_i \phi_0, e^{T_j - T_i}\Phi_j \rangle \\ &= \langle \tilde{\Phi}_i, \Phi_j \rangle + \sum \lambda_{i,\mu} \langle X_\mu \phi_0, e^{T_j - T_i}\Phi_j \rangle \end{aligned}$$

IIa
Bivariational Principle

A state-specific multi-reference coupled- cluster method based on the bivariational principle J. Chem. Phys. 153, 024106 (2020); Tilmann Bodenstein and Simen Kvaal

Non-Unitary Treatment of Quantum Problems

CAS Coupled Cluster Method - Bivariational Formulation

We consider the bivariational energy functional using $\langle \psi_0, \Phi_{cas} \rangle := 1$

- optimize

$$\mathcal{E}(\tilde{\Phi}, \Phi, \mathbf{t}) := \frac{\langle \tilde{\Phi}, \overline{H}^{cas}(\mathbf{t})\Phi \rangle}{\langle \tilde{\Phi}, \Phi \rangle}$$

- subordinated to the linked amplitude equation

$$0 = \mathbf{f}(\mu) := \langle X_\mu \phi_0, e^{-T(\mathbf{t})} H e^{T(\mathbf{t})} \Phi \rangle \forall \mu \in \mathcal{I}_{ext}$$

(constraint optimization)
Following S. Kvaal, let us introduce the Lagrangian

$$\mathcal{L}(\tilde{\Phi}, \Phi, \mathbf{t}, \lambda) \quad := \quad \mathcal{E}(\tilde{\Phi}, \Phi, \mathbf{t}) + \frac{1}{\langle \tilde{\Phi}, \Phi \rangle} \boldsymbol{\lambda}^T \mathbf{f}(\mathbf{t})$$

We are looking for the stationary points $(\tilde{\Phi}, \Phi, \mathbf{t}, \boldsymbol{\lambda})^*$ of $\mathcal{L}$, then $\mathcal{L}((\tilde{\Phi}, \Phi, \mathbf{t}, \boldsymbol{\lambda})^*)$ are (approximate) eigenvalues of the original H

CAS Coupled Cluster Method - Bivariational Formulation

Equivalently we can use the Lagrangian

$$\mathcal{L}(\tilde{\Phi}, \Phi, \mathbf{t}, \Lambda, E) \quad := \quad \langle \tilde{\Phi}, \overline{H}^{cas}(\mathbf{t})\Phi \rangle + \boldsymbol{\lambda}^T \mathbf{f}(\mathbf{t}) + E(1 - \langle \tilde{\Phi}, \Phi \rangle)$$

Working equations for $E, \Phi_{cas} \in \mathscr{H}_{cas}$ and external amplitudes $\mathbf{t}$ are given by differentiation of $\mathcal{L}$ w.r.t. $\tilde{\Phi}$, $\boldsymbol{\lambda}$, Φ and $\mathbf{t}$:

$$\begin{aligned}
\langle \delta\tilde{\Phi}, (\overline{H}^{cas}(\mathbf{t}) - E)\Phi_{cas} \rangle &= 0 \ \forall \delta\tilde{\Phi} \in \mathscr{H}_{cas} \\
\langle X_\mu \phi_0, e^{-T^{ext}(\mathbf{t})} H e^{T^{ext}(\mathbf{t})} \Phi_{cas} \rangle &= 0 \ \forall \mu \in \mathcal{I}_{ext} \\
\langle \delta\Phi, (\overline{H}^{cas}(\mathbf{t}) - E)^\dagger \tilde{\Phi}_{cas} \rangle &= \langle \delta\Phi, \sum_\mu \lambda_\mu X_\mu \phi_0 \rangle \ \forall \delta\Phi \in \mathscr{H}_{cas} \\
(D\mathbf{f})_\mathbf{t} \boldsymbol{\lambda} &= \partial_\mathbf{t} \mathcal{L} = \partial_\mathbf{t} E(\mathbf{t}) \\
\text{where } (D\mathbf{f})_{\nu,\mu} &:= \langle X_\mu \phi_0, e^{-T^{ext}} [H, X_\nu] e^{T^{ext}} \Phi_{cas} \rangle
\end{aligned}$$

denotes the CC Jacobian

In Bodenstein & Kvaal they considered $\tilde{\Psi} := e^{-T^\dagger}(\tilde{\Phi} + \sum_\mu \lambda_\mu X_\mu \tilde{\Phi})$

State Universal CC with CASCC

We consider n first eigenstates (e.g. the (ground) state E_1 is degenerate), (with a positive spectral gap to the next)

$$H\Psi_i = E_i\Psi_i \ , \ i = 1, \ldots, n \ , \ , \ \langle \Psi_i, \Psi_j \rangle = \delta_{i,j}$$

Consider

$$\Psi_j \ := \ e^{T_j(\mathbf{t})}\Phi_j \ , \ T_j = (\mathbf{t}_\mu) \ , \ \mu \in \mathcal{I}_{ext} \ , \ \Lambda_j = \sum_\mu \lambda_{j,\mu} X_\mu$$

$$\tilde{\Psi}_j \ := \ e^{-T_j^\dagger}(\tilde{\Phi}_j + \Lambda_j\phi_0) \ , \ \tilde{\Phi}_j, \Phi_j \in \mathscr{H}_0 := \mathscr{H}_{cas}$$

we impose (bi-) orthogonality

$$\langle \tilde{\Psi}_i, \Psi_j \rangle = \delta_{i,j}$$

where ϕ_0 e.g is the HF determinant.

$$\begin{aligned} \delta_{i,j} = \langle \tilde{\Psi}_i, \Psi_j \rangle &= \langle \tilde{\Phi}_i, e^{T_j - T_i}\Phi_j \rangle + \langle \Lambda_i\phi_0, e^{T_j - T_i}\Phi_j \rangle \\ &= \langle \tilde{\Phi}_i, \Phi_j \rangle + \sum_\mu \lambda_{i,\mu} \langle X_\mu\phi_0, e^{T_j - T_i}\Phi_j \rangle \end{aligned}$$

State Universal Lagrangian

We modifiy the Lagrangian to enforce bi-orthogonality.Let us introduce the vector valued functions

$$\Phi := (\Phi_i)_{i=1,\dots,n}\ ,\ \tilde{\Phi} := (\tilde{\Phi}_i)_{i=1,\dots,n},\ T := (T_i)_{i=1,\dots,n}\ ,\ \Lambda_i = (\sum_{\mu} \lambda_{i,\mu} X_\mu)$$

together with a new Lagrange multiplier $\Sigma = (\Sigma_{i,j})$

$$\begin{aligned}\mathcal{L}(\Phi, \tilde{\Phi}, T, \Lambda) \quad := \quad & \sum_{i,j=1}^{n} \Big(\langle \tilde{\Phi}_i, e^{-T_i} H e^{T_j} \Phi_j \rangle + \langle \Lambda_i \phi_0, e^{-T_i} H e^{T_j} \Phi_j \rangle \Big) \\ & + \sum_{i,j=1}^{n} \Sigma_{i,j} \Big(\delta_{i,j} - \langle \Lambda_i \phi_0, e^{T_j - T_i} \Phi_j \rangle - \langle \tilde{\Phi}_i, \Phi_j \rangle \Big)\end{aligned}$$

where $e^{-T_j} H e^{T_j}$ is non symmetric! and depends on j

State Universal Lagrangian -Coupled equations

The stationary points of the Lagrangian (1st order conditions) are given in weak form by

$$\begin{aligned}
\frac{\partial J}{\partial \tilde{\Phi}}(\delta\tilde{\Phi}_i) &= \sum_{j=1}^{n}\Big(\langle \delta\tilde{\Phi}_i, e^{-T_i} H e^{T_j}\Phi_j\rangle - \langle \delta\tilde{\Phi}_i, \Phi_j\rangle\Big) = 0 \quad \forall \delta\tilde{\Phi} \in \mathscr{H}_{cas}\ ,\ i = 1,\ldots,n \\
\frac{\partial J}{\partial \Lambda_i} &= \sum_{j=1}^{n}\Big(\langle \phi_0, e^{-T_i} H e^{T_j}\Phi_j\rangle - \Sigma_{i,j}\langle \phi_0, e^{T_j - T_i}\Phi_j\rangle\Big) = 0 \quad \forall\ i = 1,\ldots,n \\
\frac{\partial J}{\partial \Phi_j}(\delta\Phi) &= \sum_{i=1}^{n}\Big(\langle \tilde{\Phi}_i, e^{-T_i} H e^{T_j}\delta\Phi\rangle + \langle \Lambda_i\phi_0, e^{-T_i} H e^{T_j}\delta\Phi\rangle\Big) \\
&\quad - \sum_{i=1}^{n}\Sigma_{i,j}\Big(\langle \Lambda_i\phi_0, e^{T_j - T_i}\delta\Phi\rangle + \langle \tilde{\Phi}_i, \delta\Phi\rangle\Big) \ \forall\ \delta\Phi \in \mathscr{H}_{cas}\ j = 1,\ldots,n \\
\frac{\partial J}{\partial T}(T_i) &= \cdots \quad \forall i = 1,\ldots,n
\end{aligned}$$

Complicated set of $4n$ coupled equations!!! Can it be decoupled?

State Universal Lagrangian

Let us consider a Lagrange to be diagonal

$$\Sigma = \text{ diag } (\delta_{i,j}) \ \Rightarrow \Sigma = \text{ diag } (E_j)$$

Then model equations becomes decoupled
We differentiate w.r.t. $\tilde{\phi}_j \in \mathscr{H}_{cas}, \Lambda_j$ and $T_j = T(\mathbf{t}_j)$ and obtain 1st order conditions

$$\begin{aligned}
\text{we set } \bar{H}_j &:= e^{-T_j} H e^{T_j} \ , \ E_j := \frac{\langle \tilde{\Psi}_j, H\Psi_j \rangle}{\langle \tilde{\Psi}_j, \Psi_j \rangle} \\
\langle \delta\tilde{\Phi}, (\bar{H}_j - E_j)\phi_j \rangle &= 0 \ \forall \delta\tilde{\phi} \in \mathscr{H}_{cas} \\
f_\mu(\mathbf{t}_j) := \langle X_\mu \phi_0, \bar{H}_j \phi_j \rangle &= 0 \ \forall \mu \in \mathcal{I}_{ext} \\
\sum_\mu \lambda_\mu \langle X_\mu \phi_0, [\bar{H}_j, X_\nu] \phi_j \rangle &= rhs_j(\nu)
\end{aligned}$$

There is another set of equations for the dual solutions $\tilde{\Phi}_j$!

State Universal Lagrangian - Dual Equations

Let us consider a diagonal $\Sigma = \text{ diag } (E_j)$
In order to compute $\tilde{\phi}_j$, we introduce $\mathscr{S} := \text{ span } \phi_j : j = 1, \ldots, n\}$
and we $\mathscr{W} \perp \mathscr{S}$ s.t. $\mathscr{H}_{cas} = \mathscr{S} \oplus \mathscr{W}$ and decompose

$$\tilde{\phi}_j := \phi'_j + \chi_j \text{ where } \chi_j \in \mathscr{W} \ , \ \phi'_j \in \mathscr{S}$$

In order to compute $\chi_j \in \mathscr{W}$ we consider

$$\begin{aligned} \langle \delta\phi, (\bar{H}_j - E_j)^\dagger (\tilde{\phi}_j + \Lambda_j \phi_0) \rangle &= 0 \ \forall \delta\phi \in \mathscr{W} \\ \langle \delta\phi, (\bar{H}_j - E_j)^\dagger \chi_j \rangle &= \langle \delta\phi, E_j \Lambda_j \phi_0 - \bar{H}_j^T \phi'_j \rangle \end{aligned}$$

the unknown $\phi'_j = \sum_\ell c_{j,\ell} \phi_\ell \in \mathscr{S}$ can be computed applying bi-orthogonality

$$\delta_{i,j} = \langle \Lambda_i \phi_0, e^{T_j - T_i} \phi_j \rangle + \langle \phi'_i, \phi_j \rangle = \langle \Lambda_i \phi_0, e^{T_j - T_i} \phi_j \rangle + \sum_\ell c_{i,\ell} \langle \phi_\ell, \phi_j \rangle$$

$$I = R + CM \Rightarrow \ C = (I - R) M^{-1} \text{ where } m_{i,j} = \langle \phi_i, \phi_j \rangle$$

Density Matrix

In order to check the previous results, we compute the matrix entries

$$\begin{aligned}\langle\tilde{\psi}_k, H\psi_j\rangle &= \langle\tilde{\phi}_k, e^{-T_k} H e^{T_j}\phi_j\rangle + \langle\Lambda_k\phi_0, e^{-T_k} H e^{T_j}\phi_j\rangle \\ &= E_j(\langle\phi'_k, \phi_j\rangle + \langle\chi_k, \phi_j\rangle) + E_j\langle\Lambda_k\phi_0, e^{T_j - T_k}\phi_j\rangle \\ &= E_j(\langle\phi'_k, \phi_j\rangle + \langle\Lambda_k\phi_0, e^{T_j - T_k}\phi_j\rangle) = E_j\delta_{k,j}\end{aligned}$$

Here we have used

$$\langle\delta, \bar{H}_j\phi_j\rangle = E_j\langle\delta, \phi_j\rangle \text{ for all } \delta \in \mathscr{H}_{cas}$$

since

$$\langle X_\mu\phi_0, e^{-T_j} H e^{T_j}\phi_j\rangle = 0 \text{ for all } \mu \in \mathcal{I}_{ext} \ .$$

This shows that

$$P = \sum_{j=1}^{n} |\psi_j\rangle\langle\tilde{\psi}_j|$$

is the desired projection (density matrix). Moreover it is of diagonal form.

Remarks: CC Energy.

Let us suppress the index $j = 1, \ldots n$. Let $T^{ext} = T_1 + T_2$ (CCSD), due to normalization $\langle \phi_0, \Psi \rangle = \langle \phi_0, \Phi \rangle := 1$.

$$
\begin{aligned}
E(\mathbf{t}) &= \langle \tilde{\Phi} + \Lambda \phi_0, e^{-T} H e^{T} \Phi \rangle = \langle \phi_0, H\Phi \rangle + E_{ext} \\
&=: E_{cas} + \langle \phi_0, H(I + T_1 + T_2 + \frac{1}{2}(T_1)^2 + T_1^{cas} T_1)\phi_0 \rangle \\
\text{if } T_1^{ext} = T_1 &:= \text{0 terms in brown are 0}
\end{aligned}
$$

We frequently choose $T_1^{ext} := 0$.

Remarks: Projected CAS Coupled Cluster Method

Let $T(\mathbf{t}) := T^{ext} = \sum_{\mu \in \mathcal{I}_{ext}} t_\mu X_\mu \ , \ 0 \neq \mu \in \mathcal{I}_{ext} \subset \mathcal{J}$
The unlinked projected Coupled Cluster formulation

$$0 = \langle X_\mu \phi_0, (H - E(\mathbf{t}))e^{T(\mathbf{t})+T^{cas}}\phi_0 \rangle =: g_\mu(\mathbf{t}), \mathbf{t} = (t_\nu)_{\nu \in \mathcal{I}_{ext}}, \mu \in \mathcal{I}_{ext}$$

The linked projected Coupled Cluster formulation consists in

$$0 = \langle X_\mu \phi_0, e^{-T(\mathbf{t})} H e^{T(\mathbf{t})} \Phi \rangle =: f_\mu(\mathbf{t}) \ , \ \mathbf{t} = (t_\nu)_{\nu \in \mathcal{I}_{ext}}, \ \mu \in \mathcal{I}_{ext}$$

In the sequel, we suppress (neglect) T_1^{ext} terms

Theorem

(S.& Faulstich & Laestadius) If $T_1^{ext} = 0$, the both methods are equivalent

$$\Psi^{CC}_{linked} = \Psi^{CC}_{unlinked}$$

This needs not to hold if $T_1^{ext} \neq 0$!

Projected CAS - Coupled Cluster Method

Let us consider the linked CC equations

$$0 = \mathbf{f}(t_\mu) := \langle X_\mu \phi_0, e^{-T(\mathbf{t})} H e^{T(\mathbf{t})} \Phi \rangle \quad , \quad \forall \mu \in \mathcal{I}_{ext}$$

Theorem

The solution does not depend on T_k^{cas}, S_k^{cas}, for $k > 3$ (!), in particular, we obtain the equations

$$0 = \mathbf{f}(t_\mu) = \langle X_\mu \phi_0, e^{-T} H e^{T} \Phi \rangle = \langle X_\mu \phi_0, (I - T_2) H (I + T_2 + \frac{1}{2}(\hat{T}_2)^2) \Phi \rangle$$

for all $\mu \in \mathcal{I}_{ext}$.

Solving this problem is not essentially more expensive than single reference CC!

Here we have dropped the index j since the equations decouple

The problem is to solve the FCI CAS equations, for large CAS space.

CAS Eigenvalue Problem

For external excitations $T = T_2 = \sum_{\mu \in \mathcal{I}_{ext}} t_\mu X_\mu$ we obtain (we neglect T_1 in the sequel)

Lemma

$$\begin{aligned}
\overline{H}^{cas}(\mathbf{t}) &= P_{\mathscr{H}_{cas}} e^{-T(\mathbf{t})} H e^{T(\mathbf{t})} P_{\mathscr{H}_{cas}} \\
&= P_{\mathscr{H}_{cas}} H P_{\mathscr{H}_{cas}} + P_{\mathscr{H}_{cas}} H T_2 P_{\mathscr{H}_{cas}} + \frac{1}{2} P_{\mathscr{H}_{cas}} H \hat{T}_2^2 P_{\mathscr{H}_{cas}} \\
&= P_{\mathscr{H}_{cas}} H (I + T_2 + \frac{1}{2} \hat{T}_2^2) P_{\mathscr{H}_{cas}}
\end{aligned}$$

$T_2 = \tilde{T}_2 + \hat{T}_2$ where $\hat{T}_2$ contains the mixed excitation terms $u_{i,j}^{a,v} X_i^a X_j^v$, and $\tilde{T}_2$ no mixed terms .

Numerical Solution of FCI Problem

Remark:

$$P_{\mathscr{H}_{cas}} H(I + T_2 + \frac{1}{2}\hat{T}_2^2) P_{\mathscr{H}_{cas}}$$

involves 3-particle operators!

We recommend to use an approximate FCI solver either

- QC-DMRG (tensor trains $\simeq$ matrix product states) or
- Monte Carlo FCI (Alavi et al.)

Simplifications: Tailored CC

$\Phi \approx \Phi_{cas}$

$$\langle \delta\tilde{\Phi}, (H - E_{cas})\Phi_{cas} \rangle = 0 \ \forall \delta\tilde{\Phi} \in \mathscr{H}_{cas}$$

$\Rightarrow$ Φ_{cas} and E_{cas} do NOT depend on $\mathbf{t}$!

Numerical results for TCC-DMRG

L. Veis, A. Antalik, J. Brabec, F. Neese, Ö. Legeza, and J. Pittner, *Coupled Cluster Method with Single and Double Excitations Tailored by Matrix Product State Wave Functions*, J. Phys. Chem. Lett., 2016, 7 (20), pp 4072 - 4078

In their approach the T_3^{cas} amplitudes are neglected!!!

Table: TCCSD Energies (E+2086 in au) of the Cr_2 *Molecule*(r = 1.5 Å)

Method	E + 2086	Δ E
DMRG(12,12)	0.071746	0.373
TCCSD(12,12)	0.424826	0.020
DMRG(12,21)	0.252552	0.192
TCCSD(12,21)	0.437171	0.007
CCSD	0.344277	0.100
CCSD(T)(45)	0.422229	0.022
CCSDTQ(45)	0.430244	0.014
DMRG(48,42)	0.444784	-

Table: Spectroscopic paramet. N_2, calculated by cc-pVTZ Basis

	ω (cm^{-1})	$\Delta\omega$	ω (cm^{-1})	$\Delta\omega$	r_0 (Å)	Δr_0
CCSD	2423.3	64.7	12.75	1.57	1.0967	0.0010
TCCSD(6,6)	2376.3	17.7	13.57	0.75	1.1009	0.0032
DMRG(10,19)	2298.8	59.8	13.72	0.60	1.1112	0.0135
TCCSD(10,19)	2347.3	11.3	13.91	0.41	1.1036	0.0059
experiment	2358.57	-	14.324	-	1.09768	-

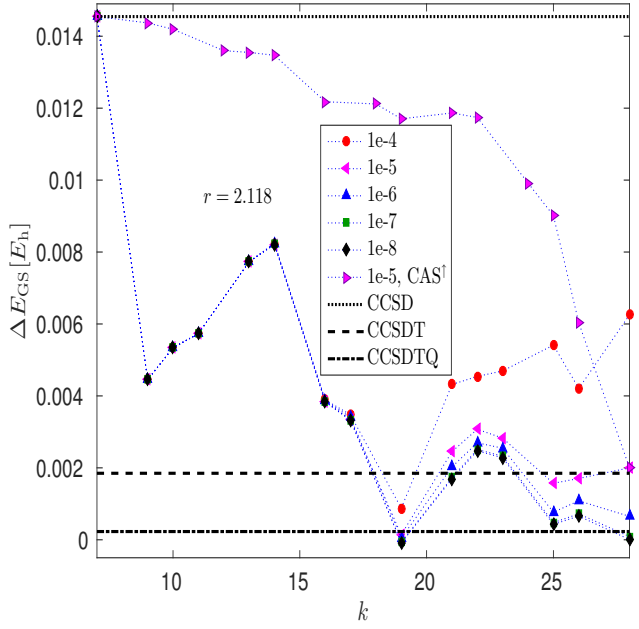
Early Numerical Experiments - TCC

Error N_2 ground state energies at bond length $r = 2.118$ equilibrium. $\frac{K}{2} = 28$, $d = 2k$ size of CAS basis set.
FCI Reference solution computed by CCSDTQVH

Numerical and theoretical aspects of the DMRG-TCC method exemplified by the nitrogen dimer,
Journal of chemical theory and computation, 15 (2019), pp. 2206 – 2220.

F. M. Faulstich, M. Mate, A. Laestadius, M. A. Csirik, L. Veis, A. Antalik, J. Brabec,

R. Schneider, J. Pittner, S. Kvaal,



Theoretical Results

The previous results from tailored CC can be extended to CAS-CC and improved. (`work in progress `) *Numerical and theoretical aspects of the DMRG-TCC method exemplified by the nitrogen dimer*,
Journal of chemical theory and computation, 15 (2019), pp. 2206 – 2220.
F. M. Faulstich, M. Mate, A. Laestadius, M. A. Csirik, L. Veis, A. Antalik, J. Brabec, R. Schneider, J. Pittner, S. Kvaal,

Analysis of the tailored coupled-cluster method in quantum chemistry,
SIAM Journal on Numerical Analysis, 57 (2019), pp. 2579 – 2607
F. M. Faulstich, A. Laestadius, O. Legeza, R. Schneider, and S. Kvaal,

work in progress

The use of (large) spaces $\mathscr{H}_{cas}$ improves the stability (inf-sup constant) of the amplitude equations

Conclusions

- CAS CC avoids most problems of single reference CCSD, without compromising the elegant numerical treatment of single reference formalism
- excited states can be treated well, great improvement compared to equation of motion (EOM)
- Tailored CC is more a perturbational approach for improving a reference solution Ψ_{cas}, 1st iteration.
- Analysis is only local, i.e. T^{ext} small, but it shows
  - importance of quality of reference solution Ψ_{cas}
  - importance of of stability
  - degenerate and quasi-degenerate ground state can be computed as well
- computational cost: CCSD (+ DMRG (for FCI))
- the *CAS* space must be sufficiently large (DMRG or MCFCI)!
- the solution is (only) slightly biased by the choice of reference determinant Ψ_0, i.e. the choice of the occupied space,

Bi-variational Formulation and Expectation Values

Why we are interested in the dual solution $\tilde{\Psi}$?
However: approximating expectation values of an operator $O : \mathscr{H} \to \mathscr{H}$, $\langle O \rangle := \langle \Psi, O\Psi \rangle$, let $\langle \tilde{\Psi}, \Psi \rangle := 1$.

- $\langle \tilde{\Phi}, (e^T)^\dagger O e^T \Phi \rangle \approx \langle \Psi, O\Psi \rangle$ is not computable!
- alternative: $\langle (\tilde{\Phi} + \Lambda\phi_0), e^{-T} O e^T \Phi \rangle = \langle \tilde{\Psi}, O\Psi_{cc} \rangle \approx \langle \Psi, O\Psi \rangle$

We may estimate

$$|\langle \tilde{\Psi}, O e^T \Phi \rangle - \langle \Psi, O\Psi \rangle| \leq c_1 \|\Psi - \tilde{\Psi}\| + c_2 \|\Psi - e^T \Phi\|$$

Note that $e^{-T^\dagger}$ is a de-excitation operator and $e^{-T^\dagger} \mathscr{H}_{cas} = \mathscr{H}_{cas}$.
Thus the first term $\|\Psi - e^{-T^\dagger} \tilde{\Phi}\|$ is relatively large!!!
(In the single reference case $\tilde{\Phi} = \phi_0$!) But $\tilde{\Psi}$ is a poor approximation of Ψ
This shows the importance of computing $\tilde{\Psi}$!!!
`to be extended in future!!!  - work in progress`

Appendix - Two Lagrangian

Better: Consider the CC Lagrangian

$$\mathcal{L}(\Phi, \tilde{\Phi}, T, \Lambda) := \frac{\langle \tilde{\Phi}, L\Phi \rangle}{\langle \tilde{\Phi}, \Phi \rangle} + \frac{1}{\langle \tilde{\Phi}, \Phi \rangle} \langle \Lambda \phi_0, L\Phi \rangle$$

we differentiate w.r.t. $\tilde{\Phi}, \Lambda$ and Φ and $T = T(\mathbf{t})$

$$\begin{aligned}
L = L(\mathbf{t}) &:= e^{-T} H e^{T} \ , \ E := \frac{\langle \tilde{\Phi}, L\Phi \rangle}{\langle \tilde{\Phi}, \Phi \rangle} \\
\langle \delta\tilde{\Phi}, (L - E)\Phi \rangle &= 0 \ \forall \delta\tilde{\Phi} \in Y_h \\
f_\mu(\mathbf{t}) = \langle X_\mu \phi_0, L\Phi \rangle &= 0 \ \forall \mu \in \mathcal{I}_{ext} \\
\sum_\mu \langle \tilde{\Phi} + \Lambda_\mu \phi_0, [L, X_\nu]\Phi \rangle &= 0 \ \ \forall \nu \in \mathcal{I}_{ext} \\
\langle (L^\dagger - E)\tilde{\Phi}, \delta\Phi \rangle &= -\langle \Lambda\phi_0, L\delta\Phi \rangle \ \ \forall \delta\Phi \in X_h (!!!)
\end{aligned}$$

here $\tilde{\Psi} \in V_{cas} \oplus \text{span} \left\{ X_\mu \phi_0 : \mu \in \mathcal{I}_{ext} \right\}$

Projection Methods - Petrov Galerkin Methods

Alternative (Bodenstein & Kvaal) Consider the CC Lagrangian

$$\mathcal{L}(\Phi, \tilde{\Phi}, T, \Lambda) := \frac{\langle \tilde{\Phi}, L\Phi \rangle}{\langle \tilde{\Phi}, \Phi \rangle} + \frac{1}{\langle \tilde{\Phi}, \Phi \rangle} \langle \Lambda \tilde{\Phi}, L\Phi \rangle$$

we differentiate w.r.t. $\tilde{\Phi}, \Lambda$ and Φ and $T = T(\mathbf{t})$, $\langle \tilde{\Phi}, \Phi \rangle := 1$,

$$\begin{aligned}
L = L(\mathbf{t}) &:= e^{-T} H e^{T} \\
\langle \delta\tilde{\Phi}, (L - E)\Phi \rangle &= 0 \ \forall \delta\tilde{\Phi} \in Y_h \\
f(\mathbf{t}) = \langle X_\mu \tilde{\Phi}, L\Phi \rangle &= 0 \ \forall \mu \in \mathcal{I}_{ext} \\
\langle (L^\dagger - E)\tilde{\Phi}, \delta\Phi \rangle + \langle \Lambda\tilde{\Phi}, L\delta\Phi \rangle &= 0 \ \ \forall \delta\Phi \in X_h (!!!) \\
\sum_\mu \langle \tilde{\Phi} + \Lambda_\mu \tilde{\Phi}, [L, X_\nu]\Phi \rangle &= 0 \ \ \forall \nu \in \mathcal{I}_{ext}
\end{aligned}$$

$\tilde{\Psi} \in V_{cas} \oplus \text{span} \{X_\mu \tilde{\Phi} : \mu \in \mathcal{I}_{ext}\}$