Explicitly Correlated Driven Similarity Renormalized Group

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Background

Strongly correlated systems requires methods that extend beyond mean-field theory due to their inherently multiconfigurational nature. Dynamic correlation plays a critical role in refining predictions.
Recent advancementsof Driven Similarity Renormalization Group (DSRG) method, offer intruder-state-free frameworks with promising applications in challenging systems like the Cr_2 dimer and organic molecule singlet-triplet gap calculations.
Basis Set Incompleteness Error (BSIE) remains a key limitation in wavefunction-based ab initio electronic structure theory. Explicitly correlated F12 theory has emerged as a robust solution, systematically accelerating basis set convergence by incorporating explicit electron correlation terms.
In this work, we demonstrate that the Canonical Transformed F12 (CT-F12) method provides a universal, accurate, and computationally efficient strategy to eliminate BSIE in multireference systems. T his approach enables high-precision electronic structure calculations while maintaining simplicity in implementation.

Canonical Transformed F12

In nonrelativistic quantum chemistry ,the exact hamiltonian can be written as

$$\hat{H} = h^{\mu}_{\nu}\hat{E}^{\nu}_{\mu} + \frac{1}{2}v^{\mu\lambda}_{\nu\kappa}\hat{E}^{\nu\kappa}_{\mu\lambda} \tag{1}$$

where h^{μ}_{ν} and $v^{\mu\lambda}_{\nu\kappa}$ are one electron integral and two electron repulsion integral respectivly. $\mu, \nu, \lambda, \kappa, \cdots$ indicates infinitly numbers of complete one-particle basis.
Because Hamiltonian is an infinitly large matrix, CT-F12 use an Unitary Transformation $e^{\hat{A}}$ to downfold this into a finite basisset hamiltonian $\hat{\bar{H}}$.

$$\hat{\bar{H}} = e^{\hat{A}^{\dagger}}\hat{H}e^{\hat{A}} \tag{2}$$

The transofrmation is determinated by cusp conditon, and the operator

$$\hat{A} = \frac{1}{2}G^{\alpha\beta}_{ij}(\hat{E}^{\alpha\beta}_{ij} - \hat{E}^{ij}_{\alpha\beta}) \tag{3}$$

where $\hat{E}^{\alpha\beta}_{ij}$ is spin-free excitation operator (from occupied$(A \cup C)$ to virtual $(V \cup CABS \cup \infty)$ .The amplitude is

$$G^{\alpha\beta}_{ij} = \frac{3}{8}\langle\alpha\beta|\hat{Q}_{12}F_{12}|ij\rangle + \frac{1}{8}\langle\alpha\beta|\hat{Q}_{12}F_{12}|ji\rangle \tag{4}$$

$$F_{12} = -\frac{1}{\gamma}e^{-\gamma r_{12}} \tag{5}$$

Where the F_{12} is used to model cusp condition ,$\hat{Q}_{12}$ aims to avoid double-count of configuration in downfoled hamiltonian.And the factor $\frac{3}{8}, \frac{1}{8}$ in G distinguishes the coalescence of same-spin or opposite-spin electrons.
Finallyl use BCH formula ,and ommit operator more than two body (three body operator is approximted by cumulent approximation),we get

$$\hat{\bar{H}} \approx \hat{H} + [\hat{H}, \hat{A}]_{1,2} + \frac{1}{2}[[\hat{F}, \hat{A}]_{1,2}, \hat{A}]_{1,2} \tag{6}$$

$$= \bar{h}^{q}_{p}\hat{E}^{p}_{q} + \frac{1}{2}\bar{v}^{rs}_{pq}\hat{E}^{pq}_{rs} \tag{7}$$

F12-DSRG-PT2

In F12-DSRG the dressed hamiltonian $\hat{\bar{H}}$ is transformed by another unitary transformation,which drives the dressed hamiltonian toward block diagonal format.

$$\hat{\bar{H}}(s) = U(s)^{\dagger}\hat{\bar{H}}U(s) \tag{8}$$

The unitary transformation is determinated by the condition

$$[\hat{\bar{H}}(s)]_N = \hat{R}(s) \tag{9}$$

where $[\bar{H}(s)]_N$ is nondiagonal part of hamiltonian and $\hat{R}(s)$ is source operator.
$U(s)$ is parameterzed similar to Unitary coupled cluster

$$U(s) = e^{\hat{S}(s)} \quad \hat{S}(s) = \sum_k \hat{T}_k - \hat{T}^{\dagger}_k \quad \hat{T}_k(s) = \frac{1}{(k!)^2}\sum_{ij\cdots}\sum_{ab\cdots} t^{ij\cdots}_{ab\cdots}\{\hat{a}^{ab}_{ij}\} \tag{10}$$

And the source operator is choosed to make off-diagonal matrix elements

$$\tilde{v}^{ab}_{ij}(s) = \tilde{v}^{ab}_{ij}(0)e^{-s(\Delta^{ij\cdots}_{ab\cdots})^2} \tag{11}$$

In DSRG-PT2 , after perturbative analysis,we get

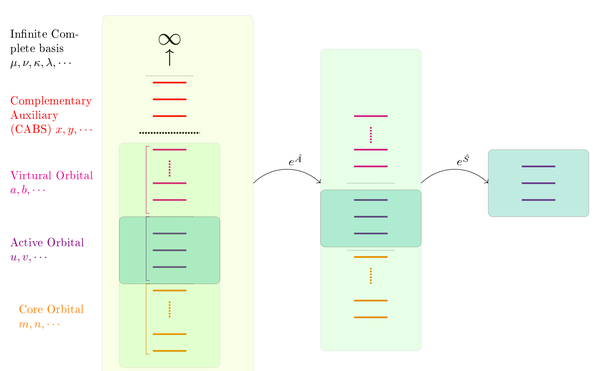
$$t^{i}_{a}(s) = \frac{[f^{i}_{a} + \sum_{ux}\Delta^{x}_{u}t^{iu}_{ax}(s)\gamma^{x}_{u}][1 - e^{-s(\Delta^{ij}_{ab})^2}]}{\Delta^{i}_{a}} \tag{12}$$

$$t^{ij}_{ab}(s) = \frac{v^{ij}_{ab}[1 - e^{-s(\Delta^{ij}_{ab})^2}]}{\Delta^{ij}_{ab}} \tag{13}$$

The energy is determined from the eigenvalue of transformed hamiltonina

$$E = \langle\Phi|\hat{\bar{H}}(s)|\Phi\rangle \tag{14}$$

Where $|\Phi\rangle$ is eigenvector of dressed hamiltonian $\hat{\bar{H}}$.



Result

Discussion

- We do not take the basisset incompletness error of casscf into account.
- Most time consumming step is calculation of integral
- Machine Learning (like DeepH)is a promissing way to accelerate this calculation.

References

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