Developments in Truncating the Unitary Coupled Cluster Functional

Harper Grimsley

Virginia Tech

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What is UCC?

Coupled Cluster (CC) Ansatz:

$$|\Psi_{CC}\rangle = \exp\left(\sum_{ia} t_a^i \hat{a}_i^a + \frac{1}{4}\sum_{ijab} t_{ab}^{ij} \hat{a}_{ij}^{ab} + \dots\right)|\phi_0\rangle$$
$$= \exp\left(\hat{T}_1 + \hat{T}_2 + \dots\right)|\phi_0\rangle$$

Unitary Coupled Cluster (UCC) Ansatz:

$$|\Psi_{UCC}\rangle = \exp\left(\sum_{ia} \kappa_a^i \left(\hat{a}_i^a - \hat{a}_a^i\right) + \frac{1}{4}\sum_{ijab} \kappa_{ab}^{ij} \left(\hat{a}_{ij}^{ab} - \hat{a}_{ab}^{ij}\right) + \dots\right)|\phi_0\rangle$$
$$= \exp\left(\hat{K}_1 + \hat{K}_2 + \dots\right)$$

UCC Pros and Cons

Pros:

1. Variational- Unitary rotations are norm-preserving
2. Size-extensive- Exponential ansatz is separable
3. *Probably* exact in limit of untruncated $\hat{K}$- (Cite Evangelista)
4. Theoretically efficient to implement on a quantum computer, particularly in approximate *Trotter* form

$$|\Psi_{tUCC}\rangle = \prod_{ia} \exp\left(\kappa_a^i \left(\hat{a}_i^a - \hat{a}_a^i\right)\right) \prod_{\substack{i<j \\ a<b}} \exp\left(\kappa_{ab}^{ij} \left(\hat{a}_{ij}^{ab} - \hat{a}_{ab}^{ij}\right)\right) \ldots |\phi_0\rangle$$

Cons:

1. Classically intractable- BCH is infinite, even if $\hat{K}$ is truncated!

$$E_{UCC} = \langle\phi_0|\hat{H} + [\hat{H}, \hat{K}] + \frac{1}{2}[[\hat{H}, \hat{K}], \hat{K}] + \ldots |\phi_0\rangle$$

Truncated BCH UCC

- The simplest truncation scheme is by BCH order
- Equivalent to a Taylor approximation of the energy in $\vec{\kappa}$
- In the simplest version, $\hat{K}$ includes only doubles, and the expansion stops at second order (i.e. a single Newton step)

$$E_{UCCD} \approx \min(\langle\phi_0|\hat{H} + [\hat{H}, \hat{K}_2] + \frac{1}{2}[[\hat{H}, \hat{K}_2], \hat{K}_2]|\phi_0\rangle$$
$$= \sum_{\substack{i<j,k<l \\ a<b,c<d}} \langle\phi_0|\hat{H}_N|\phi_{ij}^{ab}\rangle \langle\phi_{ij}^{ab}|\hat{H}_N^{-1}|\phi_{kl}^{cd}\rangle \langle\phi_0|\hat{H}_N|\phi_{kl}^{cd}\rangle$$

- This is equivalent to LCCD/CEPA(0)/D-MBPT(∞), but it is obvious how to systematically improve it

Single Excitations

When singles are introduced, this approach becomes different than LCCSD, due to terms like

$$\langle \phi_0 | \hat{H}_N \hat{a}_i^a \hat{a}_j^b | \phi_0 \rangle$$

and

$$\langle \phi_0 | \hat{H}_N \hat{a}_a^i \hat{a}_{ij}^{ab} | \phi_0 \rangle$$

The second term can repair size-inconsistency in CEPA for non-HF references, partially cancelling terms like:

$$\langle \phi_0 | \hat{a}_{ab}^{ij} \hat{H}_N \hat{a}_i^a | \phi_0 \rangle$$

For 2nd-order UCCSD, size consistency is fully restored by using a Trotter approximation where the doubles are applied to $|\phi_0\rangle$ before the singles

Size Consistency Restoration

Monomer 1	Monomer 2	UCCSD (a.u.)	tUCCSD (a.u.)
Water	Water	-1.464728×10^{-6}	1.826663×10^{-10}
Water	Methane	-1.049710×10^{-6}	3.109335×10^{-11}
Methane	Methane	-6.567442×10^{-7}	$-4.530420 \times 10^{-11}$

Table: Size-inconsistency errors in the 2nd-order Taylor energies from Untrotterized and Trotterized UCCSD. Kohn-Sham orbitals from B3LYP were used to introduce non-Brillouin singles. All calculations were performed in the 6-31G(d,p) basis.

- Using a "doubles-then-singles" Trotter ordering is equivalent to deleting disconnected terms from the energy functional, but is less complex
- If the correct operator ordering is used, tUCCSD...N is exact for N electrons (Cite Evangelista)

Singular Hessians: A National Crisis

- In quadratic methods like ours, singular values in $\hat{H}_N$ cause the energy to diverge
- Negative singular values in the matrix to be inverted can make these methods yield an energy **above** the reference