

Extending Single-Reference Coupled-Cluster Methods to Multireference Problems with the Help of Configuration Interaction and Connected Moment Expansions



Second Year Oral Examination

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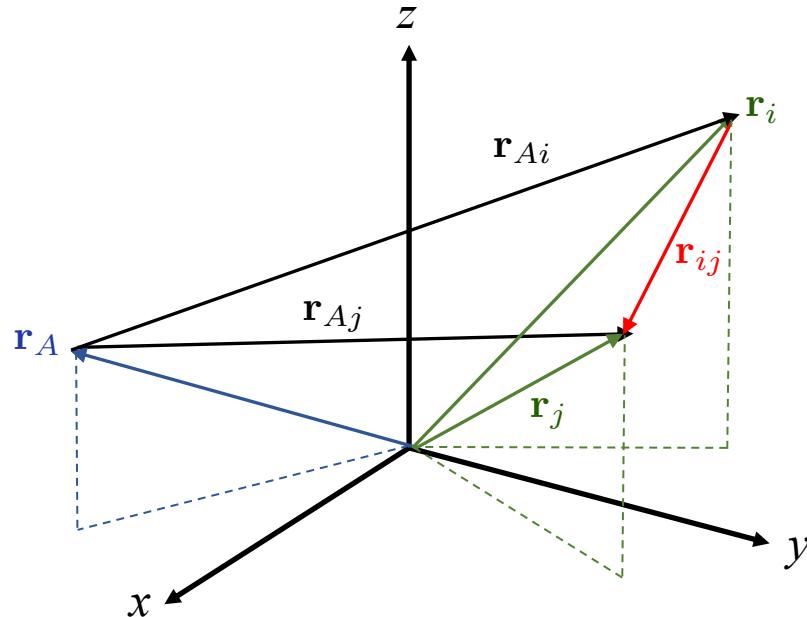
Contents

❖ Introduction to Electronic Structure Theory



Introduction to Electronic Structure Theory

- The goal of the electronic structure theory is to solve the time-independent Schrödinger equation for many-electron systems.



$$H\Psi_\mu(\mathbf{X};\mathbf{R}) = E_\mu(\mathbf{R})\Psi_\mu(\mathbf{X};\mathbf{R})$$

$$\mathbf{X} = (\mathbf{x}_1, \dots, \mathbf{x}_N)$$

Electronic Coordinates
 $\mathbf{x}_i = (\mathbf{r}_i, \sigma_i)$

$$H = \boxed{-\frac{1}{2} \sum_i \nabla_i^2 - \sum_{A,i} \frac{Z_A}{r_{Ai}}} + \boxed{\sum_{i>j} \frac{1}{r_{ij}}}$$

One-body Term

Two-body Term

- This equation is analytically solvable only for one-electron systems, such as, H, He^+ , and H_2^+ . For many-electron systems, this problem must be solved numerically, typically using an approach that employs a pre-designed basis set.

Introduction to Electronic Structure Theory

- Define single-particle basis functions (e.g., LCAO-type molecular spin-orbitals) obtained by solving mean-field equations, such as Hartree–Fock, using a pre-determined atomic orbital basis set.

$$V \equiv \{\phi_p(\mathbf{x}), p = 1, \dots, \dim V\}$$

Exact Solution: $\dim V = \infty$

In Practice: $\dim V < \infty$

- Construct Slater determinants using the given single-particle basis.

$$\Phi_{p_1 \dots p_N}(\mathbf{x}_1, \dots, \mathbf{x}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_{p_1}(\mathbf{x}_1) & \phi_{p_2}(\mathbf{x}_1) & \dots & \phi_{p_N}(\mathbf{x}_1) \\ \phi_{p_1}(\mathbf{x}_2) & \phi_{p_2}(\mathbf{x}_2) & \dots & \phi_{p_N}(\mathbf{x}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_{p_1}(\mathbf{x}_N) & \phi_{p_2}(\mathbf{x}_N) & \dots & \phi_{p_N}(\mathbf{x}_N) \end{vmatrix}$$



Introduction to Electronic Structure Theory

- The exact wavefunction is the linear combination of all Slater determinants

$$\Psi_\mu(\mathbf{x}_1, \dots, \mathbf{x}_N) = \sum_{p_1 < \dots < p_N} c_{p_1 \dots p_N}^\mu \Phi_{p_1 \dots p_N}(\mathbf{x}_1, \dots, \mathbf{x}_N) = \sum_I c_I^\mu \Phi_I(\mathbf{x}_1, \dots, \mathbf{x}_N).$$

- Determine the coefficients c_I^μ and the energies E_μ by solving the matrix eigenvalue problem

$$\mathbf{H}\mathbf{C}^\mu = E_\mu \mathbf{C}^\mu ,$$

where the matrix elements of the Hamiltonian are

$$H_{IJ} = \langle \Phi_I | H | \Phi_J \rangle = \int d\mathbf{x}_1 \dots d\mathbf{x}_N \Phi_I^*(\mathbf{x}_1, \dots, \mathbf{x}_N) H \Phi_J(\mathbf{x}_1, \dots, \mathbf{x}_N).$$

- This procedure, known as the **full configuration interaction (FCI)**, produces the exact solution to the Schrödinger equation within a given single-particle basis set.

Introduction to Electronic Structure Theory

$$D_{KNS} = \frac{2S+1}{K+1} \binom{K+1}{N/2-S} \binom{K+1}{N/2+S+1}$$



Weyl-Paldus Formula [H. Weyl, 1946 and J. Paldus, 1974] Counts the number of configuration state functions spanning the many-electron Hilbert space

Dimensions of $S = 0$ FCI spaces of molecules using correlation-consistent valence basis sets (frozen-core approximation)

Basis Set	System and Number of Correlated Electrons			
	C_2H_2 ($N=10$)	C_2H_4 ($N=12$)	...	C_6H_6 ($N=30$)
cc-pVDZ	2.7×10^{10}	1.4×10^{13}		5.6×10^{34}
cc-pVTZ	2.1×10^{14}	1.1×10^{18}		3.8×10^{46}
cc-pVQZ	1.9×10^{17}	4.9×10^{21}		2.9×10^{55}

- The rapidly growing dimensionality of the FCI eigenvalue problem makes it **inapplicable to systems with more than a few correlated electrons and realistic basis sets.**
- Alternative approaches are required to study the most chemical problems of interest.

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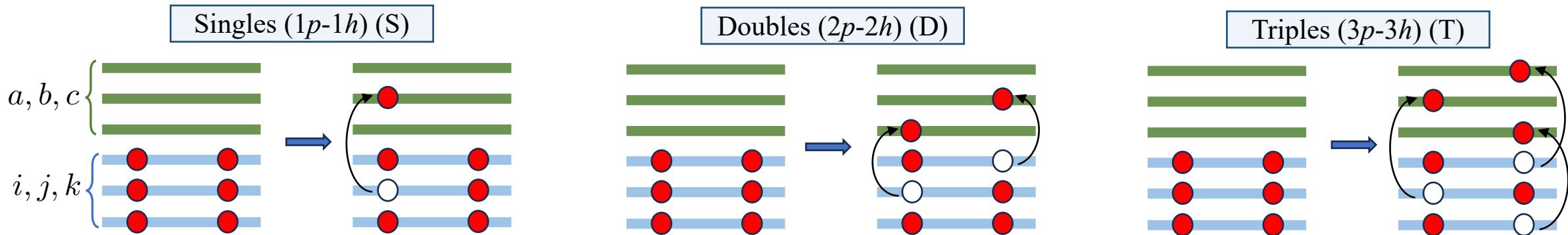
Single-Reference Coupled-Cluster (CC) Theory

$$|\Psi_0^{(A)}\rangle = e^{T^{(A)}} |\Phi_0\rangle \quad T^{(A)} = \sum_{n=1}^{m_A} T_n$$

$$T_1 |\Phi_0\rangle = \sum_{i,a} t_a^i |\Phi_i^a\rangle$$

$$T_2 |\Phi_0\rangle = \sum_{\substack{i < j \\ a < b}} t_{ab}^{ij} |\Phi_{ij}^{ab}\rangle$$

$$T_3 |\Phi_0\rangle = \sum_{\substack{i < j < k \\ a < b < c}} t_{abc}^{ijk} |\Phi_{ijk}^{abc}\rangle$$



$$m_A \leq N, m_A = N \Rightarrow \text{FCI}$$

$$m_A = 2$$

$$T^{(\text{CCSD})} = T_1 + T_2$$

$$m_A = 3$$

$$T^{(\text{CCSDT})} = T_1 + T_2 + T_3$$

$$m_A = 4$$

$$T^{(\text{CCSDTQ})} = T_1 + T_2 + T_3 + T_4$$

$$\text{CCSD} \quad n_{\text{o}}^2 n_{\text{u}}^4 (\mathcal{N}^6)$$

$$\text{CCSDT} \quad n_{\text{o}}^3 n_{\text{u}}^5 (\mathcal{N}^8)$$

$$\text{CCSDTQ} \quad n_{\text{o}}^4 n_{\text{u}}^6 (\mathcal{N}^{10})$$

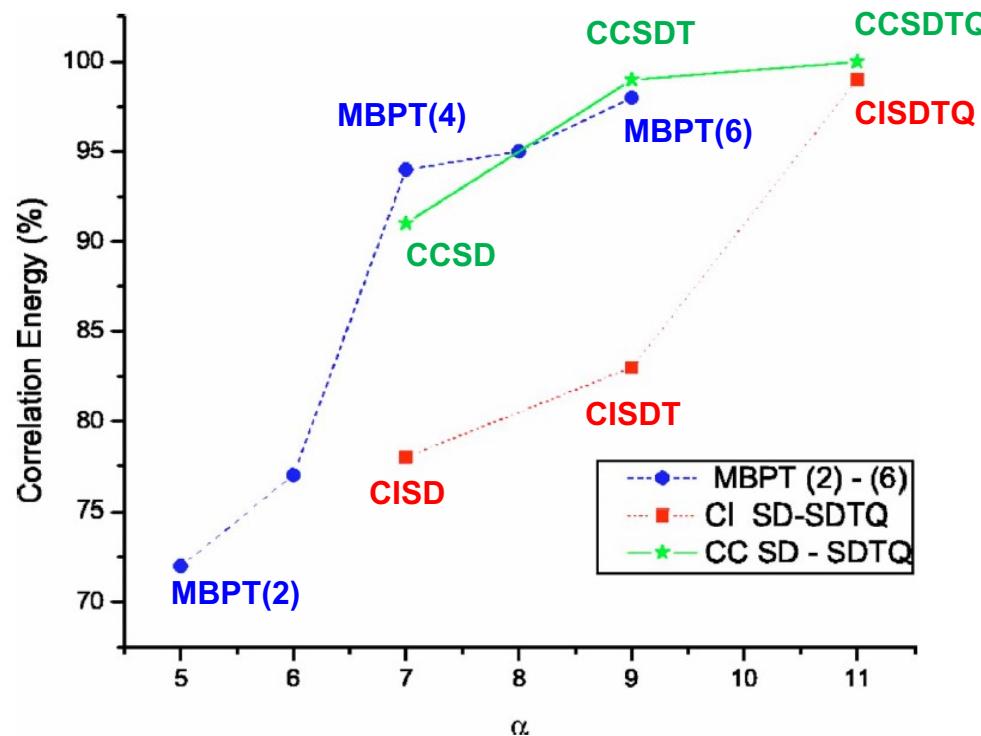
$$\langle \Phi_{i_1 \dots i_k}^{a_1 \dots a_k} | \bar{H}^{(A)} | \Phi_0 \rangle = 0, \quad k = 1, \dots, m_A; \quad \bar{H}^{(A)} = e^{-T^{(A)}} H e^{T^{(A)}} = (H e^{T^{(A)}})_C$$

$$E_0^{(A)} = \langle \Phi_0 | \bar{H}^{(A)} | \Phi_0 \rangle$$



Why CC Theory?

- **Size-extensivity of CC approximations:** No loss of accuracy when system size is made larger.
- **Separability or size consistency:** CC wave functions separate correctly if the reference determinant is separable.
- **Fast convergence** toward the exact, FCI, limit.

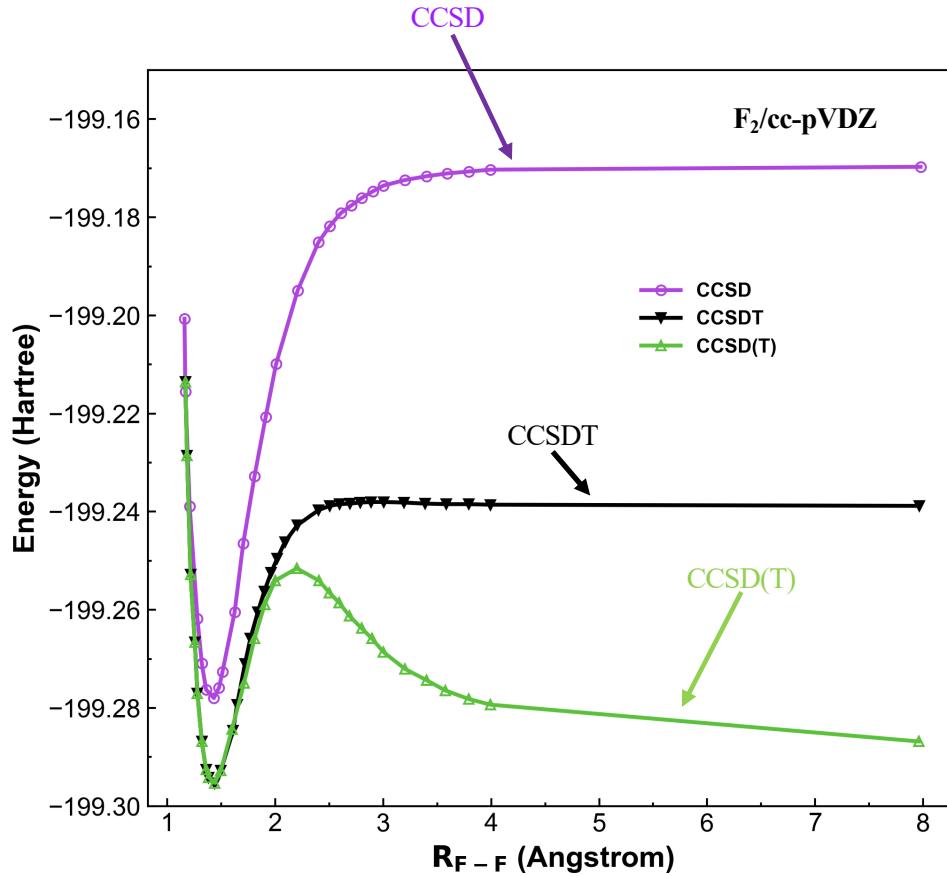


BH, HF, H₂O, SiH₂, CH₂
C₂, N₂



Challenges of Single-Reference CC Theory

How to incorporate T_n components with $n > 2$, needed to achieve a quantitative description, without running into prohibitive computational costs of CCSDT, CCSDTQ, and similar schemes?



Traditional Approaches

Add non-iterative perturbative corrections to CCSD, e.g., of the CCSD(T) type (i.e., replace iterative \mathcal{N}^8 steps of CCSDT by iterative \mathcal{N}^6 steps plus \mathcal{N}^7 noniterative operations).



How can one develop methods and algorithms within the SRCC framework to achieve that desired accuracy of high-level CC methods, such as CCSDT and CCSDTQ, while mitigating the pitfalls associated with various perturbative schemes, such as CCSD(T)?

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High-Level CC Energetics via CC($P;Q$) Moment Expansions

$$E_0^{(P+Q)} = E_0^{(P)} + \delta_0(P;Q)$$

CC(P) energy obtained in the P space $\mathcal{H}^{(P)}$.

Correction due to correlation effects captured with the help of the Q space $\mathcal{H}^{(Q)}$.

$$\delta_0(P; Q) = \sum_{|\Phi_K\rangle \in \mathcal{H}^{(Q)}} \ell_{0,K}(P) \mathfrak{M}_{0,K}(P)$$

Moments of CC Equation

$$\mathfrak{M}_{0,K}(P) = \langle \Phi_K | \bar{H}^{(P)} | \Phi_0 \rangle$$

$$\ell_{0,K}(P) = \langle \Phi_0 | (1 + \Lambda^{(P)}) \bar{H}^{(P)} | \Phi_K \rangle / D_{0,K}(P)$$

$$\bar{H}^{(P)} = e^{-T^{(P)}} H e^{T^{(P)}} = (H e^{T^{(P)}})_C$$

$$D_{0,K}(P) = E_0^{(P)} - \langle \Phi_K | \bar{H}^{(P)} | \Phi_K \rangle$$



High-Level CC Energetics via CC($P;Q$) Moment Expansions

$$E_0^{(P+Q)} = E_0^{(P)} + \delta_0(P;Q)$$

$\mathcal{G}^{(S)}$ \equiv set of all singles
 $\mathcal{G}^{(D)}$ \equiv set of all doubles

CC(P) energy obtained in the P space $\mathcal{H}^{(P)}$.

Correction due to correlation effects captured with the help of the Q space $\mathcal{H}^{(Q)}$.

Example of a target: **CCSDT**

Conventional

$$\begin{aligned}\mathcal{H}^{(P)} &= \mathcal{G}^{(S)} \oplus \mathcal{G}^{(D)} \\ \mathcal{H}^{(Q)} &= \mathcal{G}^{(T)}\end{aligned}\xrightarrow{\hspace{1cm}} \text{CR-CC}(2,3)$$

M. Włoch, J. R. Gour, and P. Piecuch

Active-Orbital-based

$$\begin{aligned}\mathcal{H}^{(P)} &= \mathcal{G}^{(S)} \oplus \mathcal{G}^{(D)} \oplus \mathcal{G}^{(t)} \\ \mathcal{H}^{(Q)} &= \mathcal{G}^{(T)} \ominus \mathcal{G}^{(t)}\end{aligned}\xrightarrow{\hspace{1cm}} \text{CC}(t;3)$$

J. Shen, N. P. Bauman, and P. Piecuch

Quantum-Monte-Carlo-driven

$$\begin{aligned}\mathcal{H}^{(P)} &= \mathcal{G}^{(S)} \oplus \mathcal{G}^{(D)} \oplus \mathcal{G}^{(t^{(MC)})} \\ \mathcal{H}^{(Q)} &= \mathcal{G}^{(T)} \ominus \mathcal{G}^{(t^{(MC)})}\end{aligned}\xrightarrow{\hspace{1cm}} \text{CC}(t^{(MC)};3)$$

J. E. Deustua, S. H. Yuwono, A. Chakraborty, J. Shen, and P. Piecuch

Selected-CI-driven

$$\begin{aligned}\mathcal{H}^{(P)} &= \mathcal{G}^{(S)} \oplus \mathcal{G}^{(D)} \oplus \mathcal{G}^{(t^{(CIPSI)})} \\ \mathcal{H}^{(Q)} &= \mathcal{G}^{(T)} \ominus \mathcal{G}^{(t^{(CIPSI)})}\end{aligned}\xrightarrow{\hspace{1cm}} \text{CC}(t^{(CIPSI)};3)$$

K. Gururangan, S. S. Priyadarsini, J. Shen, and P. Piecuch

Adaptive CC($P;Q$)

$$\begin{aligned}\mathcal{H}^{(P)} &= \mathcal{G}^{(S)} \oplus \mathcal{G}^{(D)} \oplus \mathcal{G}^{(t^{(Ad)})} \\ \mathcal{H}^{(Q)} &= \mathcal{G}^{(T)} \ominus \mathcal{G}^{(t^{(Ad)})}\end{aligned}\xrightarrow{\hspace{1cm}} \text{CC}(t^{(Ad)};3)$$

K. Gururangan and P. Piecuch



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$$E_0^{(P+Q)} = E_0^{(P)} + \delta_0(P;Q)$$

$\mathcal{G}^{(S)}$ \equiv set of all singles
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Correction due to correlation effects captured with the help of the Q space $\mathcal{H}^{(Q)}$.

Example of a target: **CCSDT**

Conventional

$$\begin{aligned} \mathcal{H}^{(P)} &= \mathcal{G}^{(S)} \oplus \mathcal{G}^{(D)} \\ \mathcal{H}^{(Q)} &= \mathcal{G}^{(T)} \end{aligned} \xrightarrow{\hspace{1cm}} \text{CR-CC}(2,3)$$

M. Włoch, J. R. Gour, and P. Piecuch

Active-Orbital-based

$$\begin{aligned} \mathcal{H}^{(P)} &= \mathcal{G}^{(S)} \oplus \mathcal{G}^{(D)} \oplus \mathcal{G}^{(t)} \\ \mathcal{H}^{(Q)} &= \mathcal{G}^{(T)} \ominus \mathcal{G}^{(t)} \end{aligned} \xrightarrow{\hspace{1cm}} \text{CC}(t;3)$$

J. Shen, N. P. Bauman, and P. Piecuch

Quantum-Monte-Carlo-driven

$$\begin{aligned} \mathcal{H}^{(P)} &= \mathcal{G}^{(S)} \oplus \mathcal{G}^{(D)} \oplus \mathcal{G}^{(t^{(MC)})} \\ \mathcal{H}^{(Q)} &= \mathcal{G}^{(T)} \ominus \mathcal{G}^{(t^{(MC)})} \end{aligned} \xrightarrow{\hspace{1cm}} \text{CC}(t^{(MC)};3)$$

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Selected-CI-driven

$$\begin{aligned} \mathcal{H}^{(P)} &= \mathcal{G}^{(S)} \oplus \mathcal{G}^{(D)} \oplus \mathcal{G}^{(t^{(CIPSI)})} \\ \mathcal{H}^{(Q)} &= \mathcal{G}^{(T)} \ominus \mathcal{G}^{(t^{(CIPSI)})} \end{aligned} \xrightarrow{\hspace{1cm}} \text{CC}(t^{(CIPSI)};3)$$

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Adaptive CC($P;Q$)

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K. Gururangan and P. Piecuch

ORMAS-CI-driven

$$\begin{aligned} \mathcal{H}^{(P)} &= \mathcal{G}^{(S)} \oplus \mathcal{G}^{(D)} \oplus \mathcal{G}^{(t^{(ORMAS)})} \\ \mathcal{H}^{(Q)} &= \mathcal{G}^{(T)} \ominus \mathcal{G}^{(t^{(ORMAS)})} \end{aligned} \xrightarrow{\hspace{1cm}} \text{CC}(t^{(ORMAS)};3)$$



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Brief Summary of CIQMC

- It is well known in quantum mechanics that if we start from a trial wave function $|\Phi_0\rangle$ that has a non-zero overlap with the exact ground state $|\Psi_0\rangle$, and if we propagate it along the imaginary-time axis, then in the limit of infinite time, we will project the exact ground-state $|\Psi_0\rangle$.

$$|\Phi_0\rangle = \sum_K c_K |\Psi_K\rangle, \quad c_K = \langle \Psi_K | \Phi_0 \rangle$$

$$\lim_{\tau \rightarrow \infty} |\Psi(\tau)\rangle = e^{-(H-S)\tau} |\Phi_0\rangle$$

$$= \sum_K c_K e^{-(H-S)\tau} |\Psi_K\rangle$$

$$= c_0 e^{-(E_0-S)\tau} |\Psi_0\rangle + \sum_{K>0} c_K e^{-(E_K-S)\tau} |\Psi_K\rangle$$

$$\left. \begin{array}{ll} \lim_{\tau \rightarrow \infty} |\Psi(\tau)\rangle = c_0 |\Psi_0\rangle & \text{for } S = E_0 \\ \lim_{\tau \rightarrow \infty} |\Psi(\tau)\rangle = \infty & \text{for } S > E_0 \\ \lim_{\tau \rightarrow \infty} |\Psi(\tau)\rangle = 0 & \text{for } S < E_0 \end{array} \right\}$$

$$|\Psi(\tau)\rangle = c_0(\tau) |\Phi_0\rangle + \sum_K c_K(\tau) |\Phi_K\rangle$$

$$\frac{\partial c_K(\tau)}{\partial \tau} = -(H_{KK} - S) c_K(\tau) - \sum_{L(\neq K)} H_{KL} c_L(\tau)$$

- If $S \rightarrow E_0$, $\frac{\partial c_K(\tau)}{\partial \tau} = 0$, and we obtain $\sum_L H_{KL} c_L(\infty) = E_0 c_K(\infty)$.



Brief Summary of CIQMC

Walker Population Dynamics

$$c_K(\tau) \sim N_K = \sum_{\alpha} s_{\alpha} \delta_{K, K_{\alpha}}, \quad s_{\alpha} = \pm 1$$

$$\frac{\partial c_K(\tau)}{\partial \tau} = -(H_{KK} - S) c_K(\tau) - \sum_{L(\neq K)} H_{KL} c_L(\tau)$$

birth and death 

spawning 

$$c_K(\tau + \Delta\tau) = [1 - (H_{KK} - S)\Delta\tau]c_K(\tau) \quad c_K(\tau + \Delta\tau) = c_K(\tau) - \Delta\tau \sum_{L(\neq K)} H_{KL} c_L(\tau)$$

$ \Phi_0\rangle^{(1)}$	$ \Phi_{S_1}\rangle$	$ \Phi_{D_1}\rangle$	$ \Phi_{T_1}\rangle$	$ \Phi_{Q_1}\rangle$	$ \Phi_{P_1}\rangle$...
	$ \Phi_{S_2}\rangle$	$ \Phi_{D_2}\rangle$	$ \Phi_{T_2}\rangle$	$ \Phi_{Q_2}\rangle$	$ \Phi_{P_2}\rangle$...
	$ \Phi_{S_3}\rangle$	$ \Phi_{D_3}\rangle$	$ \Phi_{T_3}\rangle$	$ \Phi_{Q_3}\rangle$	$ \Phi_{P_3}\rangle$...
	$ \Phi_{S_4}\rangle$	$ \Phi_{D_4}\rangle$	$ \Phi_{T_4}\rangle$	$ \Phi_{Q_4}\rangle$	$ \Phi_{P_4}\rangle$...
	$ \Phi_{S_5}\rangle$	$ \Phi_{D_5}\rangle$	$ \Phi_{T_5}\rangle$	$ \Phi_{Q_5}\rangle$	$ \Phi_{P_5}\rangle$...
:	:	:	:	:	:	..

Brief Summary of CIQMC

Walker Population Dynamics

$$c_K(\tau) \sim N_K = \sum_{\alpha} s_{\alpha} \delta_{K, K_{\alpha}}, \quad s_{\alpha} = \pm 1$$

$$\frac{\partial c_K(\tau)}{\partial \tau} = -(H_{KK} - S) c_K(\tau) - \sum_{L(\neq K)} H_{KL} c_L(\tau)$$

birth and death 

$$c_K(\tau + \Delta\tau) = [1 - (H_{KK} - S)\Delta\tau]c_K(\tau)$$

spawning 

$$c_K(\tau + \Delta\tau) = c_K(\tau) - \Delta\tau \sum_{L(\neq K)} H_{KL} c_L(\tau)$$

$ \Phi_0\rangle^{(1)}$	$ \Phi_{S_1}\rangle$	$ \Phi_{D_1}\rangle$	$ \Phi_{T_1}\rangle$	$ \Phi_{Q_1}\rangle$	$ \Phi_{P_1}\rangle$...
	$ \Phi_{S_2}\rangle$	$ \Phi_{D_2}\rangle$	$ \Phi_{T_2}\rangle$	$ \Phi_{Q_2}\rangle$	$ \Phi_{P_2}\rangle$...
	$ \Phi_{S_3}\rangle$	$ \Phi_{D_3}\rangle$	$ \Phi_{T_3}\rangle$	$ \Phi_{Q_3}\rangle$	$ \Phi_{P_3}\rangle$...
	$ \Phi_{S_4}\rangle$	$ \Phi_{D_4}\rangle$	$ \Phi_{T_4}\rangle$	$ \Phi_{Q_4}\rangle$	$ \Phi_{P_4}\rangle$...
	$ \Phi_{S_5}\rangle$	$ \Phi_{D_5}\rangle$	$ \Phi_{T_5}\rangle$	$ \Phi_{Q_5}\rangle$	$ \Phi_{P_5}\rangle$...
	\vdots	\vdots	\vdots	\vdots	\vdots	\ddots

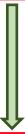
The Ground State Semi-Stochastic CC($P;Q$) Approach

Start a CIQMC (e.g., i -CIQMC) propagation by placing a certain number of walkers on the reference determinant.



Extract a list of the higher-than-doubly excited determinants relevant to the CC theory of interest (e.g., triples for CCSDT) from the CIQMC propagation at a given time τ to define the P space for CC(P) calculation as follows:

- If the target approach is CCSDT, the P space is defined as all singles, all doubles, and a subset of triples having at least n_p (e.g., one) positive or negative walkers on them.



Solve the CC(P) and left-CC(P) equations by defining the cluster and linear de-excitation operators in the P space as follows:

Target: **CCSDT**

$$T^{(P)} = T_1 + T_2 + \textcolor{red}{T}_3^{(\text{MC})}$$

$$\Lambda^{(P)} = \Lambda_1 + \Lambda_2 + \textcolor{red}{\Lambda}_3^{(\text{MC})}$$



Correct CC(P) energies for remaining triples (in case of CCSDT) using non-iterative $\delta_0(P;Q)$ correction.



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[Repository icon] **cct3** Public

CCT3: A PSI4 plugin which performs active-space coupled-cluster CCSDt calculations and which can determine non-iterative corrections to CCSDt defining the CC(t;3) approach.

● Fortran ⭐ 12 📂 6

[Repository icon] **ccq** Public

A research coupled-cluster program (CC) capable of performing various CC calculations, including up to quadruply excited cluster components.

● Fortran ⭐ 4 📂 1

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Coupled-cluster package written in Python.

● Fortran ⭐ 12

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A general spin-orbital coupled-cluster package written in Python.



● Python ⭐ 0 📂 BSD-3-Clause 📂 1 ⏺ 0 ⏺ 0 Updated 5 days ago

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CCT3: A PSI4 plugin which performs active-space coupled-cluster CCSDt calculations and which can determine non-iterative corrections to CCSDt defining the CC(t;3) approach.



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- 1.MP2
- 2.MP3
- 3.CCD
- 4.CCSD
- 5.CCSD(T)
- 6.CR-CC(2,3)
- 7. CC3
- 8. CCSDt
- 9. CC(t;3)
- 10. CIPSI-driven CC($P;Q$)
aimed at converging CCSDT
- 11. Adaptive CC($P;Q$) aimed at
converging CCSDT
- 12. CCSDT
- 13. CCSDTAQ
- 14. CR-CC(2,4)
- 15. CCSDTQ
- 16. ec-CC-II
- 17. ec-CC-II₃
- 18. ec-CC-II_{3,4}



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CQA: A PSI4 plugin which performs active-space coupled-cluster CCSDt calculations and which can determine non-iterative corrections to CCSDt defining the CC(t;3) approach.

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[ec-CC-II](#) Public

A research coupled-cluster program (CC) capable of performing various CC calculations, including up to quadruply excited cluster components.

Fortran 4 LGPL-2.1 1 0

[ec-CC-II₃](#) Public

A research coupled-cluster program (CC) capable of performing various CC calculations, including up to quadruply excited cluster components.

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Methods

- 19. EOMCCSD
- 20. SF-EOMCCSD
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- 22. CR-EOMCC(2,3) and its size-intensive δ-CR-EOMCC(2,3) extension
- 23. EOM-CC3
- 24. EOMCCSDt
- 25. EOMCCSDT
- 26. IP-EOMCCSD(2h-1p)
- 27. IP-EOMCCSD(3h-2p)
- 28. EA-EOMCCSD(2p-1h)
- 29. EA-EOMCCSD(3p-2h)
- 30. DIP-EOMCCSD(3h-1p)
- 31. DIP-EOMCCSD(4h-2p)
- 32. DEA-EOMCCSD(3p-1h)
- 33. DEA-EOMCCSD(4p-2h)
- 34. Active-space IP-EOMCCSD(3h-2p){N_o} (also known as IP-EOMCCSDt)
- 35. Active-space EA-EOMCCSD(3p-2h){N_u} (also known as EA-EOMCCSDt)

- 36. Excited-state CC(t;3)
- 37. ACCD
- 38. ACCSD
- 39. ACCSDt
- 40. ACC(2,3)
- 41. ACC(t;3)

People

This organization has no members to see.

Top languages

Fortran Python





1.MP2

2.MP3

3.CCD

4.CCSD

5.CCSD(T)

6.CR-CC(2,3)

7. CC3

8. CCSDt

9. CC(t;3)

10. CIPSI-driven CC($P;Q$)

aimed at converging CCSDT

11. Adaptive CC($P;Q$) aimed at

converging CCSDT

12. CCSDT miniccp

13. CCSDTAQ

14. CR-CC(2,4)

15. CCSDTQ

16. ec-CC-II

17. ec-CC-II_{3,4}18. ec-CC-II_{3,4}

Piecuch Research Group

5 followers East Lansing, MI https://www2.chemistry.msu.edu/fac...

piecuch@chemistry.msu.edu

Overview

Repositories 5

Projects

Packages

People

Pinned

cct3 Public

CCT3: A PSI4 plugin which performs active-space coupled-cluster CCSDt calculations and which can determine non-iterative corrections to CCSDt defining the CC(t;3) approach.

Fortran 12 6

ccq Public

A research coupled-cluster program (CC) capable of performing various calculations, including up to quadruply excited cluster components.

Fortran 4 1

Repositories

Find a repository...

Methods

19. EOMCCSD

20. SF-EOMCCSD

21. SF-EOMCC(2,3)

22. CR-EOMCC(2,3) and its size-

intensive δ-CR-EOMCC(2,3) extension

23. EOM-CC3

24. EOMCCSDt

25. EOMCCSDT

26. IP-EOMCCSD(2h-1p)

27. IP-EOMCCSD(3h-2p)

28. EA-EOMCCSD(2p-1h)

29. EA-EOMCCSD(3p-2h)

30. DIP-EOMCCSD(3h-1p)

31. DIP-EOMCCSD(4h-2p)

32. DEA-EOMCCSD(3p-1h)

33. DEA-EOMCCSD(4p-2h)

34. Active-space IP-EOMCCSD(3h-

2p){N_o} (also known as IP-EOMCCSDt)

35. Active-space EA-EOMCCSD(3p-

2h){N_u} (also known as EA-EOMCCSDt)

36. Excited-state CC(t;3)

37. ACCD

38. ACCSD

39. ACCSDt

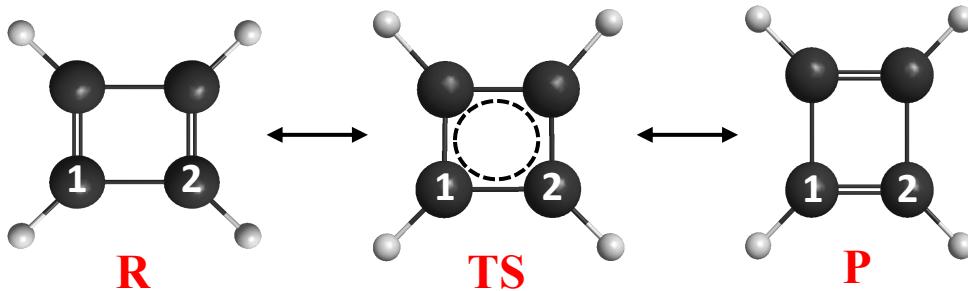
40. ACC(2,3)

41. ACC(t;3)

42. CIQMC-driven CC($P;Q$)
aimed at converging CCSDT

Performance of the CIQMC-driven CC($P;Q$)

Example: Automerization of Cyclobutadiene



Experimental Barriers: 1.6-10 kcal/mol
Theoretical Estimates: 6-10 kcal/mol

CC energies of different methods (in millihartree) relative to full CCSDT (in hartree) obtained with cc-pVDZ basis set

Methods	Reactant	TS	Barrier Height (kcal/mol)	
CCSD	26.827	47.979	20.9	
<i>T</i> ₁ and <i>T</i> ₂ are decoupled from <i>T</i> ₃	{ CCSD(T) CR-CC(2,3)	1.123 0.848	14.198 14.636	15.8 16.3
CCSDt	20.786	20.274	7.3	
CC(t;3)	-0.137	0.071	7.8	
CCSDT	-154.244157	-154.232002	7.6	

Performance of the CIQMC-driven CC($P;Q$)

Monte Carlo (MC) Approach = i -CISDTQ-MC ($\delta\tau = 0.0001$ a.u., $n_\alpha = 3$)

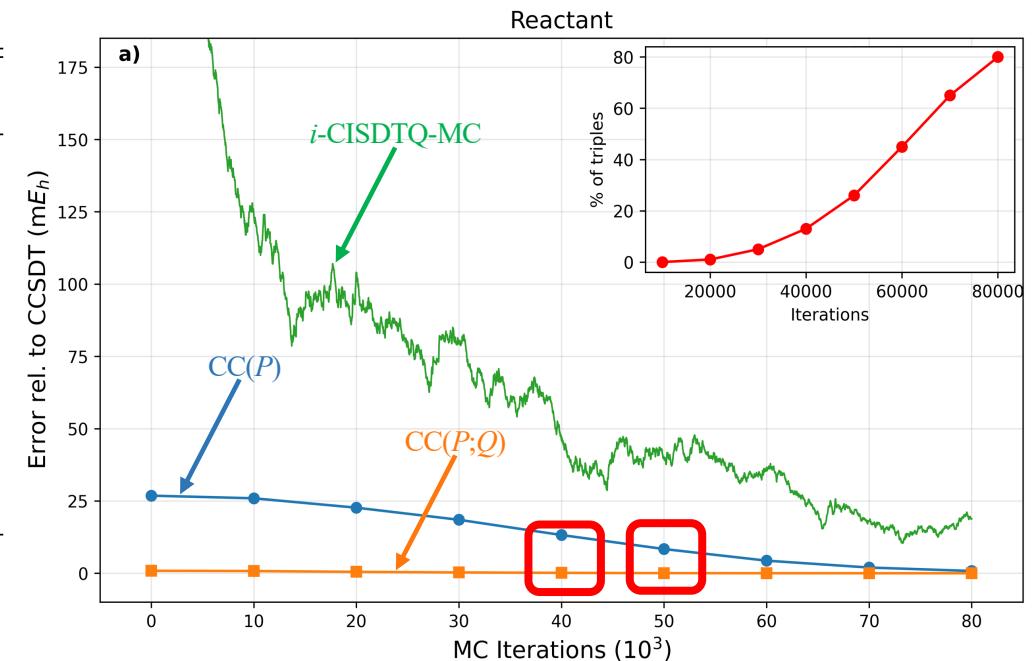
Species	MC iterations	% of triples	$CC(P)^a$	$CC(P;Q)^a$
R	0	0	26.827 ^b	0.848 ^c CR-CC(2,3)
	40000	13	13.220	0.130
	50000	26	8.370	0.036
	60000	45	4.353	0.006
	∞	100	-154.244157 ^d	

^aErrors relative to CCSDT in millihartree for the reactant.

^bEquivalent to CCSD.

^cEquivalent to CR-CC(2,3).

^dTotal CCSDT energy in hartree.



Performance of the CIQMC-driven CC($P;Q$)

Monte Carlo (MC) Approach = i -CISDTQ-MC ($\delta\tau = 0.0001$ a.u., $n_\alpha = 3$)

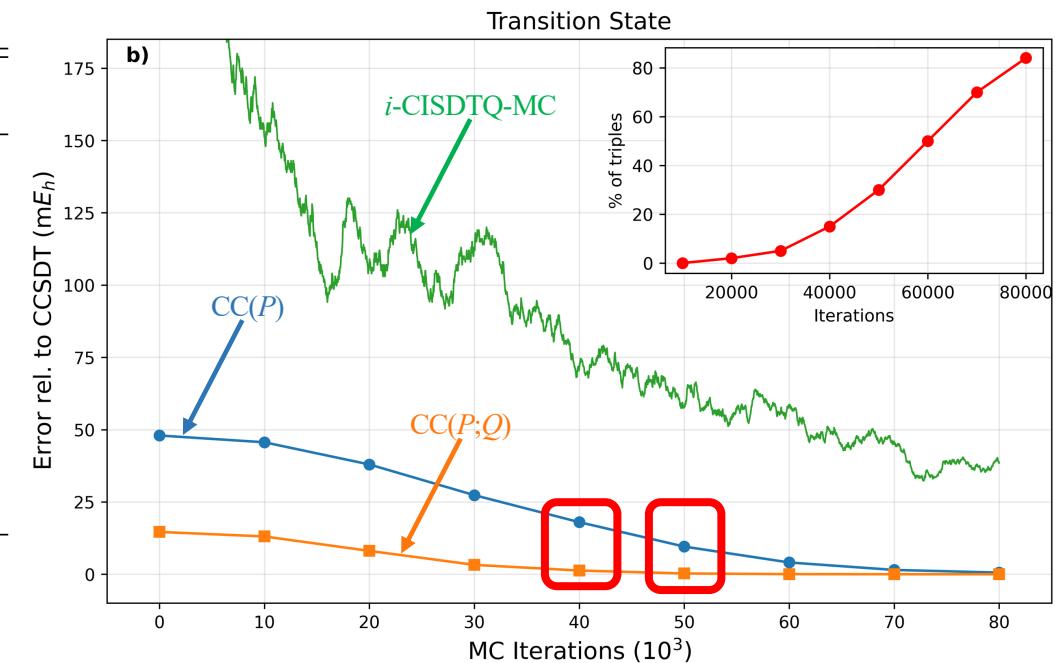
Species	MC iterations	% of triples	$CC(P)^a$	$CC(P;Q)^a$
TS				
	0	0	47.979 ^b	14.636 ^c CR-CC(2,3)
	40000	15	18.011	1.283
	50000	30	9.568	0.267
	60000	50	4.075	0.033
	∞	100	-154.232002 ^d	

^aErrors relative to CCSDT in millihartree for the transition state.

^bEquivalent to CCSD.

^cEquivalent to CR-CC(2,3).

^dTotal CCSDT energy in hartree.



Performance of the CIQMC-driven CC($P;Q$)

Monte Carlo (MC) Approach = i -CISDTQ-MC ($\delta\tau = 0.0001a.u.$, $n_\alpha = 3$)

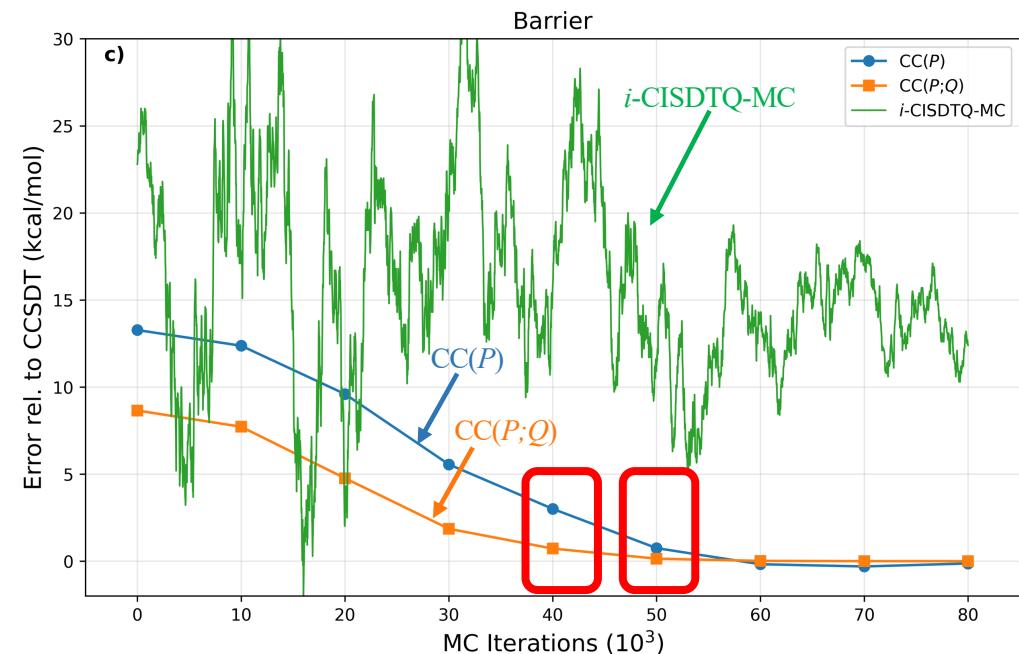
Species	MC iterations	% of triples	CC(P) ^a	CC($P;Q$) ^a
Barrier				
	0	0/0	13.274 ^b	8.653 ^c
	40000	13/15	3.007	0.724
	50000	26/30	0.752	0.145
	60000	45/50	-0.175	0.018
	∞	100/100	7.627 ^e	

^aErrors relative to CCSDT in kcal/mol for the activation barrier.

^bEquivalent to CCSD.

^cEquivalent to CR-CC(2,3).

^dCCSDT activation barrier in kcal/mol.



Performance of the CIQMC-driven CC($P;Q$)

Computational timings of the various CC calculations for the cyclobutadiene / cc-pVDZ system in the transition-state geometry

CPU Time(min)

Method	P Space Determination ^a	Iterative Steps ^b	Noniterative Steps ^c	Total	Error rel. to CCSDT (mE _h)		
					MC iterations	CC(P)	CC($P;Q$)
→ CCSD	...	0.5	...	0.5			
CCSD(T)	...	0.5	0.1	0.6			
→ CR-CC(2,3)	...	0.8	0.3	1.1	0	47.979	14.636
MC iterations = 40000 ← CC($P;Q$)[%T=15]	10.7	24.1	13.9	48.9	40000	18.011	1.283
MC iterations = 50000 ← CC($P;Q$)[%T=30]	23.4	53.4	11.8	88.7	50000	9.568	0.267
CC($P;Q$)[%T=50]	55.3	77.8	10.2	143.3	60000	4.075	0.033
CCSDT	...	455.8	...	455.8			

^a P space determination = i-CISDTQ-MC calculation and obtaining the P space.

^bIterative Steps = Constructing and solving the relevant CC amplitude equations and companion left eigenstate problems (Convergence threshold = 10^{-7} hartree).

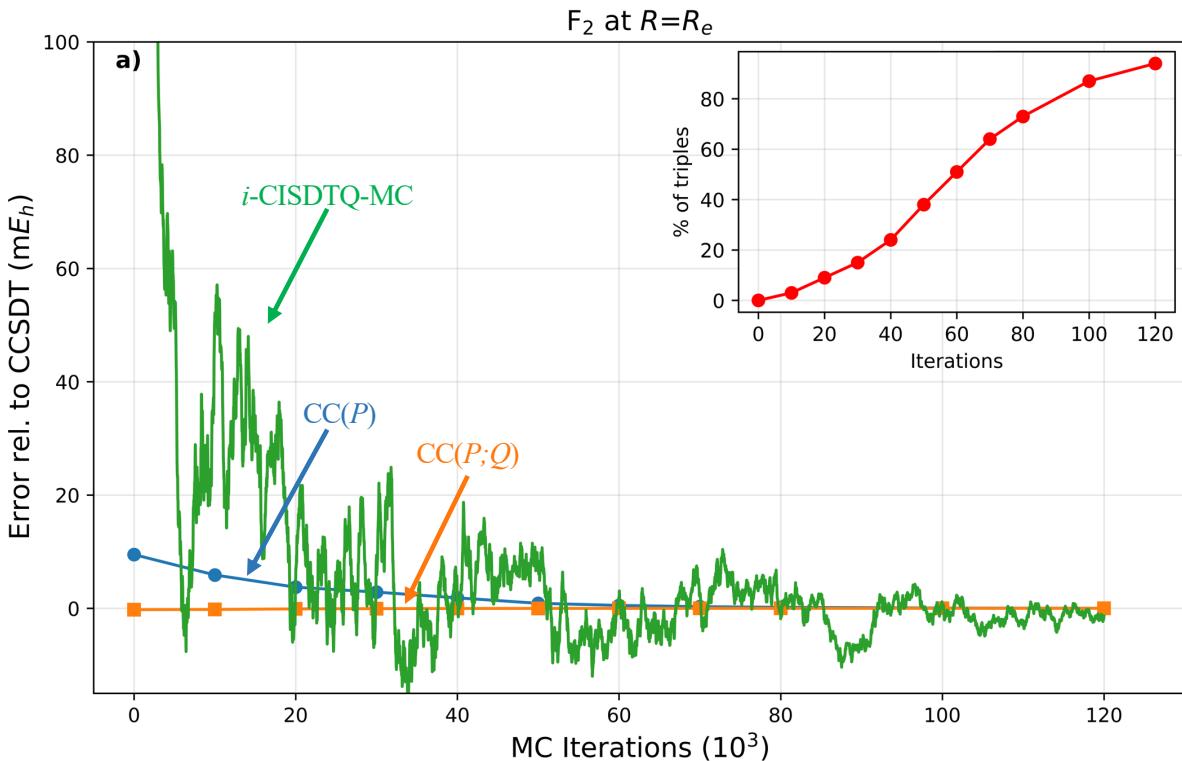
^cNoniterative Steps = The computational times required to determine the noniterative triples corrections correspond to all triples in the case of CCSD(T) and CR-CC(2,3) and the remaining ($100 - x$) percent of triples not included in the relevant P spaces in the case of CC($P;Q$) [%T = x].



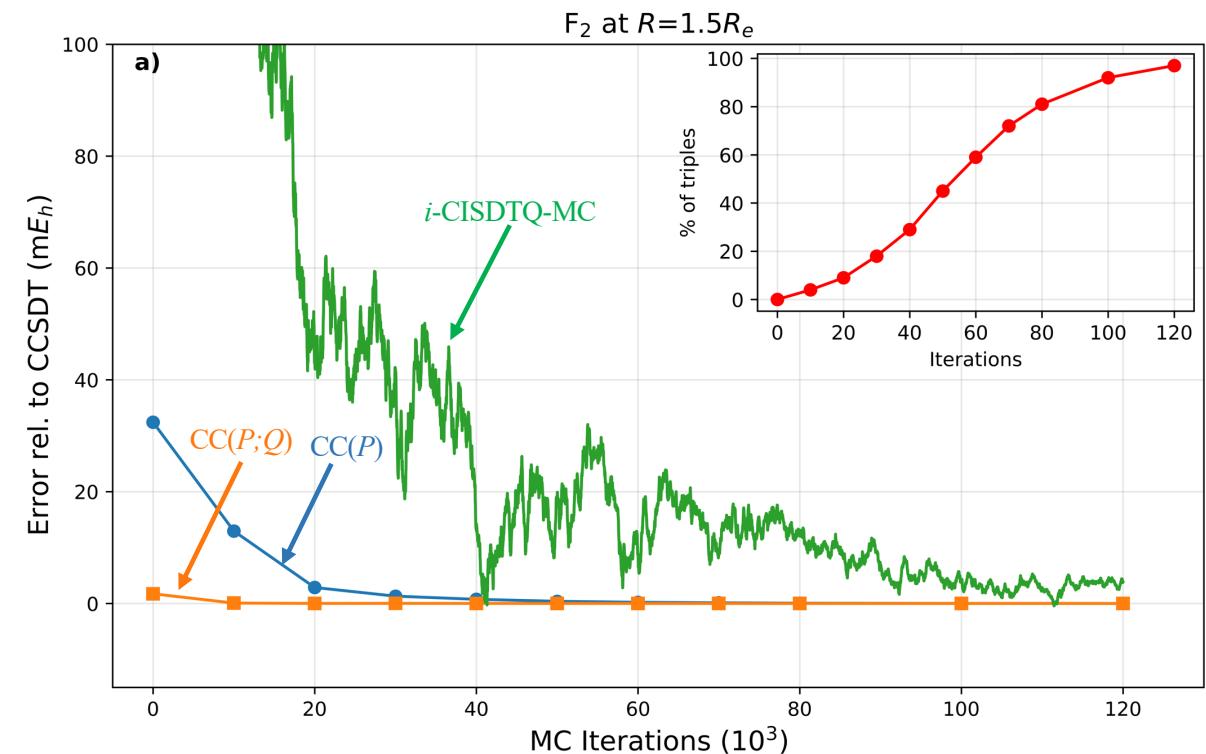
Performance of the CIQMC-driven CC($P;Q$)

F_2 / cc-pVDZ

Monte Carlo (MC) Approach = i -CISDTQ-MC ($\delta\tau = 0.0001$ a.u., $n_\alpha = 3$)



F–F internuclear distance $R = R_e = 2.66816$ bohr



F–F internuclear distance $R = 1.5R_e = 4.00224$ bohr

Contents

- ❖ Introduction to Electronic Structure Theory
- ❖ Coupled-Cluster Theory
 - Key Elements of the Single-Reference Coupled-Cluster (CC) Formalism
 - Challenges of Single-Reference CC Theory
- ❖ High-Level CC Energetics via $\text{CC}(P;Q)$ Moment Expansions
- ❖ Accomplishment to Date: Efficient Implementation of the Semi-Stochastic $\text{CC}(P;Q)$ Approach in the CCpy
 - Brief Summary of the Configuration Interaction Quantum Monte Carlo (CIQMC)
 - CIQMC-driven $\text{CC}(P;Q)$
 - Performance of the CIQMC-driven $\text{CC}(P;Q)$
- ❖ Future Research Plans
 - Integrating $\text{CC}(P;Q)$ Moment Expansions with Occupation Restricted Multiple Active Spaces-Configuration Interaction (ORMAS-CI)
 - Combining Externally Corrected (ec) CC methodology with (ORMAS-CI)
 - Exploring Connected Moment Expansions (CMX)



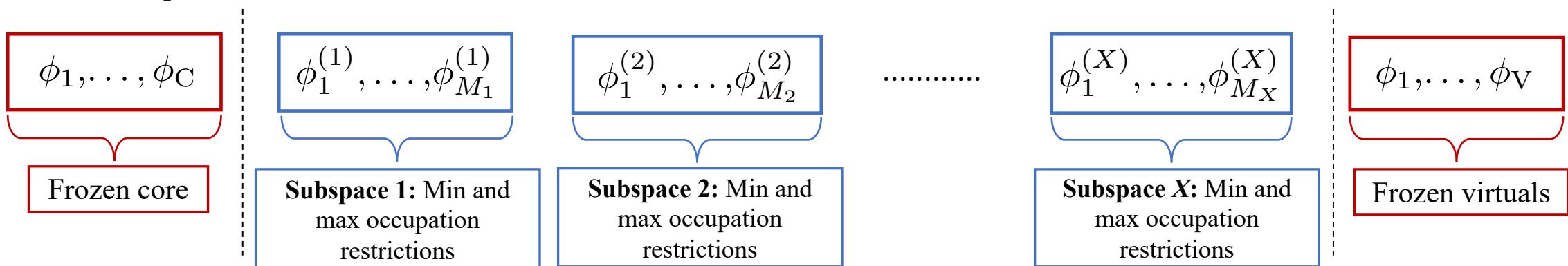
Occupation-Restricted Multiple Active-Space (ORMAS)-CI

- Occupation-Restricted Multiple Active-Space (ORMAS)-CI, which is available in the GAMESS package, is a direct determinant-based configuration interaction method.
- In the first step of this approach, the orbital active space is $\phi_p (p = 1, \dots, M_A)$ divided into an arbitrary number of subspaces, $\phi_p^{(1)} (p = 1, \dots, M_1)$, $\phi_p^{(2)} (p = 1, \dots, M_2)$, ..., $\phi_p^{(X)} (p = 1, \dots, M_X)$, so that

$$\sum_{I=1}^X M_I = M_A,$$

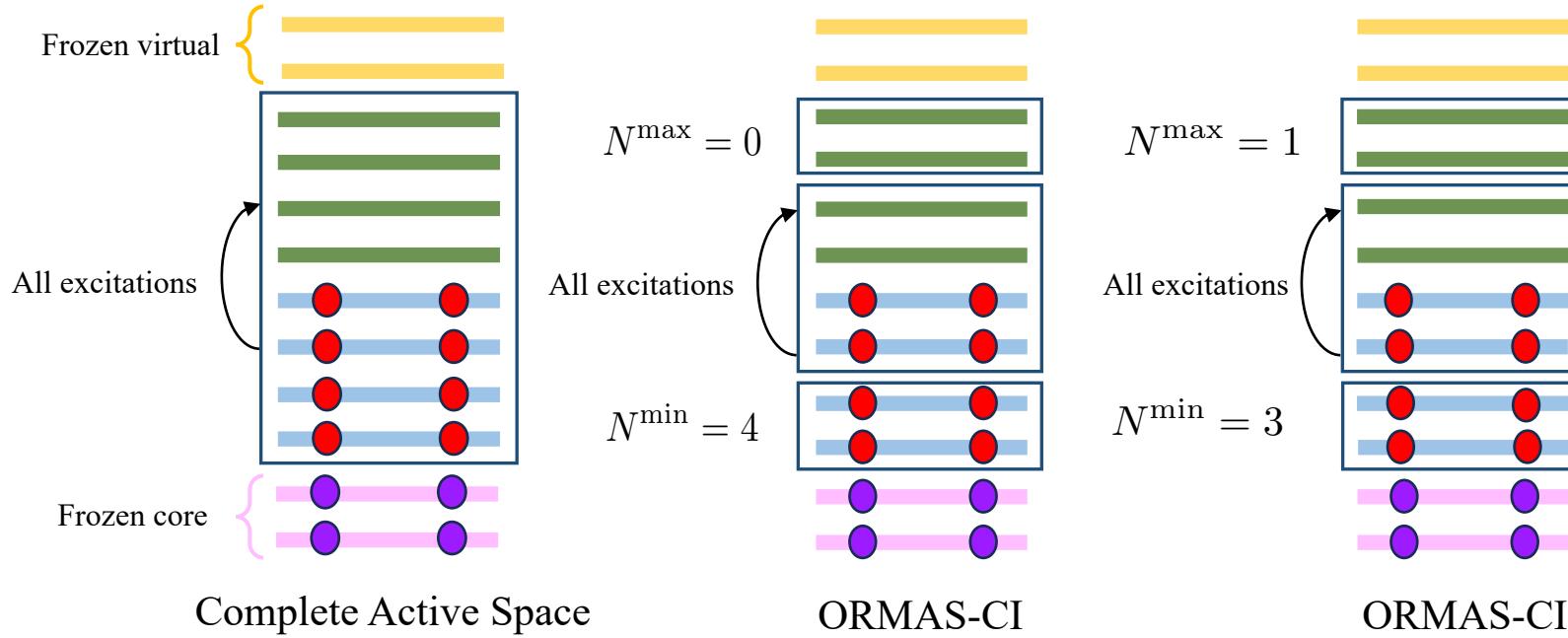
where M_I is the number of orbitals in group I .

- Limitations upon the number of electrons that can occupy each of these orbital groups are provided in the form of minimum, N_I^{\min} , and maximum, N_I^{\max} , values.

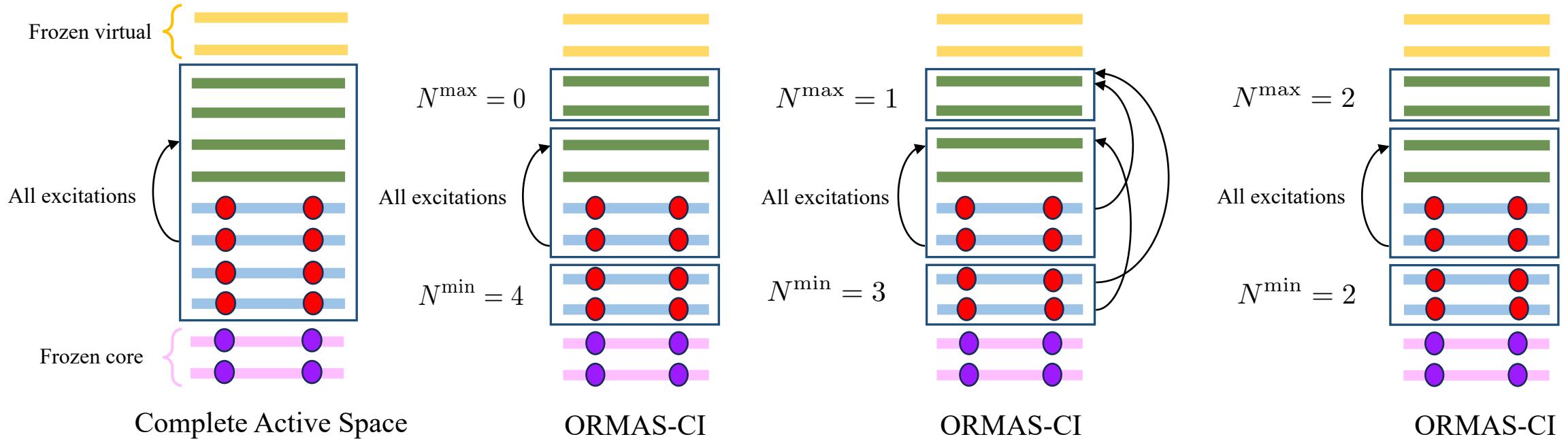


- The configuration space is then chosen to contain all determinants which satisfy these above restrictions.

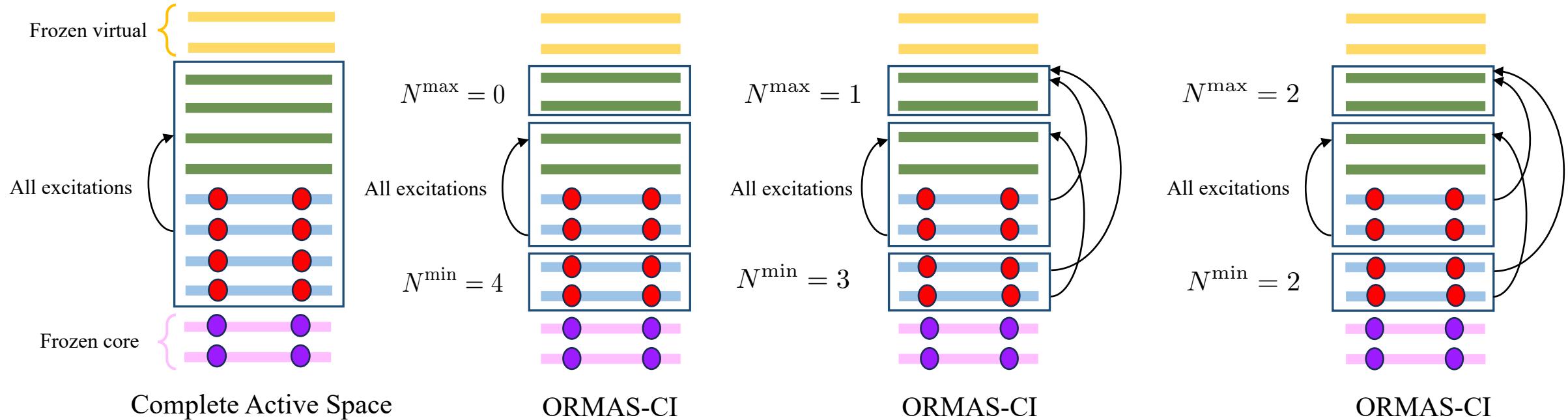
Occupation-Restricted Multiple Active-Space (ORMAS)-CI



Occupation-Restricted Multiple Active-Space (ORMAS)-CI



Occupation-Restricted Multiple Active-Space (ORMAS)-CI



ORMAS-CI

CC($P;Q$) Approach

$$\mathcal{H}^{(P)} = \mathcal{G}^{(\text{S})} \oplus \mathcal{G}^{(\text{D})} \oplus \mathcal{G}^{(\text{t}^{(\text{ORMAS})})}$$

$$T^{(P)} = T_1 + T_2 + T_3^{(\text{ORMAS})}$$



The Externally Corrected (ec) CC Formalism

The electronic Hamiltonian H is two-body.

The Ground-State CC Amplitude Equations:

$$\langle \Phi_i^a | [H_N(1 + T_1 + T_2 + (1/2)T_1^2 + \textcolor{blue}{T}_3 + T_1T_2 + (1/6)T_1^3)]_C | \Phi_0 \rangle = 0$$

$$\begin{aligned} \langle \Phi_{ij}^{ab} | [H_N(1 + T_1 + T_2 + (1/2)T_1^2 + \textcolor{blue}{T}_3 + T_1T_2 + (1/6)T_1^3 + \textcolor{blue}{T}_4 + T_1\textcolor{blue}{T}_3 + (1/2)T_2^2 \\ + (1/2)T_1^2T_2 + (1/24)T_1^4)]_C | \Phi_0 \rangle = 0 \end{aligned}$$

The Ground-State CC Energy:

$$E_0 = \langle \Phi_0 | H | \Phi_0 \rangle + \langle \Phi_0 | [H_N(T_1 + T_2 + (1/2)T_1^2)]_C | \Phi_0 \rangle$$

OBSERVATION: T_3 and T_4 extracted from the FCI $\longrightarrow E_0$ becomes exact!

ec-CC approaches

Solve for T_1 and T_2 in the presence of T_3 and T_4 extracted from a well-behaved non-CC source.

- ❖ PUHF, valence-bond, and CASSCF wave functions
- ❖ MRCI wave functions used in the RMRCC approaches
- ❖ FCIQMC wave functions (CAD-FCIQMC), CIPSI, ACI, HCI, and DMRG



The Externally Corrected (ec) CC Formalism

$$|\Psi_0\rangle = (1 + C)|\Phi_0\rangle = e^T|\Phi_0\rangle$$

$$|\Psi_0\rangle = \underbrace{(1 + C_1 + C_2 + \dots)}_{\text{CI expansion}} |\Phi_0\rangle = \underbrace{e^{T_1 + T_2 + \dots}}_{\text{CC expansion}} |\Phi_0\rangle$$

$$T = \ln(1 + C) = \sum_{m=1}^N \frac{(-1)^{m-1}}{m} C^m$$

$$T_1 = C_1$$

$$T_2 = C_2 - \frac{1}{2}C_1^2$$

$$\textcircled{T}_3 = C_3 - C_1C_2 + \frac{1}{3}C_1^3$$

$$\textcircled{T}_4 = C_4 - C_1C_3 - \frac{1}{2}C_2^2 + C_1^2C_2 - \frac{1}{4}C_1^4$$

The above defines **ec-CC-I**, where we do not make any *a posteriori* modifications in T_3 and T_4 .

$$T_1 = C_1$$

$$T_2 = C_2 - \frac{1}{2}C_1^2$$

$$\textcircled{T}_3 = C_3 - C_1C_2 + \frac{1}{3}C_1^3$$

$$\textcircled{T}_4 = C_4 - C_1C_3 - \frac{1}{2}C_2^2 + C_1^2C_2 - \frac{1}{4}C_1^4$$

In the **ec-CC-II** approach, one removes those T_3 and T_4 components that do not have the companion C_3 and C_4 amplitudes.



The Externally Corrected (ec) CC Formalism

Theorem 1:

The ec-CC-I calculation in which T_3 and T_4 are obtained by cluster analysis of the CI wave function that describes singles and doubles fully, as in CISD, CISDT, CISDTQ, etc., or any other CI method that provides a complete treatment of the single and double excitation manifolds, returns the underlying CI energy.

Theorem 2:

The ec-CC-II calculation in which T_3 and T_4 are obtained by cluster analysis of the CI wave function that captures all singles, doubles, triples, and quadruples, as in CISDTQ, CISDTQP, CISDTQPH, etc., or any other CI method that provides a complete treatment of the single, double, triple, and quadruple excitation manifolds, returns the underlying CI energy.

Good Non-CC Sources

Truncated CI wave functions that can effectively sample the many-electron Hilbert space without saturating lower-rank excitation manifolds.

Further Acceleration

ec-CC-II + Moment Corrections

ORMAS-CI



Solve for T_1 and T_2 in the presence of $T_3^{(\text{ORMAS})}$ and $T_4^{(\text{ORMAS})}$ obtained from ORMAS-CI.



Exploring Connected Moment Expansions (CMX)

- Horn and Weinstein in their seminal work published in 1984, where one expresses the exact ground-state energy and properties of any quantum system as a power series in the variable t (formally corresponding to the imaginary-time propagation) in which the connected moments of the Hamiltonian or their analogs corresponding to the property of interest, define the expansion coefficients.
- It is on the well-established fact that one can always converge the exact ground state $|\Psi_0\rangle$ of a quantum system by applying the operator e^{-tH} to a trial wave function $|\Phi_0\rangle$, which has a non-zero overlap with $|\Psi_0\rangle$, and making the variable t in the resulting expression infinitely large, $\lim_{t \rightarrow \infty} E(t) \rightarrow E_0$, where

$$E(t) = \frac{\langle \Phi_0 | H e^{-tH} | \Phi_0 \rangle}{\langle \Phi_0 | e^{-tH} | \Phi_0 \rangle}.$$

- Horn and Weinstein demonstrated that

$$E(t) = \frac{\langle \Phi_0 | H \exp(-tH) | \Phi_0 \rangle}{\langle \Phi_0 | \exp(-tH) | \Phi_0 \rangle} = \sum_{k=0}^{\infty} \frac{(-t)^k}{k!} I_{k+1},$$

where the **connected moments of the Hamiltonian** I_{k+1} is defined recursively as

$$I_k = \langle H^k \rangle - \sum_{i=0}^{k-2} \binom{k-1}{i} I_{i+1} \langle H^{k-i-1} \rangle; \quad \langle H^k \rangle = \langle \Phi_0 | H^k | \Phi_0 \rangle.$$



Exploring Connected Moment Expansions (CMX)

$k = 1$

$$I_1 = \langle H \rangle = \langle \Phi_0 | H | \Phi_0 \rangle$$

Energy of the reference state $|\Phi_0\rangle$

$k = 2$

$$I_2 = \langle H^2 \rangle - \langle H \rangle^2$$

$k = 3$

$$I_3 = \langle H^3 \rangle - 3\langle H^2 \rangle \langle H \rangle + 2\langle H \rangle^3$$

$$E(t) = \sum_{k=0}^{\infty} (-t)^k \frac{I_{k+1}}{k!} = I_1 - I_2 t + I_3 \frac{t^2}{2!} + \dots$$

How to extrapolate $E(t)$ to $t \rightarrow \infty$?

$$E(t) = \sum_{k=0}^N \frac{(-t)^k}{k!} I_{k+1}$$

Approach 1

Form Padé approximants

Approach 2

Form Padé approximants to the derivative of the function and then integrate the approximant to reconstruct the function.

- Employed for Heisenberg model of a one-dimensional antiferromagnet and the cluster of eight hydrogen atoms described in a minimum basis set.



Exploring Connected Moment Expansions (CMX)

Original Formulation by Cioslowski

$$E_0 = I_1 - \frac{I_2^2}{I_3} - \left(\frac{1}{I_3} \right) \frac{(I_4 I_2 - I_3^2)^2}{(I_5 I_3 - I_4^2)} - \dots$$

- The K th order of CMX [$(\text{CMX}(K))$] is obtained by the truncation of the above series after the first K terms.

$$E_{\text{CMX}(K=1)} = I_1$$

$$E_{\text{CMX}(K=2)} = I_1 - \frac{I_2^2}{I_3}$$

$$E_{\text{CMX}(K=3)} = I_1 - \frac{I_2^2}{I_3} - \left(\frac{1}{I_3} \right) \frac{(I_4 I_2 - I_3^2)^2}{(I_5 I_3 - I_4^2)} \dots$$

\downarrow
 \mathcal{N}^6

\downarrow
 \mathcal{N}^8

Reformulation by Knowles

- As the correlation energy is defined as $E_{\text{corr}} = E_0 - \langle \Phi_0 | H | \Phi_0 \rangle = \lim_{t \rightarrow \infty} [E(t)] - I_1$, we can rewrite the series as follows:

$$E_{\text{corr}} = \lim_{m \rightarrow \infty} [E_{\text{corr}}^{(m)}]_{\text{CMX}}.$$



Exploring Connected Moment Expansions (CMX)

$$[E_{\text{corr}}^{(m)}]_{\text{CMX}} = -\frac{S_{2,1}^2}{S_{3,1}} \left(1 + \frac{S_{2,2}^2}{S_{2,1}^2 S_{3,2}} \left(1 + \frac{S_{2,3}^2}{S_{2,2}^2 S_{3,3}} \left(1 + \cdots \left(1 + \frac{S_{2,m}^2}{S_{2,m-1}^2 S_{3,m}} \right) \cdots \right) \right) \right)$$

$$S_{k,1} = I_k, k = 2, 3, \dots,$$

$$S_{k,i+1} = S_{k,i} S_{k+2,i} - S_{k+1,i}^2; i \geq 1$$

$m = 1$: 1st-order approximation

$$[E_{\text{corr}}^{(m=1)}]_{\text{CMX}} = -\frac{I_2^2}{I_3}$$

$m = 2$: 2nd-order approximation

$$[E_{\text{corr}}^{(m=2)}]_{\text{CMX}} = -\frac{I_2^2}{I_3} - \left(\frac{1}{I_3} \right) \frac{(I_4 I_2 - I_3^2)^2}{(I_5 I_3 - I_4^2)} \dots$$

DCM(N) Implementation

- This implementation constrains the excited determinants entering I_K to the doubly excited determinants only to reduce the computational cost of CMX calculations to noniterative \mathcal{N}^6 , independent of the order of N .
- For I_2 and I_3 there will be contributions only from the doubly excited determinants. But for higher order moments, I_K , $K > 3$, there will be contribution from higher-order terms, but only the doubly excited determinants were considered.



Exploring Connected Moment Expansions (CMX)

Our Proposed Formulation

$$I_k = \langle H^k \rangle - \sum_{i=0}^{k-2} \binom{k-1}{i} I_{i+1} \langle H^{k-i-1} \rangle; \quad \langle H^k \rangle = \underbrace{\langle \Phi_0 | H^k | \Phi_0 \rangle}$$

$$\langle H^k \rangle = \langle \tilde{\Psi}_0 | H^k | \Psi_0 \rangle$$

$$\langle \tilde{\Psi}_0 | = \langle \Phi_0 | (1 + \Lambda) e^{-T} \quad | \Psi_0 \rangle = e^T | \Phi_0 \rangle$$

$$\langle H^k \rangle = \langle \Phi_0 | (1 + \Lambda) e^{-T} H^k e^T | \Phi_0 \rangle = \langle \Phi_0 | (1 + \Lambda) \bar{H}^k | \Phi_0 \rangle$$

$$T = T_1 + T_2, \quad \Lambda = \Lambda_1 + \Lambda_2$$

$$\begin{aligned} \bar{H} &= e^{-T} H e^T \\ &\quad (e^T e^{-T}) \\ H^k &= H H \dots H \end{aligned}$$

$$\langle H^k \rangle^{(\text{CCSD})} = \langle \Phi_0 | (1 + \Lambda_1 + \Lambda_2) e^{-T_1 - T_2} H^k e^{T_1 + T_2} | \Phi_0 \rangle$$

$$\langle H^k \rangle^{(\text{CCSD})} = \langle \Phi_0 | (1 + \Lambda_1 + \Lambda_2) \left[\bar{H}^{(\text{CCSD})} \right]^k | \Phi_0 \rangle$$

$$\bar{H}^{(\text{CCSD})} = e^{-T_1 - T_2} H e^{T_1 + T_2}$$

Derivation of I_1

$$I_1 = \langle H \rangle$$

$$I_1 = \langle \Phi_0 | (1 + \Lambda_1 + \Lambda_2) \bar{H}^{(\text{CCSD})} | \Phi_0 \rangle \rightarrow E_0^{(\text{CCSD})}$$



Exploring Connected Moment Expansions (CMX)

Derivation of I_2

$$\begin{aligned}
 I_2 &= \langle H^2 \rangle - \langle H \rangle^2 = \langle \Phi_0 | (1 + \Lambda_1 + \Lambda_2) \left[\bar{H}^{(\text{CCSD})} \right]^2 | \Phi_0 \rangle - I_1^2 \\
 &= \langle \Phi_0 | (1 + \Lambda_1 + \Lambda_2) \bar{H}^{(\text{CCSD})} \bar{H}^{(\text{CCSD})} | \Phi_0 \rangle - \left[E_0^{(\text{CCSD})} \right]^2 \\
 &\quad \uparrow \text{Resolution of identity} \quad 1 = |\Phi_0\rangle\langle\Phi_0| + \sum_{n \neq 0} |\Phi_n\rangle\langle\Phi_n| \\
 I_2 &= \langle \Phi_0 | (1 + \Lambda_1 + \Lambda_2) \bar{H}^{(\text{CCSD})} | \Phi_0 \rangle \langle \Phi_0 | \bar{H}^{(\text{CCSD})} | \Phi_0 \rangle \equiv \left[E_0^{(\text{CCSD})} \right]^2 \\
 &\quad + \sum_{i,a} \langle \Phi_0 | (1 + \Lambda_1 + \Lambda_2) \bar{H}^{(\text{CCSD})} | \Phi_i^a \rangle \underbrace{\langle \Phi_i^a | \bar{H}^{(\text{CCSD})} | \Phi_0 \rangle}_0 \\
 &\quad + \sum_{i < j, a < b} \langle \Phi_0 | (1 + \Lambda_1 + \Lambda_2) \bar{H}^{(\text{CCSD})} | \Phi_{ij}^{ab} \rangle \underbrace{\langle \Phi_{ij}^{ab} | \bar{H}^{(\text{CCSD})} | \Phi_0 \rangle}_0 \\
 &\quad + \sum_{i < j < k, a < b < c} \langle \Phi_0 | (1 + \Lambda_1 + \Lambda_2) \bar{H}^{(\text{CCSD})} | \Phi_{ijk}^{abc} \rangle \underbrace{\langle \Phi_{ijk}^{abc} | \bar{H}^{(\text{CCSD})} | \Phi_0 \rangle}_{\mathfrak{M}_{abc}^{ijk}(\text{CCSD})} \\
 &\quad + \sum_{i < j < k < l, a < b < c < d} \langle \Phi_0 | (1 + \Lambda_1 + \Lambda_2) \bar{H}^{(\text{CCSD})} | \Phi_{ijkl}^{abcd} \rangle \underbrace{\langle \Phi_{ijkl}^{abcd} | \bar{H}^{(\text{CCSD})} | \Phi_0 \rangle}_{\mathfrak{M}_{abcd}^{ijkl}(\text{CCSD})} - \left[E_0^{(\text{CCSD})} \right]^2
 \end{aligned}$$



Exploring Connected Moment Expansions (CMX)

Derivation of I_2

$$I_2 = \sum_{i < j < k, a < b < c} \langle \Phi_0 | (1 + \Lambda_1 + \Lambda_2) \bar{H}^{(\text{CCSD})} | \Phi_{ijk}^{abc} \rangle \mathfrak{M}_{abc}^{ijk}(\text{CCSD}) \\ + \sum_{i < j < k < l, a < b < c < d} \langle \Phi_0 | (1 + \Lambda_1 + \Lambda_2) \bar{H}^{(\text{CCSD})} | \Phi_{ijkl}^{abcd} \rangle \mathfrak{M}_{abcd}^{ijkl}(\text{CCSD})$$

Similar to $\delta_0(2,3) = \sum_{i < j < k, a < b < c} \langle \Phi_0 | (1 + \Lambda_1 + \Lambda_2) \bar{H}^{(\text{CCSD})} | \Phi_{ijk}^{abc} \rangle \mathfrak{M}_{abc}^{ijk}(\text{CCSD}) / D_{abc}^{ijk}$ of CR-CC(2,3)

Derivation of I_3

$$I_3 = \langle H^3 \rangle - 3\langle H^2 \rangle \langle H \rangle + 2\langle H \rangle^3$$

$$I_3 = \sum_{i < j < k, a < b < c} \langle \Phi_0 | (1 + \Lambda_1 + \Lambda_2) \left[\bar{H}^{(\text{CCSD})} \right]^2 | \Phi_{ijk}^{abc} \rangle \mathfrak{M}_{abc}^{ijk}(\text{CCSD}) + \dots - 2I_2 E_0^{(\text{CCSD})}$$



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