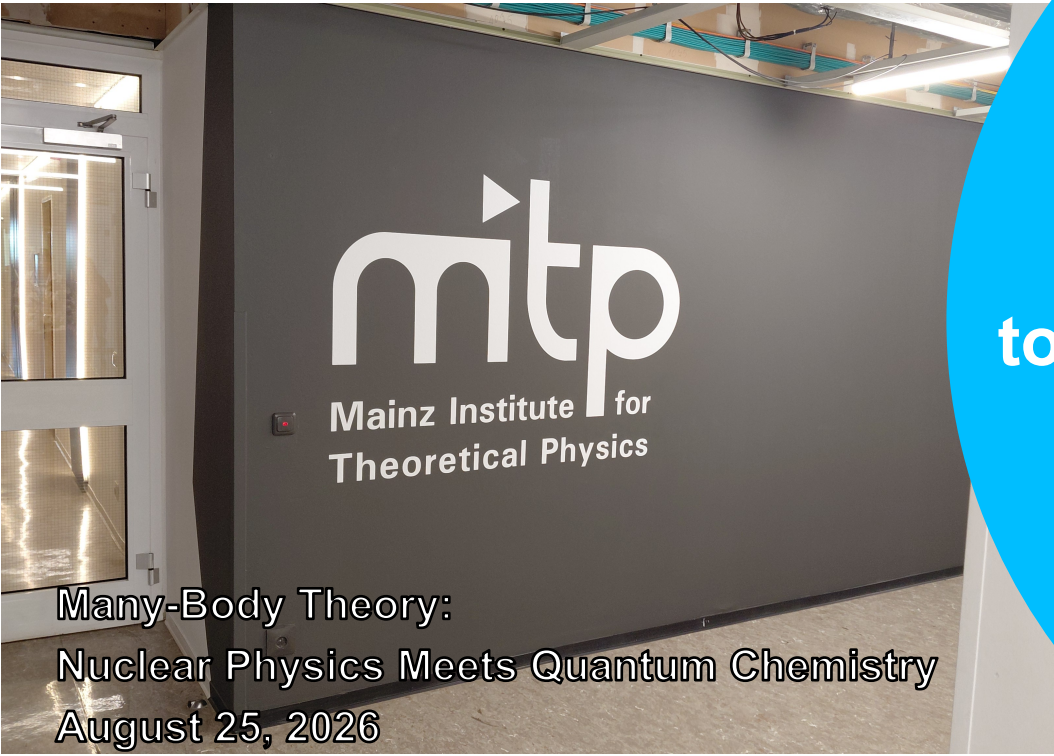
University of Stuttgart
Institute for Theoretical Chemistry



Taking Coupled-Cluster Theory to the Multireference Stage

Andreas Köhn

Many-Body Theory:
Nuclear Physics Meets Quantum Chemistry
August 25, 2026

Merits of coupled-cluster theory

Product-separable wavefunctions $e^{\hat{T}_{\mathrm{A}\cdots\mathrm{B}}}|\Phi_0^{\mathrm{A}\cdots\mathrm{B}}\rangle = e^{\hat{T}_{\mathrm{A}}}|\Phi_0^{\mathrm{A}}\rangle e^{\hat{T}_{\mathrm{B}}}|\Phi_0^{\mathrm{B}}\rangle$

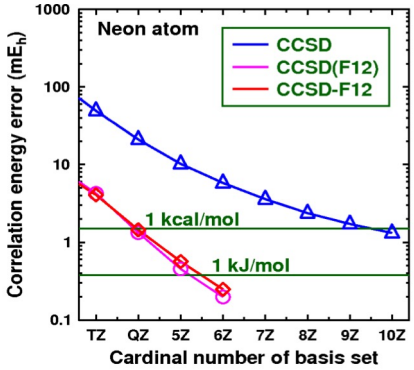
Correct scaling of correlation energy $E_{\mathrm{c}}(N\mathrm{A}) = NE_{\mathrm{c}}(\mathrm{A})$

Systematic and quickly converging hierarchy CCSD, CCSD(T), CCSDT, CCSDTQ, …

➡ Very accurate computations are possible

E.g. thermochemistry: HEAT, W3, FPD, …

Stanton, Gauss, Martin, Karton, Feller, Peterson, Dixon, …



Challenges:

- Basis set convergence: Extrapolation; F12 methods
  Klopper, Kutzelnigg, Tew, Ten-no, Hättig, Werner, Valeev, …
- Steep scaling: Local correlation (PNO)
  Meyer, Pulay, Werner, Neese, Tew, Hättig, …
- Open shells?

PNO-LCCSD(T)-F12 / cc-pVTZ-F12

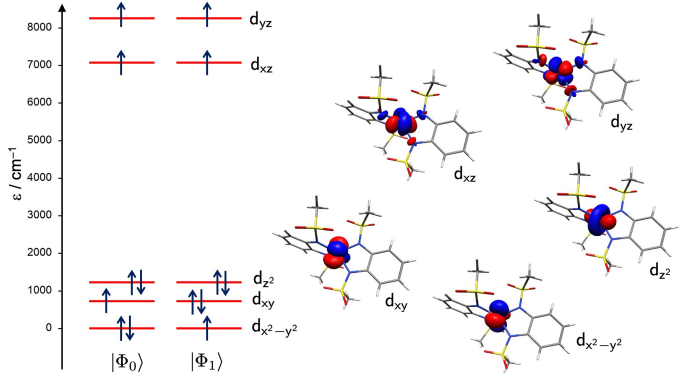
- 92 atoms
- 3345 basis functions

Computational time: 9.4 h (80 cores on 4 nodes)

Ma, Werner, JCTC 2018, 14, 198

Open shells

- incompletely filled atomic shells (d shell, f shell)



CC-BY

Hunger, Netz, …, AK, van Slageren, *Nat. commun.* **2025**, 16, 2157

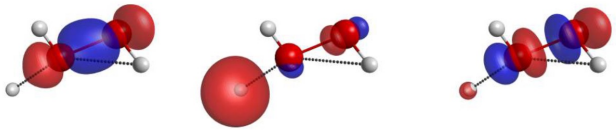
- (poly)-radicals

picture of m-$(TTM)_2$

Kopp, Nakamura, …, Wasielewski, *J. Am. Chem. Soc.* **2024**, *146*, 27935

- Bond cleavage/formation (radicalic pathway)

$H + H_2O_2 \rightarrow H_2O + OH$



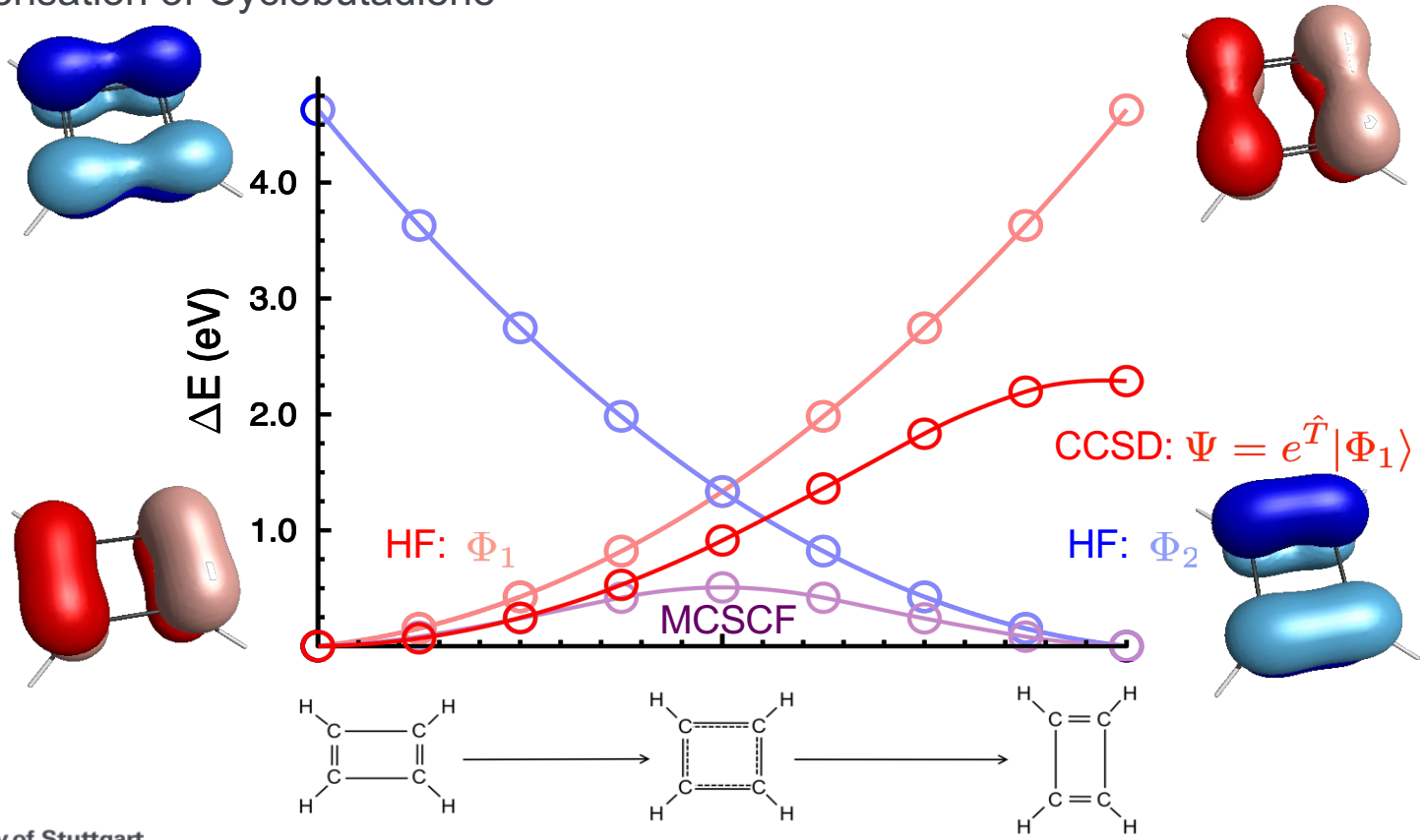
Lamberts, Samanta, AK, Kästner, *Phys. Chem. Chem. Phys.* **2016**, *18*, 33021

In many cases:

- two or more energetically close-lying determinants
- need for spin-adapted functions

Degenerate configurations

Automerisation of Cyclobutadiene



Extension of the single-reference CC ansatz

Two aspects – two starting points

(a) generalise reference function

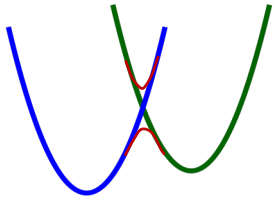
$$|\Phi_0\rangle \Rightarrow |\psi_0\rangle = \sum_\mu |\Phi_\mu\rangle c_\mu$$

required for spin-adapted wfns.

$$|\Psi_{\mathrm{CC}}\rangle = e^{\hat{T}}|\Phi_0\rangle$$

(b) multistate ansatz

required for (near-)degeneracies



$$|\tilde{\Psi}_{\mathrm{CC}}\rangle = c_A|\Psi^A_{\mathrm{CC}}\rangle + c_B|\Psi^B_{\mathrm{CC}}\rangle$$

Generalisation of reference function

Čížek, Adv. Chem. Phys. XIV, 35, 1968

which are described in detail in articles by Jucys,[36] Lefebvre,[37] Löwdin,[38] and Moser,[39] suggest themselves. How to use these methods as an initial approximation for the method described here or, in other words, how to proceed in the case that the exact wave function is written in the form

$$|\Psi\rangle = e^{\hat{R}}|\Phi'\rangle$$

where $|\Phi'\rangle$ is a multideterminantal wave function, will be the subject of a future communication.[40]

Banerjee, Simons, IJQC 1981, 19, 207

Laidig, Saxe, Bartlett, JCP 1987, 86, 887

Fink, Staemmler, TCA 1993, 87, 129

Li, Paldus JCP 1994, 101, 8812

Evangelista, Gauss, JCP 2011, 134, 114102
Hanauer, AK, JCP 2011, 134, 204111

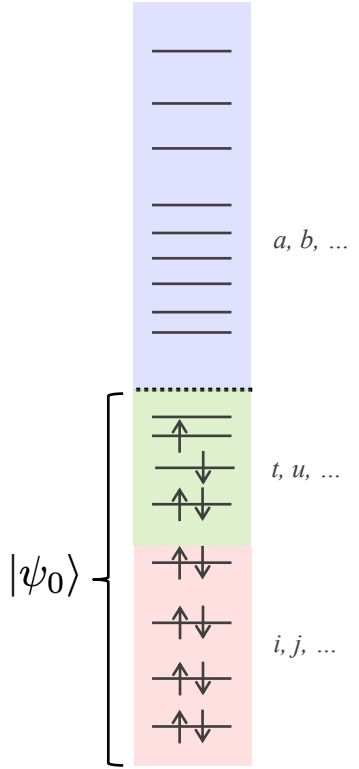
$$|\psi_0\rangle = \sum_\mu |\Phi_\mu\rangle c_\mu \qquad \hat{T} = \sum_\rho t_\rho \hat{\tau}_\rho$$

$$|\Psi_{\mathrm{MRCC}}\rangle = e^{\hat{T}}|\psi_0\rangle \qquad \hat{\tau}_\rho \in \{\hat{E}^a_i, \hat{E}^t_i, \hat{E}^a_t, \hat{E}^{ab}_{ij}, \ldots\}$$

It becomes significantly more complex: $[\hat{E}^a_i, \hat{E}^c_k] = 0$

$$[\hat{E}^u_i, \hat{E}^c_v] = -\delta^u_v \hat{E}^c_i \neq 0$$

→ many more terms, no simple truncation of $e^{-\hat{T}}\hat{H}e^{\hat{T}}$



Generalisation of reference function

$$|\psi_0\rangle = \sum_\mu |\Phi_\mu\rangle c_\mu$$

$$|\Psi_{\mathrm{MRCC}}\rangle = e^{\hat{T}}|\psi_0\rangle \qquad \hat{T} = \sum_\rho t_\rho \hat{\tau}_\rho$$

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Banerjee, Simons, IJQC 1981, 19, 207

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Fink, Staemmler, TCA 1993, 87, 129

Li, Paldus JCP 1994, 101, 8812

Evangelista, Gauss, JCP 2011, 134, 114102
Hanauer, AK, JCP 2011, 134, 204111

$$\hat{E}^{ab}_{ij}|\Phi_0\rangle = |\Phi^{ab}_{ij}\rangle \qquad \hat{E}^{ab}_{uv}\Big(c_{1\bar{1}}|\Phi_{1\bar{1}}\rangle + c_{2\bar{2}}|\Phi_{2\bar{2}}\rangle\Big) = \delta_{uv,11}c_{1\bar{1}}|\Phi^{ab}_{\square}\rangle + \delta_{uv,22}c_{2\bar{2}}|\Phi^{ab}_{\square}\rangle$$

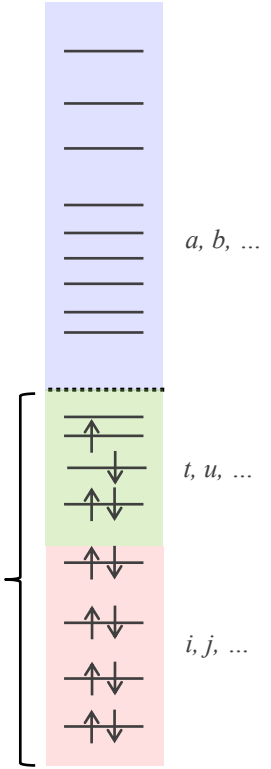
$\Rightarrow$ $\hat{E}^{ab}_{11}|\psi_0\rangle$ and $\hat{E}^{ab}_{22}|\psi_0\rangle$ are linearly dependent

$S_{\rho\sigma} = \langle\psi_0|\hat{\tau}^\dagger_\rho\hat{\tau}_\sigma|\psi_0\rangle$ not diagonal, singular $\Rightarrow$ transform to non-singular orthogonal subspace $\{\hat{\tau}'_\rho|\psi_0\rangle\}$

known from internally contracted CI theory: Werner Adv. Chem. Phys. **1987**, *69*, 1

catch for CC: $\{\hat{\tau}_\rho\} \to \{\hat{\tau}'_\rho\} \cup \{\hat{\tau}^\perp_\rho\}$ have only $\langle\psi_0|\hat{\tau}'^\dagger_\rho e^{-\hat{T}}\hat{H}e^{\hat{T}}|\psi_0\rangle = 0$

but these can give non-zero contributions!



Multistate perspective

The Bloch equations Claude Bloch, *Nucl. Phys.* **1958**, *6*, 329

Zeroth-order states: $\hat{H}_0|\psi_i\rangle = |\psi_i\rangle E_i^{(0)}$

$\mathcal{M}_0$ space: $|\psi_1\rangle, |\psi_2\rangle, \ldots$ Projector: $\hat{P} = \sum_i |\psi_i\rangle\langle\psi_i| \qquad \hat{P}\hat{P} = \hat{P}$

Exact states: $\hat{H}|\Psi_\alpha\rangle = |\Psi_\alpha\rangle E_\alpha \qquad \hat{P}\hat{H}|\Psi_\alpha\rangle = \hat{P}|\Psi_\alpha\rangle E_\alpha$

intermediate normalization: $\langle\Psi_\alpha|\hat{P}|\Psi_\alpha\rangle = 1 \qquad |\tilde{\psi}_\alpha\rangle = \sum_i |\psi_i\rangle C_\alpha^i$

Wave operator: $\hat{\Omega}|\tilde{\psi}_\alpha\rangle = |\Psi_\alpha\rangle \qquad \hat{\Omega}|\tilde{\psi}_\alpha\rangle = \sum_i \hat{\Omega}|\psi_i\rangle C_\alpha^i = \sum_i |\tilde{\Psi}_i\rangle C_\alpha^i$

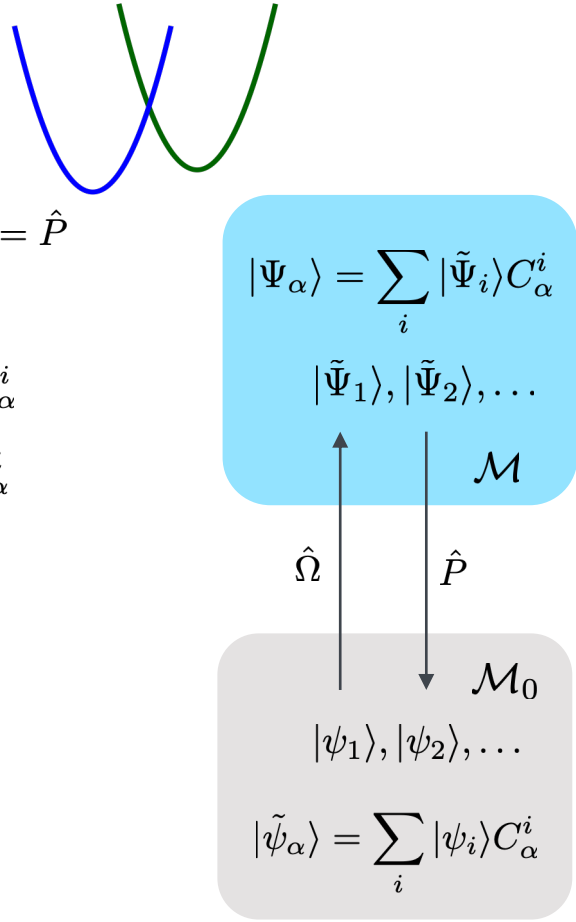
$$\hat{\Omega} = \sum_i |\tilde{\Psi}_i\rangle\langle\psi_i|$$

Properties: $\hat{P}\hat{\Omega} = \hat{P} \qquad \hat{\Omega}\hat{P} = \hat{\Omega} \qquad \hat{\Omega}\hat{\Omega} = \hat{\Omega}$

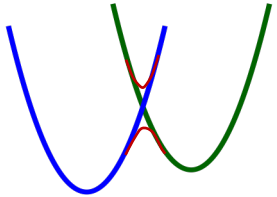
$$\hat{H}|\Psi_\alpha\rangle = |\Psi_\alpha\rangle E_\alpha$$
$$\hat{\Omega}\hat{H}|\Psi_\alpha\rangle = |\Psi_\alpha\rangle E_\alpha$$
$$\left(\hat{H} - \hat{\Omega}\hat{H}\right)|\Psi_\alpha\rangle = 0$$
$$\left(\hat{H} - \hat{\Omega}\hat{H}\right)\hat{\Omega}|\tilde{\psi}_\alpha\rangle = 0$$

equation for wave op.

$$\hat{H}\hat{\Omega} = \hat{\Omega}\hat{H}\hat{\Omega}$$



Multistate perspective



Jeziorski & Monkhorst: State-Universal MRCC (SU-MRCC)
Multiple reference determinants, Bloch equations

$$\hat{H}\hat{\Omega} = \hat{\Omega}\hat{H}\hat{\Omega} \qquad \hat{\Omega} = \sum_{\mu} e^{\hat{T}(\mu)} |\Phi_\mu\rangle\langle\Phi_\mu|$$

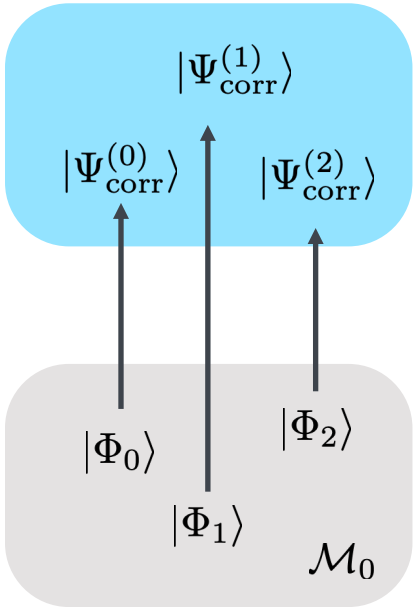
$$\langle\Phi_\mu|\hat{\tau}_\rho^{(\mu)\dagger} e^{-\hat{T}(\mu)} \hat{H} e^{\hat{T}(\mu)} |\Phi_\mu\rangle = \sum_{\nu\neq\mu} \langle\Phi_\mu|\hat{\tau}_\rho^{(\mu)\dagger} e^{-\hat{T}(\mu)} e^{\hat{T}(\nu)} |\Phi_\nu\rangle H_{\nu\mu}^{\mathrm{eff}}$$

$$H_{\nu\mu}^{\mathrm{eff}} = \langle\Phi_\nu| e^{-\hat{T}(\mu)} \hat{H} e^{\hat{T}(\mu)} |\Phi_\mu\rangle$$

further conditions: $\{|\Phi_\mu\rangle\}$ complete

$$\hat{T}(\mu)^\dagger |\Phi_\nu\rangle = 0 \quad \forall \mu, \nu$$

$$|\Psi_{\mathrm{JM}}^{(a)}\rangle = \sum_{\mu} e^{\hat{T}(\mu)} |\Phi_\mu\rangle C_\mu^{(a)}$$



Drawbacks: Many amplitudes, convergence issues,
spin-adaption difficult, depends on orbital rotations inside active space

Jeziorski, Monkhorst, PR A **24**, 1668 (1981)

Multistate perspective with internal contraction

Generalise states in model space:

$$|\psi_i\rangle = \sum_\mu |\Phi_\mu\rangle c_\mu^{(i)} \qquad \hat{\Omega} = \sum_i e^{\hat{T}(i)}|\psi_i\rangle\langle\bar{\psi}_i|$$

Only require biorthogonality of ref. states

Generalised JM (GJM)

Internally contracted MRCC state

Internally contracted projection

$$\langle\psi_i|\hat{\tau}_\rho'^{(i)\dagger} e^{-\hat{T}(i)}\hat{H}e^{\hat{T}(i)}|\psi_i\rangle = \sum_{j\neq i}\langle\psi_i|\hat{\tau}_\rho'^{(i)\dagger} e^{-\hat{T}(i)}e^{\hat{T}(j)}|\psi_j\rangle H_{ji}^{\text{eff}}$$

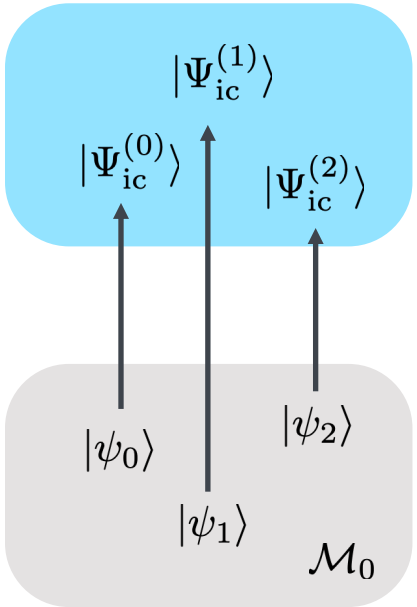
$$H_{ji}^{\text{eff}} = \langle\bar{\psi}_j|e^{-\hat{T}(i)}\hat{H}e^{\hat{T}(i)}|\psi_i\rangle$$

Q: Optimal zeroth-order states?

A: Choose ref. states such that the multistate equations decouple

$$\langle\Phi_\mu|e^{-\hat{T}(i)}(\hat{H}-E_i)e^{\hat{T}(i)}|\psi_i\rangle = 0$$

$H_{ji}^{\text{eff}} = 0$ for $j \neq i$ → Theory becomes state-specific!

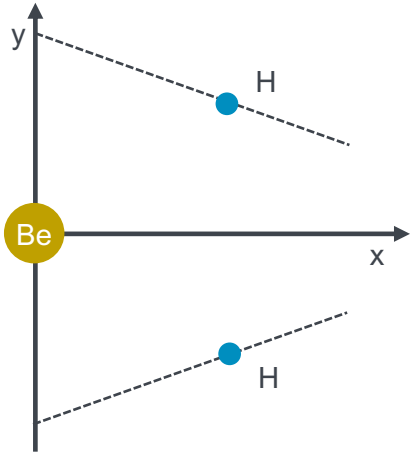


Aoto, AK, JCP 144, 074103 (2016)
see also: Adam, Waigum, AK, WIRes 15, e70023 (2025)

Numerical illustration I

BeH_2

DZ, CAS(2,2)



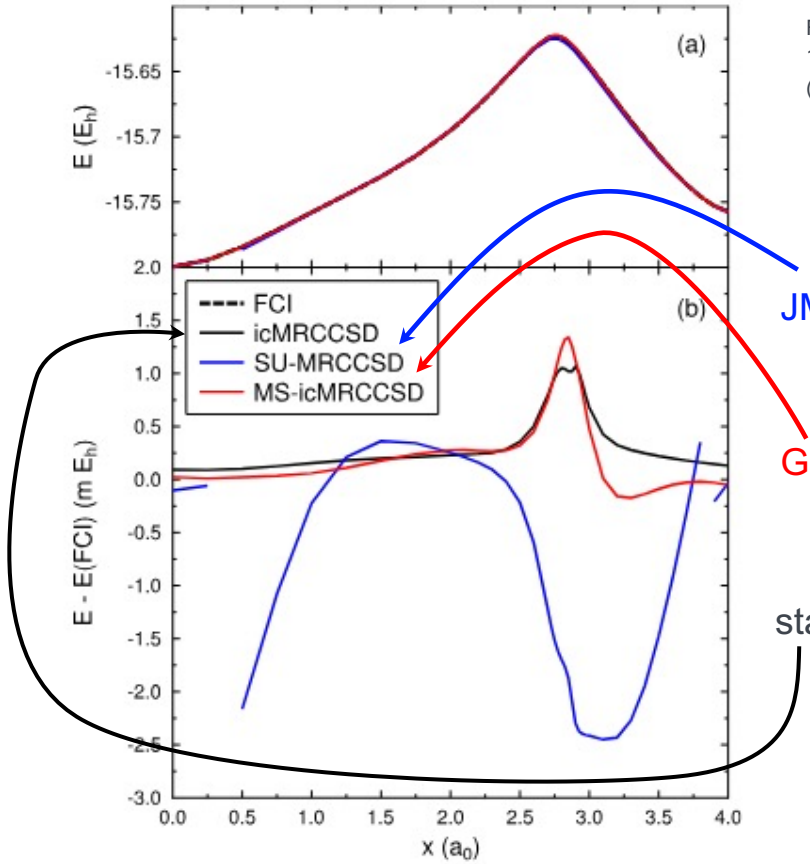


Figure reprinted from Aoto, Köhn, J. Chem. Phys. 144, 074103 (2016) with the permission of AIP (permission #6337630085125)

JM: $\hat{\Omega} = \sum_{\mu} e^{\hat{T}(\mu)} |\Phi_\mu\rangle\langle\Phi_\mu|$ determinants

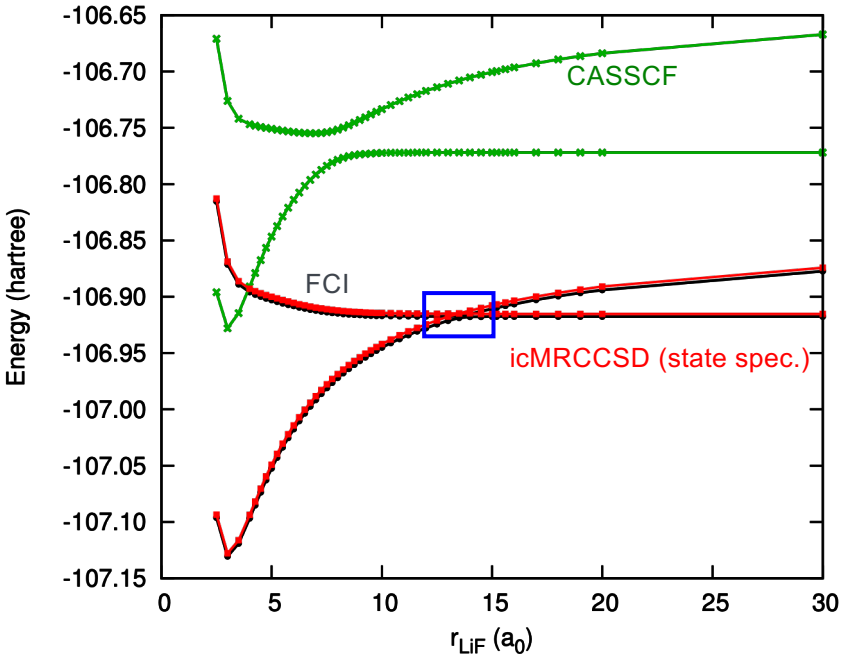
GJM: $\hat{\Omega} = \sum_{i} e^{\hat{T}(i)} |\psi_i\rangle\langle\psi_i|$ CASCI states

state-specific: $e^{\hat{T}} |\psi_0\rangle$ optimised

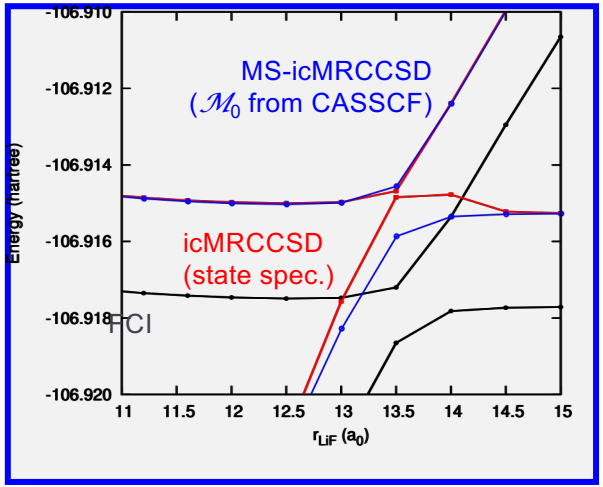
Aoto, Köhn, JCP 144, 074103 (2016)

Numerical illustration II

LiF dissociation



Li: cc-pVDZ
F: aug-cc-pVDZ
frozen core
CAS(2,2)



Aoto, Köhn, JCP 144, 074103 (2016)

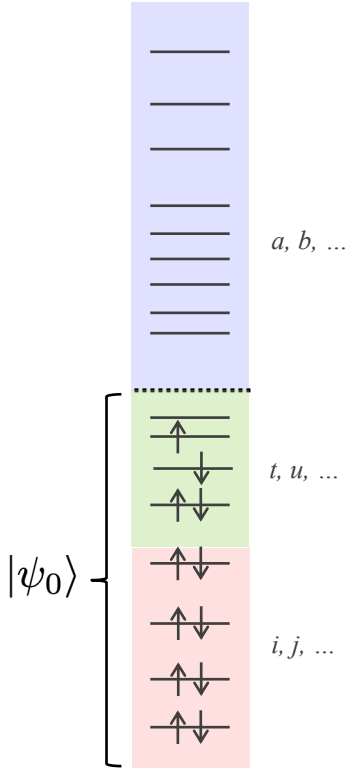
Internally contracted MRCC

Evangelista, Gauss, JCP 134, 114102 (2011)
Hanauer, Köhn, JCP 134, 204111 (2011)
Hanauer, Köhn, JCP 136, 204107 (2012)
Evangelista, Gauss, Hanauer, Köhn, JCP 136, 204108 (2012)
Hanauer, Köhn, JCP 137, 131103 (2012)

older work (same ansatz, but strong simplifications):
Banerjee, Simons, IJQC 19, 207 (1981)
Laidig, Saxe, Bartlett, JCP 86, 887 (1987)
Fink, Staemmler, TCA 87, 129 (1993)

$$|\Psi\rangle = e^{\hat{T}}|\psi_0\rangle = e^{\hat{T}}\sum_\mu |\Phi_\mu\rangle c_\mu$$

$$\hat{T} = \sum t_\rho \hat{\tau}_\rho$$



exclude active-active excitations
instead: optimize reference $|\psi_0\rangle = \sum_\mu |\Phi_\mu\rangle c_\mu$

Amplitude equations: $\langle\psi_0|\hat{\tau}'^\dagger_\rho e^{-\hat{T}}\hat{H}e^{\hat{T}}|\psi_0\rangle = 0$

$\hat{H} + [\hat{H},\hat{T}] + \frac{1}{2}[[\hat{H},\hat{T}],\hat{T}]$
approx. BCH expansion

Coefficient equations: $\sum_\nu \langle\Phi_\mu|e^{-\hat{T}}\hat{H}e^{\hat{T}}|\Phi_\nu\rangle c_\nu = E c_\mu$

orthogonalized excitation manifold (lin. dep. → threshold)

$$\hat{\tau}'_\rho = \sum_\sigma \hat{\tau}_\sigma X^\sigma_\rho \qquad \langle\psi_0|\hat{\tau}'^\dagger_\rho \hat{\tau}'_\sigma|\psi_0\rangle = \delta_{\rho\sigma}$$

(icMRCCSD: diagonalize up to 3-RDM)

Fully spin-adapted!

efficient CAS(2,2) impl.
since Molpro 2023.1

recent summary: WIRes 15 (2025) e70023

Internally contracted MRCC – (T)

Hanauer, Köhn, JCP 136, 204107 (2012)
Köhn, Black, Aoto, Hanauer, Mol. Phys. 118, e1743889 (2020)
For some updates see: Waigum, Ertürk, Köhn, JPC A 128, 10053 (2024)

Perturbative triples: icMRCCSD(T)

Based on Dyall Hamiltonian

$$\langle\Psi_0|\hat{\tau}'^{\dagger}_{\rho_3}[\hat{H}_0,\hat{T}_3]|\Psi_0\rangle = -\langle\Psi_0|\hat{\tau}'^{\dagger}_{\rho_3}[\hat{H},\hat{T}_2]|\Psi_0\rangle$$

$$\Delta E_{(\mathrm{T})} = \langle\Psi_0|(\hat{T}_1^{\dagger}+\hat{T}_2^{\dagger})[\hat{H},\hat{T}_3]|\Psi_0\rangle$$

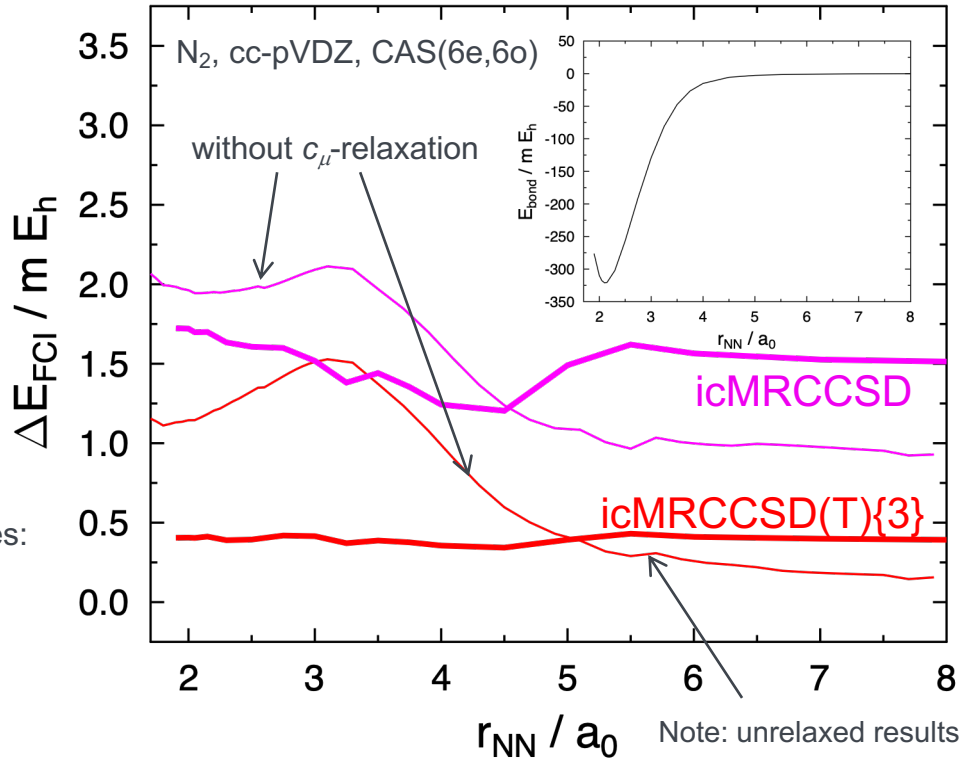
Approximation: Try to avoid T_3
with too many active indices

orthogonalization requires:

{3}: e.g. $t^{tuv}_{abc}\ t^{iuv}_{abt}$ 3-RDM

{4}: e.g. $t^{tuv}_{abw}\ t^{itu}_{avw}$ 4-RDM

{5}: e.g. t^{tuv}_{awx} 5-RDM



Note: unrelaxed results use CAS(10e,8o)

Application examples

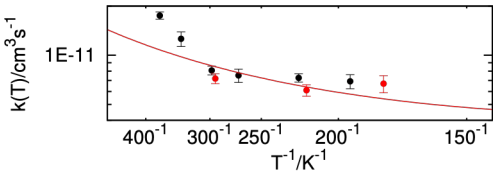
[F,H,Cl] global PES

Aoto, AK, PCCP 18, 30241 (2016)

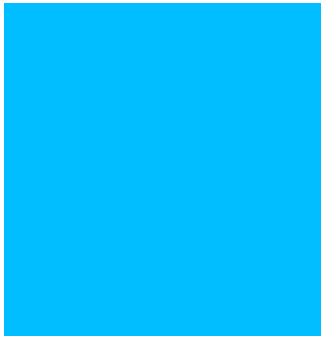
$F + HCl \longrightarrow Cl + HF$

Barrier height

Best estimate	1.21 kcal mol^{-1}
+ Spin-Orbit	1.59 kcal mol^{-1}
Previous work (MRCI)	3.8 kcal mol^{-1}



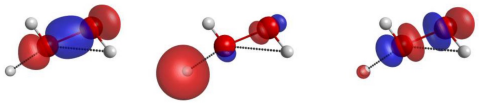
CoH



de Moraes, Aoto, *Theor. Chem. Acc.* **2020**, *139*, 71

$H + H_2O_2 \longrightarrow H_2O + OH$ tunnelling rates

benchmarking of RE and barriers



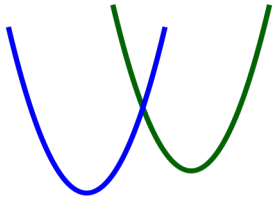
Lamberts, Samanta, AK, Kästner, *PCCP* **2016**, *18*, 33021

Benchmarking mechanisms in mechano-chemistry

Germann, Meisner, *J. Phys. Chem. A* **2024**, 128, 10224

Summary and Outlook

spin-adapted
general references



unbiased treatment of
near-degeneracies

$$\hat{\Omega} = \sum_i e^{\hat{T}(i)} |\psi_i\rangle\langle\bar{\psi}_i|$$

Generalised Jeziorski-Monkhorst ansatz

$|\psi_i\rangle \rightarrow |\Phi_\mu\rangle$

$$\hat{\Omega} = \sum_\mu e^{\hat{T}(\mu)} |\Phi_\mu\rangle\langle\Phi_\mu|$$

Jeziorski-Monkhorst ansatz

state-specific variants
(e.g. by Mukherjee)

$H^{\text{eff}}_{ji} = 0$

$e^{\hat{T}}|\psi_0\rangle$

state specific
icMRCC theory

+ unbiased ref. state
+ spin-adapted
+ extensive
+ compact & accurate

– implementation diff.
– numerical stability

alternatives: active-space CC;
DIP/DEA-EOM-CC
not covered: Fock-Space CC

possible alternatives: e.g. ric-MRCCSD (Feldmann/Reiher), DSRG by Evangelista

open issue: active space scaling