

# **String-based methods for state-selective multi-reference coupled-cluster**

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# Outline

- 1 Implementation of single-reference CC theories**
- 2 State-specific multi-reference CC theories**
- 3 Implementation of the SR-MRCC ansatz**
- 4 Implementation of Mukherjee's SS-MRCC ansatz**
- 5 Assessment of state-specific MRCC methods**
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# 1

# Implementation of single-reference CC theories

# Coupled-cluster theory

Coupled-cluster wave function:

$$|\Psi\rangle = e^{\hat{T}}|0\rangle \quad \hat{T} = \sum_{k=1}^n \hat{T}_k$$

$$\hat{T}_k = \sum_{\substack{a_1 < a_2 \dots < a_k \\ i_1 < i_2 \dots < i_k}} t_{i_1 i_2 \dots i_k}^{a_1 a_2 \dots a_k} a_1^+ i_1^- a_2^+ i_2^- \dots a_k^+ i_k^-$$

$i, j, k \dots (a, b, c \dots)$ : occupied (virtual) orbitals

$p, q, r \dots$ : generic indices

$t_{i_1 i_2 \dots i_k}^{a_1 a_2 \dots a_k}$ : cluster amplitudes

## Coupled-cluster equations:

$$\langle 0 | e^{-\hat{T}} \hat{H} e^{\hat{T}} | 0 \rangle = E$$

$$\langle \Psi_{i_1 i_2 \dots i_k}^{a_1 a_2 \dots a_k} | e^{-\hat{T}} \hat{H} e^{\hat{T}} | 0 \rangle = 0 \quad (k = 1, \dots, n)$$

$$e^{-\hat{T}} \hat{H} e^{\hat{T}} = 1 + [\hat{H}, \hat{T}] + \frac{1}{2!} [[\hat{H}, \hat{T}], \hat{T}] + \dots =$$

$$\{ \hat{H} (1 + \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \dots + \frac{1}{2!} \hat{T}_1^2 + \hat{T}_1 \hat{T}_2 + \frac{1}{3!} \hat{T}_1^3 + \dots) \}_C$$

Consequence: only connected terms in operator  $e^{-\hat{T}} \hat{H} e^{\hat{T}}$   
 Two-body Hamiltonian  $\Rightarrow$  at most the fourth power of  $\hat{T}$

# Solution of CC equations

Our goal is to solve the CC equations up to infinite order minimizing the costs of the calculation.

1. Derivation of CC equations in terms of antisymmetrized (Brandow-type) diagrams
2. Factorization of these diagrams and the definition of intermediates
3. The numerical calculation itself which corresponds to successive evaluation of contractions of cluster amplitudes with intermediates.

## Automated diagram generation

Antisymmetrized diagrams are represented by 13-membered integer sequences:

$$\mu_{1,1} \mu_{1,2} \mu_{1,3} \quad \mu_{2,1} \mu_{2,2} \mu_{2,3} \quad \mu_{3,1} \mu_{3,2} \mu_{3,3} \quad \mu_{4,1} \mu_{4,2} \mu_{4,3} \quad \mu_5$$

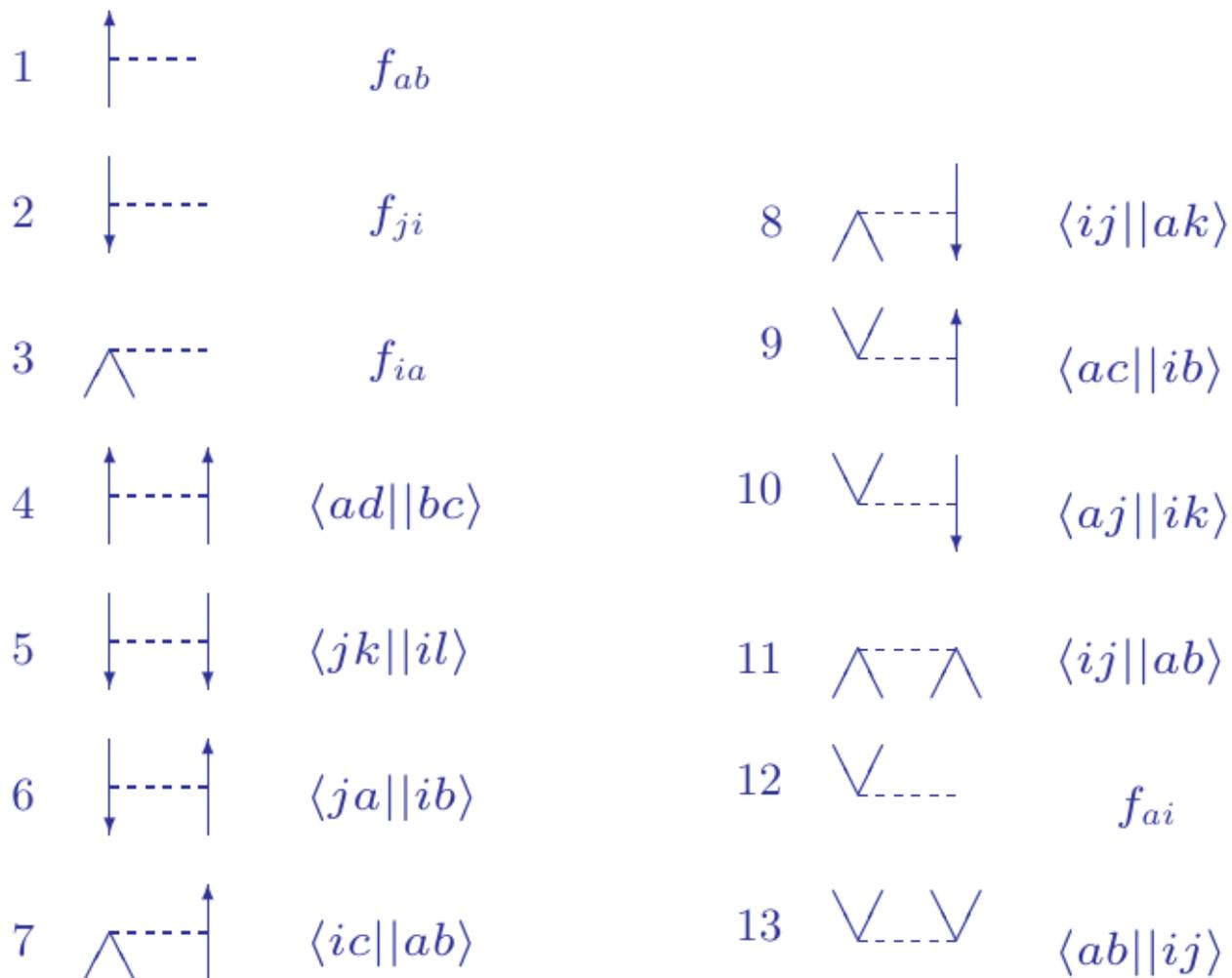
a triplet of numbers ( $\{\mu_{i,j}\}_{j=1}^3$ ) for each amplitude vertex (or zeros if there are less than four  $\hat{T}$  vertices) and the serial number ( $\mu_5$ ) of the integral list.

$\mu_{i,1}$ : excitation level of the amplitude vertex

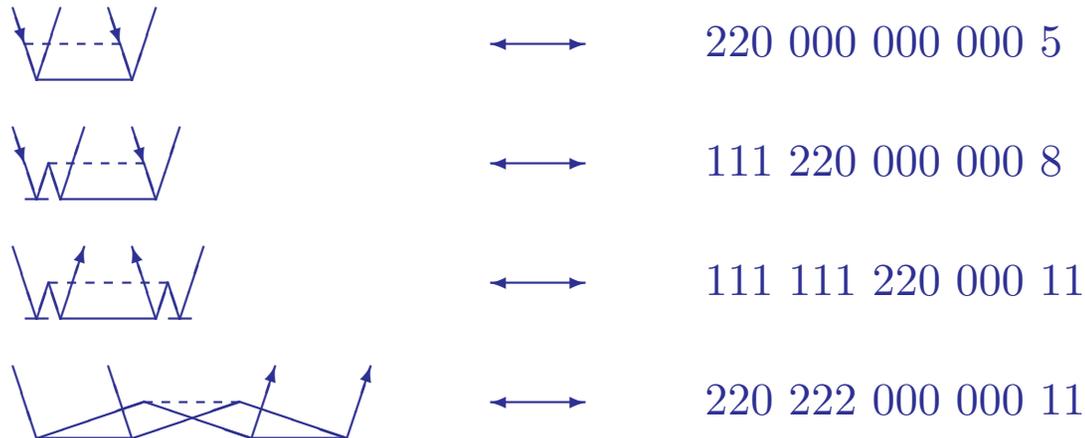
$\mu_{i,2}$ : number of internal lines attached to the  $\hat{T}$  vertex

$\mu_{i,3}$ : number of internal particle lines

# Automated diagram generation: Hamiltonian



# Automated diagram generation: examples



Intermediates can also be symbolized by such sequences of integers.

In general: any expression can be represented by such sequences (a multiplet of integers for each factor) provided that there are only excitation operators or only one of them is a de-excitation operator.

# Diagram factorization

## What does factorization mean?

- diagrams in CC equations are usually non-linear in cluster amplitudes
- however, contractions of Fock-matrix elements or two-electron integrals with cluster amplitudes can be carried out by linear operations
- we can sum over internal lines connected to a  $\hat{T}$  vertex independently
- a non-linear term can be calculated as successive contractions between appropriately defined intermediates (partial sums) and cluster amplitudes.

Example:

$$W_{ij}^{ab} = -\hat{P}(i|j) \sum_{c<d,k,l} \langle kl||cd \rangle t_{ki}^{ab} t_{lj}^{cd} \quad [\sim n_b^8]$$

It can be factorized in two different ways:

$$W_{l,i}^{cd,ab} = \sum_k \langle kl||cd \rangle t_{ki}^{ab} \quad [\sim n_b^7]$$

$$W_{ij}^{ab} = -\hat{P}(i|j) \sum_{c<d,l} W_{l,i}^{cd,ab} t_{lj}^{cd} \quad [\sim n_b^7]$$

or

$$W_{k,j} = \sum_{c<d,l} \langle kl||cd \rangle t_{lj}^{cd} \quad [\sim n_b^5]$$

$$W_{ij}^{ab} = -\hat{P}(i|j) \sum_k W_{k,j} t_{ki}^{ab} \quad [\sim n_b^5]$$

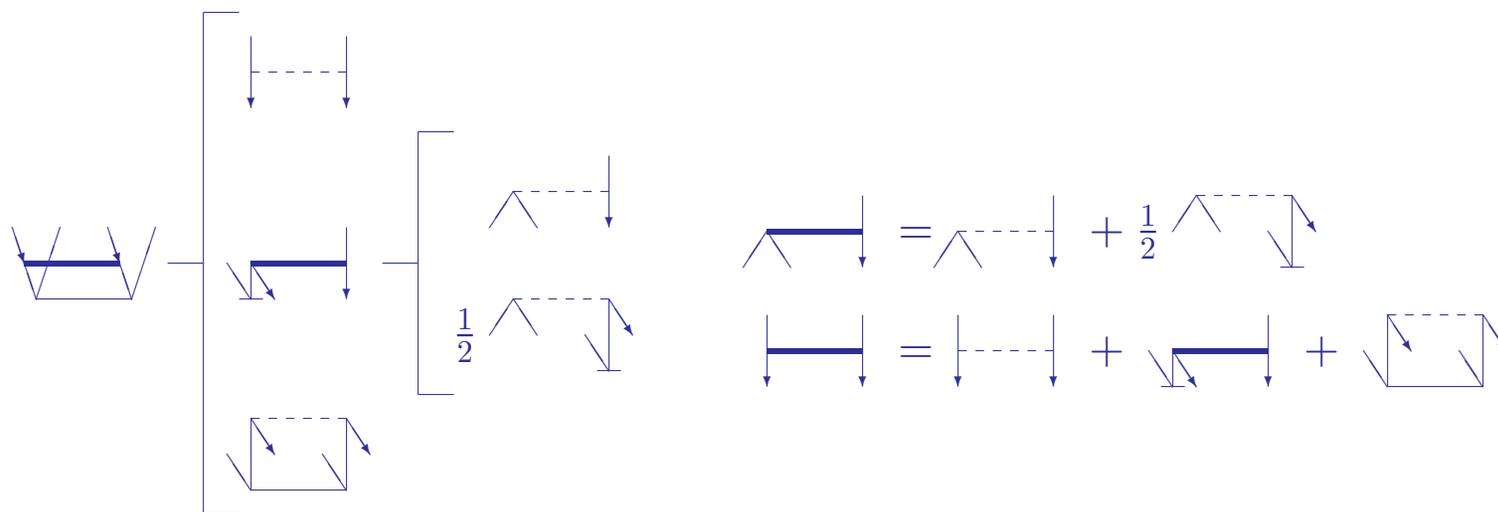
## Identification of intermediates

- further intermediates can be defined by adding those ones together that have identical labels and will be contracted with the same amplitude vertices
- rearrange integer triples within each 13-membered sequence: last contracted amplitude vertex to the left then the next-to-the-last etc.
- the 13-membered integer sequences can be regarded as 13-digit integers and can be ordered into ascending order
- consider consecutive diagrams: supposing that the  $m$ th integer triple is identical in the sequences, but the  $(m + 1)$ th one is different, intermediates  $\mu_{m+1,1} \mu_{m+1,2} \dots \mu_{4,3} \mu_5$  can be added together

# Example: above four diagrams (CCSD, $\hat{T}_2$ equations)

$$\begin{array}{l}
 220 \ 000 \ 000 \ 000 \ 5 \\
 220 \ 111 \ 000 \ 000 \ 8 \\
 220 \ 111 \ 111 \ 000 \ 11 \\
 220 \ 222 \ 000 \ 000 \ 11
 \end{array}
 \longrightarrow
 220 \left[ \begin{array}{l}
 000 \quad \left[ \begin{array}{l} 000 \ 000 \ 5 \\ 000 \ 000 \ 8 \end{array} \right. \\
 111 \quad \left[ \begin{array}{l} 111 \ 000 \ 11 \\ 000 \ 000 \ 11 \end{array} \right. \\
 222 \quad \left[ \begin{array}{l} 000 \ 000 \ 11 \end{array} \right.
 \end{array} \right.$$

This scheme with the conventional diagrams:



# String-based algorithm

## What does term “string” mean?

A string is an ordered set of (spin-)orbital indices ( $p$ ):

$$\mathcal{P} = p_1 p_2 p_3 \dots \quad (p_1 < p_2 < p_3 < \dots)$$

E.g., in the case of four orbitals, the three-membered strings are:

$$1\ 2\ 3 \quad 1\ 2\ 4 \quad 1\ 3\ 4 \quad 2\ 3\ 4$$

The concept of strings was introduced into quantum chemistry by Handy four decades ago for addressing the determinants in a full CI calculation.

# String-based algorithm

## Why do we need strings?

- in conventional many-body codes, quantities are stored in terms of orbital indices, loops run over orbitals
- a general procedure is desired which is independent of the number of indices.
- solution: string-based algorithm – quantities in terms of strings, loops over strings

Cluster amplitudes and intermediates with strings:

$$t_{i_1 i_2 \dots i_n}^{a_1 a_2 \dots a_n} \rightarrow t_{\mathcal{I}}^{\mathcal{A}}$$

$$W_{k_1 k_2, i_1 i_2 \dots i_n}^{c_1 c_2, a_1 a_2 \dots a_n} \rightarrow W_{\mathcal{K}\mathcal{I}}^{\mathcal{C}\mathcal{A}}$$

$\mathcal{I}, \mathcal{J}, \mathcal{K} \dots (\mathcal{A}, \mathcal{B}, \mathcal{C} \dots)$ : strings of occupied (virtual) indices

# Concept of string multiplication

Product of two strings of the same type:

$$\mathcal{R} = \text{sgn}_{\mathcal{P}\mathcal{Q}} \mathcal{P} \cdot \mathcal{Q}$$

$\mathcal{R}$  is a string that consists of the elements of  $\mathcal{P}$  and  $\mathcal{Q}$

$\text{sgn}_{\mathcal{P}\mathcal{Q}} = 0$  if  $\mathcal{P}$  and  $\mathcal{Q}$  contain any common index

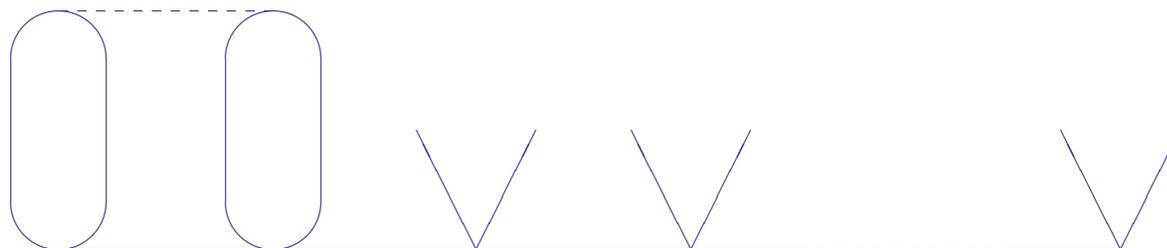
$\text{sgn}_{\mathcal{P}\mathcal{Q}} = (-1)^p$  otherwise

$p$  is the parity of the permutation which arranges elements into ascending order

All operations with cluster amplitudes and intermediates can be expressed in terms of string multiplications.

# Evaluation of contractions

An example:



In terms of spin-orbital indices:

$$V_{i_3 i_4 \dots i_n}^{a_3 a_4 \dots a_n} = \sum_{a_1 < a_2 \quad i_1 < i_2} \langle a_1 a_2 || i_1 i_2 \rangle t_{i_1 i_2 \dots i_n}^{a_1 a_2 \dots a_n}$$

In terms of strings:

$$V_{\mathcal{I}}^{\mathcal{A}} = \sum_{\mathcal{B}\mathcal{J}} \text{sgn}_{\mathcal{B}\mathcal{A}} \text{sgn}_{\mathcal{J}\mathcal{I}} W_{\mathcal{J}}^{\mathcal{B}} t_{\mathcal{J}\cdot\mathcal{I}}^{\mathcal{B}\cdot\mathcal{A}}$$

$$\mathcal{A} = a_3 a_4 \dots a_n \quad \mathcal{I} = i_3 i_4 \dots i_n \quad \mathcal{B} = a_1 a_2 \quad \mathcal{J} = i_1 i_2$$

# Algorithm for contractions

Loop over  $\mathcal{A}$

Loop over  $\mathcal{I}$

Initialize an array  $F$  to zero

Loop over  $\mathcal{J}$  ( $\mathcal{J} \cdot \mathcal{I} \neq 0$ )

$$\mathcal{K} = \mathcal{J} \cdot \mathcal{I}$$

Loop over  $\mathcal{B}$  ( $\mathcal{B} \cdot \mathcal{A} \neq 0$ )

$$C = \mathcal{B} \cdot \mathcal{A}$$

$$F_{\mathcal{J}}^{\mathcal{B}} = \text{sgn}_{\mathcal{B}\mathcal{A}} \text{sgn}_{\mathcal{J}\mathcal{I}} t_{\mathcal{K}}^C$$

End of loop over  $\mathcal{B}$

End of loop over  $\mathcal{J}$

$$V_{\mathcal{I}}^{\mathcal{A}} = \sum_{\mathcal{B}\mathcal{J}} W_{\mathcal{J}}^{\mathcal{B}} F_{\mathcal{J}}^{\mathcal{B}}$$

End of loop over  $\mathcal{I}$

End of loop over  $\mathcal{A}$

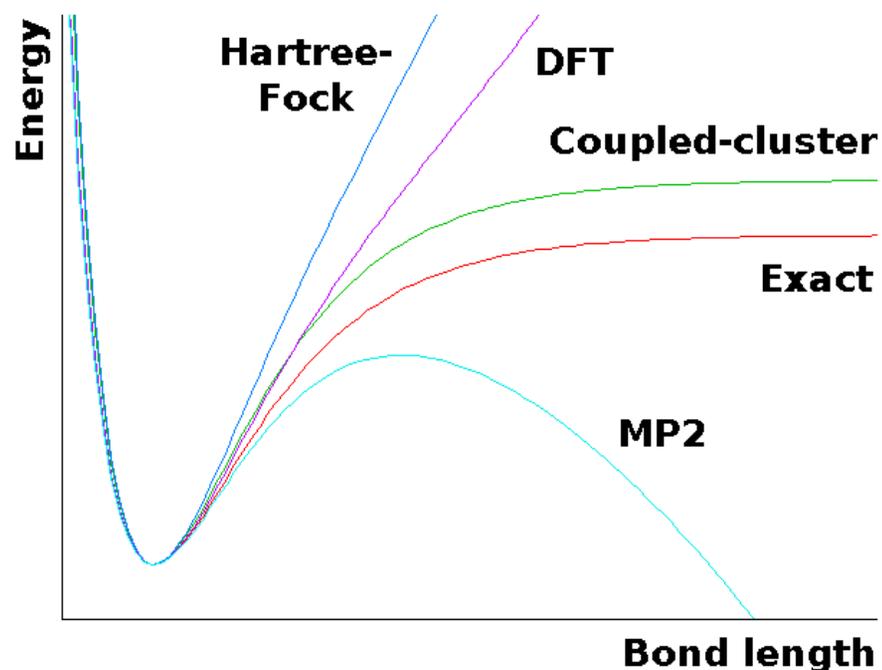
# 2

# State-specific multi-reference CC theories

# Why are multi-reference coupled-cluster models required?

- the majority of the quantum chemical methods only work at the equilibrium

E.g., the dissociation curve of the fluorine molecule



- configuration interaction (CI) methods, which can describe multi-reference problems, are not size-extensive, thus not applicable to large molecules

# The Jeziorski–Monkhorst ansatz

Jeziorski and Monkhorst, *Phys. Rev. A* **24**, 1668 (1981).  
Silverstone and Sinanoglu, *J. Chem. Phys.* **44**, 1899 (1966).

**The wave function ansatz:**

$$\psi = \sum_{\mu} \exp(T^{\mu}) \phi_{\mu} c_{\mu}$$

$\phi_{\mu}$  – reference function

$c_{\mu}$  – combining coefficients

$T^{\mu}$  – cluster operator for  $\phi_{\mu}$ :  $T^{\mu} = \sum_l t_{l\mu}^{\mu} a^{+} \dots i^{-} \dots$  where

the summation runs through all single and double excitations out of  $\phi_{\mu}$  generating a virtual determinant  $|\chi_l\rangle$

## The effective Hamiltonian:

$$\bar{H}_\mu = \exp(-T^\mu) H \exp(T^\mu)$$

**The equations for the  $c_\mu$  coefficients:** diagonalize the effective Hamiltonian in the model space

$$\sum_\nu \tilde{H}_{\mu\nu} c_\nu = E c_\mu$$

where  $\tilde{H}_{\mu\nu} = \langle \phi_\mu | \bar{H}_\nu | \phi_\nu \rangle$ .

**The equations for the cluster amplitudes:** derived from the Bloch equation, no Schrödinger equation

$$\langle \chi_l | \bar{H}_\mu | \phi_\mu \rangle - \sum_\nu \langle \chi_l | \exp(-T^\mu) \exp(T^\nu) | \phi_\nu \rangle \tilde{H}_{\nu\mu} = 0$$

## Problems with the ansatz:

- one has to consider several eigenstates simultaneously whose majority is irrelevant to the problem—it is not state-specific
- high number of cluster amplitudes
- appearance of intruder states—convergence problems

$$t_{l\mu}^{\mu} = \frac{H_{l\mu} + \sum_{m \neq l} H_{lm} t_{m\mu}^{\mu} + \dots + \sum_{\nu} (t_{l\nu}^{\nu} - t_{l\nu}^{\mu} + \dots) \tilde{H}_{\nu\mu}}{\tilde{H}_{\mu\mu} - H_{ll}}$$

where  $H_{lm} = \langle \chi_l | H | \chi_m \rangle$

# State-specific MRCC theories based on the Jeziorski–Monkhorst ansatz

- **Mukherjee's state-specific MRCC theory (SS-MRCC)**  
Mahapatra, Datta, and Mukherjee, *J. Chem. Phys.* **110**, 6171 (1999).
- **Multi-reference Brillouin-Wigner CC theory (MRBWCC)**  
Mášik, Hubač, and Mach, *J. Chem. Phys.* **108**, 6571 (1998).
- **Hanrath's MRexpT model**  
Hanrath, *J. Chem. Phys.* **123**, 084102 (2005).

# Mukherjee's state-specific MRCC theory

**The equations for the cluster amplitudes:** derived from the Schrödinger equation invoking sufficiency conditions

$$\langle \chi_l | \bar{H}_\mu | \phi_\mu \rangle c_\mu + \sum_\nu \langle \chi_l | \exp(-T^\mu) \exp(T^\nu) | \phi_\mu \rangle \tilde{H}_{\mu\nu} c_\nu = 0$$

**Properties of the ansatz:**

- state-specific
- size-extensive and size-consistent with localized orbitals
- not invariant to transformation among the active orbitals
- no intruder states

$$t_{l\mu}^\mu = \frac{H_{l\mu} + \sum_{m \neq l} H_{lm} t_{m\mu}^\mu + \dots + \sum_\nu (t_{l\mu}^\nu + \dots) \tilde{H}_{\mu\nu} c_\nu / c_\mu}{E - H_{ll}}$$

# Multi-reference Brillouin-Wigner CC theory

**The equations for the cluster amplitudes:** derived from the Schrödinger equation invoking sufficiency conditions

$$\langle \chi_l | H \exp(T^\mu) | \phi_\mu \rangle = E \langle \chi_l | \exp(T^\mu) | \phi_\mu \rangle$$

## Properties of the ansatz:

- state-specific
- not size-extensive and size-consistent
- no intruder states
- size-extensivity corrections are possible but result in intruder state problems

# Hanrath's MRexpT model

**Modified wave function ansatz:** cluster amplitudes generating  $|\chi_l\rangle$  from different reference determinants are constrained to be equal

**The equations for the cluster amplitudes:** derived from the Schrödinger equation

$$\sum_{\mu} \langle \chi_l | H \exp(T^{\mu}) | \phi_{\mu} \rangle c_{\mu} = E \sum_{\mu} \langle \chi_l | \exp(T^{\mu}) | \phi_{\mu} \rangle c_{\mu}$$

**Properties of the ansatz:**

- state-specific
- not size-extensive
- no intruder states

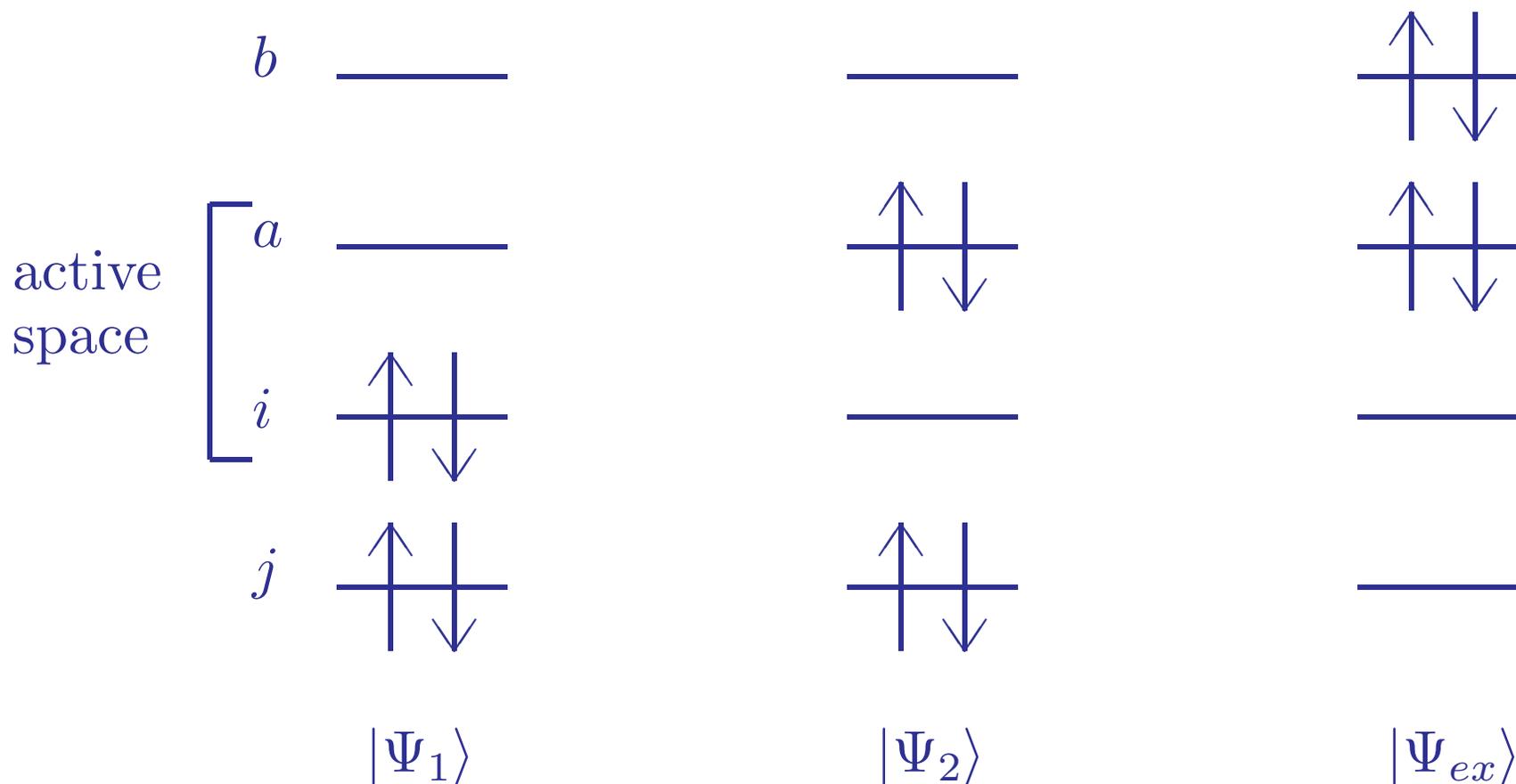
## An alternative formulation: the “single-reference” multi-reference CC ansatz

Oliphant and Adamowicz, *J. Chem. Phys.* **94**, 1229 (1991).

Piecuch, Oliphant, and Adamowicz, *J. Chem. Phys.* **99**, 1875 (1993).

MK, Szalay, and Surján, *J. Chem. Phys.* **117**, 980 (2002).

- assuming a complete active space, one of the reference determinants can be chosen as a formal Fermi-vacuum
- all single, double (or higher) excitations out of the other reference functions can be regarded as higher excitations out of this single determinant



$|0\rangle = |\Psi_1\rangle$  – Fermi-vacuum

$|\Psi_2\rangle = a_\alpha^+ a_\beta^+ i_\alpha^- i_\beta^- |0\rangle$  – another reference determinant

$|\Psi_{ex}\rangle = a_\alpha^+ a_\beta^+ b_\alpha^+ b_\beta^+ i_\alpha^- i_\beta^- j_\alpha^- j_\beta^- |0\rangle$  – double excitation from  $|\Psi_2\rangle$

## Properties of the ansatz:

- the single-reference formalism can be applied, however, only selected excitations are included
- it retains the simplicity and the size-extensivity of the single-reference CC methods, state-specific, no intruder states
- disturbing feature: the method is not invariant with respect to the choice of the Fermi-vacuum
- however, the error resulting from the lack of invariance is usually smaller than the absolute error of the method
- it can be regarded as a selection scheme for single reference wave functions

# 3

## Implementation of the SR-MRCC ansatz

# Automated diagram generation

Multi-reference case: amplitudes are classified according to the number of inactive labels

Two additional integers per  $\hat{T}$  vertex  $\rightarrow$  21-membered integer strings

$$\mu_{1,1} \mu_{1,2} \mu_{1,3} \mu_{1,4} \mu_{1,5} \quad \dots \quad \mu_{4,1} \mu_{4,2} \mu_{4,3} \mu_{4,4} \mu_{4,5} \quad \mu_5$$

$\mu_{i,1}$ : excitation level of the amplitude vertex

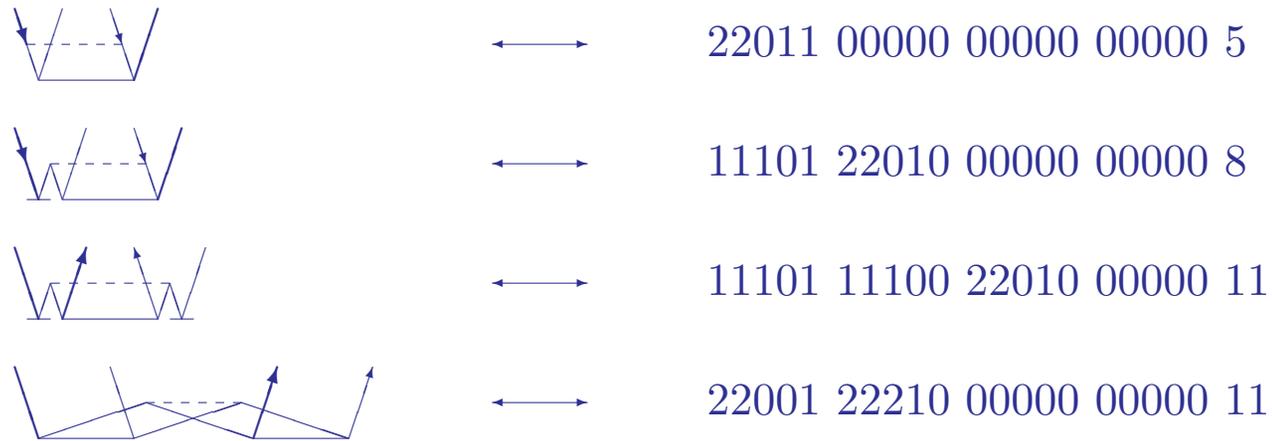
$\mu_{i,2}$ : number of internal lines attached to the  $\hat{T}$  vertex

$\mu_{i,3}$ : number of internal particle lines

$\mu_{i,4}$ : number of inactive fixed particle lines

$\mu_{i,5}$ : number of inactive fixed hole lines

# Automated diagram generation: examples



Inactive labels: thick lines

The projecting amplitude has one particle and one hole inactive index.

With these modifications, the single-reference machinery can be employed.

# 4

## Implementation of Mukherjee's SS-MRCC ansatz

## Previous implementations

- **Mukherjee and co-workers:** the active space is limited to two closed-shell determinants  
Mahapatra, Datta, and Mukherjee, *J. Chem. Phys.* **110**, 6171 (1999).
- **Evangelista and co-workers:** the active space is limited to two electrons  
Evangelista, Allen, and Schaefer, *J. Chem. Phys.* **125**, 154113 (2006); **127**, 024102 (2007).
- **Pittner and co-workers:** general active spaces; single, double, and triple excitations  
Bhaskaran-Nair, Demel, and Pittner, *J. Chem. Phys.* **132**, 154105 (2010).

# Our implementation

## Features:

- string-based techniques
- arbitrary complete active spaces
- no restriction on the number of electrons, number of active orbitals, spin multiplicity
- arbitrarily high excitations in the cluster operators
- other implemented methods: SS-MRCEPA, SS-MRPT, MRBWCC

## The working equations:

$$\langle \chi_l | \bar{H}_\mu | \phi_\mu \rangle c_\mu + \sum_\nu \langle \chi_l | \exp(-T^\mu) \exp(T^\nu) | \phi_\mu \rangle \tilde{H}_{\mu\nu} c_\nu = 0$$

$$\sum_\nu \tilde{H}_{\mu\nu} c_\nu = E c_\mu \quad \text{where} \quad \tilde{H}_{\mu\nu} = \langle \phi_\mu | \bar{H}_\nu | \phi_\nu \rangle$$

## Implementation of $\langle \chi_l | \bar{H}_\mu | \phi_\mu \rangle$ and $\tilde{H}_{\mu\nu}$ :

- similar to the matrix elements for the SRMRCC approach
- the all-active excitations are dropped from  $T^\mu$
- the projecting space is limited to excitations corresponding to  $T^\mu$  as well as to the reference determinants

## Implementation of $\langle \chi_l | \exp(-T^\mu) \exp(T^\nu) | \phi_\mu \rangle$ :

- new term
- the non-vanishing component of  $T^\nu$ ,  $\overline{T^\nu}(\mu)$ , has exactly the same excitation structure as  $T^\mu$
- $\overline{T^\nu}(\mu)$  and  $T^\mu$  commute  $\Rightarrow$  one can rewrite the matrix element as  $\langle \chi_l | \exp[-T^\mu + \overline{T^\nu}(\mu)] | \phi_\mu \rangle$
- operator  $-T^\mu + \overline{T^\nu}(\mu)$  is constructed by calculating the addresses of excitation operators in  $\overline{T^\nu}(\mu)$  wrt  $\phi_\mu$  using graphical techniques
- the matrix element is calculated by means of the power series expansion of the exponential
- the powers of operator  $-T^\mu + \overline{T^\nu}(\mu)$  are evaluated by a string-based algorithm

# Convergence problems

Iteration formula for the cluster amplitudes:

$$t_{l\mu}^{\mu} = \frac{H_{l\mu} + \sum_{m \neq l} H_{lm} t_{m\mu}^{\mu} + \dots + \sum_{\nu} (t_{l\mu}^{\nu} + \dots) \tilde{H}_{\mu\nu} c_{\nu} / c_{\mu}}{E - H_{ll}}$$

- numerical instability when  $c_{\mu}$  is much smaller than  $c_{\nu}$
- this effect is different from the inherent intruder problem of the Jeziorski–Monkhorst ansatz and is less severe
- it can be resolved using various techniques, however, our experience shows that no universal solution exists and each system requires special attention

## Possible solutions:

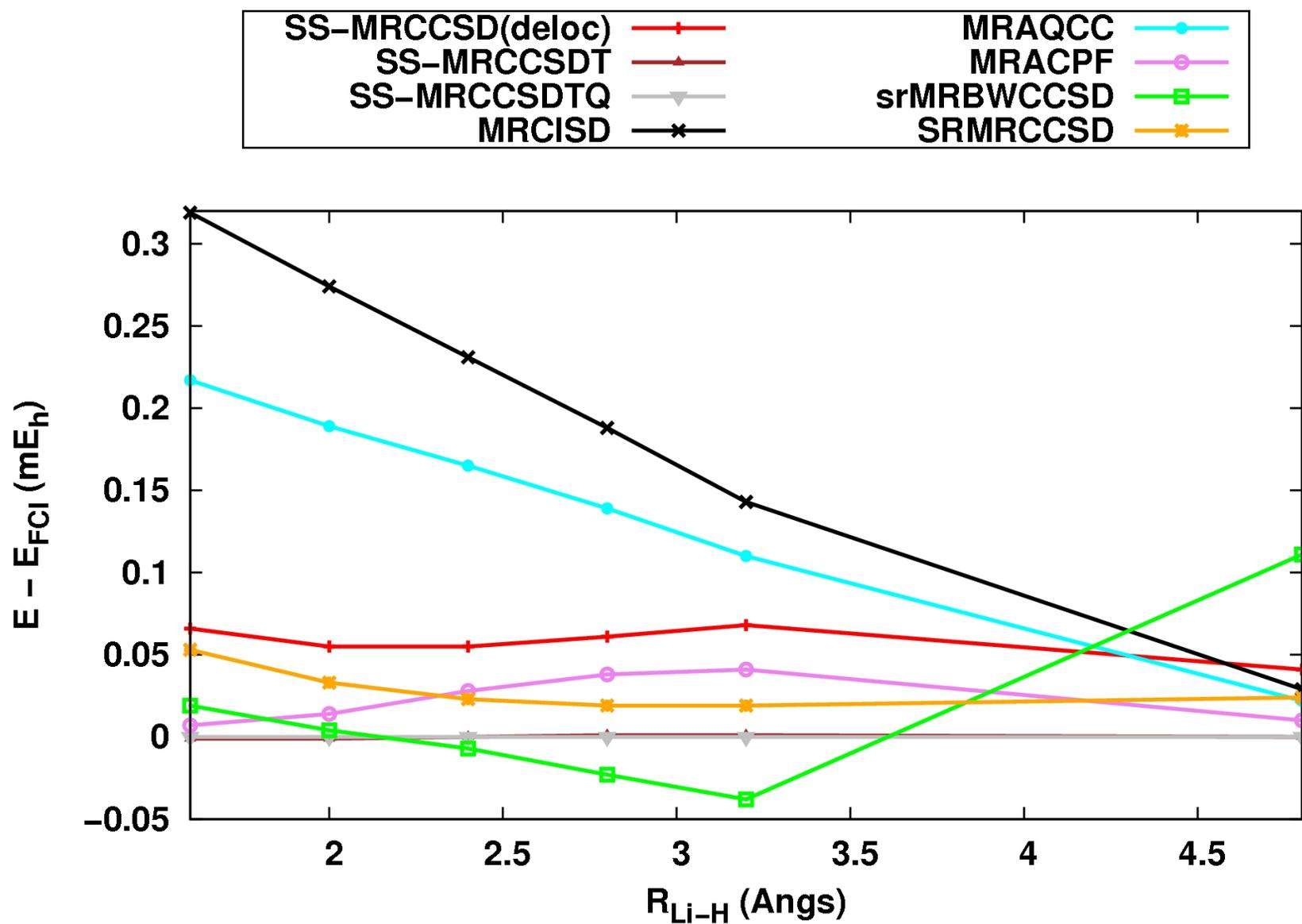
- (i) **Ignore problematic reference determinants:** drop the cluster amplitudes for the determinants with combining coefficient less than  $10^{-6}$ , results in negligible change in the energy
- (ii) **Tikhonov regularization:** replace  $c_\nu/c_\mu$  in the iteration formula by  $c_\nu c_\mu / (c_\mu^2 + \omega^2)$ , no change in the energy if used only in the first iteration cycles, small change in the energy if used throughout,  $\omega = 0.01$  is sufficient in most cases
- (iii) **Restarting cluster amplitudes:** restart from the converged SS-MRCEPA(0) cluster amplitudes, no change in the energy

# 5

## Assessment of state-specific MRCC methods

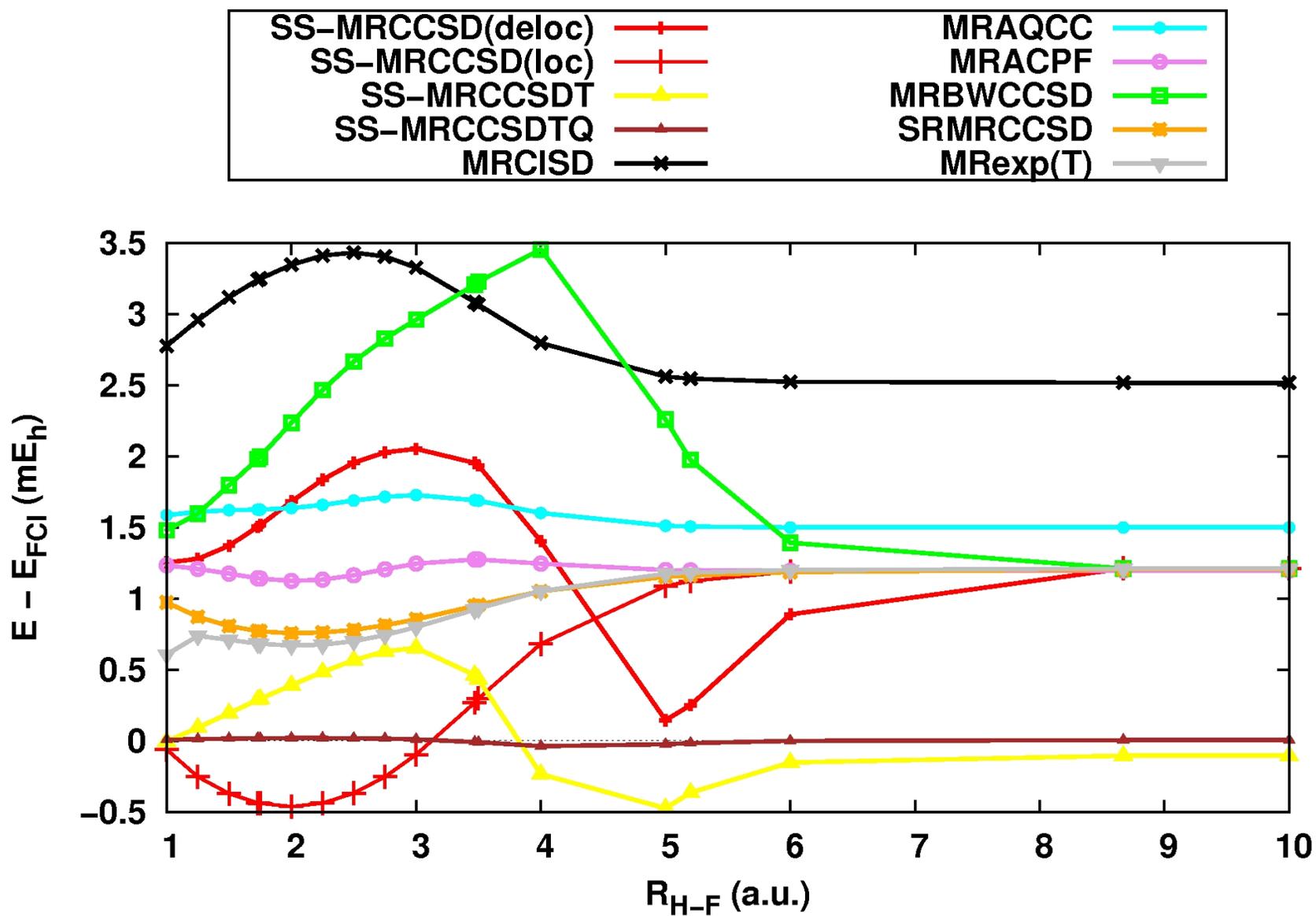
# The lithium hydride molecule

- single bond dissociation
- active space:  $2 \times 2$  CAS including the  $2\sigma$  and  $3\sigma$  orbitals
- 4 reference determinants
- basis set: cc-pVTZ
- Tikhonov regularization with  $\omega=0.01$  for the first ten iteration cycles, dropping cluster amplitudes for determinants with  $c_\mu$ 's less than  $10^{-6}$



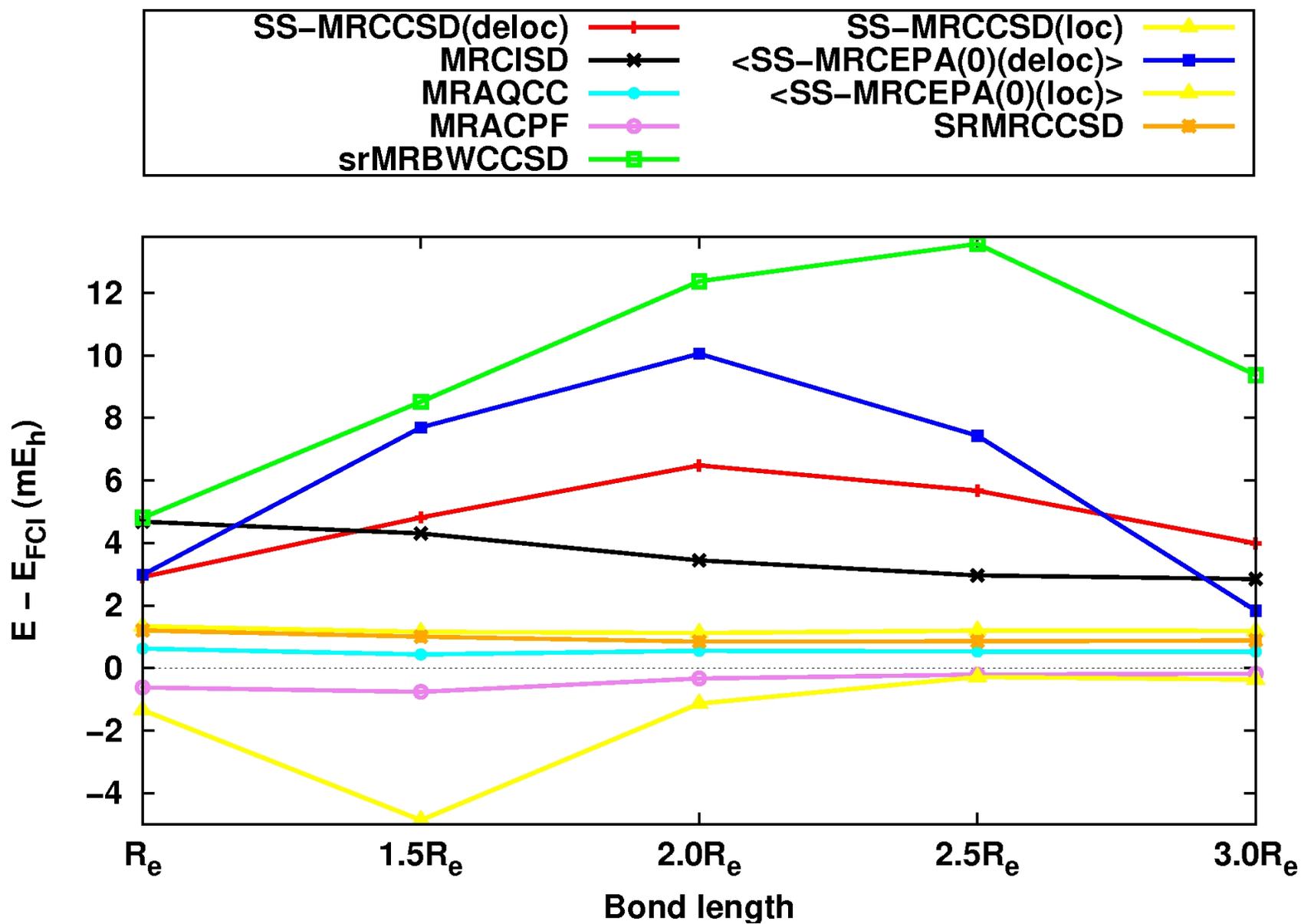
# The hydrogen fluoride molecule

- single bond dissociation
- active space:  $2 \times 2$  CAS including the  $3a_1$  and  $4a_1$  orbitals
- 4 reference determinants
- basis set: valence double-zeta (Dunning-Hay)
- no regularization, but cluster amplitudes for determinants with  $c_\mu$ 's less than  $10^{-6}$  are dropped



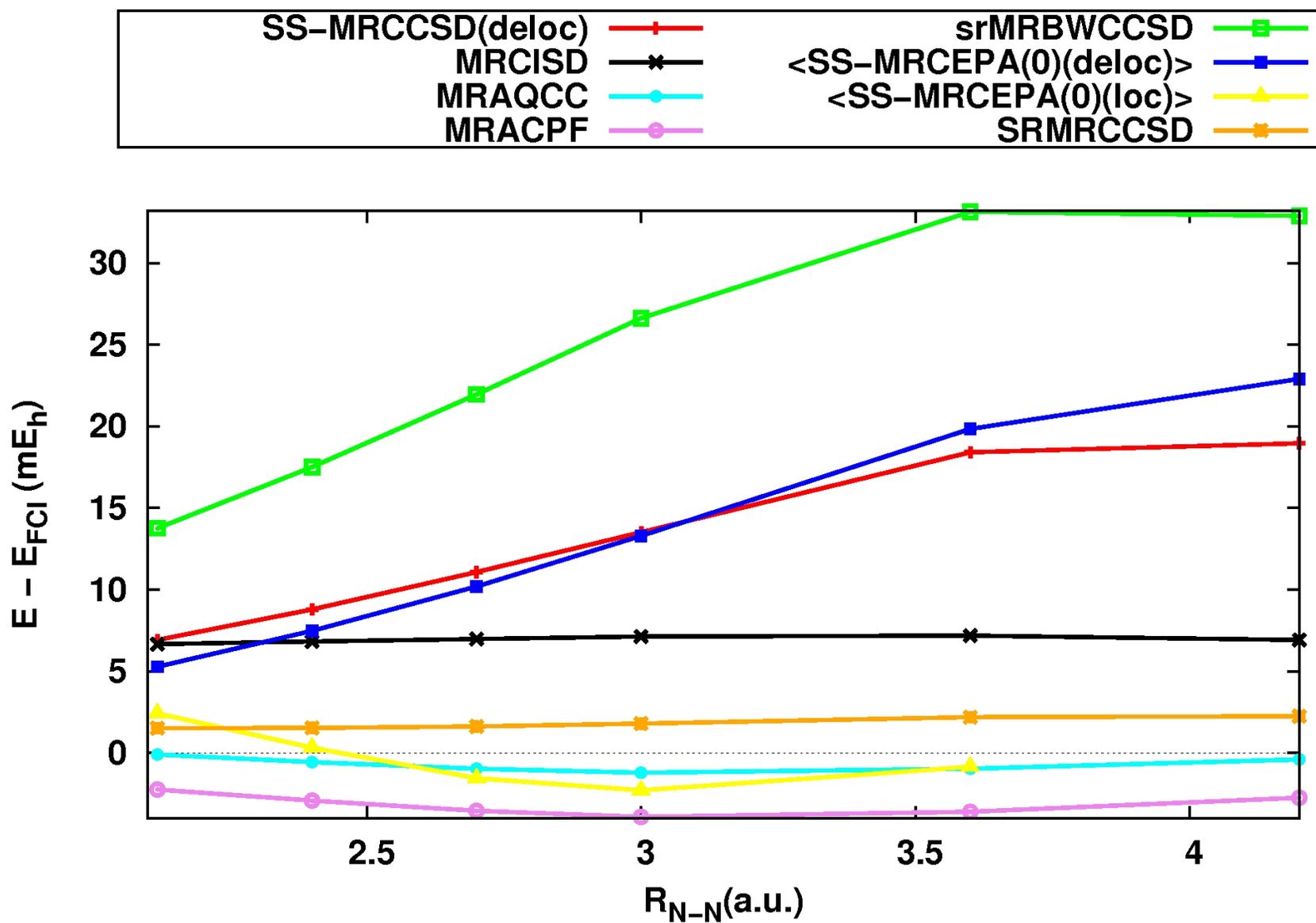
# The water molecule

- simultaneous dissociation of two single bonds
- active space:  $4 \times 4$  CAS including the  $3a_1$ ,  $4a_1$ ,  $1b_2$ , and  $2b_2$  orbitals
- 20 reference determinants
- basis set: cc-pVDZ
- Tikhonov regularization with  $\omega=0.01$  for the first ten iteration cycles, dropping cluster amplitudes for determinants with  $c_\mu$ 's less than  $10^{-6}$



# The nitrogen molecule

- triple bond dissociation
- active space:  $6 \times 6$  CAS including the  $3\sigma_g^+$ ,  $1\pi_u$ ,  $1\pi_g$ , and  $3\sigma_u^+$  orbitals
- 36 reference determinants
- basis set: cc-pVDZ
- Tikhonov regularization with  $\omega=0.01$  for all the iteration cycles, dropping cluster amplitudes for determinants with  $c_\mu$ 's less than  $10^{-6}$



## Performance in multi-reference regions

- the performance of SS-MRCC usually falls behind that of extensivity-corrected MRCI variants, SRMRCC, and MRexpT
- fundamental difference between SS-MRCC and the other ansätze: different coupling terms for virtual determinants
- in the SS-MRCC equations the virtual determinants derived from different reference functions are only indirectly coupled
- in the case of the other methods these determinants are coupled directly through the Hamiltonian
- localized orbitals improve the performance

## 6 Conclusions

- the string-based approach enables the general implementation of single- and multi-reference CC methods
- the full implementation of the SR-MRCC ansatz and Mukherjee's SS-MRCC theory has been presented
- the performance of various state-specific MRCC methods has been assessed
- the iterative solution of the SS-MRCC equations is prone to convergence problems
- the performance of the SS-MRCC method is often not satisfactory in the multi-reference regions of potential energy surfaces especially for multiple bond cleavage

# Acknowledgments

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## Program availability

<http://www.mrcc.hu>