Aspects of Spin-Adaptation in Multi-Reference Coupled Cluster Formalisms using Multi-exponential Type Cluster Ansatz: State-universal and State-specific Approaches

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Dynamical vs Non-Dynamical Correlations:

Use of active space and multi-reference (MR) many-electron correlation theories

❖ **Multi-reference formulations appear as the natural, though beguiling, mode of description of electron correlation when there is quasi-degeneracy among the reference functions essential for the conceptually minimal description.**

❖ **One starts by dividing correlation contribution into static (or non-dynamical) correlations, due to near-degeneracy and dynamical correlations (short-range, stemming from admixture with the virtual functions).**

❖ **The two effects are NOT additive due to quantum-mechanical interference. I will use the term non-dynamical correlation oftener than the term static correlation (I am simply more used to it).**

❖ **We will discuss the coupled cluster (CC) approach to study non-dynamical as well as dynamical correlations**

Two distinct Situations for Open-shell States

Simple open-shell configurations

- can be described by a single determinant or just one CSF

- the combining coefficients are determined by spin-symmetry

We think of invoking open-shell (OS) CC theory here.

A genuine multi-reference case

- the reference function is a combination of more than one CSFs

-can think of several variants:

- target many roots simultaneously via an H_{eff} formalism (**STATE-UNIVERSAL**)
- target just one root of interest (**STATE-SPECIFIC**)

Spin-orbital based OS-CC approach and Spin-contamination

- The open-shell (ROHF) determinant $|\varphi_\alpha\rangle \equiv |i\uparrow i\downarrow j\uparrow j\downarrow .....\alpha\uparrow\rangle$
- Different cluster amplitudes are needed for the single excitations $i\uparrow => a\uparrow$ and $i\downarrow => a\downarrow$ excitations.

$$\hat{T}_1 |\varphi_\alpha\rangle = (\hat{T}_{i\uparrow}^{a\uparrow} + \hat{T}_{i\downarrow}^{a\downarrow}) |\varphi_\alpha\rangle = x|a\uparrow i\downarrow ...\alpha\uparrow\rangle + y|i\uparrow a\downarrow ...\alpha\uparrow\rangle$$

- Three singly occupied orbitals. Could be the M_s =+1/2 of a spin-doublet also the M_s=+1/2 of a spin-quartet.
- With three open-shell orbitals, three linearly independent doublets are possible. The third possibility is $|i\uparrow a\uparrow .....\alpha\downarrow\rangle$
- This requires a two-body excitation amplitude $\hat{T}_{\alpha\uparrow i\downarrow}^{a\uparrow\alpha\downarrow}$
- It is, therefore, not possible to span the full spin-space at any fixed level of truncation of the rank of the cluster operators

Spin-adaptation using generators of the unitary group

- Spin adaptation of the wave-operator can be easily performed using the spin-free generators of the unitary group.

$$\hat{E}_q^p = \sum_{\sigma=\alpha,\beta} \hat{a}^+_{p_\sigma} \hat{a}_{q_\sigma}$$

- The wave-operator components are characterized by the ***spatial orbitals*** only. This requires that the ***vacuum state should be a closed-shell***, such that each spatial orbital is either doubly occupied or empty in the vacuum determinant. **The model functions are CSFs rather than determinants.**
- In a multi-exponential type cluster Ansatz such as the Jeziorski-Monkhorst Ansatz, **it is necessary to use some convenient closed-shell part of every model function as the vacuum.**

Spin-adaptation using generators of the unitary group (cont.)

- **Unlike in the spin-orbital case, all the cluster operators have annihilation operators labeled by the open-shell (*active*) orbitals.**

- **Janssen and Schaefer[1] first pointed out that to maintain the exact spin-symmetry, spin-free cluster operators should be employed and in addition to the excitation operators, one must include operators with "spectator scattering" involving the labels of the open-shell orbitals.**

- **The open-shell orbitals appear both as creation and as annihilation operators. Hence, the cluster operators can be contracted among themselves through the spectator orbitals and not all of them commute.** ***The Baker-Hausdorff expansion does not terminate at the quartic power of the cluster amplitudes.***

1) C. L. Janssen and H. F. Schaefer III, *Theor. Chim. Acta.*, **79**, 1 (1991).

State-universal Multi-reference Coupled Cluster Theories Using Jeziorski-Monkhorst Ansatz

The multi-exponential type Jeziorski Monkhorst (JM) Ansatz[1]

$$\Psi_k = \sum_{\mu} \exp(T^{\mu}) \Phi_{\mu} c_{\mu k}$$

uses every model function Φ_{μ} as vacuum to define the cluster operators T^{μ} . The cluster operators are therefore all closed-shell-like excitation operators. This feature leads to a compact set of working equations for the cluster amplitudes via the Baker-Hausdorff expansion.

$$\langle \chi_l | \{\overline{H}\}_{\mu} | \Phi_{\mu} \rangle = \sum_{\nu \neq \mu} \langle \chi_l | e^{-T^{\mu}} e^{T^{\nu}} | \Phi_{\nu} \rangle H_{eff\ \nu\mu}$$

Direct Term **Coupling Term**

The direct term is at most quartic in the cluster amplitudes. Whereas, termination of the coupling term depends on the number of active orbitals distinguishing the model functions Φ_{μ} and Φ_{ν} .

1. B. Jeziorski and H. J. Monkhorst, *Phys. Rev. A* **24**, 1668 (1981).

Shortcomings of the Jeziorski-Monkhorst Ansatz

- In the general cases, the model functions are not necessarily closed-shell singlets. In such cases, therefore, the cluster operators **have to be defined in terms of spin-orbitals.**
- The number of independent spin-orbital based cluster amplitudes is roughly three times more than the number of amplitudes defined in orbital basis, which leads to an **increased computational cost.**
- The naive use of a spin-orbital based formalism **leads to spin-broken solutions for non-singlet cases.**
- **Although the Jeziorski-Monkhorst Ansatz has a simple structure in spin-orbital basis, its spin-adaptation turns out to be quite non-trivial[1,2].**

1. B. Jeziorski and J. Paldus, *J. Chem. Phys.* **88**, 5673 (1988).
2. B. Jeziorski, J. Paldus, and P. Jankowski, *Int. J. Quantum Chem.* **56**, 129 (1995).

OUR GOAL

- Our intention is to choose a fully spin-adapted version of open-shell, state-universal and state-specific theories using spin-free cluster operators with unitary generators

- Also, at the same time avoid appearance of more than four-fold commutators for the direct term in the equations determining the cluster amplitudes.

- We discuss the choice of the cluster operators and of the ansatz for the wave operator in turn.

Exponential Wave-operator with Commuting Cluster operators

- The physical content of an ordinary exponential, exp(S^{μ}), where S^{μ}'s commute, is very different from that of an ordinary exponential when the operators are non-commuting.

- Let us consider a quadratic term $\frac{1}{2}(S^{\mu})^2 \equiv \frac{1}{2} \Sigma_{i,j} S^{\mu}_i S^{\mu}_j$. For distinct i,j, both $S^{\mu}_i S^{\mu}_j$ and $S^{\mu}_j S^{\mu}_i$ will induce exactly the same product excitation by their action on the model function Φ_{μ}. This essentially means that the same excited state is generated twice via the products $S^{\mu}_i S^{\mu}_j$ and $S^{\mu}_j S^{\mu}_i$, which together with the factor ½ implies that each excited state is generated precisely *once* via the product excitations.

This, therefore, implies that the factor 1/n! accompanying $(S^{\mu})^n$ takes care of the fact that we want each n^{th} power of product excitation to generate each distinct excited state precisely once.

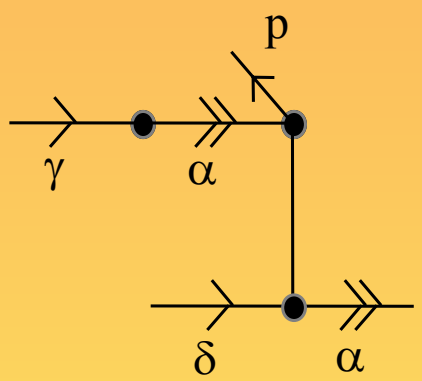
Exponential Wave-operator with Non-commuting Cluster operators

- The situation is dramatically different when the cluster operators are *non-commuting*.

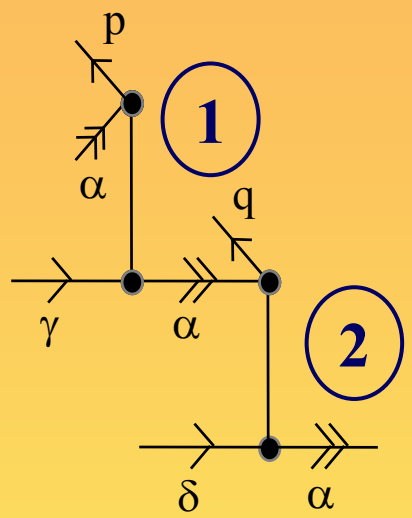
- The *pure exponential wave-operator* will have certain terms with no S_μ-S_μ contractions and certain other terms with the operators contracted among themselves. The terms with no contractions do not pose any problem in generating each distinct excited state just once. The terms with contractions are quite different.

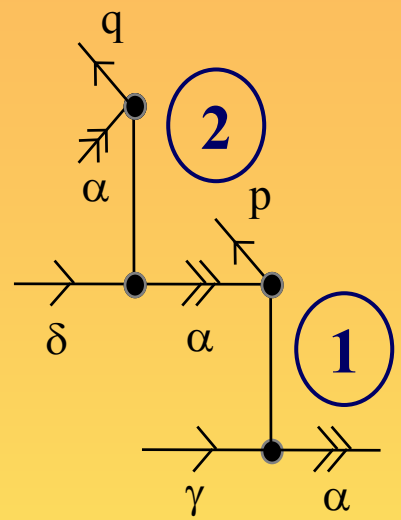
- Let us consider a term like $\frac{1}{2}\sum_{i,j}\{\overline{S_i^\mu S_j^\mu}\}$. For the two terms $\{\overline{S_i^\mu S_j^\mu}\}$ and $\{\overline{S_j^\mu S_i^\mu}\}$ the excited states reached are completely different because of the non-commuting nature of the cluster operators. Let us illustrate this by taking two specific examples.

Exponential Wave-operator with Non-commuting Cluster operators



Factors 1/2





Factor of each composite should be 1

Each excited function, however, appears with a factor ½ stemming from the quadratic power of a pure exponential wave-operator. The excited functions reached by the action of the contracted composites are thus saddled with unnecessary factors, thereby undermining their presence in the full wave function.

Towards a Multi-reference Combanitaoric Exponential Ansatz

On the other hand, if we put the factors $1/f_{ij}$ and $1/f_{ji}$ with $\{S_i^\mu S_j^\mu\}$ and $\{S_j^\mu S_i^\mu\}$ respectively, where f_{ij} and f_{ji} are the number of ways of joining S_i^μ and S_j^μ leading to the same excitation, then this extraneous undermining can be fully avoided. In the current case, $f_{ij} = f_{ji} = 1$, and each distinct excited function appears only once.

Thus, one of the major physical deficiencies of the pure exponential Ansatz for non-commuting operators can be avoided if we use factors $1/f_n$ for a composite with n S^μ operators, where f_n is the number of ways the n operators can be joined leading to the same excited state. In the combinatoric terminology, f_n is called the "*automorphic*" factor of the composite of n non-commuting operators.

In our new Ansatz for the wave-operator Ω, we replace the factors of the contracted composites with the inverse of the *appropriate automorphic factors*. We will call these generically as combinatoric open-shell cc Ansatz

The Combinatoric Simple Open-shell (COSCC) and SU Coupled Cluster (SU-COSCC) Ansatz

$$\Psi_k = \sum_{\mu} \{\{e^{(T^{\mu}+S^{\mu})}\}\} |\Phi_{\mu}\rangle c_{\mu k}$$

with

$$\{\{e^{(T^{\mu}+S^{\mu})}\}\} = 1 + \{T^{\mu}\} + \{S^{\mu}\} + \frac{1}{2!}\{T^{\mu^2}\} + .. \frac{1}{2!}\{T^{\mu}S^{\mu}\} + \frac{1}{2!}\{S^{\mu}T^{\mu}\} + ..$$

$$= \sum_{i,j} \frac{1}{f_{ij}} \{\overline{S_i^{\mu} S_j^{\mu}}\} + \sum_{i,j,k} \frac{1}{f_{ijk}} \{\overline{S_i^{\mu} S_j^{\mu} S_k^{\mu}}\} + \ldots$$

$$\frac{1}{2!}\sum_{i,j} \frac{1}{f_{ij}} \{T^{\mu}\overline{S_i^{\mu} S_j^{\mu}}\} + \frac{1}{2!}\sum_{i,j} \frac{1}{f_{ij}} \{\overline{S_i^{\mu} S_j^{\mu}} T^{\mu}\} + \ldots$$

1. D. Datta and D. Mukherjee, *Int. J. Quantum Chem.* **108**, 2211 (2008).
2. D. Jana, D. Datta and D. Mukherjee, *Chem. Phys.* **329**, 290 (2006).
3. D. Datta and D. Mukherjee, Submitted to *J. Chem. Phys.* (Under review).

"*Local*" nature of the Automorphic Factors

Let us distinguish two qualitatively distinct modes of joining of the cluster operators among them and with the Hamiltonian.

1. **We define terms like** $\overline{\overline{\{HS^{\mu}S^{\mu}\}}}$ **, where every** S^{μ} **is joined to** H **via at least one non-spectator orbital, as "*strongly connected*".**

2. **And terms like** $\overline{\{HS^{\mu}(S^{\mu})_{w}\}}$**, where the second** S^{μ} **is joined to the first through the spectator orbital only and *not* to** H**, as "*weakly connected*".**

In our COSCC Ansatz, a term like $\overline{\{H(S^{\mu})^{p}(S^{\mu})^{q}{}_{w}\}}$ **having *p* strongly connected and *q* weakly connected operators has two separate "*local*" factors** $1/f_p$ **and** $1/f_q$ **generated from the power** $(S^{\mu})^{(p+q)}$ **instead of a single "*global*" factor** $1/(p+q)!$ **, as would be the case for a pure exponential Ansatz.**

Therefore, despite the fact that the S^{μ}***'s are non-commuting, a factorization of the weakly connected terms follow, thus resulting in a compact structure for the working equations.***

Structure of the COSCC Equations: The Automorpihc Factors

Writing the product **{*H* exp(*S*$^{\mu}$)}** in normal order.

- ***Commuting Cluster Operators:***

  Any typical term of $\overline{\{H\exp(S^{\mu})\}}$ **will invariably have the structure**

$$\frac{1}{n!}\overline{\{HS^{\mu}S^{\mu}S^{\mu}....S^{\mu}\}}$$

  Thus, the commutativity of the cluster operators confers two distinct features:

(a) no contraction between *S*$^{\mu}$s, and

(b) all *S*$^{\mu}$s connect to *H*. Since *H* has only 4 creation/annihilation operators, the series $\overline{\{H\exp(S^{\mu})\}}$ ***terminates exactly at the quartic power*.**

Structure of the COSCC Equations: The Automorpihc Factors

Non-commuting cluster operators:

The crux of the problem in a pure exponential Ansatz involving non-commuting cluster operators is that any term of $\{H\exp(S^{\mu})\}$ contains S^{μ}-S^{μ} contractions, with some S^{μ} operators thus contracted being attached entirely to other S^{μ} 's and not to *H*.

As a result, two awkward features show up, The most obvious difficulty is the non-terminating nature of the connected quantities $\{H\exp(S^{\mu})\}$.

Several S^{μ} 's joined in a chain-like fashion with the other S^{μ} operators and not to H, does not lead to a series that terminates at the quartic power.

The COSCC Ansatz: An alternative representation (A suggestion by Prof. Marcel Nooijen)

An alternative form of our Ansatz could be

$$\Psi_k = \sum_{\mu} e^{T^{\mu}} e^{S_e{}^{\mu}} \{\{e^{S_{re}{}^{\mu}}\}\} |\Phi_{\mu}\rangle c_{\mu k}$$

which can be further simplified as

$$\Psi_k = \sum_{\mu} e^{T^{\mu}} e^{S_e{}^{\mu}} \{e^{\sigma^{\mu}}\} |\Phi_{\mu}\rangle c_{\mu k}$$

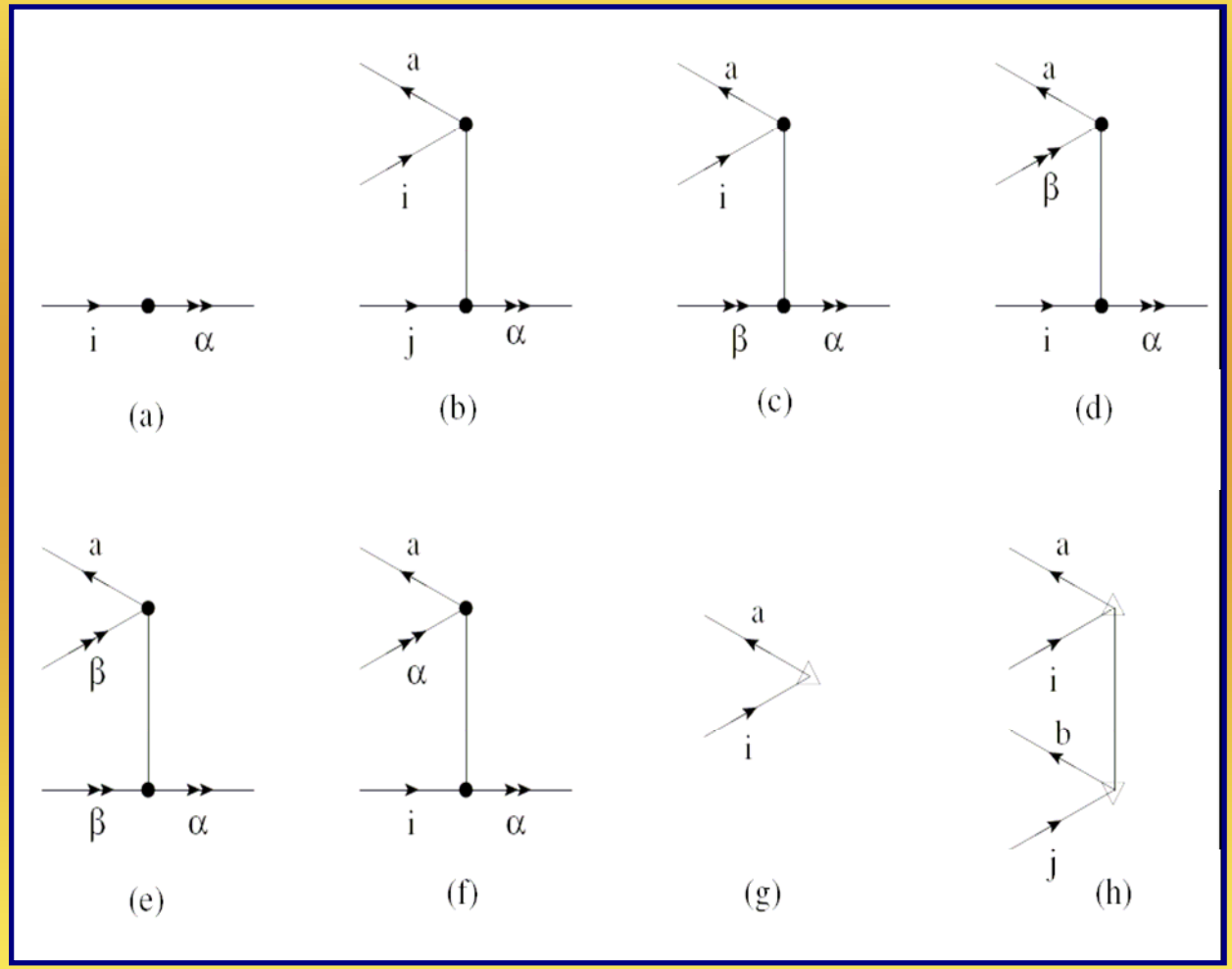
with $\sigma^{\mu} = \sigma_1^{\mu} + \sigma_2^{\mu} + \sigma_3^{\mu} + \ldots$ **where,** $\sigma_1^{\mu} = S_{re}^{\mu}$

$$\sigma_2^{\mu} = {}^{1}\!/\!_{f_{ij}} \sum_{i,j} \{\overline{(S_{re}^{\mu})_i (S_{re}^{\mu})_j}\}$$

$$\sigma_3^{\mu} = {}^{1}\!/\!_{f_{ijk}} \sum_{i,j,k} \{\overline{(S_{re}^{\mu})_i (S_{re}^{\mu})_j (S_{re}^{\mu})_k}\}$$

This is a simpler and compact representation of our Ansatz. However, in order to arrive at a compact set of working equations containing up to quartic powers of the original cluster operators, we have to consider the mode of joining of each component of σ_n^{μ} with the other operators and the Hamiltonian and distinguish terms as strongly and weakly connected.

Spin-free Cluster Operators for the One Hole-Valence Multi-reference Case



- Every model function has just one active hole orbital, e.g., $\Phi_\mu = a_\alpha \left| \Phi_0 \right\rangle$ and $\Phi_\nu = a_\beta \left| \Phi_0 \right\rangle$, Φ_0 being the common closed-shell core vacuum.

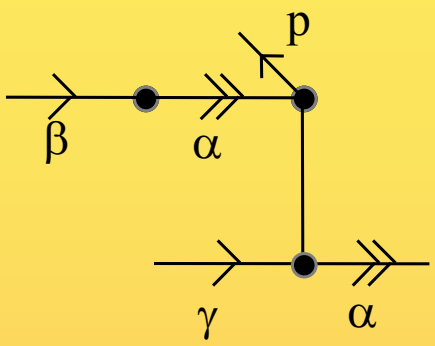
- (a)-(e) are the excitation operators denoted by S_e^μ and (f) is the cluster operator with exchange valence spectator scattering denoted by S_{re}^μ

- We choose the closed-shell–like excitation operators (g) and (h), T^μ instead of direct spectators. This is the most economic choice in terms of the excitation rank.

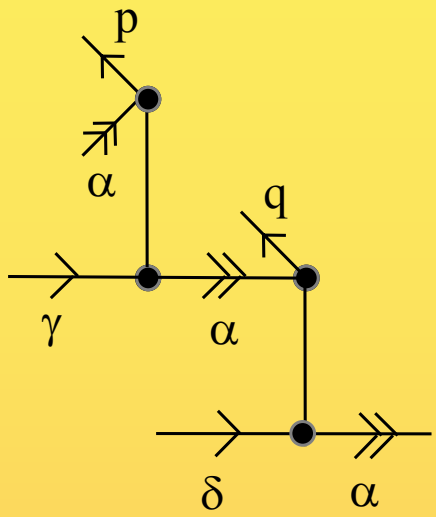
We argue that a multi-exponential type cluster expansion Ansatz using cluster operators defined in terms of spin-free unitary generators, where contraction among exchange spectators in the various cluster operators are allowed , is the closest spin-free analogue of the Jeziorski-Monkhorst Ansatz.

Use of our new Ansatz in the Bloch equation leads to a set of compact working equations for determining the cluster amplitudes. The 'direct term' is *almost* quartic in the cluster amplitudes and termination of the 'coupling term' is dictated by the valence rank of the effective Hamiltonian operator and the excitation rank at which the theory is truncated.

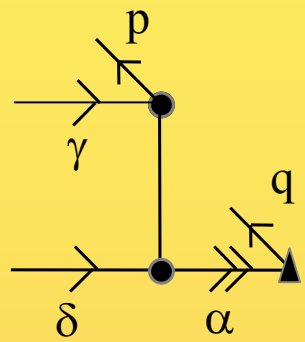
Allowed Contractions in our Ansatz



(a)



(b)



(c) **NOT ALLOWED**

- The S^{μ}_{re} operators are allowed to contract among them through the spectator valence orbitals and the S^{μ}_{e} operators are allowed to contract with the S^{μ}_{re} operators from the left through the spectator orbitals in S^{μ}_{re}.

- Contractions of type T^{μ} -S^{μ} (c) do not have any analogue in the spin-orbital based SU-MRCC theory using the JM Ansatz. These contractions arise only because of the spin-free choice of the cluster operators. **We do not allow these contractions in our Ansatz. Thus, the T^{μ} operators are not allowed to contract with any other operator in our Ansatz.**

Specific Features of the SU-COS-MRCC Ansatz

- In the combinatoric language, f_{ijk} etc. are called the *"Automorphic Factors"* of the composites of non-commuting cluster operators.

- In a pure exponential Ansatz, the factor associated with a contracted composite of n non-commuting operators is $1/n!$, which is a *"global factor"*. The automorphic factors in the COSCC Ansatz, on the other hand, have a *"local"* nature. These factors do not depend on the number of cluster operators in a composite, they rather depend on the number of ways the non-commuting cluster operators can be contracted among them generating the same excitation.

- **Choice of the correct automorphic factors is crucial for the generation of a set of compact working equations for the cluster amplitudes.**

Working Equations for the State-Universal Combinatoric Open-Shell MRCC (SU-COS-MRCC) theory

$$Z_\mu = \{[\{e^{S_e^\mu}\}_h H_{eff_{\mu\mu}}]\}_{op} + \sum_{\nu\neq\mu}\{[(e^{-T^\mu}e^{T^\nu})\{e^{S_e^\nu}\}_h\{e^{-S_e^\mu}\}_{wt}\{e^{S_e^\nu}\}_{wt} \times\{\{e^{S_{re}^\nu}\}\}_w H_{eff_{\nu\mu}}\{\{e^{-S_{re}^\mu}\}\}_w]\}_{op}$$

Where $Z_\mu = \{\{\overline{He^{(T^\mu+S^\mu)}}\}\}_{strong,op}$ **and** $\sum_\nu H_{eff_{\mu\nu}} c_{\nu k} = E_k c_{\mu k}$

"*h*" indicates that the S_e^μ operators are joined from the left to the operator $\{He^{T^\mu}\}$ in H_{eff} . "*w*" indicates weakly joined chains of the exchange spectators and the subscript "*wt*" indicates that the S_e^μ operators are joined weakly from the left to the exchange spectators.

Effect of core-hole localization on the core-ionized state energy of N_2 (Basis: cc-pVTZ, R(N-N) = 1.0977 Å)

Delocalized core-hole D_{2h} framework	Single-reference COSCC	σ_g^{-1}	-94.294509 a.u.	
		σ_u^{-1}	-94.298476 a.u.	
		Δ_{g-u}	0.108 eV	
Localized core-hole C_{2v} framework	Single-reference COSCC	$1a_1^{-1}$	-94.351257 a.u.	Experimental Δ_{g-u} = 0.11[a] eV
	SU-COS-MRCC	$1a_1^{-1}$	-94.349693 a.u.	
		$2a_1^{-1}$	-94.352771 a.u.	
		Δ_{1-2}	0.084 eV	

a. M. Alagia, R. Richter, S. Stranges *et al.*, Phys. Rev. A **71**, 012506 (2005).

Calculations with a two-dimensional model space using both $1a_1$ and $2a_1$ orbitals and within the localized core-hole framework, tries to destroy the effect of core-hole localization, and we get two roots with almost the same splitting as the delocalized core-hole description. The individual state energies, however, are not equal to those with the delocalized core-hole orbitals, this is because *our theory is not orbital invariant*.

Energies of the Valence- and Inner-shell Ionized States of H_2O Molecule

Basis: cc-pVDZ, Geometry: r_{O-H} = 1.84345 a.u., θ_{H-O-H} = 110.6°

State/ Method	Core-ionized (a.u.)	$^2B_1$ (a.u.)	$^2A_1$ (a.u.)	$^2B_2$ (a.u.)
FCI[a]	-	-75.558233	-75.732910	-75.806892
COSCC[b]	-56.316115	-75.556294	-75.731459	-75.804342
VSCC	-56.315339	-75.553028	-75.729324	-75.803116
{exp(S)}	-56.277688	-75.557271	-75.735742	-75.810530
ROHF-CCSD[a]	-	-75.555214	-75.730282	-75.804255
UHF-CCSD[a]	-	-75.555278	-75.730319	-75.804287

a. J. Olsen, P. Jørgensen, H. Koch, A. Balkova and R. J. Bartlett, *J. Chem. Phys.* **104**, 8007 (1996).

b. D. Datta and D. Mukherjee, *Int. J. Quantum Chem. (Jankowski festschrift, to appear)*

Comparison of total energies (in a.u.) for the cationic states of N_2; R = 1.116Å, TZ2P basis, spherical d-orbitals. All orbitals correlated.

Method	$^2\Sigma_{1u}$	$^2\Pi_{1g}$	$^2\Sigma_{1u}$
IP-EOM-CCSD[a]	-108.79477	-108.74046	-108.67330
IP-OS-CCSD-0[a]	-108.79716	-108.75699	-108.66766
IP-OS-CCSD-M[a]	-108.79803	-108.75798	-108.66811
QROHF-IP-OS-CCSD-0[a]	-108.79780	-108.75760	-108.66903
UHF-CCSD[a]	-108.79542	-108.75722	-108.66602
ROHF-CCSD[a]	-108.79452	-108.75717	-108.66542
COSCC	-108.79502	-108.76180	-108.65736
UHF-CCSD(T)[a]	-108.81813	-108.77015	-108.69581

[a] Reference: M. Nooijen and V. Lotrich, *J. Mol. Struct. (THEOCHEM)*, **547**, 253(2001)

Table VII: C 1s and O 1s IP's of CO (in eV)

Ionized States	Basis Sets	This work				Other Methods		Expt.
		$E^{ion}_{COSCC} - E^{ground}_{CCSD}$	$E^{ion}_{COSCC} - E^{ground}_{CCSD(T)}$	$E^{ion}_{\{exp(S)\}} - E^{ground}_{CCSD}$	$E^{ion}_{\{exp(S)\}} - E^{ground}_{CCSD(T)}$	SAC-CI general R [a]	ADC(4) [b]	
C 1s $^{-1}$ ($2s^{-1}$)	cc-pVTZ	295.28	295.75	296.66	297.13	296.13	295.13	296.069 [c]
	cc-pCVTZ	295.71	296.20	-	-	-	-	
O 1s $^{-1}$ ($1s^{-1}$)	cc-pVTZ	541.98	542.45	543.47	543.94	542.34	541.56	542.57 [b]
	cc-pCVTZ	542.18	542.68	-	-	-	-	

[a] Reference: H. Nakatsuji *et. al*, *J. Chem. Phys.* **125**, 114304 (2006)
[b] Reference: G. Angonoa, I. Walter, J. Schirmer, *J. Chem. Phys.* **87**, 6789 (1987)
[c] Reference: V. Myrseth, J. D. Bozek, E. Kukk, L. J. Sæthre, T. D. Thomas, *J. Electron Spectrosc. Relat. Phenom.* **122**, 57 (2002)

Intruder problem and its resolution in the active space effective operator framework

- **The traditional correlation theories based on effective Hamiltonian formalism are plagued by the ubiquitous 'intruder state problem'. They can be alleviated somewhat by working in incomplete model space abandoning intermediate normalization (Mukherjee), or via Intermediate Hamiltonian formalism (Malrieu, Mukherjee, Kaldor, Eliav). Generation of a size-extensive Intermediate Hamiltonian is rather nontrivial (Mukhopadhyay and Mukherjee).**

- **An extreme example of an intermediate Hamiltonian strategy is the suite of State-Specific formalisms, where one demands that only one eigenvalue of the effective operator is an eigenvalue of H. Here one targets only one state, starting from a multi-reference zeroth order description.**

State-Specific Multi-reference Coupled Cluster Formalism

- A proper formulation using the JM ansatz requires resolution of the theoretical problem of redundancy of the cluster amplitudes:

$$\Psi=\Sigma_\mu\, e^{T^\mu}\, \Phi_\mu\, C_\mu$$

- Since the same virtual function χ_l can be generated from several model functions.The redundancy has to be resolved either by deleting some cluster amplitudes (Simons et al, Hanrath), which is difficult, or by imposing suitable sufficiency conditions (Malrieu et al, Mukherjee et al, Hubac, Carski, Pittner).

- The sufficiency conditions should be physically sensible and should ensure both size-extensivity and avoidance of intruders in a manifest manner (Mukherjee et al).

We call this a state-specific MRCC (SS-MRCC) theory

Working equations for the Original SS-MRCC[1] Theory

$$H\psi = E\psi \qquad \psi = \sum_{\mu} e^{T^{\mu}} \phi_{\mu} c_{\mu}, \{\phi_{\mu}\}$$ spans a CAS

The amplitude equations of the SS-MRCC formalism :

$$\left\langle \chi_l \middle| \overline{H}_{\mu} \middle| \phi_{\mu} \right\rangle c_{\mu} + \sum_{\nu} \left\langle \chi_l \middle| e^{-T^{\mu}} e^{T^{\nu}} \middle| \phi_{\mu} \right\rangle \tilde{H}_{\mu\nu} c_{\nu} = 0 \quad \forall \quad l, \mu$$

Direct term **Coupling term**

$$\overline{H}_{\mu} = e^{-T^{\mu}} H e^{T^{\mu}} \quad \text{and} \quad \tilde{H}_{\mu\nu} = \left\langle \phi_{\mu} \middle| \overline{H}_{\nu} \middle| \phi_{\nu} \right\rangle$$

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

1. U. S. Mahapatra, B. Datta and D. Mukherjee, *J. Chem. Phys.* **110**, 6171 (1999).

Working equations for the SS-COS-MRCC formalism for the special case of one active hole in every model CSF

Z_μ is a strongly connected term leading to excitations out of the model space, defined by

$$Z_\mu = \{\{\overline{He^{(T^\mu + S^\mu)}}\}\}_{strong,op}$$

Where most of the terms are at most quartic in the cluster amplitudes, barring only a very few.

and $\langle \Phi_\mu | \tilde{H} | \Phi_\nu \rangle = \langle \Phi_\mu | \{\{\overline{He^{(T^\nu + S^\nu)}}\}\}_{strong,closed} | \Phi_\nu \rangle$

consists of strongly connected terms only. $\tilde{H}_{\mu\nu}$ furnishes the desired state energy on diagonalization in the model space

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

State-Specific Combinatoric Open-Shell MRCC (SS-COS-MRCC) formalism

$$\Psi = \sum_{\mu} \{\{e^{(T^{\mu}+S^{\mu})}\}\}|\Phi_{\mu}\rangle c_{\mu}$$

Working equations for the SS-COS-MRCC formalism for the special case of one active hole in every model CSF

$$Z_{\mu}c_{\mu} + \sum_{\nu\neq\mu}[\{\{\{e^{-(T^{\mu}+S^{\mu})}\}\}e^{T^{\nu}}\widetilde{H}_{\mu\nu}\}]_{op}c_{\nu}$$

Term I **Term II**

$$-\sum_{\nu\neq\mu}[\{\{e^{S_e^{\mu}}\}_h\{\{e^{S_{re}^{\mu}}\}\}_w\widetilde{H}_{\mu\nu}\}]_{op}c_{\nu} - [\{\{e^{S_e^{\mu}}\}_h\widetilde{H}_{\mu\mu}\}]_{op}c_{\mu} = 0$$

Term III **Term IV**

1. **Term II is just a normal ordered product of $\widetilde{H}_{\mu\nu}$ and the rest of the terms without any contraction.**
2. **In Term III, the S_e^{μ} and S_{re}^{μ} operators are contracted to H in $\widetilde{H}_{\mu\nu}$ from the left and not to any T^{ν} or S^{ν} operators in $\widetilde{H}_{\mu\nu}$.**
3. **The S_e^{μ} operators in Term IV, on the other hand, joined to $\overline{\{He^{T^{\mu}}\}}$ composite in $\widetilde{H}_{\mu\mu}$.**

Principal features of SS-COS-MRCC method

1. It is manifestly extensive.

2. The formalism employs the description using the relaxed coefficients of the multi-configurational reference function (though it can also be used with unrelaxed coefficients, if so desired).

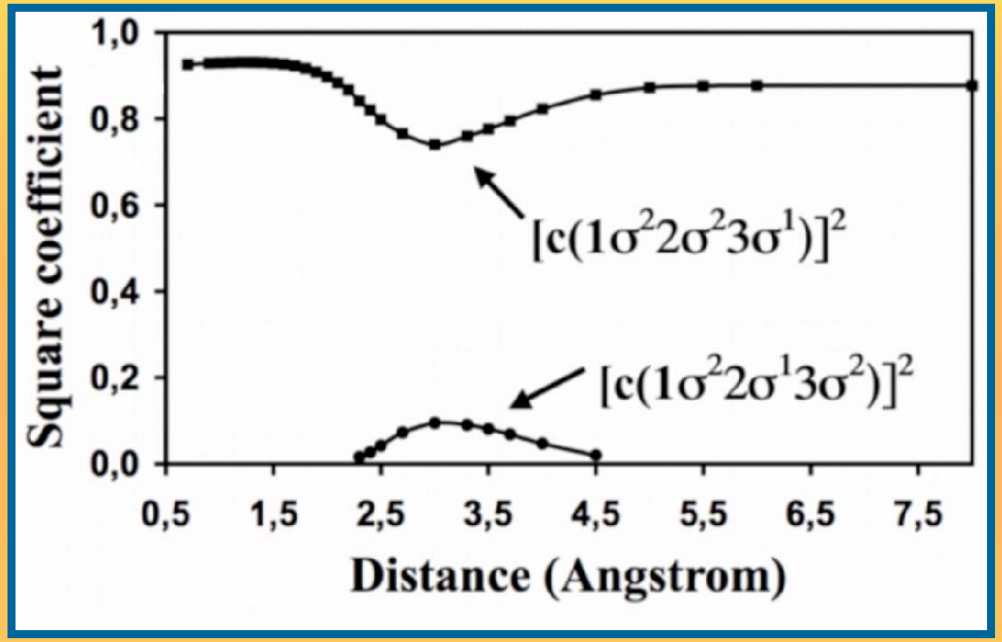
3. The sufficiency conditions invoked by us avoid intruders as long as the target state energy *E* remains well-separated from those of the virtual states.

Potential Energy Curve for the ground ($^2\Sigma^+$) state of BeH radical using the RHF orbitals of BeH^- ion

Basis: Be: 4s3p2d1f+4s4p2d Rydberg ANOs and H: 3s2p1d ANO Basis

Relatively small 2s-2p gap of Be atom increases the relevance of the $(2\sigma)^{-1}$ $(3\sigma)^{+1}$ excitation for the lower states of BeH.

For the ground state, weight of the main configuration $(1\sigma^2 2\sigma^2 3\sigma^1)$ diminishes in magnitude between 2.0 Å to 4.5 Å, reaching a minimum at ~3.0 Å.



Plot of squared coefficients for the configurations $(1\sigma^2 2\sigma^2 3\sigma^1)$ & $(1\sigma^2 2\sigma^1 3\sigma^2)$ for the ground state of BeH.
FCI results from Ref.[1]

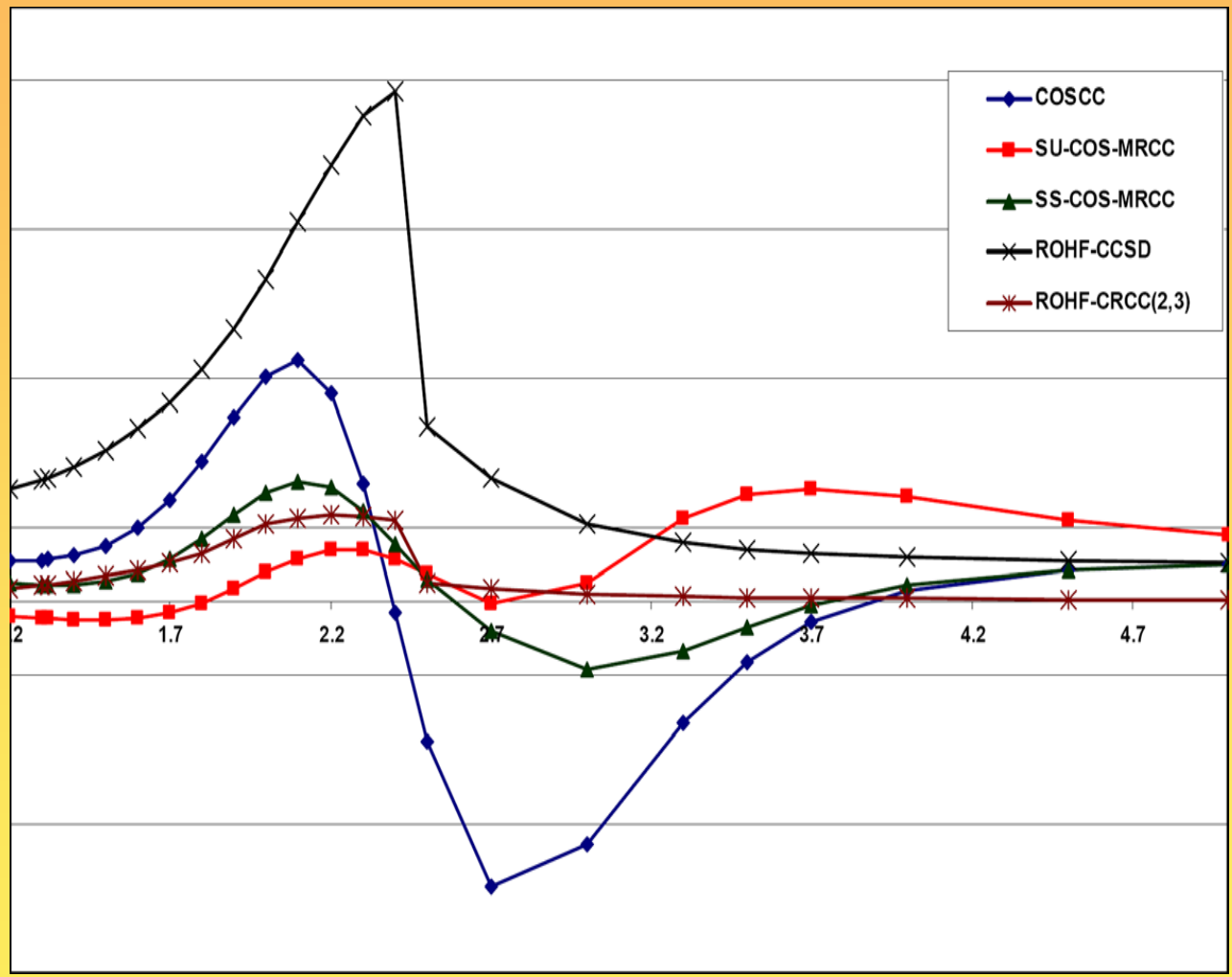
1. J. Pitarch-Ruiz, J. Sánchez-Marin, A. M. Velasco, and I. Martin, *J. Chem. Phys.* **129**, 054310 (2008).

Plot of energy difference ($E_{Method} - E_{FCI}$) (in mE_h) for the ground ($^2\Sigma^+$) state of BeH radical

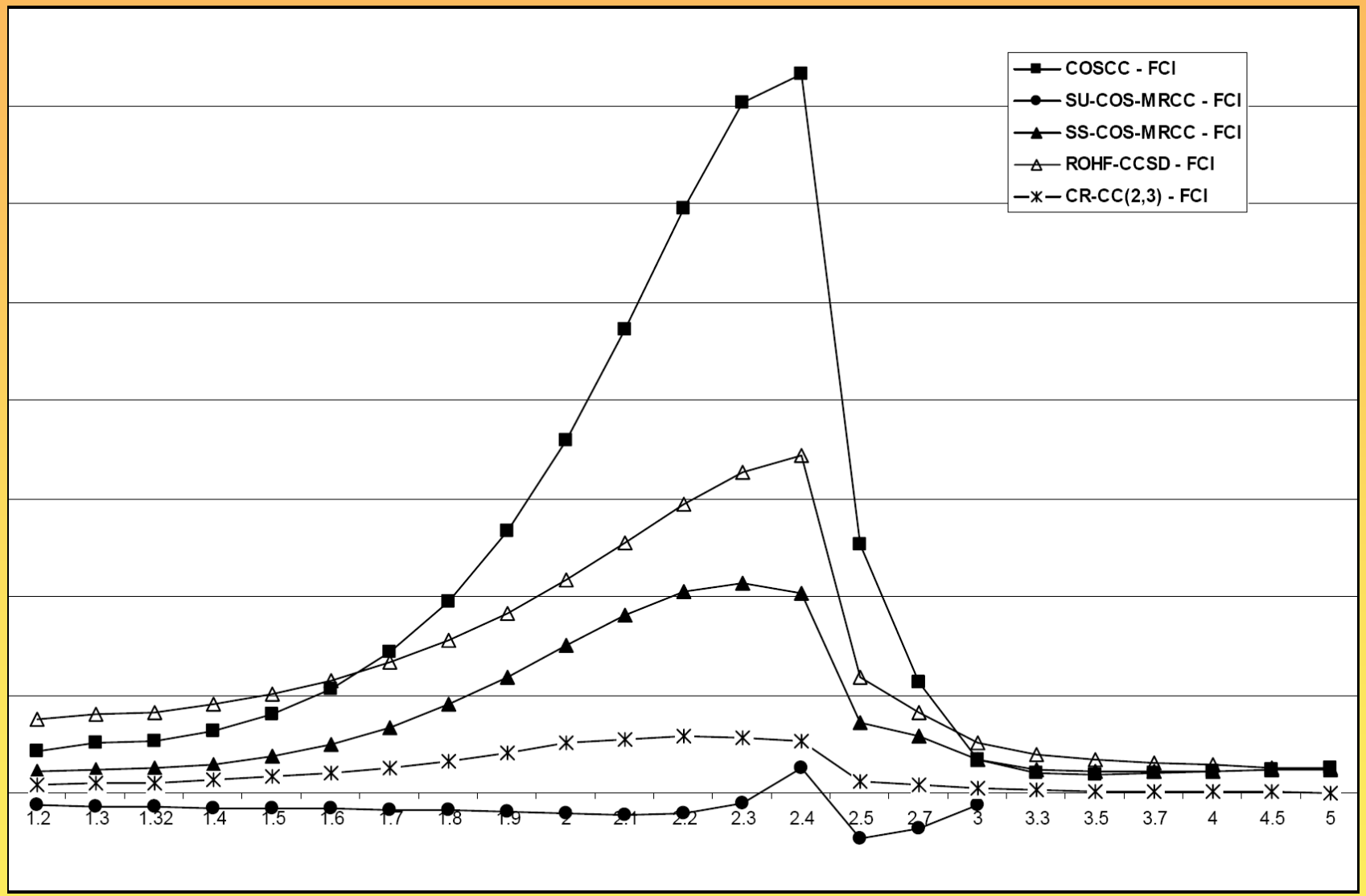
SU-COS-MRCC overestimates the FCI energies and SS-COS-MRCC performs better near equilibrium.

At large distances (say, within the range 3.2-5.0 Å) the SU-COS-MRCC results are affected by the inner-valence shake-up states encountered by the excited states.

The excitation amplitudes for the configuration ($1\sigma^2 2\sigma^1 3\sigma^2$) are difficult to converge.



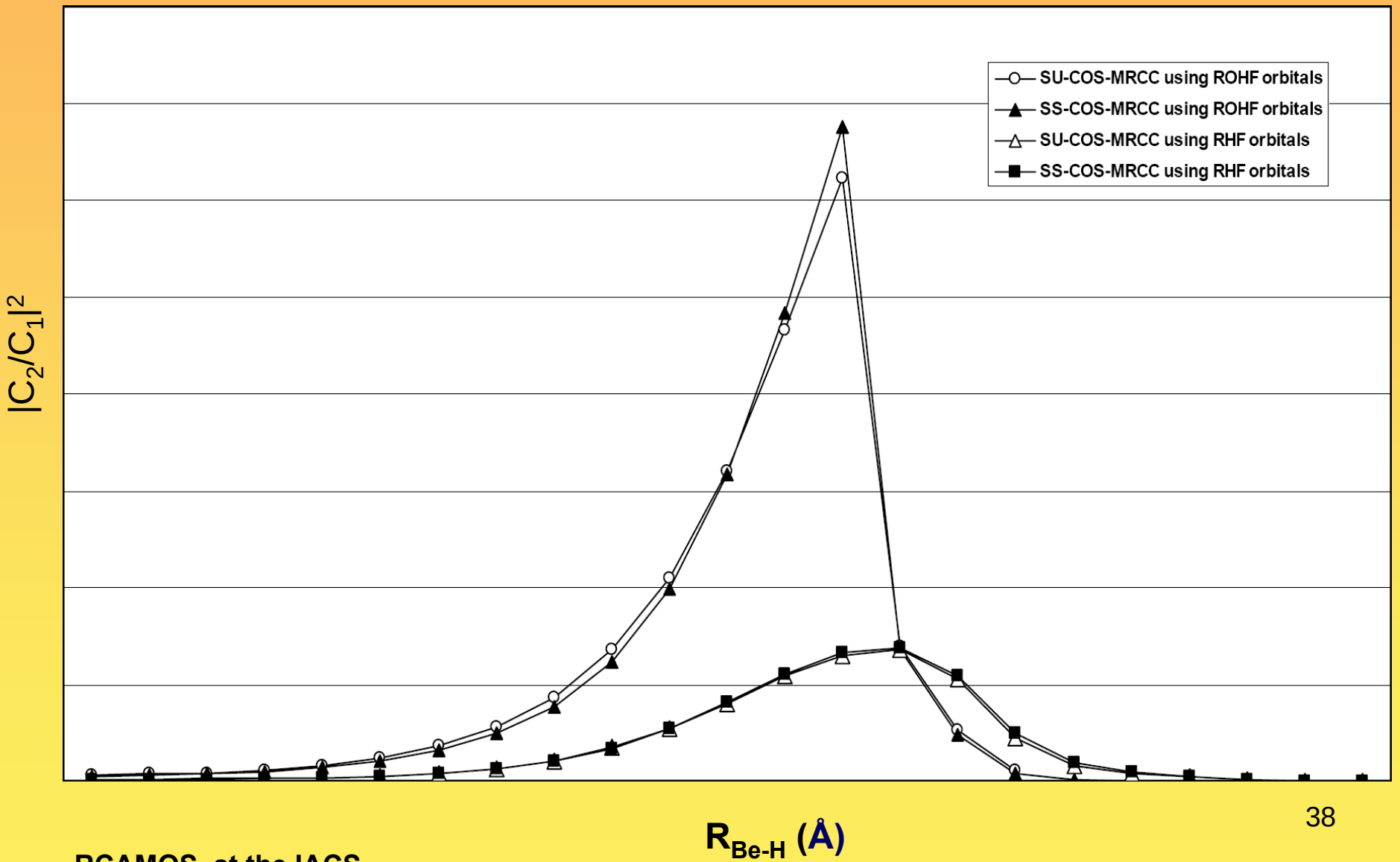
Plot of energy difference ($E_{Method} - E_{FCI}$) (in mE_h) for the ground ($^2\Sigma^+$) state of BeH radical using the ROHF orbitals of BeH radical



$E_{Method} - E_{FCI}$ (mE_h)

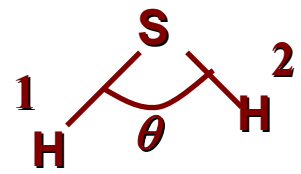
R_{Be-H} (Å)

Plot of the renormalized coefficient of the $1\sigma^2 2\sigma^1 3\sigma^2$ configuration (C_2) after including Dynamical Correlation for the ground state of BeH radical



Potential Energy Surface for the first excited $^2A'$ state of Asymmetric H_2S^+ ion with respect to H-S-H angle variation

Basis: cc-pVDZ
Orbitals: RHF orbitals of the neutral H_2S molecule
1s, 2s and 2p electrons of S were not correlated



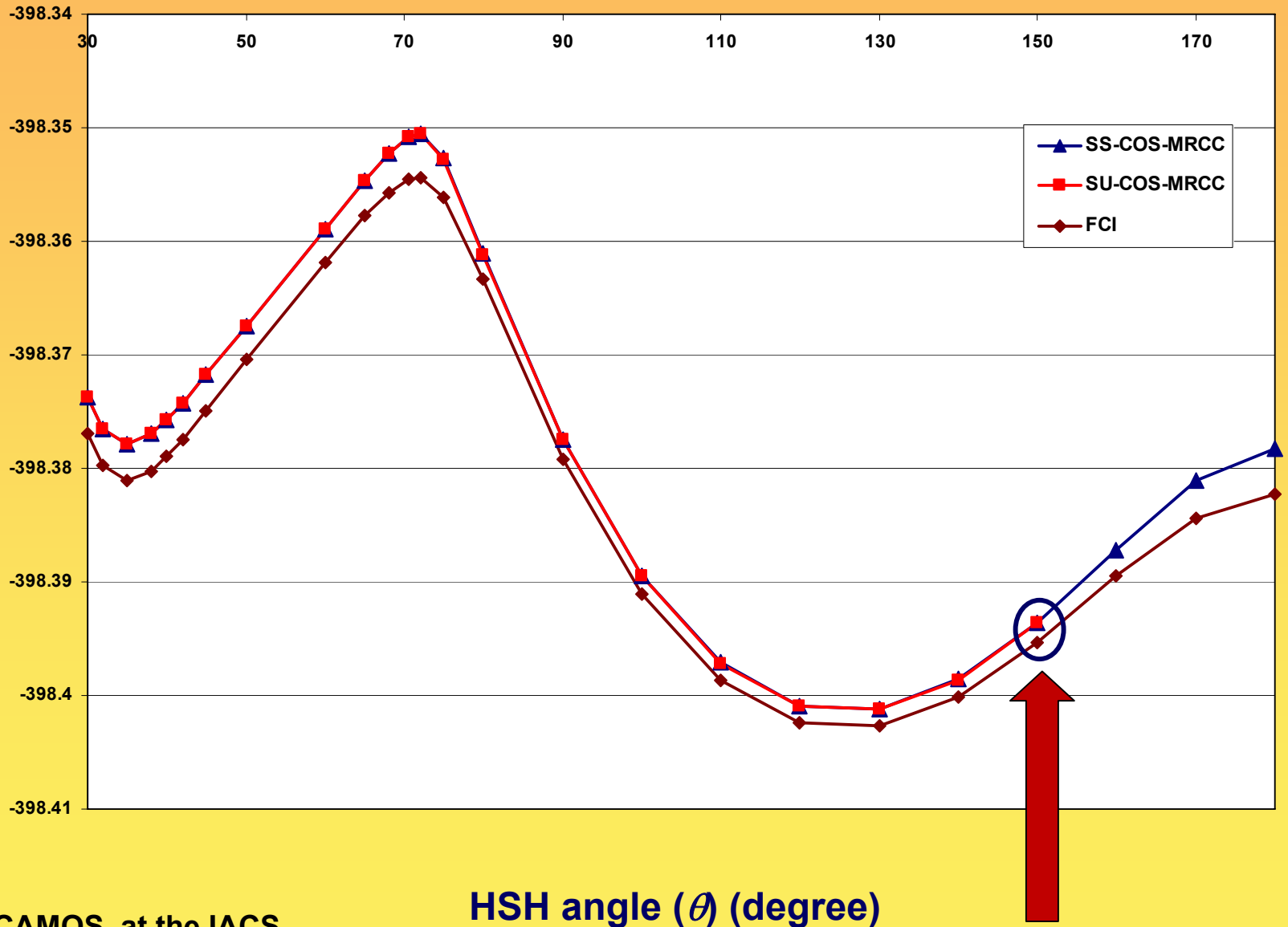
S-H1 = 1.595 Å
S-H2 = 1.399 Å

1. This model system is interesting for our purpose because the first excited state ($1^2A'$) of H_2S^+ ion exhibits avoided crossing with the second excited state ($2^2A'$), which is also of the same symmetry. The potential energy surface, therefore passes through a transition state and has two minima.

2. The model space in our study consists of two configurations: $(6a')^2(7a')^1$ and $(6a')^1(7a')^2$

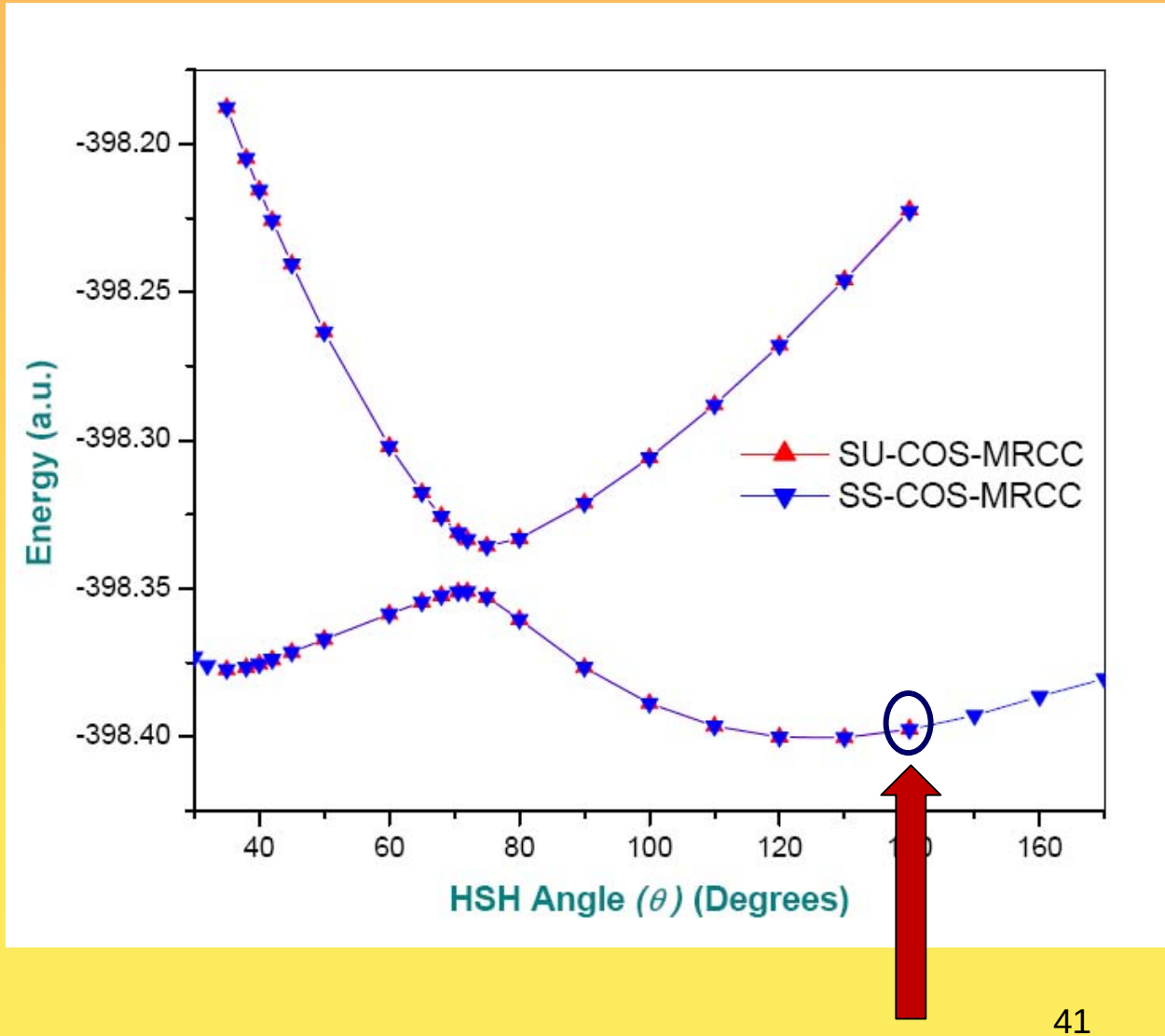
3. FCI calculations in the same basis indicate that around the transition state geometry (70°), the coefficient of the $(6a')^1(7a')^2$ configuration is large, warranting a multi-reference formulation. Both SU-COS-MRCC and SS-COS-MRCC perform equally well in this region.

PES of for the first excited $^2A'$ state of Asymmetric H_2S^+ ion with respect to H-S-H angle variation

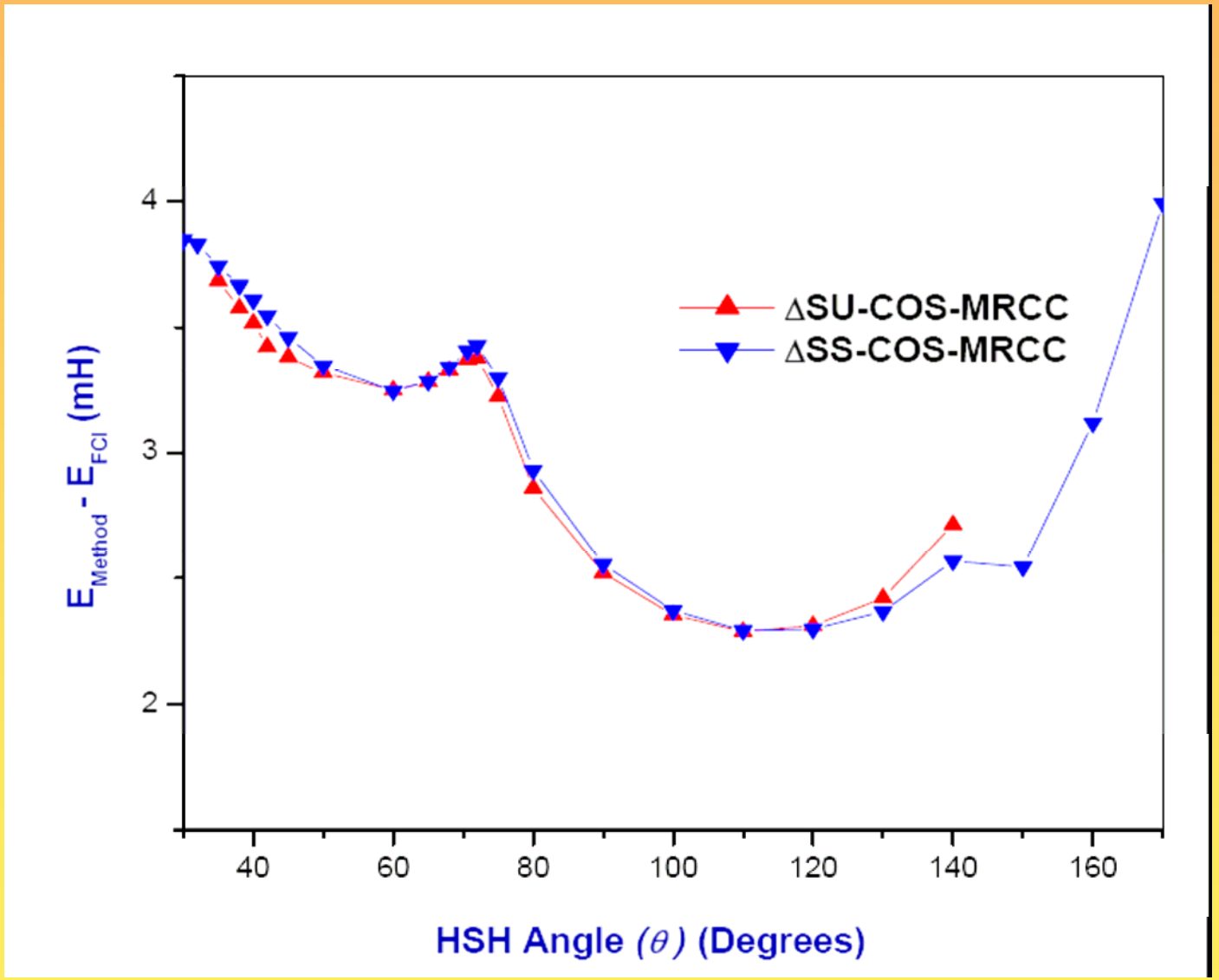


PES for the first two excited $^2A'$ states of Asymmetric H_2S^+ ion with respect to H-S-H angle variation

- At small (30º-32º) and large (150º-170º) H-S-H angles, the excited $2^2A'$ state encounters a strong intruder due to the excitation $5a' \rightarrow 6a'$.
- The SU-COS-MRCC amplitudes fail to converge at these points and only SS-COS-MRCC works.
- The SS-COS-MRCC amplitudes for the excited state also fail to converge in these regions.



Plot of energy difference ($E_{Method} - E_{FCI}$) (in mE_h) for the first excited $^2A'$ state of H_2S^+ ion



Summarizing Remarks

- We have developed a spin-free analogue of the Jeziorski-Monkhorst Ansatz using the common closed-shell component of every model CSF as the vacuum and defining cluster operators in terms of spin-free unitary generators.

- Choice of an appropriate automorphic factor in our Ansatz associated with every contracted composite of non-commuting cluster operators leads to SU-COS-MRCC amplitude equations where the direct term terminates at the quartic power of the cluster amplitudes, except a very few terms. And the termination of the coupling term is dictated by the valence rank of the effective Hamiltonian operator and the excitation rank of cluster operators at which the theory is truncated.

- The method is much more compact compared to the UGA based formalisms currently in use.

- We have also formulated a State-Specific (SS) MRCC formalism using our spin-free combinatoric Ansatz.

- Our numerical applications to study the potential energy surfaces using the SU-COS-MRCC and SS-COS-MRCC formalisms reveal that the later has the desirable feature of being intruder free. At geometries where the SU-COS-MRCC encounters intruder states and the amplitudes fail to converge or lead to poorer description of the state under consideration, SS-COS-MRCC provides reasonably good description of the state.

- The numerical applications and comparison with benchmark Full CI results show the efficacy of the methods.

THANK YOU