Applicability of Various Coupled Cluster and Perturbation Theory Methods within the Correlation Consistent Composite Approach (ccCA)

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INTRODUCTION

Developing *ab initio* computational methods to predict **physical and thermodynamic properties** of molecules has been of great interest. To reduce the computational costs (CPU time, disk space and memory) while maintaining a high level of accuracy, approaches have been made. In the **correlation consistent composite approach**[1], we achieve high accuracy by combining the result of several lower level of theory calculations. In this work, the **spin-component scaled MP2**[2] (SCS-MP2) method and **active space coupled cluster**[3] (CCSDTA) methods have been utilized within the ccCA framework. The enthalpies of formations have been calculated for the molecules of the G2/97 molecule test set and were compared against the standard ccCA.
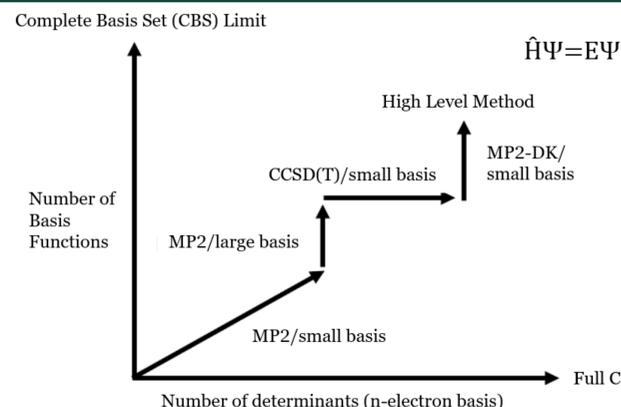
METHODS

$$\hat{H}\Psi = E\Psi$$

Figure 1: General schematic of a composite method, which uses a series of additive corrections to approximate results of a higher level calculation.

$$E_{ccCA} = E_{MP2/CBS} + \Delta CC + \Delta CV + \Delta DK + \Delta SO + ZPE$$

	ccCA[3]
Geometry Optimization	B3LYP/cc-pVTZ
E_{ref}	MP2/aug-cc-pV∞Z Uses aug-cc-pVnZ (n = D,T,Q) extrapolated to CBS limit
ΔCC	CCSD(T)/cc-pVTZ – MP2/cc-pVTZ
ΔCV	MP2(FC1)/aug-cc-pCVTZ –MP2/aug-cc-pVTZ
ΔDK	MP2-DK/cc-pVTZ-DK –MP2/cc-pVTZ
ΔSO	Experimental atomic values
ZPE	Frequencies scaled by 0.989

Figure 2: The steps for calculating ccCA energies. E_{ref} - reference energy, ΔCC - core-core correlation, ΔCV - core-valence correlation, ΔDK - scalar relativistic correction, ΔSO - spin-orbit correction, ZPE - zero point energy correction.

- ORCA[4] and NWChem[5] program
- 148 molecules from G2/97 molecule set
- SCS-ccCA: replace MP2 with SCS-MP2
- Active space ccCA: replace CCSD(T) with active space CC
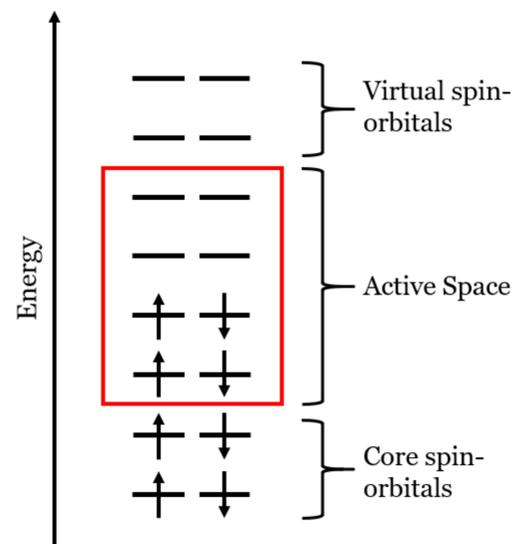
RESULTS

Active space ccCA

Figure 3: Representation of an active space for molecules.

- Includes coupled cluster single, double and active triple excitation
- Alpha- and beta-spinorbital treated individually (spin up, spin down)
- Active space is uniquely defined for each molecule
- Between ten and 16 active spinorbitals depending on orbital occupation
- Level 1 uses triply excited amplitudes defined by at least one occupied and one unoccupied active spinorbital labels
- Level 2 uses triply excited amplitudes that carry at least two occupied and unoccupied active spinorbital labels
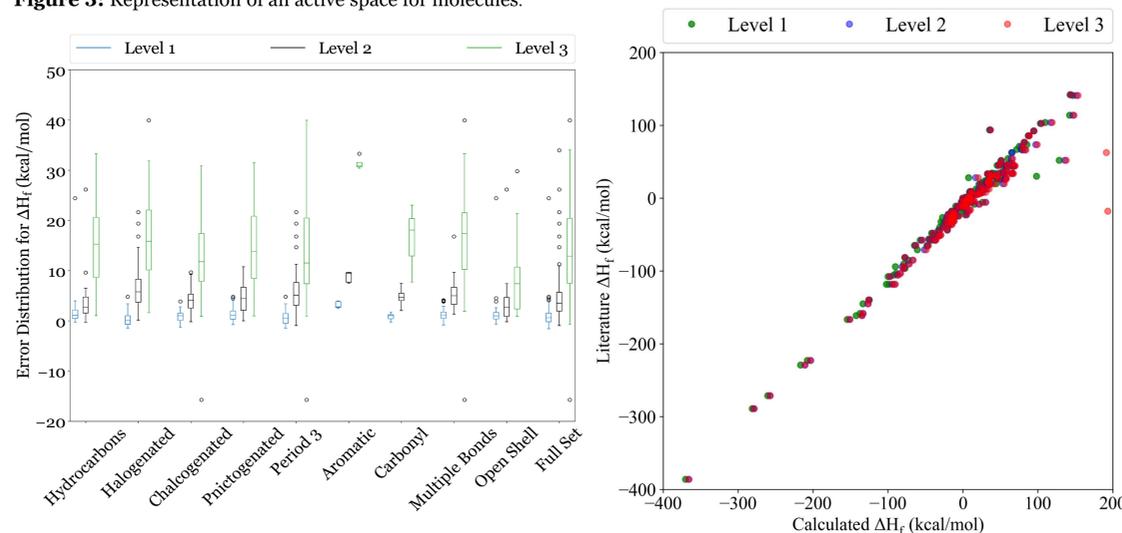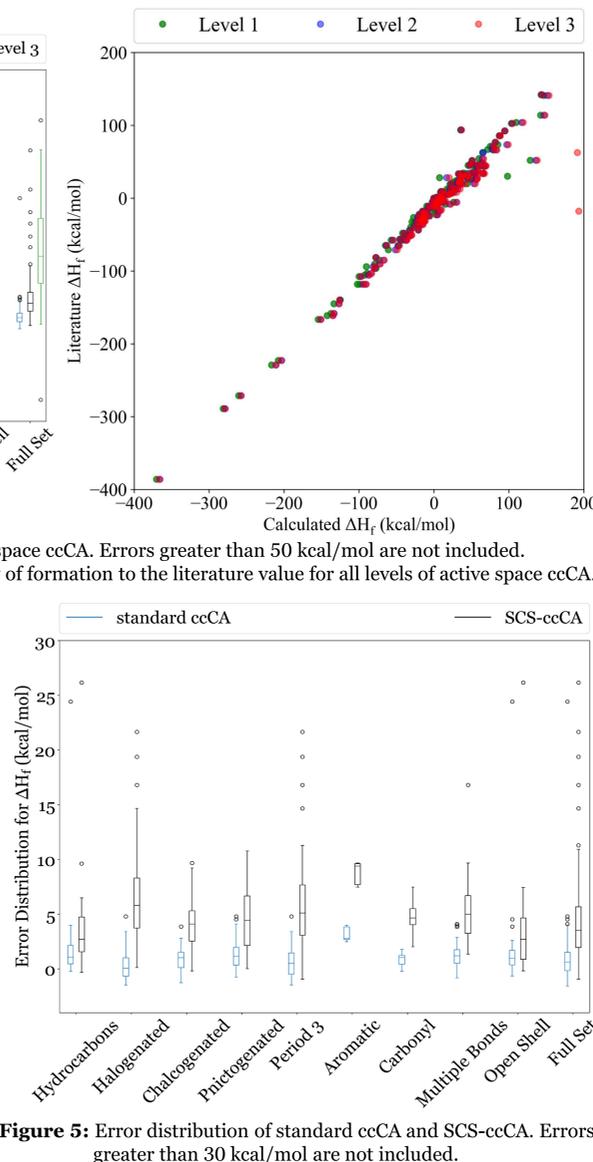- Level 3 uses triply excited amplitudes that are defined by active indices only

Figure 4: Left: Error distribution of all levels of active space ccCA. Errors greater than 50 kcal/mol are not included. **Right:** Comparison of the calculated enthalpy of formation to the literature value for all levels of active space ccCA.

SCS-ccCA

- Energy contributions of parallel- and antiparallel-spin (singlet and triplet electon pairs) are scaled seperatley
- General overestimation of the enthalpy of formation
- Overall larger median error, larger spread, and more outlieres for SCS-ccCA
- Largest median error for aromatic systems (with delocalized π-electrons)

Figure 5: Error distribution of standard ccCA and SCS-ccCA. Errors greater than 30 kcal/mol are not included.

RESULTS

- For open-shell systems unrestricted Hartree-Fock method (UHF) was used for SCF energy
- Enthalpies of formation are more likely to be overestimated than underestimated
- Supposedly there are problems with input files of outlier molecules
- Regarding the large errors of the active space ccCA, a combination of active space CC and SCS-MP2 within ccCA does not seem reasonable

Table 1: The mean absolute deviation (MAD), standard deviation (STDEV) in kcal mol^{-1} for all standard ccCA, SCS-ccCA, all levels of active space ccCA.

	ccCA	SCS-ccCA	Active space ccCA (1)	Active space ccCA (2)	Active space ccCA (3)
MAD	1.30	2.22	9.69	12.73	15.90
STDEV	2.33	3.99	9.71	9.97	20.95

- The standard ccCA has the smallest MAD
- MAD increases with higher level of active space CC within ccCA and smaller set of triply excited amplitudes

CONCLUSION

- Level 1 of active space coupled cluster shows smallest errors in the active space ccCA but overall large errors
- SCS-ccCA slightly increases MAD and STDEV in comparison to standard ccCA
- Our work shows the potential applicability of active space CC within the ccCA

Future work:

- Refine number of active space orbitals
- Further investigate applicability to open-shell systems
- Examine the influence of using restricted open-shell Hartree-Fock method (ROHF) for the SCF calculation

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ACKNOWLEDGEMENTS