

EOM-CC is equivalent to SAC-CI which is original

Reference: SAC-CI GUIDE (https://qcri.or.jp/sacci/SAC-CI-GUIDE_121215.pdf)

The EOM-CC(1989,1993)[1] and the CC-LRT methods(1979,1990)[2] are equivalent to the SAC-CI method(1978). This was obvious theoretically from the beginning, however, this fact has not been properly understood by some investigators. Here, we give some numerical proofs that show the equivalence of EOM-CC and CC-LRT to SAC-CI both in the SD level. We performed the SAC-CI SD-*R* calculations for CH₂ and CH⁺ for which the EOM-CCSD[4] and CCSD-LRT[5] calculations were reported.

We also show that the approximation of neglecting the unimportant unlinked terms and the perturbation selection of the linked operators are both accurate and useful. It should be noted that the program system MEG/EX-MEG[6] coded in 1985 can perform both SAC-CI SD-*R* and general-*R* calculations as special cases of more general MEG/EX-MEG calculations [7-10] without introducing any approximations.

The excitation energies of the singlet and triplet excited states of CH₂ and singlet excited states of CH⁺ are compared in Tables 1 and 2, respectively. The basis sets and geometries are identical to those used in the EOM-CCSD and CCSD-LRT calculations. The SAC-CI SD-*R* results obtained without any selections are given in the column under Full. From Table 1 we see that the results of the SAC-CI SD-*R* and EOM-CCSD are identical, and from Table 2 those of the SAC-CI SD-*R* and CCSD-LRT are identical: This is a numerical proof of the equivalence of the three methods.

Table 1. Excitation energy (in eV) of singlet and triplet excited states for CH₂ with 6-31G*

State	SAC-CI-NV			EOM-CC	Full-CI
	Full	#1	#2		
Singlet					
A ₁	0.0	0.0	
	5.844	5.871	5.796	5.844	4.517
	9.120	9.109	9.111	9.120	9.053
A ₂	6.101	6.105	6.105	6.101	6.093
B ₁	1.668	1.669	1.692	1.668	1.679
B ₂	9.692	9.660	9.637	9.692	8.254
Triplet					
A ₁	8.389	8.376	8.405	8.389	8.327
A ₂	5.300	5.305	5.324	5.300	5.315
B ₁	-.344	-.344	-.319	-.344	-.310
B ₂	8.382	8.370	8.342	8.382	6.904
	9.304	9.299	9.304	9.304	9.150
CPU time (sec) ^[a]					
SAC-CI	1m17s	29s	25s		

#1: Unlinked terms of R1*S2 and R2*S2 are included and others are neglected. All the thresholds are zero; EThreS2=EThreR2=CThreULS2G=CThreULR1=CThreULR2=0.0

#2: Unlinked terms are same as #1 and further selection is performed with default thresholds; EThreS2=1.d-6, EThreR2=1.d-7, CThreULS2G=5.d-3, CThreULR1=CThreULR2=5.d-2, CThreULS2E=0.0

Table 2. Excitation energy (in eV) of singlet excited states for CH⁺ with [5s3p1d/3s1p].

State	SAC-CI-NV			SAC-CI-V		CC-LRT	full-CI
	Full	#1	#2	#1	#2		
Σ^+	0.000	0.000	0.000
	9.109	9.120	9.076	9.114	9.074	9.109	8.549
	13.580	13.578	13.582	13.574	13.578	13.580	13.525
Π	3.261	3.265	3.271	3.262	3.268	3.261	3.230
	14.454	14.450	14.479	14.444	14.473	14.454	14.127

#1,#2: Same as those of table 1.

A policy of the SAC/SAC-CI program is we calculate only important terms, and we neglect terms if they are certainly negligibly small. By doing so, we can make programs more efficient, so that we can calculate larger and more complex systems, and the physics and chemistry of the calculated results becomes clearer than otherwise. It is by this virtue that we could have been able to apply our SAC-CI method to the porphyrin systems and to the reaction center of photosynthesis of *Rhodospseudomonas viridis*. For this purpose, we may introduce the following approximations.

- (1) Some classes of unimportant unlinked terms are neglected from the beginning.
- (2) The perturbation selection of the linked operators and further the selection among the unlinked terms composed of the selected linked terms are performed.

The accuracy of these approximations is also shown in Tables 1 and 2. #1 means that we adopt the approximation (1) given above, and #2 means that the approximation (2) is further done together with the approximation (1). It is seen that both approximations give reliable results within chemical accuracy. The results of SAC-CI-V method are also given for CH⁺, and we can see the reliability of this method.

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