Generalization of the Projection Space Improves the SAC-SD
(symmetry-adapted cluster-singles and doubles) Method in Bond-breaking Systems

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The equation for nonvariational SAC-SD method has been
generalized to have multireference projection space. The results show
significant improvements in the description of the potential
curves especially in the bond-breaking region.

The SAC method¹ ² is well-known as an accurate method for
treating the electron correlations which is indispensable to
achieve chemical accuracy. The computational program has
been published by through Gaussian 03 package.³ The nonvaria-
tional SAC-SD (SAC-SD-NV) equation works very nicely for
systems where the Hartree–Fock description is a good approxi-
mation. However, the single-reference wave function including
single- and double-excitation operators such as SAC-SD breaks
down in bond-breaking systems.⁴ On the other hand, it was
pointed out that the generalized valence bond perfect pairing
(GVB-PP)⁵ wave function, which is applicable to the bond-
breaking systems, is a special case of the SAC-SD wave func-
tion.⁶ Apparently, there is an inconsistency between the theoreti-
cal analysis and numerical results. In this study, we analyzed the
structure of the SAC-SD wave function and clarified the reason
of the failure in the bond-breaking systems. We then proposed
the generalization of the projection space in the SAC-SD-NV
working equation which effectively improves the numerical
performance in the bond-breaking systems.

The structure of the GVB-PP⁵ wave function is equivalent to
a special case of the SAC-SD wave function,⁶

$$\psi_{GVB-PP}^{\text{SAC}} = \exp \left( \sum_i \sum_m C_m \hat{S}_m^{GVB-PP} \right) \Psi_0,$$  (1)

where the symmetry-adapted excitation operator,

$$\hat{S}_m^{GVB-PP} = \hat{a}_{i_m \sigma}^\dagger \hat{a}_{i_m \sigma} \hat{a}_{i_m \alpha}^\dagger \hat{a}_{i_m \alpha},$$  (2)

describes the pair excitation from bonding orbital \(i_m\) to its corre-
sponding anti-bonding orbital \(a_m\). \(\Psi_0\) is the reference determi-
nant, and \(C_m\) is coefficient for the corresponding excitation oper-
ator, eq 2. In homolytic bond-breaking, the GVB-PP wave func-
tion describes the biradical electronic structure by enlarging \(C_m\).
In multiple bond-breaking, several coefficients in eq 1 enlarge at
the same time. For example in \(N_2\) molecule, the GVB-PP solu-
tion shows large coefficients for three pairs of electrons in one \(\sigma\)
and two \(\pi\) orbitals, which describes 2p electrons in the quartet
state of the \(N\) atom. In terms of the cluster expansion as shown in
eq 1, this electronic structure corresponds to a sextuple excita-
tion described by the third-order product of the pair excitation
operators. In this way, the electronic configuration generated by
the high-order expansion becomes main configuration. This
analysis indicates that the SAC-SD wave function is actually ap-
plicable to the bond-breaking system.

Next we investigate the SAC-SD-NV working equations,
which are derived by projecting \((\hat{H} - E_{SAC}) \psi_{\text{SAC}} = 0\) onto a
bra function \((\psi_{\text{bra}})\) to calculate energy and onto single and double
excitations from the bra function \((\psi_{\text{bra}} | \hat{S}_K^m \hat{S}_K^n)\) to determine
the coefficients of the wave function. The \(\hat{S}_K^m\) operators are the same
as those included in the SAC-SD wave function and defined as
the excitation from occupied to unoccupied orbitals in the refer-
ence determinant \(\Psi_0\).

$$E = N \cdot \langle \psi_{\text{bra}} | \hat{H} \exp(\hat{S}) | \Psi_0 \rangle,$$  (3)

$$\langle \psi_{\text{bra}} | \hat{S}_K^m (\hat{H} - E) \exp(\hat{S}) | \Psi_0 \rangle = 0.$$  (4)

\(N\) in the eq 3 is a normalization factor.

$$N = \langle \psi_{\text{bra}} | \exp(\hat{S}) | \Psi_0 \rangle^{-1}.$$  (5)

In these equations, single determinant is used for the bra func-
tion, and the projection space consists of up to double excitation.
Consequently, the SAC expansion naturally truncates at the
quadruple excitations. Apparently, this is an inadequate property
of the SAC-SD-NV equation, since the high-order products of
the excitation operators become main configuration in the
bond-breaking system.

There are two ways to overcome the difficulty. The first one is
to apply the variation principle to the SAC-SD wave function.
However, the variational SAC equation requires very high-order
products of the excitation operators until all electrons are excit-
ed.⁷ The other way is to generalize the bra function to multicon-
figuratuer wave function,

$$\psi_{\text{bra}} = \sum_K b_K | \Phi_K \rangle,$$  (6)

where \(\Phi_K\) and \(b_K\) express the electronic configuration and its
coefficient, respectively. The bra function describes the main
configurations of the wave function and is predetermined by a
preliminary CI calculation. Since the resulting projection space
consists of up to double excitation from the bra function, the
SAC-SD expansion reaches certain order of the products neces-
sary to describe the main configuration in the bond-breaking.

The expansion would naturally truncate at practical order of
the products, because of the nature of the projection space.
We hereafter refer this equation as “MRbra-SAC-SD-NV” eq.

We tested the present equation in the potential curve of HF,
LiF, CO, and \(N_2\). The results were compared with the conven-
tional SAC-SD-NV results and also with Full-CI or CAS-CI re-
sults depending on the active space. The basis sets used were 6-
31G sets⁸ in all calculations. The calculations were performed
with the development version of Gaussian 03.³

Figure 1 shows the potential curve of HF molecule. All or-
potential curve by SAC-SD-NV has an artificial hump around 9
bohr. SAC-SD-NV solution follows RHF one, since the bra
function in the MRbra-SAC-SD-NV calculation was CISD with
the active space of 1 occupied (2p\textsubscript{C27}) and 1 unoccupied
orbitals. At 3.0 bohr separation, double excitation (2p\textsuperscript{2}\sigma \rightarrow (2p\textsuperscript{2}\sigma)\textsuperscript{2}) has coefficient very close to the HF configu-
ration. The original SAC-SD-NV eq gives correct behavior even
in the bond-breaking region, but the error from Full-CI becomes
12 mhartree at 3.0 Å. The MRbra equation improved the error to
be 7.5 mhartree (4.7 kcal/mol).

In LiF case, both ionic and covalent states cross each other at
around 9.0 bohr. The restricted Hartree–Fock (RHF) configura-
tion has ionic character and becomes excited state in the bond
length larger than 9.0 bohr. The active space was composed of
4 occupied (1s frozen core) and 8 unoccupied orbitals. The bra
function of the MRbra-SAC-SD-NV eq was CISD with the ac-
tive space of 1 highest-occupied and 2 lowest-unoccupied orbi-
tals. RHF describes the ionic state and become excited state over
9.0 bohr. SAC-SD-NV solution follows RHF one, since the bra
function in the equation is ionic configuration (HF configu-
ration). The MRbra result smoothly follows the ground state
CAS-CI potential curve.

Figure 3 shows the result for CO molecule. Five occupied
(1s core) and 7 unoccupied orbitals were correlated. The bra
function in the MRbra-SAC-SD-NV calculation was CISD with
4 highest-occupied and 3 lowest-unoccupied active orbitals. Al-
though the error in the SAC-SD-NV energy significantly
increases with the elongated bond distance, the MRbra equation
performs much better than the SAC-SD-NV.

Figure 4 shows the potential curve for triple bond breaking
in N\textsubscript{2} molecule. Only 1s orbital was excluded from the active
space. The bra function used in the MRbra-SAC-SD-NV calcu-
lation is CI up to sextuple excitations having 3 highest occupied
and 3 lowest unoccupied in the active space. As Figure 4 shows,
potential curve by SAC-SD-NV has an artificial hump around
1.75 Å. The MRbra approach significantly improves in all bond
distances and shows correct dissociation in the potential curve.
However, the error from the Full-CI increases with the bond dis-
tance. The amount of the error reaches 34 mhartree (21 kcal/
mol) at 3.0 Å.

In conclusion, the present approach significantly improved
the bond-breaking potential curve. However, the error still re-
mains at elongated bond distances. The error could originate
from the treatment of the semi-internal correlations. Further
improvement would be provided in the future study.

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References and Notes
2 H. Nakatsuji, in “Computational Chemistry - Reviews of
Current Trends,” ed. by J. Leszczynski, World Scientific,
3 M. J. Frisch et al., “Gaussian 03,” Gaussian Inc., Pittsburgh
PA (2003).
4 MR-SAC (H. Nakatsuji, J. Chem. Phys., 83, 713 (1985)) and
MEG (H. Nakatsuji, J. Chem. Phys., 95, 4296 (1991)) meth-
ods treat the electron correlation in the quasi-degenerate
electronic structure.
5 F. W. Bobrowicz and W. A. Goddard, III, in “Methods or
Electronic Structure Theory,” ed. by H. F. Schaefer, III,
7 W. J. Hehre, R. Ditchfield, and J. A. Pople, J. Chem. Phys.,
56, 2257 (1972).