

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 method^{1,2} 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 nonvariational SAC-SD (SAC-SD-NV) equation works very nicely for systems where the Hartree–Fock description is a good approximation. 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 function.⁶ Apparently, there is an inconsistency between the theoretical 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

$$\Psi^{\text{GVB-PP}} = \exp\left(\sum_m^{N_{\text{Pair}}} C_m \hat{S}_m^{\text{GVB-PP}}\right) \Psi_0, \quad (1)$$

where the symmetry-adapted excitation operator,

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

describes the pair excitation from bonding orbital i_m to its corresponding anti-bonding orbital a_m . Ψ_0 is the reference determinant, and C_m is coefficient for the corresponding excitation operator, eq 2. In homolytic bond-breaking, the GVB-PP wave function 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 solution shows large coefficients for three pairs of electrons in one σ and two π 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 excitation 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 $(\hat{H} - E_{\text{SAC}})|\Psi_{\text{SAC}}\rangle = 0$ onto a bra function $\langle\Psi_{\text{bra}}|$ to calculate energy and onto single and double excitations from the bra function $\langle\Psi_{\text{bra}}|\hat{S}_K^\dagger$ to determine the coefficients of the wave function. The \hat{S}_K^\dagger 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 reference determinant $|\Psi_0\rangle$.

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

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

N in the eq 3 is a normalization factor.

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

In these equations, single determinant is used for the bra function, 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 excited.¹ The other way is to generalize the bra function to multiconfigurational wave function,

$$\langle\Psi_{\text{bra}}| = \sum_K b_K \langle\Phi_K|, \quad (6)$$

where Φ_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 necessary 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 conventional SAC-SD-NV results and also with Full-CI or CAS-CI results depending on the active space. The basis sets used were 6-31G sets⁷ 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-

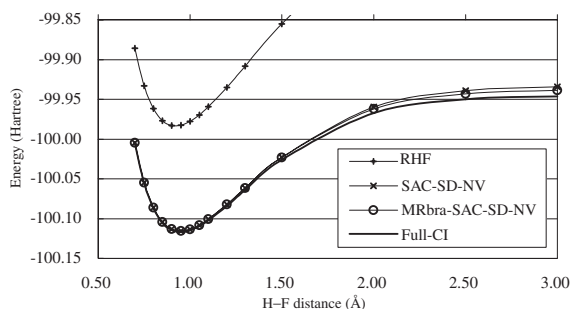


Figure 1. Potential curve of the ground state of HF molecule.

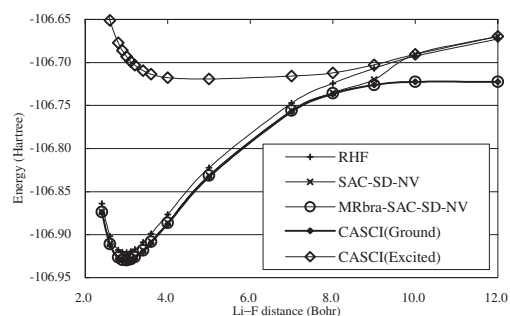


Figure 2. Potential curve of the ground state of LiF molecule.

bitals are correlated. The bra function of MRbra-SAC-SD-NV was CISD with the active space of 1 occupied ($2p\sigma$) and 1 unoccupied ($2p\sigma^*$) orbitals. At 3.0 Å separation, double excitation $(2p\sigma)^2 \rightarrow (2p\sigma^*)^2$ has coefficient very close to the HF configuration. 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, ionic and covalent states cross each other at around 9.0 bohr. The restricted Hartree-Fock (RHF) configuration 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 active space of 1 highest-occupied and 2 lowest-unoccupied orbitals. 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 configuration). 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 CISDTQ with 4 highest occupied and 3 lowest unoccupied active orbitals. Although the error in the SAC-SD-NV energy significantly increases with the elongated bond length, the MRbra equation performs much better than the SAC-SD-NV.

Figure 4 shows the potential curve for triple bond breaking in N_2 molecule. Only 1s orbital was excluded from the active space. The bra function used in the MRbra-SAC-SD-NV calculation 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

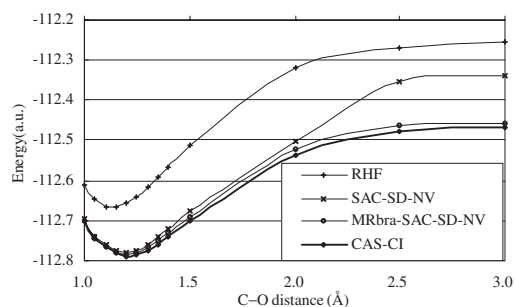


Figure 3. Potential curve of the ground state of CO molecule.

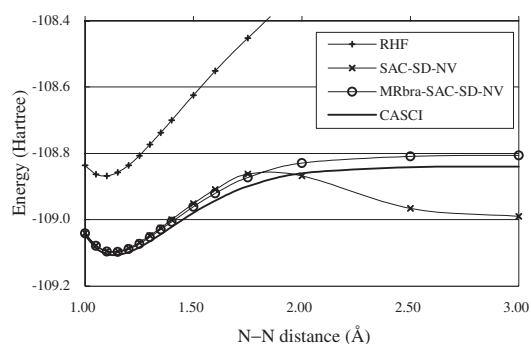


Figure 4. Potential curve of the ground state of N_2 molecule.

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 distance. 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 remains 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

- 1 H. Nakatsuji and K. Hirao, *J. Chem. Phys.*, **68**, 2053 (1978).
- 2 H. Nakatsuji, in "Computational Chemistry - Reviews of Current Trends," ed. by J. Leszczynski, World Scientific, Singapore (1997), Vol. 2.
- 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)) methods 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, Plenum Press, New York (1977), Vol. 3, p 79.
- 6 I. I. Ukrainskii, *Theor. Math. Phys.*, **32**, 816 (1978).
- 7 W. J. Hehre, R. Ditchfield, and J. A. Pople, *J. Chem. Phys.*, **56**, 2257 (1972).