Analytical energy gradients of the excited, ionized and electron-attached states calculated by the SAC-CI general-R method

Mayumi Ishida, Kazuo Toyota, Masahiro Ehara, Hiroshi Nakatsuji *

Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering,
Kyoto University, Sakyou-ku, Kyoto 606-8501, Japan

Received 1 June 2001; in final form 2 July 2001

Abstract

A method of calculating analytical energy gradients of the excited, ionized and electron-attached states calculated by the symmetry-adapted-cluster configuration-interaction (SAC-CI) general-R method is formulated and implemented. This method is expected to be a powerful tool in the studies of dynamics and properties of molecules in which two- and multi-electron processes are involved. Good performance of this method is shown for the singlet and triplet excited states of BH and for the doublet ground and excited states of CH. © 2001 Published by Elsevier Science B.V.

1. Introduction

Derivatives of the adiabatic potential energy surfaces of molecules not only in their ground states but also in their excited, ionized, and electron-attached states are key fundamental information for investigating molecular geometries, vibrations, chemical reactions, energy relaxation processes, and dynamics. Furthermore, the derivatives of energy in these states with respect to external electric and magnetic fields provide electric and magnetic properties of molecules in these different electronic states [1]. A purpose of this Letter is to give a reliable method of calculating the energy derivatives of molecules based on the symmetry adapted cluster (SAC)/SAC-CI general-R method for the excited, ionized, and electron-attached states.

The SAC/SAC-CI method [2–4] was originally published in 1978 for studying ground, excited, ionized and electron-attached (anion) states of molecules and has been successfully applied to various chemistries and physics involving many different kinds of electronic states [5,6]. The analytical gradients of the SAC/SAC-CI energy were formulated and implemented in this laboratory at the single double (SD)-R level [16,17], and applied to the calculations of equilibrium geometries, dipole moments and vibrational frequencies of molecules in various electronic states of molecules. However, as the SAC-CI SD-R method is quantitative only for the electronic states generated by the one-electron process from the ground

* Corresponding author. Fax: +81-75-753-5910.
E-mail address: hiroshi@subchem.kyoto-u.ac.jp (H. Nakatsuji).

state, we could not apply this method to the multi-electron processes that sometimes appear in the excited and ionized states and in the course of chemical reaction dynamics. Furthermore, when we study excited states of open-shell systems by the SAC-CI method, they are often described by the two-electron processes from the closed-shell SAC state. Therefore, it was anticipated to develop the analytical energy gradient method that can be applicable to such electronic states of molecules.

There are two standards in the choice of the linked operators (R) in the SAC-CI method. In the SD-R method, only single- and double-excitation operators are adopted for the R-operators, while in the general-R method [7–10], triple-, quadruple- and higher-excitation operators are further included. The SAC-CI SD-R method is reliable for ordinary single-electron excitation and ionization processes, while the general-R method is designed to describe multiple-electron processes with high accuracy and has been applied successfully, for example, in the calculations of ionization spectra involving shake-up satellite peaks [11–15].

In the present study, the analytical energy gradients of the SAC-CI general-R method were developed and implemented. The targets of the methods are the excited, ionized and electron-attached states of molecules including the multi-electron processes. The performance of the method was examined for the excited states of BH and CH molecules. More details will be given in a forthcoming paper [18].

2. Theory

The analytical gradients of the SAC-CI correlation energy with respect to the external parameter, a, are most conveniently expressed in terms of effective density matrices (EDMs) [16,17],

$$\frac{\partial \Delta E}{\partial a} = \sum_{ij}^{MO} \gamma_{ij}^{SAC\text{-}CI} \frac{\partial f_{ij}}{\partial a} + \sum_{ijkl}^{MO} \Gamma_{ijkl}^{SAC\text{-}CI} \frac{\partial (ij|kl)}{\partial a}, \qquad (1)$$

in an MO representation, where f_{ij} and $(ij|kl)$ are the Fock matrix elements and the two-electron

MO integrals, respectively. Subscripts i, j, k and l refer to the spatial orbitals. Matrix elements $\gamma_{ij}^{SAC\text{-}CI}$ and $\Gamma_{ijkl}^{SAC\text{-}CI}$ are given by

$$\gamma_{ij}^{SAC\text{-}CI}$$
$$\equiv \sum_I \left\{ \sum_K Z_K^{SAC\text{-}CI} \left(\sum_J C_J S_{KJ} \right) C_I - Z_I^{SAC\text{-}CI} \right\} \gamma_{ij}^{0I}$$
$$+ \sum_M \sum_N d_M^L d_M^R \gamma_{ij}^{MN} - \sum_K \sum_I Z_K^{SAC\text{-}CI} C_I \gamma_{ij}^{KI}$$
$$+ \sum_M \sum_N \sum_I d_M^L d_M^R C_I \gamma_{ij}^{M,NI}$$
$$- \frac{1}{2} \sum_K \sum_I \sum_J Z_K^{SAC\text{-}CI} C_I C_J \gamma_{ij}^{K,IJ} \qquad (2)$$

and

$$\Gamma_{ijkl}^{SAC\text{-}CI}$$
$$\equiv \sum_I \left\{ \sum_K Z_K^{SAC\text{-}CI} \left(\sum_J C_J S_{KJ} \right) C_I - Z_I^{SAC\text{-}CI} \right\} \Gamma_{ijkl}^{0I}$$
$$+ \sum_M \sum_N d_M^L d_M^R \Gamma_{ijkl}^{MN} - \sum_K \sum_I Z_K^{SAC\text{-}CI} C_I \Gamma_{ijkl}^{KI}$$
$$+ \sum_M \sum_N \sum_I d_M^L d_M^R C_I \Gamma_{ijkl}^{M,NI}$$
$$- \frac{1}{2} \sum_K \sum_I \sum_J Z_K^{SAC\text{-}CI} C_I C_J \Gamma_{ijkl}^{K,IJ}. \qquad (3)$$

Here, we adopt the convention that the subscripts I, J, K, and L refer to the SAC excitation operators $S^\dagger$, while M and N the SAC-CI excitation operators $R^\dagger$. γ_{ij}^{IJ} and Γ_{ijkl}^{IJ} are one-electron (1e) and two-electron (2e) coupling constants, respectively, between linked configurations $S_I^\dagger|0\rangle$ and $S_J^\dagger|0\rangle$, $\gamma_{ij}^{I,JK}$ and $\Gamma_{ijkl}^{I,JK}$ are those between linked configuration $S_I^\dagger|0\rangle$ and the unlinked configuration $S_J^\dagger S_K^\dagger|0\rangle$, γ_{ij}^{MN} and Γ_{ijkl}^{MN} are those between $R_M^\dagger|0\rangle$ and $R_N^\dagger|0\rangle$, $\gamma_{ij}^{M,NI}$ and $\Gamma_{ijkl}^{M,NI}$ are those between $R_M^\dagger|0\rangle$ and $R_N^\dagger S_I^\dagger|0\rangle$. C_I is the SAC coefficient, and d_M^L and d_M^R are the SAC-CI left- and right-vectors, respectively. S_{ij} represents the overlap matrix and is independent of the external parameters. $Z_I^{SAC\text{-}CI}$ in Eqs. (2) and (3) are the components of the SAC-CI Z-vectors, and can be obtained by the SAC-CI Z-vector equation

$$\sum_K \left\{ H_{KI} - \left(\sum_J C_J S_{KJ} \right) H_{0I} \right.$$

$$\left. - \Delta E_{SAC} S_{KI} + \sum_J C_J H_{K,IJ} \right\} Z_K^{SAC\text{-}CI} \quad (4)$$

$$= \sum_M \sum_N d_M^L d_M^R H_{M,NI},$$

where H_{IJ}, $H_{I,JK}$ and $H_{M,NI}$ are the Hamiltonian matrices, which are defined as $\langle 0|S_I H S_J^\dagger|0\rangle$, $\langle 0|S_I H S_J^\dagger S_K^\dagger|0\rangle$ and $\langle 0|R_M H R_N^\dagger S_I^\dagger|0\rangle$. In the SAC-CI analytical energy gradient method, explicit calculation of the first derivatives of the SAC coefficient $\partial C_I / \partial a$ is circumvented, introducing the interchange technique [19] (or the so-called Z-vector method [20]).

For implementing the analytical energy gradients of the SAC-CI general-R method, we have formulated $\gamma_{ij}^{SAC\text{-}CI}$ and $\Gamma_{ijkl}^{SAC\text{-}CI}$ in Eqs. (2) and (3), and the SAC-CI Z-vector equation in Eq. (4) according to the SAC-CI general-R method. The SAC-CI wave function is written as

$$\Psi^{SAC\text{-}CI} = R\Psi^{SAC}, \quad (5)$$

where

$$R = \sum_M d_M R_M^+, \quad (6)$$

and $\{R_M^+\}$ represents a set of excitation, ionization and electron-attachment operators. In the SAC-CI general-R method, $\{R_M^+\}$ includes not only single- and double-excitation operators, but also triple-, quadruple-, and higher-excitation operators. Therefore, the 1e- and 2e-EDMs in the second and fourth terms of Eqs. (2) and (3), and the SAC-CI Z-vector equation in the right-hand side of Eq. (4), should be formulated to include the contributions from the higher-excitation operators. Namely, the summation on M and N in these terms is over the SAC-CI operators including triple (T)-, quadruple (Q)-, and higher-excitation operators as

$$\sum_M \sum_N = \left(\sum_M^S + \sum_M^D + \sum_M^T + \sum_M^Q + \cdots \right)$$

$$\times \left(\sum_N^S + \sum_N^D + \sum_N^T + \sum_N^Q + \cdots \right). \quad (7)$$

Other terms are the same as in the SD-R method. In the present study, the unlinked terms that are redundant with the the linked terms are neglected.

The SAC-CI general-R analytical energy gradient code has been implemented into the SAC-CI96 program system [22] and has been incorporated into the GAUSSIAN 98 suite of programs [23]. The numerical check was done by confirming that the analytical energy gradients gave identical results to the numerical differentiations of the energies within computational accuracy.

3. Applications

The first application of the SAC-CI general-R analytical energy gradient method is the calculation of the spectroscopic constants of the singlet and triplet excited states of BH molecule and those of the doublet ground and excited states of CH molecule. BH and CH are good benchmark molecules, since the experimental data of the equilibrium internuclear distance r_e, the harmonic vibrational frequency ω_e, and the adiabatic excitation energy T_e have been reported for various electronic states [21], in which several excited states are described by the two-electron processes: in the previous paper of the SAC-CI SD-R energy gradient method [17], we studied only the one-electron excited states of these molecules.

The basis set we adopted is the double-zeta plus polarization (DZP) basis set of Huzinaga–Dunning [24,25], (9s5p1d/4s1p)/[4s2p1d/2s1p]. All the MOs were included in the active space and no configuration selection was performed. We used the approximately variational SAC-CI (SAC-CI-V) method.

3.1. BH

First, we discuss the spectroscopic properties of BH: the ground state was calculated by the SAC method and the excited states by both the SAC-CI SD-R and general-R methods. In SAC-CI general-R, the R-operators were limited up to triples. Table 1 shows the results of r_e, ω_e and T_e, compared with experiments [21]. The excitation level denotes the

Table 1
Excitation level, equilibrium internuclear distance (r_e), adiabatic excitation energy (T_e), and harmonic vibrational frequency (ω_e), for the singlet and triplet states of BH

State	Method	Excitation level	r_e (Å)	T_e (eV)	ω_e (cm^{-1})	Main configuration[a]
$X^1\Sigma_g^+$	SAC	0	1.243	–	2362	
	Exptl.[b]		1.232	–	2356	
$a^3\Pi$	SD-R	1	1.194	1.190	2664	$0.94(3\sigma^{-1}1\pi) + 0.32(3\sigma^{-1}2\pi)$
	General-R	1	1.195	1.163	2653	$0.93(3\sigma^{-1}1\pi) + 0.32(3\sigma^{-1}2\pi)$
	Exptl.[b]		1.201	–	–	
$A^1\Pi$	SD-R	1	1.236	3.074	2227	$0.94(3\sigma^{-1}1\pi)$
	General-R	1	1.241	3.018	2171	$0.93(3\sigma^{-1}1\pi)$
	Exptl.[b]		1.219	2.868	2251	
$b^3\Sigma^-$	SD-R	2	1.206	5.470	2629	$0.86(3\sigma^{-2}1\pi^2) + 0.30(3\sigma^{-2}1\pi2\pi)$ $-0.30(3\sigma^{-2}1\pi2\pi)$
	General-R	2	1.228	4.616	2405	$0.84(3\sigma^{-2}1\pi^2) + 0.30(3\sigma^{-2}1\pi2\pi)$ $-0.30(3\sigma^{-2}1\pi2\pi)$
	Exptl.[b]		1.227	–	–	
$C'^1\Delta$	SD-R	2	1.190	6.815	2776	$0.90(3\sigma^{-2}1\pi^2)$
	General-R	2	1.198	6.092	2673	$0.89(3\sigma^{-2}1\pi^2)$
	Exptl.[b]		1.196	5.701	2610	
$C^1\Sigma^+$	SD-R	2	1.191	7.550	2762	$0.63(3\sigma^{-2}1\pi^2) + 0.63(3\sigma^{-2}1\pi^2)$
	General-R	2	1.200	7.014	2657	$0.63(3\sigma^{-2}1\pi^2) + 0.63(3\sigma^{-2}1\pi^2)$
	Exptl.[b]		1.213	6.854	2475	

[a] The Hartree–Fock electronic configuration for the ground state is $(1\sigma)^2(2\sigma)^2(3\sigma)^2$.
[b] Ref. [21].

number of electrons involved in the excitation process and the excitation character is shown by the SAC-CI coefficients of the main configurations.

The low-lying $A^1\Pi$ and $a^3\Pi$ states of BH are described essentially by the one-electron excitations from the ground state, while the $C'^1\Delta$, $C^1\Sigma^+$ and $b^3\Sigma^-$ states are described by the two-electron excitations from the ground state. For the one-electron processes, the SAC-CI SD-R and general-R methods give very similar results in good agreement with experiments: the effects of the triples are negligible and within 0.005 Å, 0.03 eV, and 50 cm^{-1} for r_e, T_e, and ω_e, respectively. For the other three states generated by the two-electron processes, the general-R method gives considerably better results than the SD-R method, especially for T_e. The effect of including triples amounts up to ca. 0.8 eV for T_e of $b^3\Sigma^-$ and $C'^1\Delta$ states. The calculated r_e agrees excellently with experiments for these states; the deviations are within 0.002 Å.

Thus, for two-electron processes, we should use the SAC-CI general-R method for obtaining quantitatively reliable results. The $b^3\Sigma^-$ state has not yet been well characterized by experiment and therefore, the present results of T_e and ω_e should provide good estimates.

3.2. CH

Next, we examine the performance of the SAC-CI general-R analytical energy gradient method for the open-shell molecule CH, for which some of the excited states are described by the multi-electron processes relative to the closed-shell SAC (cation) state: we first calculate closed-shell CH$^+$ by the SAC method, and then calculate various electronic states of CH radical by the SAC-CI electron-attachment method. Table 2 summarizes r_e, ω_e and T_e calculated by the SAC-CI SD-R and general-R methods in comparison with the experiment [21]. In order to examine the effect of the R-operators in

Table 2
Excitation level, equilibrium internuclear distance (r_e), adiabatic excitation energy (T_e), and harmonic vibrational frequency (ω_e), for the doublet ground and excited states of CH

State	Method	Excitation level	r_e (Å)	T_e (eV)	ω_e (cm^{-1})	Main configuration[a]
$X^2\Pi$	SD-R	1	1.127	–	2906	$0.97(1\pi)$
	General-R (SDT)	1	1.127	–	2889	$0.95(1\pi)$
	General-R (SDTQ)	1	1.128	–	2889	$0.95(1\pi)$
	Exptl.[b]		1.120	–	2859	
$A^2\Delta$	SD-R	2	1.074	4.873	3488	$0.99(3\sigma^{-1}1\pi^2) + 0.99(3\sigma^{-1}1\pi^2)$
	General-R (SDT)	2	1.103	3.075	3045	$0.97(3\sigma^{-1}1\pi^2) + 0.97(3\sigma^{-1}1\pi^2)$
	General-R (SDTQ)	2	1.105	3.062	3006	$0.97(3\sigma^{-1}1\pi^2) + 0.97(3\sigma^{-1}1\pi^2)$
	Exptl.[b]		1.102	2.875	2931	
$B^2\Sigma^-$	SD-R	2	1.103	6.083	3142	$0.57(3\sigma^{-1}1\pi^2) - 0.57(3\sigma^{-1}1\pi^2)$
	General-R (SDT)	2	1.175	3.481	2263	$0.55(3\sigma^{-1}1\pi^2) - 0.55(3\sigma^{-1}1\pi^2)$ $-0.20(2\sigma^{-1}3\sigma^{-1}1\pi^24\sigma)$
	General-R (SDTQ)	2	1.192	3.383	2045	$0.54(3\sigma^{-1}1\pi^2) - 0.54(3\sigma^{-1}1\pi^2)$ $-0.22(2\sigma^{-1}3\sigma^{-1}1\pi^24\sigma)$
	Exptl.[b]		1.198	3.229	1795	
$C^2\Sigma^+$	SD-R	2	1.080	5.637	3381	$0.70(3\sigma^{-1}1\pi^2) + 0.70(3\sigma^{-1}1\pi^2)$
	General-R (SDT)	2	1.111	4.178	2960	$0.69(3\sigma^{-1}1\pi^2) + 0.69(3\sigma^{-1}1\pi^2)$
	General-R (SDTQ)	2	1.110	4.168	2966	$0.68(3\sigma^{-1}1\pi^2) + 0.68(3\sigma^{-1}1\pi^2)$
	Exptl.[b]		1.114	3.943	2840	

[a] The electronic configuration and the excitation level are given relative to the closed-shell CH$^+$, namely, $(1\sigma)^2(2\sigma)^2(3\sigma)^2$.
[b] Ref. [21].

different orders, systematic calculations were performed using SDT and SDTQ R-operators.

The ground state, $X^2\Pi$, is described by the one-electron process, while the other three doublet excited states, $A^2\Delta$, $B^2\Sigma^-$, and $C^2\Sigma^+$, are represented by the two-electron processes. For the ground state, both SAC-CI SD-R and general-R methods give excellent results in comparison with experiment. The deviations from the experimental values are to within 0.008 Å and 50 cm^{-1} for r_e and ω_e, respectively. For the excited states, the general-R method drastically improves the results of the SD-R method, especially for T_e and ω_e. The effects of including triples in the R-operators are as large as 1.5–2.4 eV and 420–880 cm^{-1} for T_e and ω_e, respectively. This effect is prominent for the $B^2\Sigma^-$ state. The calculation including up to quadruples further improves the results by 0.02 Å (r_e),

0.1 eV (T_e), and 220 cm^{-1} (ω_e). This is because the three-electron processes considerably mix to this state. The agreement of the general-R results with the experimental values are satisfactory regardless of the excitation levels of the states.

In these calculations, the computational cost of the SAC-CI general-R analytical energy gradient is approximately twice as much as that for its single energy calculation. Therefore, this method has the advantage over the numerical calculations of the derivatives and, in particular, is of great importance for large systems.

4. Summary

In this communication, we reported some results obtained by developing and implementing the

SAC-CI general-*R* analytical energy gradient method for the excited, ionized and electron-attached states of molecules. The reliability and usefulness of the present method are clear from the applications to the excited states of BH and CH molecules. The advantages of the SAC-CI general-*R* analytical energy gradients are summarized as follows:

- The method is quantitatively applicable to the excited, ionized, and electron-attached states including the multi-electron process.
- In particular, it is useful to study the excited states of open-shell systems, since they are often described by the two-electron process from the closed-shell SAC state.
- Detailed description can be obtained for the chemical reaction dynamics and energy relaxation processes, in which multi-electron processes sometimes play an important role.

Thus, we think that the present method should be a powerful tool for investigating the dynamics and properties in the excited, ionized and electron-attached states involving multi-electron processes.

Acknowledgements

References

[1] Y. Yamaguchi, Y. Osamura, J.D. Goddard, H.F. Shaefer, A New Dimension to Quantum Chemistry: Analytic Derivative Methods in Ab Initio Molecular Electronic Structure Theory, Oxford University Press, New York, 1994.

[2] H. Nakatsuji, K. Hirao, J. Chem. Phys. 68 (1978) 2053.

[3] H. Nakatsuji, Chem. Phys. Lett. 59 (1978) 362.

[4] H. Nakatsuji, Chem. Phys. Lett. 67 (1979) 329.

[5] H. Nakatsuji, Acta Chim. Acad. Sci. Hung. 129 (1992) 719.

[6] H. Nakatsuji, in: J. Leszczynski (Ed.), Computational Chemistry – Review of Current Trends, vol. 2, World Scientific, New Jersey, 1997, p. 62.

[7] H. Nakatsuji, Chem. Phys. Lett. 177 (1991) 331.

[8] H. Nakatsuji, J. Chem. Phys. 83 (1985) 731.

[9] H. Nakatsuji, J. Chem. Phys. 83 (1985) 5743.

[10] H. Nakatsuji, J. Chem. Phys. 94 (1991) 6716.

[11] M. Ehara, H. Nakatsuji, Chem. Phys. Lett. 282 (1998) 347.

[12] J. Hasegawa, M. Ehara, H. Nakatsuji, Chem. Phys. 230 (1998) 23.

[13] M. Ehara, P. Tomasello, J. Hasegawa, H. Nakatsuji, Theor. Chem. Acc. 102 (1999) 161.

[14] M. Ehara, H. Nakatsuji, Spectrochim. Acta A 55 (1999) 487.

[15] M. Ehara, M. Ishida, H. Nakatsuji, J. Chem. Phys. 114 (2001) 8990.

[16] T. Nakajima, H. Nakatsuji, Chem. Phys. Lett. 280 (1997) 79.

[17] T. Nakajima, H. Nakatsuji, Chem. Phys. 242 (1999) 177.

[18] M. Ishida, K. Toyota, M. Ehara, H. Nakatsuji, in preparation.

[19] A. Dalgarno, A.L. Stewart, Proc. R. Soc. London Ser. A 247 (1968) 245.

[20] N.C. Handy, H.F. Schaefer III, J. Chem. Phys. 81 (1984) 5031.

[21] K.P. Huber, G. Herzberg, Molecular Spectra and Molecular Structure, IV. Constants of Diatomic Molecules, Van Nostrand, New York, 1979.

[22] H. Nakatsuji, M. Hada, M. Ehara, J. Hasegawa, T. Nakajima, H. Nakai, O. Kitao, K. Toyota, SAC/SAC-CI program system (SAC-CI96) for calculating ground, excited, ionized, and electron-attached states having singlet to septet spin multiplicities, 1996.

[23] M.J. Frisch et al., Gaussian 98, Revision A.5, Gaussian, Inc., Pittsburgh, PA, 1998.

[24] S. Huzinaga, J. Chem. Phys. 42 (1965) 1293.

[25] T.H. Dunning Jr., J. Chem. Phys. 53 (1970) 2823.