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Analytical energy gradient of the ground, excited, ionized and electron-attached states calculated by the SAC/SAC-CI method

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Abstract

The method of calculating the analytical energy gradients for the ground, excited, ionized and electron-attached states calculated by the SAC (symmetry adapted cluster)/SAC-CI (configuration interaction) method is formulated and implemented. It is adapted with the configuration selection procedure used in the SAC/SAC-CI method. The performance of the method is investigated for the Li_2 and CO molecules. © 1997 Elsevier Science B.V.

1. Introduction

The derivatives of the adiabatic potential energies with respect to the nuclear coordinates of a molecule give fundamental information for investigating molecular geometries, vibrations, chemical reactions, etc., and the derivative of the energy with respect to the external electric or magnetic field provides the molecular properties such as the dipole, quadrupole, and magnetic moments [1]. Thus, the method of calculating the energy derivatives provides a useful and powerful tool in the field of quantum chemistry.

The SAC (symmetry adapted cluster)/SAC-CI method [2–4] was originally published in 1978 for studying the ground, excited, ionized and electron attached (anion) states of molecules and applied to various chemistries and physics involving many different electronic states [5,6]. It has also been applied to multi-electron processes [7] and the high-spin states from quartet to septet spin multiplicities [8]. It has been applied to the spectroscopies and chemical reactions of various molecular systems including surface–molecule interacting systems [9] and biochemical systems [10]. Due to these accumulated studies, the SAC/SAC-CI method has now been well established as a powerful, computationally efficient, and accurate method for calculating the ground and various excited states of molecules and molecular systems [5,6].

It is thus desirable to develop a practical method of calculating the gradients of the SAC/SAC-CI energies. This will provide a useful and efficient method for studying the dynamics and the properties of molecules in the ground and various excited and ionized states.

Two approaches have been developed for calculating the energy gradient; one calculates the direct analytical energy gradient [1], and the other uses the Hellmann–Feynman (H–F) theorem [11,12]. The use of the H–F theorem is efficient for a basis such as

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plane waves (e.g., the Car–Parrinello method [13]) and provides physically and chemically pictorial force concepts [14,15] in chemistry. Though the H–F theorem holds for the exact and stable wavefunctions, it is not satisfied for most approximate wavefunctions due to the use of the linear combination of atomic orbital (LCAO)–molecular orbital (MO) approximation. Nakatsuji and co-workers [16,17] proved a theorem which shows that there is a unique and systematic way of improving the SCF and multi-configuration SCF (MC-SCF) wavefunctions to satisfy the H–F theorem; a sufficient condition for the H–F theorem to be satisfied is that the basis set includes the derivative of any basis function included. However, the H–F theorem is not satisfied for the SAC-CI method and therefore, we have to calculate the analytical energy gradients of the SAC/SAC-CI energies.

In this Letter, we briefly summarize the SAC/SAC-CI energy gradient method for the ground, excited, ionized and electron attached states of a molecule. It assumes the usage of the configuration selection technique [18]. More details will be given in a forthcoming paper [19]. To the best of our knowledge, this is the first time that the energy gradient method has been implemented for the method using the configuration selection technique. The EOM-CC energy gradient, which is equivalent to the SAC-CI energy gradient, has been developed by Stanton and Gauss [20,21], but the method was straightforward since the configuration selection technique was not used in their formulation. We apply the present SAC/SAC-CI energy gradient method to the various electronic states of the Li_2 and CO molecules.

2. SAC/SAC-CI energy gradient method

The gradients of the SAC and SAC-CI non-variational (SAC-CI-NV) energies with respect to the external parameter a are written as

$$\frac{\partial \Delta E}{\partial a} = \sum_{ij}^{\mathrm{MO}} \gamma_{ij} \frac{\partial f_{ij}}{\partial a} + \sum_{ijkl}^{\mathrm{MO}} \Gamma_{ijkl} \frac{\partial (ij|kl)}{\partial a} \tag{1}$$

in a MO representation, where ΔE is the SAC or SAC-CI correlation energy, f_{ij} the Fock matrix element and $(ij|kl)$ the two-electron MO integral. γ_{ij} and Γ_{ijkl} are the SAC or SAC-CI one- and two-electron (1e and 2e) effective density matrices (EDMs), respectively, in the MO representation, and are given by

$$\begin{aligned}\gamma_{ij}^{\mathrm{SAC}} \equiv & \sum_I \left[\left\{ 1 + \left(\sum_K \sum_J Z_K^{\mathrm{SAC}} C_J S_{KJ} \right) \right\} C_I \right. \\ & \left. - Z_I^{\mathrm{SAC}} \right] \gamma_{ij}^{0I} - \sum_K \sum_I Z_K^{\mathrm{SAC}} C_I \gamma_{ij}^{KI} \\ & - \tfrac{1}{2} \sum_K \sum_I \sum_J Z_K^{\mathrm{SAC}} C_I C_J \gamma_{ij}^{K,IJ} \end{aligned} \tag{2}$$

and

$$\begin{aligned}\Gamma_{ijkl}^{\mathrm{SAC}} \equiv & \sum_I \left[\left\{ 1 + \left(\sum_K \sum_J Z_K^{\mathrm{SAC}} C_J S_{KJ} \right) \right\} C_I \right. \\ & \left. - Z_I^{\mathrm{SAC}} \right] \Gamma_{ijkl}^{0I} - \sum_K \sum_I Z_K^{\mathrm{SAC}} C_I \Gamma_{ijkl}^{KI} \\ & - \tfrac{1}{2} \sum_K \sum_I \sum_J Z_K^{\mathrm{SAC}} C_I C_J \Gamma_{ijkl}^{K,IJ} \end{aligned} \tag{3}$$

for the SAC method and

$$\begin{aligned}\gamma_{ij}^{\mathrm{SAC\text{-}CI}} \equiv & \sum_I \left\{ \left(\sum_K \sum_J Z_K^{\mathrm{SAC\text{-}CI}} C_J S_{KJ} \right) C_I - Z_I^{\mathrm{SAC\text{-}CI}} \right\} \gamma_{ij}^{0I} \\ & + \sum_M \sum_N d_M^{\mathscr{L}} d_N^{\mathscr{R}} \gamma_{ij}^{MN} - \sum_K \sum_I Z_K^{\mathrm{SAC\text{-}CI}} C_I \gamma_{ij}^{KI} \\ & + \sum_M \sum_N \sum_I d_M^{\mathscr{L}} d_N^{\mathscr{R}} C_I \gamma_{ij}^{M,NI} \\ & - \tfrac{1}{2} \sum_K \sum_I \sum_J Z_K^{\mathrm{SAC\text{-}CI}} C_I C_J \gamma_{ij}^{K,IJ} \end{aligned} \tag{4}$$

and

$$\begin{aligned}\Gamma_{ijkl}^{\mathrm{SAC\text{-}CI}} \equiv & \sum_I \left\{ \left(\sum_K \sum_J Z_K^{\mathrm{SAC\text{-}CI}} C_J S_{KJ} \right) C_I - Z_I^{\mathrm{SAC\text{-}CI}} \right\} \Gamma_{ijkl}^{0I} \\ & + \sum_M \sum_N d_M^{\mathscr{L}} d_N^{\mathscr{R}} \Gamma_{ijkl}^{MN} - \sum_K \sum_I Z_K^{\mathrm{SAC\text{-}CI}} C_I \Gamma_{ijkl}^{KI} \\ & + \sum_M \sum_N \sum_I d_M^{\mathscr{L}} d_N^{\mathscr{R}} C_I \Gamma_{ijkl}^{M,NI} \\ & - \tfrac{1}{2} \sum_K \sum_I \sum_J Z_K^{\mathrm{SAC\text{-}CI}} C_I C_J \Gamma_{ijkl}^{K,IJ} \end{aligned} \tag{5}$$

for the SAC-CI method. Here, γ_{ij}^{IJ} and Γ_{ijkl}^{IJ} are the one- and two-electron coupling constants between the configurations Φ_I and Φ_J, respectively, C_I the SAC coefficients, and $d_M^{\mathscr{L}}$ and $d_N^{\mathscr{R}}$ are the left- and right-vector coefficients, respectively, in the SAC-CI method. S_{IJ} represents the overlap matrix between the configurations Φ_I and Φ_J, which is a constant independent of the external parameters. Z_I in Eqs. (2)–(5) are obtained by the interchange technique [22] (or the so-called Z-vector method [23]), so that the explicit calculation of the first derivatives of the SAC coefficient $\partial C_I/\partial a$, is circumvented. Otherwise, it is a costly computational procedure involving $3N$ sets of unknowns with N being the number of atoms. Note that the formulae given by Eqs. (2)–(5) are valid for the SAC SD-*S* and SAC-CI SD-*R* methods not including the unlinked terms as products of the single excitation operators. Inclusion of such terms is straightforward.

The MO representation of the first derivatives of the SAC and SAC-CI energies is not necessarily practical since it involves the derivatives of the 2e MO integrals. However, the derivatives of the 2e atomic orbital (AO) integrals are mostly zero since only such derivative integrals which include the AO whose center is involved in the derivative calculation are non-zero, while the MO derivative integrals are generally non-zero. Therefore, instead of transforming the derivative integrals, we back-transform the effective density matrix from the MO to the AO representation [24]. The detailed discussion is given in Ref. [19].

We have also implemented the first derivative of the approximately variational SAC-CI (SAC-CI-V) energy [3]. This implementation is straightforward since the SAC-CI-V method is obtained simply by symmetrizing the SAC-CI-NV matrices. The SAC/SAC-CI energy gradient code, in addition to the CIS (singles), CISD (singles and doubles), MP2 (second-order Møller–Plesset perturbation) and SACD energy gradient, has been implemented into the SAC85 and SAC-CI96 program system [25–27] in the SD-*R* approximation. The SCF calculation is performed by the GAUSSIAN94 [28] or HONDO8 [29] program systems.

A numerical check for the implemented program was carried out by a comparison with the result of the numerical differentiations.

3. GSUM method

A feature of the present SAC/SAC-CI energy gradient method is that it is adapted with the configuration selection scheme used in the SAC/SAC-CI calculations. This is advantageous for the study of dynamics and properties of large molecules. However, for example in the geometry optimization procedure, an independent selection of operators for independent geometries may lead to a discontinuity in the potential surface. To avoid this discontinuity, we adopt the GSUM method proposed previously [30]: we use the group sum of the operators selected at different points in the geometrical domain of interest. We applied it in the calculations of the potential energy curves of the Li_2 and Li_2^+ molecules [30].

The geometry optimization using the GSUM method is summarized as follows. Before the optimization, we take the group sum of the linked and unlinked operators selected for all the representative points in the nuclear configuration space which covers the reaction under consideration. The geometry optimization is performed within this configuration space. The usefulness of this method is confirmed in the applications given below.

4. Applications

4.1. Li_2

As an example of applications of the present SAC/SAC-CI energy gradient method, we calculate the spectroscopic constants of the ground, singlet and triplet excited and ionized states of the Li_2 molecule. Li_2 is a good benchmark molecule, since the experimental results, data for the equilibrium internuclear distance r_e, the harmonic vibrational frequency ω_e and the adiabatic transition energy T_e are reported for various states [31], and in a previous paper we numerically calculated these spectroscopic constants of Li_2 and Li_2^+ by the SAC/SAC-CI method [30]. We here calculate these properties by the SAC/SAC-CI energy gradient method; the singlet ground state is evaluated by the SAC energy gradient method and the other excited states by the SAC-CI energy gradient method. The doublet ionized state

was obtained by the electron attachment to the corresponding di-cationic closed-shell Li_2 molecule. The SAC-CI calculations are performed by both the non-variational and approximate variational methods, SAC-CI-NV and SAC-CI-V, respectively. The basis set is 6-311 + + G** [32,33]. No configuration selection was done for this molecule.

The calculated results are shown in Table 1 and compared with the experiment [31]. The results calculated by the SAC/SAC-CI energy gradient method generally give good agreement with experiment. The differences between the SAC/SAC-CI and experimental results are to within 0.03 Å for the equilibrium distance, to within 10 cm^{-1} for the harmonic vibrational frequency, and within 0.15 eV for the adiabatic transition energy.

The SAC-CI-V results are close to the SAC-CI-NV results. The adiabatic transition energies calculated by the SAC-CI-V method are generally a little smaller than those by the SAC-CI-NV method. The differences in the equilibrium distance between SAC-CI-NV and SAC-CI-V are to within a few 10^{-3} Å for the states for which the vibrational frequencies are larger than 200 cm^{-1}. Thus, the accuracies of the SAC-CI-NV and SAC-CI-V methods are similar.

4.2. CO — with the GSUM method

In the next example, we show the performance of the GSUM method used in the configuration selection technique. We calculate the equilibrium internuclear distance r_e and the adiabatic transition energy T_e of the ground, singlet and triplet states of the CO molecule. In a previous paper [34], we numerically calculated these spectroscopic constants of CO by the SAC/SAC-CI method.

Table 1
Equilibrium internuclear distances, harmonic vibrational frequencies and adiabatic transition energies of Li_2 in the singlet, triplet and ionized states

State		Equilibrium internuclear distance, r_e (Å)	Harmonic vibrational frequency ω_e (cm^{-1})	Adiabatic transition energy, T_e (eV)
singlet state				
$X\,^1\Sigma_g^+$	SAC	2.698	347	0.0
	exptl. [a]	2.673	351	0.0
$A\,^1\Sigma_u^+$	SAC-CI-NV	3.093	258	1.844
	SAC-CI-V	3.094	254	1.843
	exptl. [a]	3.108	255	1.744
$B\,^1\Pi_u$	SAC-CI-NV	2.968	269	2.725
	SAC-CI-V	2.968	272	2.725
	exptl. [a]	2.935	270	2.534
$2\,^1\Sigma_g^+$	SAC-CI-NV	3.366	173	2.718
	SAC-CI-V	3.343	165	2.718
$1\,^1\Pi_g$	SAC-CI-NV	3.693	149	2.725
	SAC-CI-V	3.718	145	2.725
triplet state				
$a\,^3\Sigma_u^+$	SAC-CI-NV	4.225	74	0.978
	SAC-CI-V	4.215	76	0.977
$1\,^3\Pi_u$	SAC-CI-NV	2.589	348	1.428
	SAC-CI-V	2.586	344	1.428
$b\,^3\Sigma_g^+$	SAC-CI-NV	3.082	251	2.014
	SAC-CI-V	3.083	244	2.014
ionized state				
$1\,^2\Sigma_g^+$	SAC-CI-NV	3.134	184	5.161 [b]
	SAC-CI-V	3.131	183	5.161 [b]

[a] Ref. [31].
[b] Ionization potential (IP) calculated as the difference energy from the Li_2 ground state. Experimental IP is 5.15 or 4.86 eV from Ref. [31].

Table 2
Equilibrium internuclear distances, adiabatic transition energies and dipole moments of CO in the singlet and triplet states

State		Equiliblium internuclear distance, r_e (Å)	Adiabatic transition energy, T_e (eV)	Dipole moment [a], μ_e (debye)
$X\,^1\Sigma^+$	SAC	1.122	0.0	+0.079
	exptl. [b]	1.128	0.0	+0.122
$a\,^3\Pi$	SAC-CI	1.195	6.207	−1.763
	exptl. [b]	1.206	6.036	−1.374
$a'\,^3\Sigma^+$	SAC-CI	1.336	6.889	+1.099
	exptl. [b]	1.352	6.922	$+1.0_6$
$d\,^3\Delta$	SAC-CI	1.351	7.728	+0.746
	exptl. [b]	1.370	7.578	–
$A^1\Pi$	SAC-CI	1.231	8.442	−0.625
	exptl. [b]	1.235	8.068	−0.335 [c]
$D^1\Delta$	SAC-CI	1.368	8.411	+0.520
	exptl. [b]	1.399	8.174	–

[a] Polarity C^-O^+.
[b] Ref. [31].
[c] Ref. [35].

The basis set is 6-311++G** [32,33]. The singlet ground state was calculated by the SAC energy gradient method and the excited singlet and triplet states by the SAC-CI energy gradient method. The SAC-CI calculations are performed by the SAC-CI-NV method. The energy thresholds of 1×10^{-5} and 1×10^{-7} hartree are used in the configuration selection scheme for the ground and excited states, respectively. The geometry optimization is performed by using the GSUM method. The configuration space in the experimental geometry is preliminarily determined by using the configuration selection technique and the equilibrium distance is calculated by the geometry optimization method keeping this configuration space. Though the experimental geometries are used as the initial starting geometries in the present calculations, other adequate geometries such as the optimized ones at the HF/CIS level can be used, as we have checked that the dependence on the initial geometry is small if a proper geometry one is used.

The calculated results are shown in Table 2 and compared with experiment [31,35]. We also calculate the dipole moments using the energy derivative method. The results calculated by the SAC/SAC-CI energy gradient method generally give good agreement with experiment. This shows that the SAC/SAC-CI energy gradient method is effective and also useful when the configuration selection scheme is used.

5. Concluding remarks

In this Letter, we briefly summarize the SAC/SAC-CI analytical energy gradient method for the ground, excited, ionized and electron attached states. The configuration selection technique can be applied to our SAC/SAC-CI energy gradient method. The reliability and the usefulness of the present method are confirmed, based on applications to the Li_2 and CO molecules. We expect that the present method will be used efficiently for studies of the dynamics and properties of molecules in the ground, excited, ionized and electron attached states.

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