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Singularity-free analytical energy gradients for the SAC/SAC-CI method: coupled perturbed minimum orbital-deformation (CPMOD) approach

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Abstract

A new procedure for evaluating energy gradients in a singularity-free manner is presented for use in the SAC/SAC-CI program in which computational dimensions are reduced by the perturbation selection method. The singularity in the energy gradients stemming from a breakdown of the unitary invariance is effectively removed by the minimum orbital-deformation (MOD) method proposed in the previous study. All calculations can be done analytically via new two sets of linear equations combined with the coupled-perturbed Hartree–Fock method. Geometry optimizations for malonaldehyde in the ground and lowest singlet excited states are performed by the new method.

1. Introduction

The SAC/SAC-CI method [1–9] proposed by Nakatsuji in 1978 is an elegant theory of electronic structure for the ground and the excited states, however, computational cost for solving the SAC/SAC-CI equations formally scales as $O(N^6)$, N being the number of basis functions, if all single and double R excitation operators are considered. This scaling property can be relaxed by suitable selections of the excitation operators, for example, the so-called perturbation selection, but the efficiency of such selections strongly depends on the choice of the MO set. To exploit the short-range nature [10] of the correlation effects, it is rational to choose the localized MOs (LMOs) as the basis.

Use of the localizability of electron correlation [11–14] has been extensively studied but limited to single point calculation except for a few examples [15–18]. This may be partly because that the localization of occupied or unoccupied MOs is no longer invariant transformation for the energies

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and properties of a wavefunction determined within selected operators. If the localization degrees of freedom are determined by such standard procedures as the Boys [19] and the Pipek–Mezey [20] methods, the MOs are not necessarily continuous functions of external parameters [21]. Therefore, singularities may appear in the first derivatives of wavefunctions described by the selected operators. Needless to say, the singularities are pure artifact and must be eliminated. This is why the minimum orbital-deformation (MOD) method was proposed in the previous work [21].

In this communication, we present new expressions for evaluating the SAC/SAC-CI energy gradients [5–8], by which the divergence of the CPHF coefficients is effectively circumvented. This realizes an economical calculation of the gradients by virtue of the localizability in a singularity-free manner.

2. Theory

The following conventions are used throughout the text: doubly occupied orbitals are denoted by i, j, k, l, unoccupied orbitals by a, b, c, d, and general orbitals by p, q, r, s. Atomic orbitals (AOs) are denoted by Greek letters μ, ν, ρ, σ. We assume the MOs to be real, orthonormal, and the linear combinations of AOs, $\psi_p = \sum_\mu \chi_\mu C_{\mu p}$.

The analytical energy gradients for the SAC/SAC-CI method were formulated by Nakajima and Nakatsuji [5,6] and implemented in the SAC/SAC-CI code for singlet, doublet, and triplet states within SD-R, i.e., the singles and doubles excitations from the SAC wavefunction. Recently, the method was extended to the higher order R operators up to sextuples [7] and spin multiplicities up to septet state [8]. The SAC/SAC-CI energy gradients with respect to the external parameters α such as nuclear coordinates, electric field, etc., can be expressed in common form as

$$\frac{\partial E_{\text{corr.}}}{\partial \alpha} = \sum_{pq} \gamma_{pq} F_{pq}^{\alpha} + \sum_{pq,rs} \Gamma_{pq,rs} (pq|rs)^{\alpha} - \sum_{pq} X_{pq} S_{pq}^{\alpha} + \sum_{p>q} \left(X_{pq} - X_{qp}\right) T_{pq}^{\alpha}, \tag{1}$$

where the skeleton Fock, two-electron, and overlap derivative integrals [22] are denoted by F_{pq}^{α}, $(pq|rs)^{\alpha}$ and S_{pq}^{α} , respectively. The elements of the effective one- and two-electron density matrices (EDMs) [5–8] are denoted by γ_{pq} and $\Gamma_{pq,rs}$, respectively. The matrix elements X_{pq} are given by

$$X_{pq} = \sum_{r} F_{pr} \gamma_{rq} + 2 \sum_{rst} (pr|st) \Gamma_{qr,st} + \frac{1}{2} \sum_{irs} \delta_{qi} \{4(pq|rs) - (pr|qs) - (ps|qr)\} \gamma_{rs}, \tag{2}$$

where F_{pq} and $(pq|rs)$ denote the Fock and two-electron integrals, respectively. The symmetries of the EDMs, i.e., $\gamma_{pq} = \gamma_{qp}$ and $\Gamma_{pq,rs} = \Gamma_{pq,sr} = \Gamma_{qp,rs} = \Gamma_{rs,pq}$, are used in deriving Eq. (2). In this communication, we assume that all MOs are correlated to avoid unnecessary complexity. The anti-symmetric matrix $\mathbf{T}^{\alpha} = \mathbf{U}^{\alpha} - \mathbf{U}^{\alpha^{\dagger}}$ represents dynamical mixing among MOs, where the matrix elements U_{pq}^{α} denote the CPHF coefficients [23]. When the MOs are determined by the SCF procedure, the ai elements of the matrix $\mathbf{T}^{\alpha}$ are attributed to the α-dependence of the SCF MOs and are explicitly obtained by solving a set of CPHF equations [23]. On the other hand, the ij and ab elements of the matrix $\mathbf{T}^{\alpha}$ are redundant, i.e., $X_{ij} - X_{ji} = 0$ and $X_{ab} - X_{ba} = 0$ for all i, j and a, b in such conventional theories as MP2, CISD [15,24] and CCSD [18]. However, to exploit the localizability, we must allow energies to depend on the localization degrees of freedom. Thus, T_{ij}^{α} and T_{ab}^{α} elements become nonredundant in the local approach.

Explicit equations for the Pipek–Mezey localizations were derived by El Azhary et al. [15] and adopted for analytical energy gradients [15–18] of the local methods originally proposed by Pulay [11]. Rauhut et al. [16] mentioned that in calculating the local MP2 energies and gradients for benzene, artificial errors might be caused by redundant degrees of freedom for the Pipek–Mezey localization. The redundant degrees of freedom may cause divergence of some ij and ab elements of the matrix $\mathbf{T}^{\alpha}$, and hence the energy gradients may diverge to the infinity. To avoid this behavior, an alternative procedure, the MOD method was proposed in the previous work [21].

The spirit of the MOD method is a suppression of orbital rotation among occupied or unoccupied MOs against external perturbations. That is achieved by imposing the conditions, $T^{\alpha}_{ij} = 0$ and $T^{\alpha}_{ab} = 0$ for all $i > j$ and $a > b$ since the elements of $\mathbf{T}^{\alpha}$ represent the 'speed' of orbital rotation induced by the perturbation. Satisfying these conditions for arbitrary geometry is practically difficult, but alternative conditions

$$M_{ij} - M_{ji} = 0 \quad \text{and} \quad M_{ab} - M_{ba} = 0 \tag{3}$$

for all $i > j$ and $a > b$, can be very easily imposed on the MOs. The matrix elements of $\mathbf{M}$ are defined by the overlap between MOs for the current α and externally given constant α_0 as

$$\mathbf{M} = \mathbf{C}^{\dagger}(\alpha_0)\mathbf{S}(\alpha_0)\mathbf{C}(\alpha), \tag{4}$$

where $\mathbf{S}$ denotes the overlap matrix in the AO representation. Imposing Eq. (3) on the MOs effectively suppresses orbital rotation for small $\alpha - \alpha_0$ because $(\mathbf{M} - \mathbf{M}^{\dagger})/(\alpha - \alpha_0)$ coincides with $\mathbf{T}^{\alpha}$ in the limit of $\alpha \rightarrow \alpha_0$. In the practical geometry optimization, the initial guess calculated at the lower level of theory may be a good choice of α_0.

Requiring Eq. (3) to the first-order, we obtain two sets of equations to determine ij and ab elements of $\mathbf{T}^{\alpha}$ for the MOD method, which we call 'coupled perturbed MOD (CPMOD)' equations

$$\frac{\partial}{\partial \alpha}(M_{wx} - M_{xw}) = \sum_{y>z} \Lambda_{wx,yz} T^{\alpha}_{yz} + \sum_{\mu\nu} \Theta_{wx,\mu\nu} \frac{\partial S_{\mu\nu}}{\partial \alpha} + \sum_{ck} \Xi_{wx,ck} \tilde{U}^{\alpha}_{ck} = 0 \tag{5}$$

for all $w > x$, where $\{w, x, y, z\}$ stands for $\{i, j, k, l\}$ or $\{a, b, c, d\}$, and the CPHF coefficients in the CMO representation are denoted by $\tilde{U}^{\alpha}_{ck}$. The coefficients Λ_{wxyz}, $\Theta_{wx,\mu\nu}$, and $\Xi_{wx,ck}$ are given by

$$\Lambda_{wx,yz} = \frac{1}{2}(1 - \tau_{yz})(1 - \tau_{wx})\delta_{xz} M_{wy}, \tag{6}$$

$$\Theta_{ij,\mu\nu} = -\frac{1}{2}(1 - \tau_{ij}) C_{\nu j} \sum_{k} C_{\mu k} M_{ki}, \tag{7}$$

$$\Theta_{ab,\mu\nu} = -\frac{1}{2}(1 - \tau_{ab}) C_{\nu b} \left(2 \sum_{k} C_{\mu k} M_{ka} + \sum_{c} C_{\mu c} M_{ca} \right), \tag{8}$$

$$\Xi_{ij,ck} = (1 - \tau_{ij}) W_{kj} \tilde{M}_{ic}, \tag{9}$$

$$\Xi_{ab,ck} = -(1 - \tau_{ab}) W_{cb} \tilde{M}_{ak}, \tag{10}$$

$$\tilde{\mathbf{M}} = \mathbf{C}^{\dagger}(\alpha_0)\mathbf{S}(\alpha_0)\tilde{\mathbf{C}}(\alpha) = \mathbf{M}\mathbf{W}^{\dagger}, \tag{11}$$

where the CMO coefficients are denoted by $\tilde{\mathbf{C}}$ and the localization by $\mathbf{W}$. The operator τ_{yz} permutes the indices y and z.

Substituting the formal solutions of the CPHF [23] and the CPMOD equations (Eq. (5)) for the elements of the matrix $\mathbf{T}^{\alpha}$ and introducing the so-called Z-vectors [26], we can rearrange Eq. (1) in the usual form [27]

$$\frac{\partial E_{\text{corr.}}}{\partial \alpha} = \sum_{\mu\nu} P_{pq} F^{\alpha}_{pq} + \sum_{pq,rs} \Gamma_{pq,rs} (pq|rs)^{\alpha} - \sum_{\mu\nu} Q_{\mu\nu} \frac{\partial S_{\mu\nu}}{\partial \alpha}. \tag{12}$$

The matrix elements P_{pq} and $Q_{\mu\nu}$ [25] can be evaluated before generating the derivatives of the AO integrals.

A note here is that the present analytical expressions are independent of the structure of the post-SCF wavefunction, which is implicit in the matrix elements γ_{pq} and $\Gamma_{pq,rs}$. The present method is examined for the CISD and the SAC/SAC-CI in the next section.

The present method have been implemented in the development version of the GAUSSIAN 01 system of programs [28], as the SAC/SAC-CI gradients code, and used to perform geometry optimizations of molecules in the ground and excited states.

3. Test calculation

The equilibrium structures of malonaldehyde ($C_3O_2H_4$) in the ground ($1^1A'$) and the lowest singlet excited ($1^1A''$) states were optimized by the CISD and the SAC/SAC-CI methods. For SAC-CI, approximately variational (SAC-CI-V) solutions were used [4]. The basis set was the double-ζ set of Huzinaga–Dunning [29,30] plus single polarization function with exponents 0.85, 0.75 (d) and 1.0 (p) on each oxygen, carbon and hydrogen atoms, respectively, designated D95(d,p). All 100 MOs were correlated in the post-SCF calculations. The localizability of electron correlations was exploited through the perturbation selection [31] of double excitation operators in the LMO representation. The HF and CIS wavefunctions were chosen as the zeroth-order approximation of the ground and excited states, respectively. The energy thresholds for perturbation selection of 10^{-6} and 10^{-7} a.u. were used for the ground state (λ_g), and 10^{-7} and 10^{-8} a.u. for the excited state (λ_e). In the SAC/SAC-CI calculations, some less important integrals for the non-linear terms of the SAC and SAC-CI expansions were neglected [9]. A set of excitation operators selected at the initial geometry was used until the optimization procedure was completed. The geometries optimized by the conventional CISD and CIS were used as the initial geometry for the ground and the excited states, respectively. The MOs were determined by the Pipek–Mezey localizations for the initial geometries and by the MOD method during the optimization. In the latter case, the LMOs of the former geometry were used as $\mathbf{C}(\alpha_0)$.

The perturbation selection depends on the initial geometry and chosen orbital set $\mathbf{C}(\alpha_0)$. This causes to some extent ambiguity of the optimized results, however, the optimized energies and geometries converge to the exact ones when the thresholds becomes zeroes and their convergence is very fast with respect to the thresholds in the present calculations. The localization of MOs for the initial geometry may be not necessarily preserved by the MOD method in the final point of optimization if the starting point is not a good guess. Such difficulties may occur in the very flat potential energy surfaces. A possible prescription to this problem is re-localizing MOs and reselecting operators at the final point, and then re-optimizing geometry as suggested by Rauhut et al. [16]. We are planning to examine this method in the forthcoming Letter [25].

3.1. Ground state

The localizability of electron correlations for the ground state is clearly seen in Table 1. More than 95% and 98% of the correlation energies were obtained for the CISD at the levels of $\lambda_g = 10^{-6}$ and 10^{-7}, respectively, while the computational dimensions were drastically reduced to 1.8% and 5.1% of the conventional calculations, respectively. At the latter level, the SAC reproduces more than 90% of the CCSD correlation energy, though the ratio is lower than that for the CISD due to the partial neglect of integrals mentioned above.

Effect of the perturbation selection on the geometrical parameters of the ground state is very small as shown in Table 2. The RMS error is as small as 0.002 Å in bond lengths and 0.26° in valence angles for the CISD, and 0.009 Å and 0.48° for the SAC. The errors in the geometries are larger for the SAC than for the CISD, but are expected to decrease when all the integrals for the non-linear terms of the SAC and SAC-CI expansions are included. Such study is in progress in our laboratory.

Table 1
Computational dimensions and energies of the ground ($1^1A'$) state of malonaldehyde at the geometry optimized by the CISD

		CISD			SAC[a]		CCSD
	λ_g:[b]	10^{-6}	10^{-7}	0.0	10^{-6}	10^{-7}	0.0
Dimension		22 257	60 811	1 186 569	22 257	60 811	1 186 569
	(%)	(1.8)	(5.1)	(100.0)	(1.8)	(5.1)	(100.0)
E(total)	(a.u.)	−266.379453	−266.398617	−266.409056	−266.442328	−266.462622	−266.543753
E(corr.)	(a.u.)	−0.682411	−0.701574	−0.712013	−0.745285	−0.765579	−0.846710
	(%)	(95.84)	(98.53)	(100.00)	(88.02)	(90.42)	(100.00)

[a] In calculating the SAC wavefunction, some less important integrals were neglected in addition to the perturbation selection of the excitation operators (see text).

[b] Energy threshold in a.u.

Table 2
Optimized geometrical parameters and energies for the ground ($1^1A'$) state of malonaldehyde

Parameter			CISD			SAC		CCSD
		λ_g:[a]	10^{-6}	10^{-7}	0.0	10^{-6}	10^{-7}	0.0
C(2)=O(1)	(Å)		1.226	1.226	1.226	1.233	1.233	1.240
C(3)–C(2)			1.463	1.456	1.452	1.477	1.471	1.455
C(4)=C(3)			1.358	1.356	1.355	1.365	1.363	1.365
O(5)–C(4)			1.328	1.324	1.321	1.342	1.339	1.337
H(6)–O(5)			0.968	0.970	0.972	0.969	0.971	0.982
RMS error			(0.006)	(0.002)	(0.000)	(0.012)	(0.009)	(0.000)
O(1)=C(2)–C(3)	(°)		123.7	123.7	123.6	123.7	123.6	123.4
C(2)–C(3)=C(4)			120.7	120.4	120.0	121.1	120.8	120.4
C(3)=C(4)–O(5)			125.7	125.5	125.2	125.8	125.7	125.2
C(4)–O(5)–H(6)			107.6	107.5	107.4	107.4	107.4	106.7
RMS error			(0.44)	(0.26)	(0.0)	(0.60)	(0.48)	(0.0)
E(total)	(a.u.)		−266.379759	−266.398674	−266.409056	−266.443919	−266.463611	−266.544670

[a] Energy threshold in a.u.

3.2. Excited state

As seen in Table 3, the correlation effects seem to be localizable for the $1^1A''$ $(n\pi^*)$ excited state as well as for the ground state. Most of the correlation effects, $\Delta E(\text{total} - \text{CIS})$, over 94% and 98% were obtained for the CISD at the levels of $\lambda_e = 10^{-7}$ and 10^{-8}, while the computational dimensions were drastically reduced to 1.6% and 3.9% of the conventional calculations, respectively. This is quite an impressive result.

The optimized geometrical parameters for the excited state are given in Table 4. Very fast convergence of the geometry with respect to the energy threshold is observed for the CISD. The RMS error is as small as 0.003 Å and 0.71° for the CISD at $\lambda_e = 10^{-8}$. The SAC-CI calculation without selection is not presented since it takes large cpu time at present, however, fast convergence of the results is expected from the small difference between the two levels of calculations, namely, 0.007 Å and 0.2°.

The adiabatic (0–0) excitation energies $\Delta E_{0\text{–}0}$ were obtained in consistent accuracy by subtracting energies of the ground state shown in Table 2 from the corresponding energies of the excited

Table 3
Computational dimensions and energies of the excited ($1^1A''$) state of malonaldehyde at the geometry optimized by the CIS

			CISD			SAC-CI[a]	
		λ_g:[b]	–	–	–	10^{-6}	10^{-7}
		λ_e:[b]	10^{-7}	10^{-8}	0.0	10^{-7}	10^{-8}
Dimension	#*S*		–	–	–	21 286	57 369
	(%)		–	–	–	(1.8)	(4.8)
	#*R*		18 887	46 225	1 186 569	18 887	46 225
	(%)		(1.6)	(3.9)	(100.0)	(1.6)	(3.9)
E(total)	(a.u.)		−265.679825	−265.685821	−265.689220	−266.304411	−266.325374
$\Delta E(\text{total} - \text{CIS})$	(a.u.)		−0.164587	−0.170583	−0.1739815	−0.789173	−0.810136
	(%)		(94.60)	(98.05)	(100.00)		

[a] In the present calculations, some less important integrals were neglected in addition to the perturbation selection of the excitation operators (see text).

[b] Energy threshold in a.u.

Table 4
Optimized geometrical parameters and energies for the excited ($1^1A''$) state of malonaldehyde

Parameter		CISD			SAC-CI		Exp.
	λ_g:[a]	–	–	–	10^{-6}	10^{-7}	
	λ_e:[a]	10^{-7}	10^{-8}	0.0	10^{-7}	10^{-8}	
C(2)=O(1)	(Å)	1.343	1.341	1.340	1.344	1.344	
C(3)—C(2)		1.399	1.392	1.386	1.441	1.434	
C(4)=C(3)		1.371	1.374	1.378	1.372	1.369	
O(5)—C(4)		1.341	1.341	1.341	1.369	1.367	
H(6)—O(5)		0.949	0.950	0.952	0.960	0.958	
RMS error		(0.007)	(0.003)	(0.000)			
O(1)=C(2)—C(3)	(°)	122.7	122.7	122.0	122.6	122.6	
C(2)—C(3)=C(4)		125.9	125.4	124.4	127.6	127.4	
C(3)=C(4)—O(5)		126.6	126.2	125.7	128.0	127.9	
C(4)—O(5)—H(6)		112.2	112.2	112.3	110.8	111.0	
RMS error		(0.99)	(0.71)	(0.0)			
E(total)	(a.u.)	−265.687803	−265.694238	−265.698175	−266.312848	−266.333350	
ΔE_{0-0} (adiabatic ex.)[b]	(eV)	18.68	19.02	19.19	3.42	3.39	3.504[c]

[a] Energy threshold in a.u.

[b] Adiabatic excitation energy including ZPE correction (−0.15 eV) estimated by HF and CIS.

[c] Ref. [32].

state shown in Table 4. The correction of the zero-point energy (ZPE) was estimated to be −0.15 eV by HF and CIS. The adiabatic excitation energies predicted by CISD vary from 18.68 to 19.19 eV with the decrease of λ_e and are much higher than the experimental value of 3.504 eV [32]. The overestimation, however, is not attributed to the perturbation selection. The ΔE_{0-0} values by the SAC-CI are 3.42 and 3.39 eV at the levels of $\lambda_g = 10^{-6}/\lambda_e = 10^{-7}$ and $\lambda_g = 10^{-7}/\lambda_e = 10^{-8}$, respectively, in excellent agreement with the experimental value, and fairly insensitive to the thresholds.

The above results suggest that Eq. (3) can be safely used instead of the standard localization conditions for calculating geometries when the good initial guess is accessible, for example, through a lower level theory giving a good zeroth-order description of the state.

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