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Second-order perturbative approximation to the SAC/SAC-CI method

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Abstract

The second-order perturbative approximation to the SAC (symmetry-adapted cluster)/SAC-CI (configuration interaction) method is proposed. It is used in various studies of electronic structures and spectroscopic properties of large molecules in ground, excited (singlet and triplet), ionized, and electron-attached states. The performance and the reliability of the proposed method are investigated by applications to several molecules in these electronic states. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

The SAC/SAC-CI method [1–3], which was originally reported in 1978 for studying the ground, excited, ionized, and electron-attached (anion) states, has been used in various studies [4,5] of molecular electronic structures, spectroscopic properties, chemical reactions, surface–molecule interaction systems [6], and biochemical systems [7,8]. This method has been extended to high-spin states from quartet to septet spin multiplicities [9]. Furthermore, the SAC/SAC-CI energy gradient method [10] has been implemented and applied to investigate the potential energy surfaces of molecules in various electronic states. Based on these accumulated studies, the SAC/SAC-CI method has been established as a reliable and useful method for studying ground and excited states of molecules in singlet to septet spin multiplicities.

In recent years, some methods similar to the SAC-CI method have been proposed. The equation-of-motion coupled cluster (EOM-CC) method [11] and the coupled cluster linear response (CCLR) theory [12–14] are essentially the same as the SAC-CI method [15]. Furthermore, some perturbative approximations to these methods have been reported by several groups. Stanton and Gauss [16], and Gwaltney et al. [17] have proposed EOM-CCSD(2) and EOM-MBPT(2) methods, respectively. The MBPT(2)-GF method by Nooijen and Snijders [18] is equivalent to the EOM-CCSD(2) method for the ionized state. The EOM-CCSD(2) method includes up to the second-order perturbation for the ground state by the Møller–Plesset (MP) perturbation theory

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[19], whereas up to infinite-order perturbation is included for the excited state, and therefore, the method may treat the ground and excited states in an unbalanced way. This unbalanced nature was avoided in the EOM-MBPT(2) approach by applying Löwdin's partitioning technique [20], which was referred to as the partitioned (P) EOM-MBPT(2) method. The CC2 method proposed by Christiansen et al. [21] and the STEOM-PT method by Nooijien and Bartlett [22] are also considered to be the second-order perturbative approximation. Head-Gordon et al. have proposed a CI singles with second-order doubles correction, referred to as CIS(D) method [23]. It was related to the non-iterative second-order perturbative approximation and drastically reduced the errors of the CIS method for the vertical excitation energies of closed-shell molecules [23]. They extended the CIS(D) method to open-shell systems based on the unrestricted CIS and restricted open-shell CIS methods [24].

Since second-order perturbative methods are simpler than the full SAC-CI method, which includes up to infinite-order perturbation, these approximations are expected to become useful for larger molecular systems. Systematic investigation of hierarchical approximations to the SAC/SAC-CI method is important not only for assessing the reliabilities and the limitations of these methods, but also developing computationally more efficient method.

In Section 2, we propose newly developed second-order perturbative approximations to the SAC/SAC-CI method. In Section 3, the performance of these methods is investigated by applying them to some doublet radicals, formaldehyde, ethylene, butadiene, and porphin in the ground and excited states.

2. Method

Throughout this Letter, we adopt the convention that S operators refer to the excitation operators for the SAC ground state and R operators to those for the SAC-CI excited, ionized, and electron-attached states. R_{S} and R_{D} refer to the SAC-CI single- and double-excitation operators, respectively, without coefficients. We use R_1 and R_2 when their coefficients are included. Symbol $|0\rangle$ is the usual Hartree–Fock (HF) configuration. Subscripts $i, j, \ldots,$ refer to the occupied orbitals and $a, b, \ldots,$ to the virtual orbitals.

In the SD SAC equation [1–3], we diagonalize the Hamiltonian matrix,

$$\begin{bmatrix} \boldsymbol{H}_{00}-E & \boldsymbol{H}_{0\mathrm{S}} & \boldsymbol{H}_{0\mathrm{D}} \\ \boldsymbol{H}_{\mathrm{S}0} & \boldsymbol{H}_{\mathrm{SS}}-E\boldsymbol{S}_{\mathrm{SS}} & \boldsymbol{H}_{\mathrm{SD}} \\ \boldsymbol{H}_{\mathrm{D}0} & \boldsymbol{H}_{\mathrm{DS}} & \boldsymbol{H}_{\mathrm{DD}}-E\boldsymbol{S}_{\mathrm{DD}} \end{bmatrix}. \tag{1}$$

The unlinked terms, such as $\langle 0|S_{\mathrm{D}}^{\dagger} H S_{\mathrm{D}} S_2|0\rangle$, are included in this Hamiltonian matrix and $\mathbf{S}_{\mathrm{SS}}$ and $\mathbf{S}_{\mathrm{DD}}$ represent similar overlap matrices. Due to these unlinked terms, the Hamiltonian matrix becomes non-symmetric. In the SD-R SAC-CI method, we diagonalize the Hamiltonian matrix,

$$\begin{bmatrix} \boldsymbol{H}_{\mathrm{SS}}-E\boldsymbol{S}_{\mathrm{SS}} & \boldsymbol{H}_{\mathrm{SD}} \\ \boldsymbol{H}_{\mathrm{DS}} & \boldsymbol{H}_{\mathrm{DD}}-E\boldsymbol{S}_{\mathrm{DD}} \end{bmatrix}, \tag{2}$$

which is also non-symmetric. An algorithm for the iterative diagonalization of the non-symmetric matrices was given previously [25].

We adopt a second-order perturbative approximation to Eq. (1) and (2). In this Letter, the SAC/SAC-CI method based on this approximation is generally referred to as the SAC(2)-CI method. As compared with the other perturbative approaches mentioned above, our approach is straightforward. It is derived from the considerations that the S_{S} and S_{D} operators give second- and first-order contributions to the energy, respectively, for the SAC ground state, and R_{S} and R_{D} operators give zeroth- and first-order contributions, respectively, to the SAC-CI excited states.

In the SAC(2)-CI method, Eq. (1) for the ground state is approximated by

$$\begin{bmatrix} \boldsymbol{H}_{00}-E & \boldsymbol{H}_{\mathrm{D}0}^{\dagger} \\ \boldsymbol{H}_{\mathrm{D}0} & \boldsymbol{H}_{\mathrm{DD}}^{\mathrm{diag}}-E\mathbf{1} \end{bmatrix}. \tag{3}$$

In this Hamiltonian matrix, $\langle 0|S_{\mathrm{D}}^{\dagger} H|0\rangle$ is included in $\boldsymbol{H}_{\mathrm{D}0}$, and only the diagonal part of $\langle 0|S_{\mathrm{D}}^{\dagger} H S_{\mathrm{D}}|0\rangle$ in $\boldsymbol{H}_{\mathrm{DD}}^{\mathrm{diag}}$. No unlinked term is included. This *symmetric* Hamiltonian matrix is solved by the iterative diagonalization in contrast with the non-iterative one by EOM-MBPT(2) and P-EOM-MBPT(2). Note that the non-iterative second-order perturbation theory is obtained from

$$\begin{bmatrix} \boldsymbol{H}_{00} - E & \boldsymbol{H}_{\mathrm{D}0}^{\dagger} \\ \boldsymbol{H}_{\mathrm{D}0} & \boldsymbol{H}_{\mathrm{DD}}^{\mathrm{diag}} \end{bmatrix}. \tag{4}$$

In the SAC(2)-CI method for the excited state, we diagonalize the non-symmetric Hamiltonian matrix,

$$\begin{bmatrix} \boldsymbol{H}_{\mathrm{SS}} - E\boldsymbol{S}_{\mathrm{SS}} & \boldsymbol{H}_{\mathrm{DS}}^{\dagger} \\ \boldsymbol{H}_{\mathrm{DS}} & \boldsymbol{H}_{\mathrm{DD}}^{\mathrm{diag}} - E\boldsymbol{1} \end{bmatrix}. \tag{5}$$

Elements $\langle 0|R_{\mathrm{S}}^{\dagger} H R_{\mathrm{S}}|0\rangle$ and $\langle 0|R_{\mathrm{S}}^{\dagger} H R_{\mathrm{S}} S_2|0\rangle$ are included in $\boldsymbol{H}_{\mathrm{SS}}$, and $\langle 0|R_{\mathrm{D}}^{\dagger} H R_{\mathrm{S}}|0\rangle$ in $\boldsymbol{H}_{\mathrm{DS}}$. Only the diagonal part of $\langle 0|R_{\mathrm{D}}^{\dagger} H R_{\mathrm{D}}|0\rangle$ is included in $\boldsymbol{H}_{\mathrm{DD}}^{\mathrm{diag}}$. In our approximation, $\langle 0|R_{\mathrm{D}}^{\dagger} H R_{\mathrm{S}} S_2|0\rangle$ in $\boldsymbol{H}_{\mathrm{DS}}$, which is included in both EOM-MBPT(2) and P-EOM-MBPT(2), is not included, since this term does not contribute to the second-order energy when HF orbitals are used. Thus, $\boldsymbol{H}_{\mathrm{DS}}$ includes only the linked term $\langle 0|R_{\mathrm{D}}^{\dagger} H R_{\mathrm{S}}|0\rangle$ and becomes Hermitian-conjugate of $\boldsymbol{H}_{\mathrm{SD}}$. The non-symmetric nature of this Hamiltonian matrix is due to $\boldsymbol{H}_{\mathrm{SS}}$ in which the unlinked term $\langle 0|R_{\mathrm{S}}^{\dagger} H R_{\mathrm{S}} S_2|0\rangle$ is included.

Explicitly writing the perturbative contribution in each operator, $\langle 0|R_{\mathrm{D}}^{(1)\dagger} H^{(0)} R_{\mathrm{D}}^{(1)}|0\rangle$ is included in $\boldsymbol{H}_{\mathrm{DD}}^{\mathrm{diag}}$ of the SAC(2)-CI method, where the number in the bracket represents the order of the perturbation, and $H^{(0)}$ denotes the zeroth-order unperturbed Hamiltonian. Two approximations are generally done for the choice of the zeroth-order Hamiltonian. If we adopt configurational energy, $\boldsymbol{H}_{\mathrm{DD}}^{\mathrm{diag}}$ involves the configuration-energy difference, but if we adopt purely zeroth-order approximation, $\boldsymbol{H}_{\mathrm{DD}}^{\mathrm{diag}}$ is written by differences of orbital energies, like in the Møller–Plesset perturbation theory [19]. These approximations are referred to as SAC(2)-CI(1) and SAC(2)-CI(0) approximations, respectively.

The SAC(2)-CI method is considered as a natural iterative extension of the non-iterative CIS(D) method (see Appendix A). A merit is that the present method does not have a dangerous denominator problem, while CIS(D) has. Other merit is that no (vv|vv)

Table 1
Vertical excitation energies of doublet radicals

Radical	State	Nature of transition	UCIS (D)[b]	RCIS (D)[b]	Koopmans[c]	IP/EA-CIS(D)[c]	SAC(2)-CI(1)[c]	SAC(2)-CI(0)[c]	SAC-CI[c]	Exptl.[b]
BeH	$^2\Pi$	V: $s_\sigma \to v_\pi$	2.649	2.641	2.701	2.601	2.681	2.683	2.564	2.484
	$^2\Pi$	R: $s_\sigma \to v_{3p}$	6.471	6.460	6.008	6.289	6.526	6.386	6.332	6.318
BeF	$^2\Pi$	V: $s_\sigma \to v_\pi$	4.284	4.278	4.181	4.331	4.324	4.318	4.285	4.138
	$^2\Sigma^+$	R: $s_\sigma \to v_{3s}$	6.330	6.329	6.036	6.308	6.356	6.310	6.241	6.158
	$^2\Sigma^+$	R: $s_\sigma \to v_{3p}$	6.462	6.470	6.201	6.422	6.438	6.407	6.444	6.271
CH_3	$^2A'_1$	R: $s_{2p} \to v_{3s}$	5.888	5.835	4.261	5.912	6.488	6.048	5.652	5.729
	$^2A'_2$	R: $s_{2p} \to v_{3p}$	7.296	7.246	5.615	7.792	8.026	7.551	7.124	7.436
CN	$^2\Pi$	V: $d_\pi \to s_\sigma$	2.138	1.847	0.452	1.582	1.712	1.513	1.461	1.315
	$^2\Sigma^+$	V: $d_\sigma \to s_\sigma$	5.138	2.489	3.857	2.110	2.997	3.066	3.296	3.219
CO^+	$^2\Pi$	V: $d_\pi \to s_\sigma$	3.928	3.815	3.143	3.143	3.347	3.193	3.569	3.264
	$^2\Sigma^+$	V: $d_\sigma \to s_\sigma$	6.196	4.986	7.138	4.106	5.151	5.044	6.062	5.819
NO	$^2\Sigma^+$	R: $s_\pi \to v_{3s}$	5.145	5.283	5.899	6.442	6.345	6.486	6.102	5.921
	$^2\Sigma^+$	R: $s_\pi \to v_{3p}$	6.141	6.281	7.062	7.644	7.550	7.684	7.288	7.027
OH	$^2\Pi$	V: $d_\sigma \to s_\pi$	4.383	4.412	3.984	4.076	4.272	4.259	4.244	4.087
RMS deviation from experiment			0.687	0.468	0.782	0.607	0.401	0.347	0.184	–
RMS deviation from SAC-CI			0.721	0.573	0.721	0.667	0.442	0.369	–	0.184

[a] Valence (V) or Rydberg (R) in character, followed by the dominant configuration described by doubly occupied (d), singly occupied (s), and unoccupied (v) molecular orbitals.
[b] Ref. [24].
[c] Present calculation.

integrals (v = virtual) need to be calculated. The number of (vv|vv) integrals are large, and these calculations are time-consuming. Note that (vv|vv) integrals have to be calculated in the EOM-MBPT(2) approximation. Due to the Hermitian-conjugate relationship between $\boldsymbol{H}_{SD}$ and $\boldsymbol{H}_{DS}$ and to a large decrease of the two-electron MO integrals, the CPU time and core memory requirements are much saved. The SAC(2)-CI method is expected to be more efficient and economical than the other existing second-order perturbative approximations to the SAC/SAC-CI method. In addition, the present formulation is very straightforward. The SAC(2)-CI method may offer a reasonable approximation of the SAC-CI method for ordinary single-electron processes like singlet and triplet excitations, Koopmans-type ionizations and electron attachments of very large systems.

The SAC(2)-CI and CIS(D) methods have been implemented in the SAC-CI96 program system [26]. The CIS(D) method extended in this study to triplet excitation, ionization, and electron attachment is discussed in Appendix A. All methods give spin-pure results for singlet, doublet, and triplet states, since we use the spin- and space-symmetry adapted scheme. We can adopt the perturbation selection technique [27,7]. Hartree–Fock (HF) orbitals are calculated by Gaussian94 [28] and HONDO95 [29] program systems and used as reference orbitals in present calculations.

3. Applications

3.1. Doublet radicals

Head-Gordon et al. calculated the vertical excitation energies of eight radical molecules, BeH, BeF, CH, CH_3, CN, CO^+, NO and OH, by UCIS(D) and RCIS(D) methods [24]. In this study we calculate vertical excitation energies of these radicals by our IP/EA-CIS(D) and SAC(2)-CI methods. In order to calculate the doublet state by our approach, we first calculate the closed-shell (anionic or cationic) singlet state, and then calculate doublet ground and excited states by applying ionization or electron-attachment operation. Results calculated by our methods have no spin-contamination and are spin-pure, while those by UCIS(D) have. Excitation energies of BeH, BeF, CH_3 and NO are calculated by electron attachment, and those of CN, CO^+ and OH are calculated by ionization. The $^2\Delta$ and $^2\Sigma^+$ states of CH and the $^2\Sigma^+$ state of OH are not studied because these states are not obtained by ionization or electron attachment from the closed-shell singlet state. Basis sets are 6-311(2+,2+)G** [30]. Geometries used are those reported in Ref. [24].

Table 1 shows the previous [24] and present results compared with the experimental values and

Table 2
Calculations of excitation energies of CH_2O, C_2H_4, and C_4H_6 (in eV)

Molecule	State[a]	SAC(2)-CI(1)	SAC(2)-CI(0)	SAC-CI	Exptl.[c]
CH_2O	1^1A_2 (V)	3.811	4.062	3.908	4.07
	1^1B_2 (R)	6.518	6.646	7.192	7.11
	2^1B_2 (R)	7.464	7.583	8.024	7.97
	2^1A_1 (R)	7.511	7.599	8.156	8.14
	2^1A_2 (R)	7.700	7.856	8.397	8.37
	3^1B_2 (R)	8.460	8.580	9.227	8.88
	1^1B_1 (V)	9.089	9.322	9.185	–
	3^1A_1 (R)	8.798	8.859	9.356	–
	4^1B_2 (R)	8.896	9.028	9.535	–
	4^1A_1 (V)	9.005	9.127	9.642	–
C_2H_4	1^1B_{3u} (R)	7.404	7.277	7.303	7.11
	1^1B_{1u} (V)	8.036	7.995	8.041	7.60,^{ca}8.0
	1^1B_{1g} (R)	8.058	7.913	7.948	7.80
	1^1B_{2g} (R)	8.094	7.950	7.999	8.01
	2^1A_g (R)	8.430	8.280	8.363	8.29
	2^1B_{3u} (R)	8.934	8.788	8.878	8.62
	1^1A_u (R)	9.091	8.907	9.028	–
	3^1B_{3u} (R)	9.216	9.064	9.194	–
	2^1B_{1u} (R)	9.400	9.254	9.386	9.33
	2^1B_{1g} (R)	9.422	9.258	9.387	9.34
C_4H_6	1^1B_u (V)	6.117	6.155	6.298	5.91
	1^1B_g (R)	6.220	6.156	6.221	6.22
	1^1A_u (R)	6.534	6.476	6.533	–
	2^1A_u (R)	6.664	6.598	6.684	6.66
	2^1B_u (R)	7.080	7.027	7.083	7.07
	2^1B_g (R)	7.313	7.237	7.329	7.36
	2^1A_g (R)	7.201	7.203	7.210	7.4
	3^1B_g (R)	7.380	7.298	7.386	7.62
	4^1B_g (R)	7.553	7.481	7.513	7.72
	3^1A_g (R)	7.601	7.516	7.532	–
	3^1B_u (R)	8.171	8.091	8.117	8.00
	3^1A_u (R)	7.893	7.839	7.918	8.18
	4^1A_u (R)	8.045	7.963	8.010	8.21

[a] Valence (V) or Rydberg (R) in character.
[b] Refs. [17,23].
[c] Refs. [30,31].

the SAC-CI results. The RMS (root-mean-square) deviations from the experiment and SAC-CI shown in the bottom row give a quick criterion of the quality of the calculated results.

The IP/EA-CIS(D) method overall improves the results of the Koopmans theorem and has performance between UCIS(D) and RCIS(D) methods. Though our IP/EA-CIS(D) method, as well as UCIS(D) and RCIS(D), gives good results for the Π-type excitation energy, they give poor results for the Σ-type valence excitation energy. The reason for poor performance for the $^2\Sigma^+$ states of CN and CO^+ by the CIS(D) method may be that the reference orbitals of the corresponding closed-shell systems used are not adequate, and the orbital-relaxation effect is not well included. The ROHF orbitals for doublet radicals may be more appropriate as the reference orbitals. Further, the orbital-relaxation effect may be included in the iterative calculation. In Table 1, we show SAC(2)-CI results. As mentioned above, the SAC(2)-CI method is considered as a natural extension of the non-iterative CIS(D) method to an iterative method. The results of the SAC(2)-CI method give better overall agreement with experimental values and the SAC-CI results. In particular, the excitation energies for the $^2\Sigma^+$ states of CN and CO^+ are remarkably improved. Thus, the SAC(2)-CI method seems to be more reliable than the CIS(D) method with a similar computational cost.

3.2. Formaldehyde, ethylene, and butadiene

The SAC(2)-CI method is applied to calculations of singlet excited states of formaldehyde, ethylene, and butadiene. These molecules have been used for benchmark calculations by previous second-order perturbative approximations [17,23,30,31]. Basis sets are 6-311(2+,2+)G** for formaldehyde and ethylene, and 6-311(2+)G* for butadiene. Geometries used are the same as those reported in Refs. [30,31]. For butadiene, four core orbitals were frozen.

Results are shown in Table 2. RMS deviations of CIS [30,31], CIS(D) [23], P-EOM-MBPT(2) [17], SAC(2)-CI(1), and SAC(2)-CI(0) with respect to the experimental values are 0.72, 0.38, 0.22, 0.33, and 0.28 eV, respectively. Those with respect to the SAC-CI method are 0.68, 0.42, 0.19, 0.33, and 0.27 eV, respectively. Our SAC(2)-CI(1) and (0) methods

Table 3
Excited states of free-base porphin calculated by the SAC(2)-CI method (in eV)

State	Nature	Excitation energy, Δ*E*				Exptl.[a]		
		CIS	SAC-CI[a]	SAC(2)-CI(1)	SAC(2)-CI(0)	polarization	Δ*E*	band
$1B_{3u}$	$\pi\to\pi^*$	2.49	1.75	1.99	1.97	*x*	1.98	Q_x
$1B_{2u}$	$\pi\to\pi^*$	2.62	2.23	2.33	2.29	*y*	2.42	Q_y
$2B_{3u}$	$\pi\to\pi^*$	4.45	3.56	3.30	3.41	*x*	3.33	B
$2B_{2u}$	$\pi\to\pi^*$	4.79	3.75	3.37	3.49	*y*	3.65	N
$1B_{1g}$	$\pi\to\pi^*$	4.65	3.55	3.35	3.51			
$1B_{2g}$	$n\to\pi^*$	6.36	4.05	3.20	3.63			
$1A_u$	$n\to\pi^*$	6.47	4.18	3.36	3.78			
$1B_{3g}$	$n\to\pi^*$	6.25	4.37	3.53	3.96			
$1B_{1u}$	$n\to\pi^*$	6.35	4.51	3.70	4.13	*z*		L
$3B_{3u}$	$\pi\to\pi^*$	5.25	4.24	3.97	4.08	*x*	4.25	L
$2A_g$	$\pi\to\pi^*$	5.58	4.25	3.95	4.16			
$3B_{2u}$	$\pi\to\pi^*$	5.97	4.52	4.20	4.37	*y*	4.67	L
$2B_{1g}$	$\pi\to\pi^*$	6.16	4.62	4.28	4.55			
$3A_g$	$\pi\to\pi^*$	6.00	4.74	4.60	4.79			
$4B_{2u}$	$\pi\to\pi^*$	6.56	5.31	5.07	5.26	*y*		M
$4B_{3u}$	$\pi\to\pi^*$	6.99	5.45	5.09	5.27	*x*	5.50	M
$3B_{1g}$	$\pi\to\pi^*$	6.36	5.13	5.12	5.33			
$4A_g$	$\pi\to\pi^*$	6.41	5.28	5.12	5.33			

[a] Ref. [7].

give the RMS deviations between CIS(D) and P-EOM-MBPT(2) and this seems to be reasonable from the nature of the approximations. Assignments by present approximations are consist with the SAC-CI result. We conclude that the present perturbative approximation is reliable and useful though our approach is computationally more efficient than the previous ones.

3.3. Free-base porphin

Free-base porphin, $C_{20}N_4H_{14}$, is a fundamental molecule in biochemical chemistry, and the excited states of this molecule were recently calculated by various theoretical methods [7,22,32]. By the SAC/SAC-CI method, the electronic spectrum was well reproduced and new assignments for the B, N, L, and M bands were proposed [7]. In this study, the SAC(2)-CI method is used to calculate singlet excited states of the free-base porphin by using the same basis set, geometry, and active space as in the previous calculations [7]. For the ground and excited states, the energy thresholds of 1×10^{-5} and 5×10^{-7} hartree, respectively, were used for the perturbation selection.

Results of excitation energies by the SAC(2)-CI method are shown in Table 3 with the CIS and the previous SAC-CI results. Two SAC(2)-CI approximations reproduce well the experimental spectrum, and they are in good agreement with the previous SAC/SAC-CI result [7]. The CPU time per one state by the present calculation is 4.4 min on the IBM RS/6000 workstation while that by the previous SAC/SAC-CI one [7] is 80 min on the NEC SX-3 supercomputer. Therefore, it is expected that the present perturbative method will become useful and effective for larger molecular systems.

4. Conclusions

Newly developed second-order perturbative approximation to the SAC/SAC-CI method, the SAC(2)-CI method, is proposed. Performance of the present method is investigated by applications for several doublet radicals, formaldehyde, ethylene, butadiene, and free-base porphin in the ground and excited states. Results of the present method are in good agreement with those by the full SAC/SAC-CI method and the experimental values. Therefore, our SAC(2)-CI method is expected to be useful and effective in the studies of larger molecules in ground and excited states of singlet, triplet, ionized, electron-attached states.

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Appendix A

In this appendix, we extend the original CIS(D) method [23] by applying the spin-adapted scheme [1–3]. The CIS(D) correlation energy, $\Delta E_{\mathrm{CIS(D)}}$, is given as

$$\Delta E_{\mathrm{CIS(D)}} = \Delta E_{\mathrm{CIS}} + \langle 0 | R_1^{(0)\dagger} V^{(1)} R_2^{(1)} | 0 \rangle + \langle 0 | R_1^{(0)\dagger} V^{(1)} S_2^{(1)} R_1^{(0)} | 0 \rangle . \qquad (\mathrm{A.1})$$

The first term, ΔE_{CIS}, is the CIS excitation energy, which gives the sum of the zeroth- and first-order energies for the CIS(D) method. The second and third terms give the correction to the CIS(D) energy. Here, CIS coefficients are implicitly included in the R_1 operator as the zeroth-order perturbation. Note that the triple-excitation in the third term is represented as the disjoint $S_2 R_1$ operator, such as the SAC/SAC-CI method. Based on the sophistication in the SAC/SAC-CI theory, double-excitation coefficients in the S_2 operator are transferred from the ground-state ones and are given by the MP2 calculations. Double-excitation coefficients, d_M, in the R_2 operator are given by the first-order perturbation,

$$d_M = -\frac{\langle M | V R_1 | 0 \rangle}{\Delta_M - \Delta E_{\mathrm{CIS}}} , \qquad (\mathrm{A.2})$$

where M represents the doubly excited configuration (the double-excitation $i \to a$, $j \to b$ for singlet and triplet excited states, the destructive double-excitation $i \rightarrow a$, j for the ionized state, and the creative double-excitation $i \rightarrow a$, b for the electron-attached state). Symbol Δ_M is the difference of orbital energies such as $\varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j$ for singlet and triplet excited states, $\varepsilon_a + \varepsilon_b - \varepsilon_i$ for ionized state, and $\varepsilon_a - \varepsilon_i - \varepsilon_j$ for electron-attached state. Explicit expressions of the Hamiltonian matrix in Eqs. (A.1) and (A.2) are given in Ref. [15].

We compare our IP/EA-CIS(D) method with the lowest-order diagonalized approximation to the one-particle Green's function (GF) [33]. Using the second-order self-energy, which is obtained by solving the Dyson equation at the first iteration, the ionization potential by ionization from the occupied orbital labeled p is given as

$$E_{\mathrm{IP}} = -\varepsilon_p - \frac{1}{2}\sum_{ija} \frac{|\langle ij \| pa \rangle|^2}{\varepsilon_p + \varepsilon_a - \varepsilon_i - \varepsilon_j} - \frac{1}{2}\sum_{iab} \frac{|\langle ab \| pi \rangle|^2}{\varepsilon_p + \varepsilon_i - \varepsilon_a - \varepsilon_b}, \qquad (\mathrm{A.3})$$

where $\langle ij \| kl \rangle$ is the antisymmetrized two-electron integral. In this equation, the second term represents the orbital-relaxation and pair-relaxation effects, and the third term represents the pair-removal (electron correlation) effect, following the interpretation by Pickup and Goscinski [34].

Using the notation in Ref. [23], Eq. (A.1) for the IP-CIS(D) method is explicitly written as

$$\Delta E_{\mathrm{CIS(D)}} = \Delta E_{\mathrm{CIS}} - \frac{1}{2}\sum_{ija} \frac{\left(\bar{u}_{ij}^{a}\right)^2}{\varepsilon_p + \varepsilon_a - \varepsilon_i - \Delta E_{\mathrm{CIS}}} + \sum_j d_j v_j, \qquad (\mathrm{A.4})$$

where d_j is the CIS-like coefficient and becomes δ_{jp} for ionization from p, and $\bar{u}_{ij}^{a}$ and v_j are given as

$$\bar{u}_{ij}^{a} = \sum_k \langle ka \| ij \rangle d_k \qquad (\mathrm{A.5})$$

and

$$v_j = -\frac{1}{2}\sum_{kiab} \langle ki \| ba \rangle d_k C_{ji}^{ab}, \qquad (\mathrm{A.6})$$

respectively, where C_{ij}^{ab} is the MP2 coefficient and given by

$$C_{ji}^{ab} = -\frac{\langle ab \| ji \rangle}{\varepsilon_j + \varepsilon_i - \varepsilon_a - \varepsilon_b}. \qquad (\mathrm{A.7})$$

Inserting Eqs. (A.5), (A.6) and (A.7) into Eq. (A.4), we easily confirm that our IP-CIS(D) method is equivalent to the lowest-order diagonalized approximation to the one-particle GF method. The same discussion holds for the EA-CIS(D) method.

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