Description of two- and many-electron processes by the SAC-CI method

Hiroshi Nakatsuji
Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Kyoto 606, Japan

Received 24 August 1990; in final form 9 November 1990

The accuracy of the SAC-CI (symmetry-adapted-cluster configuration-interaction) method for two- and many-electron processes is improved by including triple, quadruple and higher excitation terms in the $R^\dagger$ operators of the SAC-CI formalism. This is confirmed by comparing SAC-CI results with full-CI ones for various excited, ionized, and anion states of CO and C_2.

Electron correlation in the excited and ionized states of molecules is an interesting topic to study by modern theoretical chemistry techniques. We have developed the SAC (symmetry-adapted-cluster)/ SAC-CI method [1,2] and applied it successfully to various aspects of molecular spectroscopy involving these states [3].

The SAC-CI wavefunction may be written with the use of the reaction operator $\mathscr{R}$ as

$$\Psi_e^{\text{SAC-CI}} = \mathscr{R}\,\Psi_g^{\text{SAC}} , \qquad (1)$$

where the operator $\mathscr{R}$ generates excited, ionized, or electron-attached states from the ground-state wavefunction. The subscripts g and e stand for ground and excited, respectively. In this sense, we call the operator $\mathscr{R}$ the excitator in order to distinguish it from more elementary excitation operators which are introduced below. Of course, the idea of this kind of operator is very old. In particular, it is used in the Green function method [4] and the equation-of-motion method [5]. The former has been applied extensively to ionized states by Cederbaum et al. [4], and the latter was designed to calculate relative quantities rather than absolute quantities.

In the SAC-CI method, the excitator $\mathscr{R}$ is expanded as

$$\mathscr{R} = \sum_K d_K \mathscr{P} R_K^\dagger , \qquad (2)$$

where $\mathscr{P}$ is a projector which projects out the SAC component, and $R_K^\dagger$ is an excitation, ionization, or electron-attachment operator. Important relations between the SAC and SAC-CI wavefunction are [2]

$$\langle \Psi_e^{\text{SAC-CI}} | \Psi_g^{\text{SAC}} \rangle = 0 ,$$
$$\langle \Psi_e^{\text{SAC-CI}} | H | \Psi_g^{\text{SAC}} \rangle = 0 , \qquad (3)$$

so that the excited state calculated by the SAC-CI method satisfies the correct relations with the SAC wavefunction for the ground state. The role of the excitator $\mathscr{R}$ is to describe an excitation, ionization, or electron attachment itself and the reorganization of electron correlations induced by this excitation. The electron correlations in excited states are written by modifying those in the ground state. This method should be easier than those which calculate all the correlations in excited and ionized states from the beginning without referring to those in the ground state, though this is usually done in the ordinary CI method.

The accuracy of the SAC-CI method has been examined for small molecules by comparing its results with those of full-CI [3,6]. It is quite satisfactory for ordinary single-electron processes like singlet and triplet excitations, Koopmans-type ionizations and electron attachments. This method has been applied to a number of molecules for investigating their spectroscopies [3]. Particularly, it has been effective for calculating V-type excitations of π-conjugated molecules [7], excitations and ionizations of metal complexes [8], and hyperfine splitting constants of radicals [9]. For two- and higher-electron processes, however, the accuracy of this method has not yet been examined in comparison with full-CI, though it has been applied for studying satellite peaks in ionization spectra of some organic and inorganic compounds [10]. The purpose of this communication is to report the accuracy of the SAC-CI method applied to two- and more-electron excitation and ionization processes.

We show two ways for choosing $R_K^\dagger$ operators in the SAC-CI calculation. One is to limit $R_K^\dagger$ operators to single- and double-excitation operators, and the other is to include also triple-, quadruple- and higher-excitation operators. The former is a standard choice in the SAC85 program [11], and all of the previous calculations are due to this algorithm. The second way is the topic of the present study. We designate the former as the SD-*R* method and the latter as the general-*R* method.

In the present calculations, all single- and double-excitation operators are included in both methods. Higher-excitation operators in the general-*R* method are produced by an exponential-generation algorithm [12]. Namely, triple- and quadruple-excitation operators are produced as products of single- and double-excitation operators whose coefficients in the SDCI are larger than a given threshold λ_{AA}. A different threshold λ_{AAA} is used for generating 5-ple- and 6-ple-excitation operators as products of single- and double-excitation operators. Thus, the accuracy of the exponential generation of the higher $R_K^\dagger$ operators in the general-*R* method is expressed by a set of the thresholds $(\lambda_{AA}, \lambda_{AAA}, \lambda_{AAAA}, ...)$.

Here, we apply the above methods to CO and C_2. We calculate a number of singlet and triplet excited states, ionized states and electron-attached states. The basis sets are the [4s2p] GTOs of Huzinaga and Dunning [13]. We perform full-CI reference calculations for investigating the accuracy of the present results. The active MOs are, therefore, limited to four occupied and four unoccupied MOs, $(2s\sigma)^2(p\pi)^4(p\sigma)^2(p\pi^*)(p\sigma^*)(p\sigma')$ for CO and four occupied and five unoccupied MOs, $(2s\sigma)^2(2s\sigma^*)^2(p\pi)^4(p\sigma)(p\pi^*)(p\sigma^*)(p\sigma')$ for C_2. The thresholds $(\lambda_{AA}, \lambda_{AAA}, \lambda_{AAAA})$ are (0.04, 0.2, 0.2) for CO. For C_2, λ_{AA} is 0.01 for single excitations, 0.07 for double excitations, and $(\lambda_{AAA}, \lambda_{AAAA})$ are set to (9.0, 9.0), so that the $R_K^\dagger$ operators include up to quadruple excitations.

Table 1 shows the full-CI and SAC-CI results for CO at its equilibrium bond length, 1.1283 Å [14]. "Excitation level" denotes the number of electrons involved in the excitation, ionization, or electron-attachment process. "Main configuration" shows the most important configuration in the full-CI, and "size" denotes the dimension of the matrices involved in the calculation. Δ shows the difference between the SAC-CI and full-CI energies in mhartree.

The SAC calculation is done for the singlet ground state and the result is commonly used in both general-*R* and SD-*R* SAC-CI methods. The second row shows the SAC-CI solution for the ground state.

Between the two SAC-CI methods, the general-*R* method gives results which are superior to the SD-*R* method. This is clearly seen from the average discrepancy and the standard deviation given in parentheses. The accuracy of the general-*R* method is almost constant, independent of the excitations, ionizations, and electron attachments. The error is often negative, since the method of solution is nonvariational. The error of the SD-*R* method is larger than that of the general-*R* method, but for single-electron processes, where the excitation level is unity, the results are acceptable. However, for two-electron processes, the error is large, more than 20 mhartree, except for the 3 $^1\Pi$-singlet excited state. Thus, for two-electron processes, the SD-*R* method is poor and we have to use the general-*R* method.

Table 2 shows the excitation energies, ionization potentials and electron affinities in electronvolt calculated from the results shown in table 1. The average discrepancy of the general-*R* method is 0.025 eV. That of the SD-*R* method is 0.067 eV for single-electron processes, but is as large as 0.865 eV for two-electron processes. We thus conclude that the SAC-CI SD-*R* method is reliable only for single-electron processes. For two- and many-electron processes, we should use the general-*R* method.

We next examine the general-*R* method for the C_2 molecule. Since the pσ-bonding MO is left unfilled in the low-lying region, the C_2 molecule has many doubly excited states in a relatively low-energy region. Table 3 shows the results of the SAC-CI general-*R* method as compared with the full-CI results.

Table 1
Full-CI and SAC-CI results in hartree for CO at $R = 1.1283$ Å (equilibrium distance)

State	Excitation level	Main configuration [a]	Full-CI		SAC-CI [b]					
					general-*R*			SD-*R*		
			size	energy	size	energy	$\Delta^{c)} \times 10^3$	size	energy	$\Delta^{c)} \times 10^3$
singlet										
$^1\Sigma^+$	0	0.98(2222)	492	−112.74374	51	−112.74054	3.20	51	−112.74054	3.20
					106	−112.74353	0.21	51	−112.74045	3.29
$^1\Pi$	1	0.95(22211)	432	−112.41498	85	−112.41433	0.65	36	−112.41052	4.46
$^1\Sigma^-$	1	0.69(221210−212201)	408	−112.35612	56	−112.35662	−0.50	30	−112.35434	1.78
$^1\Delta$	1	0.68(212210+221201)	492	−112.35538	56	−112.35533	0.05	51	−112.35312	2.26
$^1\Pi$	1	0.89(12221)	432	−112.21458	85	−112.21264	1.94	36	−112.20864	5.94
$^1\Sigma^+$	1	0.92(2221001)	492	−112.20140	106	−112.19829	3.11	51	−112.19655	4.85
$^1\Sigma^+$	1	0.61(212210−221201)	492	−112.11498	106	−112.11449	0.49	51	−112.12178	−6.80
$^1\Pi$	2	0.64(221111) −0.49(21212+212102)	432	−112.08857	85	−112.08731	1.26	36	−112.08426	4.31
							(1.27±1.14) [d]			(4.10±1.55)
triplet										
$^3\Pi$	1	0.96(22211)	392	−112.49703	95	−112.49644	0.59	44	−112.48977	7.26
$^3\Sigma^+$	1	0.69(21221−221201)	584	−112.40058	84	−112.40040	0.18	44	−112.40219	−1.61
$^3\Delta$	1	0.69(21221+221201)	584	−112.37771	84	−112.37756	0.15	44	−112.37747	0.24
$^3\Sigma^-$	1	0.68(22121−212201)	584	−112.36376	71	−112.36453	−0.77	40	−112.36188	1.88
$^3\Pi$	1	0.93(12221)	592	−112.26151	95	−112.25892	2.59	44	−112.25873	2.78
							(0.86±0.90) [d]			(2.75±2.40)
ion										
$^2\Sigma^+$	1	0.95(2221)	616	−112.22748	147	−112.22735	0.13	22	−112.22377	3.71
$^2\Pi$	1	0.96(2122)	588	−112.11220	143	−112.11346	−1.26	17	−112.11517	−2.97
$^2\Sigma^+$	1	0.93(1222)	616	−112.00829	147	−112.00904	−0.75	22	−112.00912	−0.83
$^2\Sigma^-$	2	0.68(22111)−0.63(212101)	560	−111.82683	146	−111.82376	3.07	12	−111.78508	41.75
$^2\Delta$	2	0.57(21211+221101)	616	−111.82500	147	−111.82262	2.38	22	−111.77826	46.74
$^2\Pi$	2	0.78(22201)−0.53(12211)	588	−111.81991	143	−111.81923	0.68	17	−111.76878	51.13
							(1.38±1.03) [d]			(24.52±22.20)
anion										
$^2\Pi$	1	0.97(22221)	588	−112.61520	84	−112.61375	1.45	17	−112.60802	7.18
$^2\Sigma^+$	1	0.97(2222001)	616	−112.44502	87	−112.44135	3.67	22	−112.43937	5.65
$^2\Delta$	2	0.68(222120−222102)	616	−112.35009	87	−112.34860	1.49	22	−112.32377	26.32
$^2\Sigma^+$	2	0.67(22212+222102)	616	−112.32870	87	−112.32651	2.19	22	−112.29876	29.94
$^2\Sigma^-$	2	0.81(222111)	560	−112.30504	64	−112.30248	2.56	12	−112.25951	45.53
							(2.27±0.82) [d]			(22.92±14.95)

[a] The MO ordering is (2s)(pπ)(pπ)(pσ)(pπ*)(pπ*)(2pσ*)(2pσ′). [b] The first row is the SAC result and all the others are the SAC-CI results.

[c] Δ shows the difference from the full-CI result.

[d] $(x \pm y)$ where x means the average discrepancy from the full-CI value and y means the standard deviation, both in mhartree.

Table 2
Excitation energies, ionization potentials and electron affinities in eV calculated by the full-CI and SAC-CI methods for CO at $R = 1.1283$ Å (equilibrium distance)

State	Excitation level	Main configuration [a]	Full-CI		SAC/SAC-CI [b]					
			size	energy	general-*R*			SD-*R*		
					size	energy	Δ [c]	size	energy	Δ [c]
singlet										
$^1\Sigma^+$	0	Hartree–Fock	492	0.0	106	0.0	0.0	51	0.0	0.0
$^1\Pi$	1	$n \to \pi^*$	432	8.946	85	8.958	0.012	36	8.978	0.032
$^1\Sigma^-$	1	$\pi \to \pi^*$	408	10.548	56	10.528	−0.020	30	10.507	−0.041
$^1\Delta$	1	$\pi \to \pi^*$	492	10.568	56	10.563	−0.005	51	10.540	−0.028
$^1\Pi$	1	$2s \to \pi^*$	432	14.399	85	14.446	0.047	36	14.471	0.072
$^1\Sigma^+$	1	$n \to 2p\sigma^*$	492	14.758	106	14.837	0.079	51	14.800	0.042
$^1\Sigma^+$	1	$\pi \to \pi^*$	492	17.109	106	17.117	0.008	51	16.835	−0.274
$^1\Pi$	2	$n \to \pi^*, \pi \to \pi^*$	432	17.828	85	17.857	0.029	36	17.856	0.028
							(0.021) [d]			(0.024) [d]
triplet										
$^3\Pi$	1	$n \to \pi^*$	392	6.713	95	6.724	0.011	44	6.821	0.108
$^3\Sigma^+$	1	$\pi \to \pi^*$	584	9.338	84	9.337	−0.001	44	9.205	−0.133
$^3\Delta$	1	$\pi \to \pi^*$	584	9.960	84	9.959	−0.001	44	9.877	−0.083
$^3\Sigma^-$	1	$\pi \to \pi^*$	584	10.340	71	10.313	−0.027	40	10.301	−0.039
$^3\Pi$	1	$2s \to \pi^*$	592	13.122	95	13.187	0.065	44	13.108	−0.014
							(0.009) [d]			(−0.032) [d]
ion										
$^2\Sigma^+$	1	$n \to \infty$	616	14.048	147	14.046	−0.002	22	14.060	0.012
$^2\Pi$	1	$\pi \to \infty$	588	17.185	143	17.145	−0.040	17	17.015	−0.170
$^2\Sigma^+$	1	$2s \to \infty$	616	20.013	147	19.986	−0.027	22	19.900	−0.113
$^2\Sigma^-$	2	$n, \pi \to \pi^*, \infty$	560	24.950	146	25.028	0.078	12	25.997	1.047
$^2\Delta$	2	$n, \pi \to \pi^*, \infty$	616	25.000	147	25.059	0.059	22	26.182	1.182
$^2\Pi$	2	$n, n \to \pi^*, \infty$	588	25.139	143	25.151	0.012	17	26.440	1.301
							(0.013) [d]			(0.543) [d]
anion										
$^2\Pi$	1	$\infty \to \pi^*$	588	−3.498	84	−3.531	−0.033	17	−3.604	−0.106
$^2\Sigma^+$	1	$\infty \to 2p\sigma^*$	616	−8.129	87	−8.223	−0.094	22	−8.193	−0.064
$^2\Delta$	2	$\infty, n \to \pi^*, \pi^*$	616	−10.712	87	−10.747	−0.035	22	−11.338	−0.626
$^2\Sigma^+$	2	$\infty, n \to \pi^*, \pi^*$	616	−11.294	87	−11.348	−0.054	22	−12.019	−0.725
$^2\Sigma^-$	2	$\infty, n \to \pi^*, \pi^*$	560	−11.938	64	−12.002	−0.064	12	−13.087	−1.149
							(−0.056) [d]			(−0.534) [d]

[a] The MO ordering is $(2s)^2(\pi)^4(n)^2(\pi^*)(p\sigma^*)(p\sigma')$. [b] Relative to the SAC-CI energy for the singlet ground state.
[c] Difference from the full-CI result. [d] Average discrepancy.

As seen from the excitation level, there are many two- and even three-electron processes. The errors of the present SAC-CI results are consistently small, independent of the excitation levels, though the sizes of the matrices involved are much smaller than those of the full-CI.

Table 4 shows the excitation energies, ionization potentials and electron affinities of C_2 calculated from the results shown in table 3. The average error from the full-CI results is 0.054 eV.

The C_2 molecule has unique excited, ionized and anion states due to the unfilled $p\sigma$ MO. The electronic structures and spectroscopic properties of C_2 and C_2^- have received much experimental [14] and theoretical [15–18] attention. In particular, the excitation energies are very small for several lower sin-

Table 3
Full-CI and SAC-CI results in hartree for C_2 at $R=1.24253$ Å (equilibrium distance)

State	Excitation level	Main configuration [a] ($C>0.3$)	Full-CI		SAC-CI (general-R) [b]		
			size	energy	size	energy	Δ [c] $\times 10^3$
singlet							
$^1\Sigma_g^+$	0	0.85(2222)−0.35(20222)	748	−75.52629	46	−75.51985	6.44
					112	−75.52378	2.51
$^1\Pi_u$	1	0.96(22121)	654	−75.45297	86	−75.45147	1.50
$^1\Sigma_g^+$	2	0.63(22202+22022)−0.32(20222)	748	−75.42469	112	−75.42195	2.74
$^1\Delta_g$	2	0.68(22202−22022)	748	−75.42356	112	−75.42130	2.26
$^1\Pi_g$	2	0.90(21212)+0.36(2211101)	654	−75.32914	69	−75.32437	4.77
$^1\Sigma_u^+$	1	0.86(21221)	688	−75.30272	111	−75.30186	0.86
$^1\Sigma_g^+$	2	0.60(20222)+0.39(2222)−0.30(212111−2112101)	748	−75.25369	112	−75.24821	5.48
$^1\Sigma_u^-$	1	0.62(221201−2221001)	620	−75.22000	79	−75.21597	4.03
$^1\Delta_u$	1	0.63(221201)+0.62(2221001)	620	−75.20743	111	−75.20551	1.92
							(2.90 ± 1.46) [d]
triplet							
$^3\Pi_u$	1	0.94(22121)	950	−75.50716	158	−75.50437	2.79
$^3\Sigma_u^+$	1	0.91(21221)	960	−75.48006	152	−75.47606	4.00
$^3\Sigma_g^-$	2	0.96(22112)	940	−75.45908	95	−75.45324	5.84
$^3\Pi_g$	2	0.90(21212)	960	−75.42354	124	−75.41957	3.97
$^3\Sigma_u^+$	1	0.57(222101−2212001)+0.31(21221)	960	−75.28156	152	−75.27305	8.51
$^3\Delta_u$	1	0.62(2221001+2212001)	940	−75.25573	152	−75.24966	6.07
$^3\Pi_g$	2	0.80(2211101)+0.48(222011)	960	−75.23213	124	−75.22675	5.38
$^3\Sigma_u^-$	1	0.62(2221001+221201)	940	−75.23070	115	−75.22491	5.79
$^3\Pi_g$	2	0.59(2211101)+0.48(222011−220211)−0.34(2211101)	960	−75.19460	124	−75.18999	4.61
$^3\Sigma_g^+$	2	0.50(212111−2112101)−0.42(212111−2112101)	920	−75.19404	124	−75.18586	8.18
							(5.51 ± 1.72) [d]
cation							
$^2\Pi_u$	1	0.84(2212)−0.39(20122)	756	−75.06396	145	−75.05952	4.44
$^2\Delta_g$	2	0.66(22201−22021)	784	−74.99347	141	−74.99174	1.73
$^2\Sigma_g^+$	2	0.61(22201+22021)−0.37(20221)	784	−74.99019	141	−74.98752	2.67
$^2\Sigma_g^-$	2	0.82(22111)−0.48(22111)	728	−74.97066	109	−74.96650	4.16
$^2\Pi_g$	2	0.85(21211)	756	−74.96718	139	−74.96376	3.42
$^2\Sigma_u^+$	1	0.90(2122)	784	−74.96041	149	−74.95513	5.28
$^2\Pi_u$	3	0.89(22102)	756	−74.95202	145	−74.94621	5.81
$^2\Delta_u$	3	0.64(21202−21022)	728	−74.89972	123	−74.89819	1.53
$^2\Sigma_u^+$	3	0.61(21202+21022)	784	−74.86227	149	−74.86018	2.09
$^2\Sigma_g^+$	2	0.81(20221)	784	−74.84186	141	−74.83864	3.22
$^2\Sigma_u^-$	3	0.78(21112)+0.45(21112)	728	−74.83681	123	−74.83394	2.87
							(3.38 ± 1.34) [d]
anion							
$^2\Sigma_g^+$	1	0.93(22221)	1164	−75.57950	133	−75.57263	6.87
$^2\Pi_u$	2	0.96(22122)	1100	−75.54346	142	−75.54102	2.44
$^2\Sigma_u^+$	2	0.87(21222)	1144	−75.48444	121	−75.48003	4.41
$^2\Pi_g$	1	0.88(222201)	1100	−75.35620	125	−75.35020	6.00
$^2\Sigma_u^+$	2	0.64(222111−2212101)	1144	−75.32372	121	−75.31868	5.04
$^2\Sigma_u^-$	2	0.66(2221101)−0.50(221211)+0.45(221211)	1056	−75.32053	125	−75.31667	3.86
$^2\Pi_g$	3	0.78(2211201)+0.56(222021)	1100	−75.31882	125	−75.31391	4.91
$^2\Delta_u$	2	0.59(221211)+0.57(2221101)+0.35(2221101)+0.32(221211)	1056	−75.31794	121	−75.31379	4.15
$^2\Delta_u$	2	0.60(221211)−0.58(2221101)+0.36(2221101)−0.33(221211)	1056	−75.30293	125	−75.29987	3.06
$^2\Sigma_u^-$	2	0.65(2221101)−0.49(221211)+0.47(221211)	1056	−75.28780	125	−75.28073	7.07
							(4.78 ± 1.45) [d]

---

[a] The MO ordering is (2sσ)(2sσ*)(pπ)(pπ)(pσ)(pπ*)(pπ*)(pσ*)(pσ′).

[b] The first row is the SAC value and all the others are the SAC-CI values.

[c] Δ shows the difference from the full-CI result.

[d] $(x \pm y)$ where x means the average discrepancy from the full-CI value and y means the standard deviation, both in mhartree.

Table 4
Excitation energies, ionization potentials and electron affinities in eV calculated by the full-CI and SAC-CI methods for C_2 at $R = 1.24253$ Å (equilibrium distance)

State	Excitation level	Main configuration [a]	Full-CI		SAC-CI (general-*R*) [b]		
			size	energy	size	energy	Δ [c]
singlet							
$^1\Sigma_g^+$	0	Hartree–Fock	748	0.0	112	0.0	0.0
$^1\Pi_u$	1	pπ→pσ	654	1.995	86	1.968	−0.027
$^1\Sigma_g^+$	2	pπ, pπ→pσ, pσ	748	2.765	112	2.771	0.006
$^1\Delta_g$	2	pπ, pπ→pσ, pσ	748	2.795	112	2.789	−0.007
$^1\Pi_g$	2	2sσ*, pπ→pσ, pσ	654	5.365	69	5.426	0.061
$^1\Sigma_u^+$	1	2sσ*→pσ	688	6.084	111	6.039	−0.045
$^1\Sigma_g^+$	2	2sσ*, 2sσ*→pσ, pσ	748	7.418	112	7.499	0.081
$^1\Sigma_u^-$	1	pπ→pπ*	620	8.335	79	8.376	0.041
$^1\Delta_u$	1	pπ→pπ*	620	8.677	111	8.661	−0.016
							(0.036) [d]
triplet							
$^3\Pi_u$	1	pπ→pσ	950	0.520	158	0.528	0.008
$^3\Sigma_u^+$	1	2sσ*→pσ	960	1.258	152	1.299	0.041
$^3\Sigma_g^-$	2	pπ, pπ→pσ, pσ	940	1.829	95	1.920	0.091
$^3\Pi_g$	2	2sσ*, pπ→pσ, pσ	960	2.796	124	2.836	0.040
$^3\Sigma_u^+$	1	pπ→pπ*	960	6.659	152	6.823	0.163
$^3\Delta_u$	1	pπ→pπ*	940	7.362	152	7.459	0.097
$^3\Pi_g$	2	pπ, pπ→pσ, pπ*	960	8.005	124	8.083	0.078
$^3\Sigma_u^-$	1	pπ→pπ*	940	8.043	115	8.133	0.089
$^3\Pi_g$	2	pπ, pπ→pσ, pπ*	960	9.026	124	9.083	0.057
$^3\Sigma_g^+$	2	2sσ*, pπ→pσ, pπ*	920	9.041	124	9.195	0.154
							(0.082) [d]
cation							
$^2\Pi_u$	1	pπ→∞	756	12.581	145	12.633	0.053
$^2\Delta_g$	2	pπ, pπ→pσ, ∞	784	14.499	141	14.478	−0.021
$^2\Sigma_g^+$	2	pπ, pπ→pσ, ∞	784	14.588	141	14.592	0.004
$^2\Sigma_g^-$	2	pπ, pπ→pσ, ∞	728	15.120	109	15.164	0.045
$^2\Pi_g$	2	2sσ*, pπ→pσ, ∞	756	15.214	139	15.239	0.025
$^2\Sigma_u^+$	1	2sσ*→∞	784	15.399	149	15.474	0.075
$^2\Pi_u$	3	pπ, pπ, pπ→pσ, pσ, ∞	756	15.627	145	15.717	0.090
$^2\Delta_u$	3	2sσ*, pπ, pπ→pσ, pσ, ∞	728	17.050	123	17.023	−0.027
$^2\Sigma_u^+$	3	2sσ*, pπ, pπ→pσ, pσ, ∞	784	18.069	149	18.058	−0.011
$^2\Sigma_g^+$	2	2sσ*, 2sσ*→pσ, ∞	784	18.624	141	18.644	0.019
$^2\Sigma_u^-$	3	2sσ*, pπ, pπ→pσ, pσ, ∞	728	18.762	123	18.772	0.010
							(0.035) [d]
anion							
$^2\Sigma_g^+$	1	∞→pσ	1164	1.488	133	1.329	−0.119
$^2\Pi_u$	2	pπ, ∞→pσ, pσ	1100	0.467	142	0.469	0.002
$^2\Sigma_u^+$	2	2sσ*, ∞→pσ, pσ	1144	−1.138	121	−1.191	−0.052
$^2\Pi_g$	1	∞→pπ*	1100	−4.628	125	−4.723	−0.095
$^2\Sigma_u^+$	2	pπ, ∞→pσ, pπ*	1144	−5.512	121	−5.581	−0.069
$^2\Sigma_u^-$	2	pπ, ∞→pσ, pπ*	1056	−5.599	125	−5.636	−0.037
$^2\Pi_g$	3	pπ, pπ, ∞→pσ, pσ, pπ*	1100	−5.646	125	−5.711	−0.065
$^2\Delta_u$	2	pπ, ∞→pσ, pπ*	1056	−5.670	121	−5.714	−0.045
$^2\Delta_u$	2	pπ, ∞→pσ, pπ*	1056	−6.078	125	−6.093	−0.015
$^2\Sigma_u^-$	2	pπ, ∞→pσ, pπ*	1056	−6.490	125	−6.614	−0.124
							(−0.062) [d]

[a] The Hartree–Fock MO ordering is (2sσ)(2sσ*)(pπ)(pπ)(pσ)(pπ*)(pπ*)(pσ*)(pσ′).

[b] Relative to the SAC-CI energy for the singlet ground state. [c] Δ shows the difference from the full-CI result. [d] Average discrepancy.

glet and triplet states, and the electron affinity is positive for some lower anion states. The lowest excitation is for the $^3\Pi_u$ state. The calculated excitation energy is 0.528 eV in comparison with the adiabatic excitation energy of 0.09 eV [14]. The lowest doubly excited state is the $1\,^3\Sigma_g^-$ state, which is 1.92 eV above the ground state. The experimental adiabatic energy is only 0.80 eV above the ground state [14]. The existence of stable excited states of the anion is particularly unique. Two anion states are calculated to be more stable than the neutral ground state. Experimentally, at least three adiabatic states of C_2^- seem to be lower than the neutral ground state [14]. In the ionized states, simultaneous excitation-ionization two- and even three-electron processes appear in a lower-energy region. However, because of the limitations in the active space and the basis set, detailed comparisons of the present results with experiment are almost meaningless.

We conclude from the present study that the accuracy of the SAC-CI method for two- and many-electron processes is improved by using the general-*R* method. For single-electron processes, the conventional SD-*R* method is reliable, as has already been confirmed.

The author thanks Mr. S. Saito for his assistance in the full-CI calculations. This study has been partially supported by the Grant-in-Aid for Scientific Research from the Ministry of Education, Science, and Culture.

References

[1] H. Nakatsuji and K. Hirao, J. Chem. Phys. 68 (1988) 2053.

[2] H. Nakatsuji, Chem. Phys. Letters 59 (1978) 362; 67 (1979) 329, 334.

[3] H. Nakatsuji, Reports in Molecular Theory, in press.

[4] L.S. Cederbaum, Mol. Phys. 28 (1974) 479;
L.S. Cederbaum, W. Domcke, J. Schirmer and W. von Niessen, Advan. Chem. Phys. 65 (1986) 115.

[5] D.J. Rowe, Rev. Mod. Phys. 40 (1968) 153;
C.W. McCurdy Jr., T.N. Rescigno, D.L. Yeager and V. McKoy, in: Modern theoretical chemistry, Vol. 3, ed. H.F. Schaefer III (Plenum Press, New York, 1977) p. 339.

[6] K. Hirao and Y. Hatano, Chem. Phys. Letters 100 (1983) 519; 111 (1984) 533;
Y. Mizukami, K. Hirao and H. Nakatsuji, submitted for publication.

[7] O. Kitao and H. Nakatsuji, J. Chem. Phys. 87 (1987) 1169; Chem. Phys. Letters 143 (1988) 528;
H. Nakatsuji, O. Kitao and M. Komori, Lecture notes in chemistry, Vol. 50 (Springer, Berlin, 1989) pp. 101–122.

[8] H. Nakatsuji and S. Saito, J. Chem. Phys. 93 (1990) 1865; Intern. J. Quantum Chem., in press.

[9] H. Nakatsuji, K. Ohta and T. Yonezawa, J. Phys. Chem. 87 (1983) 3068;
T. Momose, H. Nakatsuji and T. Shida, J. Chem. Phys. 89 (1988) 4185;
H. Nakatsuji and M. Izawa, J. Chem. Phys. 91 (1989) 6205.

[10] H. Nakatsuji and T. Yonezawa, Chem. Phys. Letters 87 (1982) 426;
H. Nakatsuji, Chem. Phys. 75 (1983) 425; Intern. J. Quantum Chem. Symp. 17 (1983) 241.

[11] H. Nakatsuji, Program system for SAC and SAC-CI calculations (SAC85), No. 146 (Y4/SAC), Data Processing Center of Kyoto University (1985); Program Library SAC85, No. 1396, Computer Center of the Institute for Molecular Science (1986).

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

[13] S. Huzinaga, J. Chem. Phys. 42 (1965) 1293;
T.H. Dunning Jr., J. Chem. Phys. 53 (1970) 2823.

[14] K.P. Huber and G. Herzberg, Molecular spectra and molecular structures, Vol. 4. Constants of diatomic molecules (Van Nostrand Reinhold, New York, 1979).

[15] K. Kirby and B. Liu, J. Chem. Phys. 70 (1979) 893;
M. Dupuis and B. Liu, J. Chem. Phys. 73 (1980) 337.

[16] J.A. Nichols and J. Simons, J. Chem. Phys. 86 (1987) 6972.

[17] W.P. Kraemer and B.O. Roos, Chem. Phys. 118 (1987) 345.

[18] C.W. Bauschlicher Jr. and S.R. Langhoff, J. Chem. Phys. 87 (1987) 2919.