

Outer- and inner-valence ionization spectra of N₂ and CO: SAC-CI (general-R) compared with full-CI spectra

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Abstract

The SAC-CI (symmetry-adapted-cluster configuration-interaction) (general-R) method describes the ionization and shake-up spectra of N₂ and CO in almost complete agreement with the full-CI results, though the computational labour of the former is much smaller than that of the latter. The SAC-CI (general-R) method is accurate for both valence and inner-valence regions of ionization spectra, while the SAC-CI (SD-R) method is good for the outer-valence region, but not always so for the shake-up region. © 1998 Elsevier Science B.V.

1. Introduction

Ionization spectra usually involve two electronic processes: one for main peaks that are described by one-electron processes, and one for shake-up satellite peaks, appearing in the inner-valence region, that are characterized by two-electron — simultaneous ionization and excitation — processes. It is sometimes difficult to give quantitative theoretical descriptions of the latter peaks because they involve multiple-electron processes and because a large number of states should be examined for studying the inner-valence region of ionization spectra.

Inner-valence ionization spectra have been extensively studied by the so-called 2ph-TDA [1] and ADC [2–4] (algebraic-diagrammatic construction) methods, both of which are based on the many-body Green function method. The ADC method has some theoretical advantages over the 2ph-TDA method,

and its reliability has been shown in many applications. In the ADC(2) and ADC(3) methods, 1h and 2h1p configurations are included while, in the ADC(4) method, configurations up to 3h2p are included. Unfortunately, application of accurate higher-order approximations such as ADC(4) has been limited only to relatively small systems because of high computational costs.

SAC/SAC-CI [5–9] is a general method applicable to both excited and ionized states and has been applied to the study of ionization spectra of various molecules [8–16]. In these applications, the SAC-CI (SD-R) method, in which the linked ionization operators R are composed of single (I_i) and double ($I_i S_j^a$) excitation operators, has reproduced the primary peaks in the outer-valence region well. However, for peaks in the inner-valence region, where many shake-up states appear, a more quantitative description of the ionization energy and intensity

was needed. The SAC-CI(general-R) method [17], in which the linked excitation operators are not limited to singles and doubles but further involve triples and higher, was proposed to effectively describe electron correlations in multiple excitation processes. The high accuracy of the SAC-CI(general-R) method was confirmed for excitation, ionization, and electron attachment processes [17]. This method is also suitable for investigating a large number of states since its calculational dimension is much smaller than that of conventional CI and MRCI methods.

In this work, we examine the accuracy and efficiency of the SAC-CI(SD-R) and SAC-CI(general-R) methods for describing primary and satellite peaks of ionization spectra. Special attention is paid to the generation algorithm of the higher-order excitation operators, namely, the exponential generation algorithm [18,19] combined with the perturbation selection scheme [10].

The ionization spectra of N₂ and CO have been studied in detail both experimentally [20–24] and theoretically [25–28]. Although the molecules are small, there already exist many shake-up states in the inner-valence regions of their ionization spectra that, therefore, are appropriate for the present examination. The outer- and inner-valence ionization spectra of these molecules are calculated by the full-CI method, and the results are used to examine the accuracy of ionization spectra calculated by the SAC-CI(SD-R) and SAC-CI(general-R) methods.

2. Method

The ionized states of N₂ and CO molecules are calculated up to the high-energy region near the double ionization threshold (~ 43 eV). The basis sets are composed of the [4s2p] GTOs of Huginaga and Dunning [29,30] augmented with the d-polariza-

Table 1
Dimensions of the SAC-CI and full-CI calculations of CO and N₂

Method	State	Singles	Doubles	Triples	Quadruples	5-ples	6-ples	7–10-ples	Total
CO									
SAC-CI(SD-R)									
	Σ, Δ	3	45	–	–	–	–	–	48
	Π	1	31	–	–	–	–	–	32
SAC-CI(general-R)									
	Σ, Δ	3	45	256	334	80	1	–	719
	Π	1	31	235	332	24	0	–	623
full-CI									
	Σ, Δ	3	45	310	1110	2128	2128	1468	7192
	Π	1	31	274	1074	2080	2080	1380	6920
N ₂									
SAC-CI(SD-R)									
	Σ_g^+, Δ_g	2	19	–	–	–	–	–	21
	Π_{g+}	0	19	–	–	–	–	–	19
	Σ_u^+, Δ_u	1	26	–	–	–	–	–	27
	Π_u	1	12	–	–	–	–	–	13
SAC-CI(general-R)									
	Σ_g^+, Δ_g	2	19	134	179	96	6	–	436
	Π_{g+}	0	19	113	194	100	4	–	430
	Σ_u^+, Δ_u	1	26	116	226	92	4	–	465
	Π_u	1	12	121	227	86	4	–	451
full-CI									
	Σ_g^+, Δ_g	2	19	164	546	1076	1052	737	3596
	Π_{g+}	0	19	128	546	1028	1052	687	3460
	Σ_u^+, Δ_u	1	26	146	564	1052	1076	731	3596
	Π_u	1	12	146	528	1052	1028	693	3460

tion functions of $\zeta_d = 0.75, 0.8,$ and 0.85 for C, N and O atoms, respectively, plus the Rydberg s function of $\zeta_s = 0.023(\text{C}), 0.028(\text{N}),$ and $0.032(\text{O})$ [31]. Both the SAC-CI(SD-R) and SAC-CI(general-R) calculations are performed to observe the effect of higher-excitation linked operators. Full-CI reference calculations are also done to examine the accuracy of the SAC-CI results. HF-SCF and reference full-CI calculations are performed with the HONDO8 program [32].

Because full-CI calculations are limited for solving many roots, the active spaces are restricted to five occupied and five unoccupied MOs for both N_2 and CO: namely, $(2\sigma_g)(2\sigma_u)(1\pi_u)(3\sigma_g)(4\sigma'_u)-(3\sigma'_u)(4\sigma_u)(1\pi_g)$ for N_2 and $(3\sigma)(4\sigma)(1\pi)(5\sigma)-(6\sigma')(7\sigma')(8\sigma^*)(2\pi^*)$ for CO. Then the resulting full-CI dimensions are about 3500 and 7000 for N_2 and CO and about 30 solutions are obtained.

SAC-CI(SD-R) calculations are performed without configuration selection for both linked and unlinked terms, and contribution of the $S(2)^*R(2)$ unlinked terms is included, i.e. the so-called ‘3,4-excited’ calculation in Ref. [10]. In the SAC-CI(general-R) method, the higher triple, quadruple, etc., excitation operators are generated by the exponential-generation algorithm described in detail in Refs. [18] and [19]. In the present study, higher-excitation operators up to 6-ple excitations are included, and the thresholds for the exponential generations are set to $(\lambda_{AA}, \lambda_{AAA}) = (0.1, 0.4)$ [18,19]. These higher-order operators are further reduced by the perturbation selection scheme [10]. Higher-excitation configurations of which the contribution of perturbation energy to the reference configurations is larger than 5×10^{-5} au are included. The reference configurations are determined by preliminary EGCI calculation [33] with the threshold of their CI coefficients being 0.05. SAC-CI calculations are performed by the SAC-CI96 program system [34]. Monopole intensity is calculated including only final-state correlation effects, for simplicity, for both full-CI and SAC-CI wave functions.

3. Results

The purpose of this study is to examine the accuracy and efficiency of the SAC-CI, in compari-

son with the full-CI, method in the calculation of outer- and inner-valence ionization spectra of N_2 and CO. Direct comparison with experimental values is not performed because of the restrictive nature of the active space and basis sets. First, we discuss the calculational efficiency of the SAC-CI method. Table 1 compares the calculational dimensions of SAC-CI and full-CI for N_2 and CO. The dimensions of the SAC-CI method are much smaller than those of the full-CI method, especially for SAC-CI(SD-R) which includes only singles and doubles for the R operators. The higher-excitation operators of SAC-CI(general-R) are effectively generated by the exponential generation algorithm combined with the per-

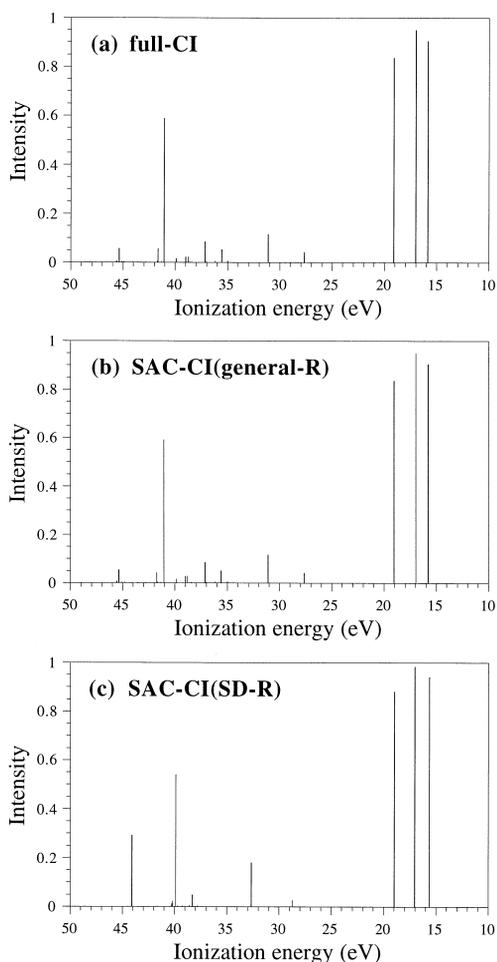


Fig. 1. Ionization spectra of N_2 calculated by the (a) full-CI, (b) SAC-CI(general-R), and (c) SAC-CI(SD-R) methods.

Table 2
Ionized states of N₂ calculated by the SAC-CI and full-CI methods

State	Excitation level	Full-CI			SAC-CI-V (general-R)			SAC-CI-V (SD-R)			
		total energy (au)	I.P. (eV)	intensity	Δ^a	I.P. (eV)	intensity	Δ^a	I.P. (eV)	intensity	
Σ_g^+	1	-1.44798	15.87	0.905	-0.14	15.83 ^b	0.905	-6.13	15.67	0.940	
	2	-0.88665	31.15	0.115	-0.20	31.11	0.116	57.57	32.68	0.180	
	2	-0.70074	36.21	0.005	-0.10	36.17	0.005	61.00	37.83	0.003	
	3	-0.66544	37.17	0.085	0.09	37.13	0.086				
	3	-0.60698	38.76	0.022	0.44	38.73	0.023				
	2	-0.59777	39.01	0.022	1.40	39.01	0.023	48.05	40.28	0.012	
	2	-0.56489	39.90	0.016	1.00	39.89	0.016	66.27	41.67	0.009	
	1	-0.52133	41.09	0.588	0.19	41.06	0.596	-42.69	39.89	0.539	
								111.95	44.10	0.291	
		3	-0.50033	41.66	0.056	1.95	41.68	0.046			
	2	-0.37217	45.15	0.004	1.26	45.14	0.004	46.44	46.37	0.003	
	3	-0.36288	45.40	0.056	0.51	45.38	0.055				
Π_u	2	-0.35444	45.63	0.006	1.42	45.63	0.006	152.15	49.73	0.007	
	1	-1.40611	17.01	0.950	-0.13	16.97 ^c	0.950	2.45	17.04	0.984	
	2	-0.91548	30.36	0.000	0.11	30.33	0.000	46.18	31.58	0.000	
	2	-0.74340	35.04	0.006	-0.12	35.01	0.006	172.38	39.70	0.002	
	2	-0.66998	37.04	0.002	0.91	37.03	0.002	82.10	39.24	0.002	
	3	-0.65659	37.41	0.000	0.19	37.38	0.000				
	3	-0.64138	37.82	0.000	0.24	37.79	0.000				
	2	-0.61092	38.65	0.001	0.58	38.63	0.001	63.65	40.35	0.002	
	3	-0.59752	39.01	0.000	0.62	39.00	0.000				
	2	-0.51258	41.33	0.002	1.78	41.34	0.002	108.03	44.23	0.002	
Σ_u^+	3	-0.49756	41.73	0.001	0.15	41.70	0.001				
	3	-0.46716	42.56	0.000	0.17	42.53	0.000				
	3	-0.43871	43.34	0.000	2.37	43.36	0.000				
	2	-0.41062	44.10	0.001	2.03	44.12	0.001	77.34	46.17	0.002	
	1	-1.32879	19.12	0.836	-0.19	19.07 ^d	0.836	-3.01	19.00	0.881	
	2	-1.01377	27.69	0.042	-0.31	27.64	0.042	40.55	28.75	0.026	
	2	-0.72396	35.57	0.052	0.06	35.54	0.052	102.08	38.32	0.049	
	2	-0.66896	37.07	0.000	0.19	37.04	0.000	56.28	38.57	0.005	
	2	-0.62056	38.39	0.001	0.63	38.37	0.001	67.93	40.20	0.024	
	2	-0.51474	41.27	0.000	2.95	41.31	0.000	68.02	43.08	0.000	
Π_g	3	-0.49771	41.73	0.005	0.83	41.72	0.005				
	2	-0.45728	42.83	0.002	0.06	42.80	0.002	62.72	44.50	0.001	
	3	-0.42822	43.62	0.001	1.64	43.63	0.001				
	2	-0.37909	44.96	0.004	0.20	44.93	0.004	168.54	49.51	0.007	
	2	-1.06328	26.34	0.000	-0.21	26.30	0.000				
	2	-1.00703	27.87	0.000	-0.17	27.83	0.000				
	2	-0.96752	28.95	0.000	-0.08	28.91	0.000				
	Δ_g	2	-0.87942	31.34	0.000	0.06	31.31	0.000	79.92	33.48	0.000
		2	-0.82297	32.88	0.000	-0.05	32.84	0.000	90.62	35.31	0.000
		3	-0.57002	39.76	0.000	0.55	39.74	0.000	49.56	41.07	0.000
Δ_u	2	-1.00727	27.86	0.000	-0.12	27.82	0.000	56.79	29.37	0.000	
	2	-0.99014	28.33	0.000	-0.19	28.29	0.000	58.62	29.89	0.000	
	2	-0.51804	41.18	0.000	2.50	41.21	0.000	48.51	42.46	0.000	
average discrepancy					0.66						

Total energies are relative to -107 au.

^a Deviation from the full-CI total energy (in mhartree).

^b Experimental I.P. 15.6 eV [20].

^c Experimental I.P. 17.0 eV [20].

^d Experimental I.P. 18.8 eV [20].

turbation selection scheme. In the present case, the numbers of triples are large, since a large number of states are calculated and many primary important doubles exist.

3.1. N_2

Fig. 1 compares the ionization spectra of N_2 calculated by full-CI, SAC-CI(general-R), and SAC-CI(SD-R). Accuracy of the method is demonstrated impressively in these theoretical spectra. Both SAC-CI(SD-R) and SAC-CI(general-R) reproduce the positions and intensities of the primary peaks of the full-CI method. As for the satellite peaks, SAC-CI(general-R) reproduces the full-CI results quite accurately, while the description using SAC-CI(SD-R) is not as satisfactory for these peaks. Actually, the theoretical spectrum of SAC-CI(general-R) almost completely superposes that of the full-CI method. In the experimental spectrum [20–24], there are band structures due to the shake-up states in the energy region of 25–46 eV which are also obtained in the present calculation. Most of these satellite peaks are explained by the intensity borrowing through the interactions with the single-hole states of $(3\sigma_g)^{-1}$ and $(2\sigma_u)^{-1}$. SAC-CI(general-R) describes these interactions precisely up to a high-energy region.

Table 2 shows detailed numerical results of SAC-CI(SD-R), SAC-CI(general-R) and full-CI calculations for the ionized states of N_2 . Total energies, ionization potentials (IP), and monopole intensities are shown for all the calculated states up to 46 eV, even if their intensities are small. Deviations of SAC-CI from full-CI total energies are given. The intensities of the Σ_g^+ , Σ_u^+ , and Π_u states are due to interactions with single-hole states. The lower three states of Π_g , Δ_u , and Δ_g , the intensities of which are trivially zero, are also given in Table 2.

For the outer-valence region, both SAC-CI(SD-R) and SAC-CI(general-R) give quantitatively good results since the primary states are described by a one-electron process. Deviations of SAC-CI(general-R) from the full-CI method are within 0.1 eV for the IPs of these states. For the inner-valence region, all of the shake-up states are described precisely by SAC-CI(general-R) due to the explicit inclusion of interactions between the dominant doubles and higher

triples and quadruples. SAC-CI(SD-R) also includes the effects of the higher-excitation terms through the unlinked terms, but the results are not satisfactory. It is interesting to note that even three-electron processes exist in this energy region, although their intensities are small; this was also pointed out by previous CI studies [25,27]. These states are also accurately calculated by the present SAC-CI (general-R) method; it is intrinsically impossible to describe these states by the SAC-CI(SD-R). Deviations in the total energy between the SAC-CI(general-R) and full-CI methods is within 3 mhartree and the

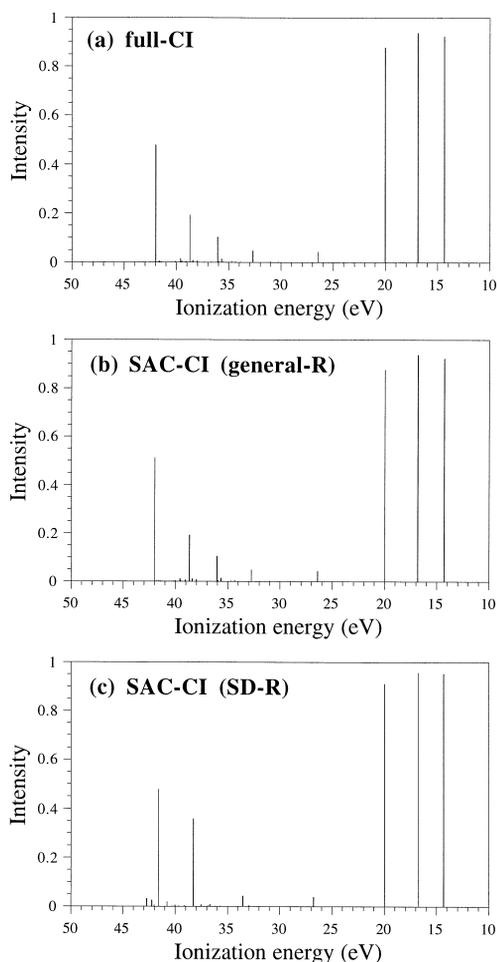


Fig. 2. Ionization spectra of CO calculated by the (a) full-CI, (b) SAC-CI(general-R), and (c) SAC-CI(SD-R) methods.

average discrepancy is only 0.66 mhartree. These results show the high accuracy of the SAC-CI(general-R) method in both outer- and inner-valence re-

gions. These results demonstrate the potential importance of including the higher-excitation $\{R_k\}$ operators in the calculations of shake-up states.

Table 3
Ionized states of CO calculated by the SAC-CI and full-CI methods

State	Excitation level	Full-CI			SAC-CI-V (general-R)			SAC-CI-V (SD-R)			
		total energy (au)	I.P. (eV)	intensity	Δ^a	I.P. (eV)	intensity	Δ^a	I.P. (eV)	intensity	
Σ	1	-1.27891	14.37	0.923	-0.38	14.30 ^b	0.923	0.87	14.33	0.952	
	1	-1.06939	20.07	0.877	0.06	20.01 ^c	0.877	-0.76	19.99	0.912	
	2	-0.83449	26.46	0.042	0.15	26.40	0.042	14.03	26.78	0.039	
	2	-0.60434	32.72	0.047	3.18	32.75	0.047	32.95	33.56	0.043	
	2	-0.53058	34.73	0.002	0.79	34.69	0.002	39.42	35.74	0.002	
	2	-0.49544	35.69	0.010	1.01	35.65	0.011	40.05	36.72	0.008	
	2	-0.48090	36.08	0.103	0.54	36.04	0.104	83.55	38.29	0.359	
	2	-0.45879	36.68	0.001	0.64	36.64	0.001	34.34	37.56	0.006	
	2	-0.40918	38.03	0.008	0.88	38.00	0.008	44.16	39.17	0.003	
	3	-0.39479	38.43	0.008	0.95	38.39	0.009				
	2	-0.38381	38.72	0.193	-0.07	38.66	0.192	329.78	47.64	0.078	
	2	-0.37080	39.08	0.004	1.08	39.05	0.004	50.00	40.38	0.001	
	2	-0.35134	39.61	0.014	1.99	39.60	0.014	99.65	42.26	0.026	
	2	-0.33358	40.09	0.004	1.22	40.06	0.004	73.66	42.03	0.006	
	2	-0.28415	41.44	0.002	4.89	41.51	0.006	50.21	42.74	0.032	
	2	-0.27851	41.59	0.006	3.88	41.63	0.001	81.75	43.75	0.000	
	1	-0.26378	41.99	0.478	1.24	41.96	0.497	-11.78	41.61	0.478	
	Π	1	-1.18623	16.89	0.937	-0.04	16.83 ^d	0.937	-2.37	16.76	0.956
		2	-0.85732	25.84	0.002	0.19	25.78	0.002	38.57	26.83	0.001
2		-0.69390	30.29	0.002	0.16	30.23	0.002	43.23	31.40	0.000	
2		-0.66560	31.06	0.002	0.28	31.00	0.002	71.78	32.95	0.003	
2		-0.64474	31.62	0.000	0.72	31.58	0.000	79.51	33.73	0.000	
2		-0.60499	32.71	0.000	1.81	32.69	0.000	76.98	34.74	0.000	
2		-0.56228	33.87	0.001	4.41	33.93	0.002	83.44	36.08	0.000	
2		-0.54465	34.35	0.003	0.63	34.30	0.003	27.31	35.03	0.000	
2		-0.53003	34.75	0.001	0.51	34.70	0.001	28.91	35.47	0.000	
2		-0.50060	35.55	0.002	0.60	35.50	0.002	26.21	36.20	0.001	
2		-0.49512	35.70	0.014	1.04	35.66	0.014	148.73	39.68	0.002	
2		-0.48404	36.00	0.004	0.54	35.95	0.003	34.81	36.88	0.004	
3		-0.42752	37.54	0.000	0.68	37.49	0.000				
3		-0.39538	38.41	0.000	0.75	38.37	0.000				
2		-0.36939	39.12	0.003	0.54	39.07	0.003	36.35	40.04	0.005	
3		-0.35590	39.48	0.004	0.74	39.44	0.005				
2		-0.34309	39.83	0.000	1.21	39.80	0.000	37.77	40.80	0.019	
2		-0.28027	41.54	0.000	3.57	41.58	0.000	216.97	47.38	0.001	
2		-0.27515	41.68	0.002	5.64	41.77	0.002	160.95	46.00	0.003	
Δ	2	-0.87486	25.36	0.000	0.05	25.30	0.000	25.70	26.00	0.000	
	2	-0.79006	27.67	0.000	0.16	27.61	0.000	22.25	28.21	0.000	
	2	-0.51510	35.15	0.000	1.04	35.12	0.000	162.87	39.52	0.000	
average discrepancy					1.29						

Total energies are relative to -111 au.

^aDeviation from the full-CI total energy (in mhartree).

^bExperimental I.P. 14.0 eV [20].

^cExperimental I.P. 19.8 eV [20].

^dExperimental I.P. 17.0 eV [20].

3.2. CO

Theoretical ionization spectra of CO calculated by full-CI and SAC-CI methods are compared in Fig. 2. The ionized states up to 42 eV are calculated. Since CO and N₂ have an isoelectronic structure, many shake-up states exist in the inner-valence region of CO. Again, the superiority of SAC-CI(general-R) to SAC-CI(SD-R) is observed in the inner-valence region, although it is not as remarkable as in the case of N₂. This is because the shake-up states of CO are mainly described by interactions within singles and doubles.

Results of SAC-CI and full-CI for the ionized states of CO are compared in Table 3. The low-lying seventeen, nineteen and three states are examined for Σ , Π and Δ symmetries, respectively. Many shake-up states are calculated in the 25–42 eV region as observed in the experimental spectra, although it is difficult to give quantitative assignment in the present level of calculations in basis set and active space. SAC-CI(general-R) results agree well with those of the full-CI method for total energy, ionization potential, and intensity. Furthermore, SAC-CI(SD-R) gives better results for CO than for N₂. For example, two small peaks at about 26.5 and 32.7 eV, and the prominent $(2\sigma)^{-1}$ peak at about 42 eV, are reproduced although a twinning of the peaks at about 36.0 eV is only reproduced by SAC-CI(general-R). The average discrepancy of the total energies between the SAC-CI(general-R) and full-CI methods is 1.29 mhartree.

These results show that SAC-CI(general-R) is an accurate, reliable method that is applicable for quantitative analysis of ionization spectra in both outer- and inner-valence regions. This is because SAC-CI(general-R) accurately and effectively describes multi-electron processes [17].

4. Conclusion

We have examined the efficiency and accuracy of the SAC-CI method for describing outer- and inner-valence ionization spectra in comparison with the full-CI method. Computational dimensions of the SAC-CI(SD-R) and SAC-CI(general-R) methods are much smaller than those of the full-CI method. Main

peaks are described precisely by the SAC-CI(SD-R) method, needing extremely little effort in calculation. For the main and shake-up peaks, SAC-CI(general-R) gives good quantitative results. The exponential generation algorithm combined with the perturbation selection technique provides compact, effective higher-excitation operators for the SAC-CI(general-R) method. We conclude that the SAC-CI(general-R) method is very useful for quantitative analysis of the shake-up states.

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References

- [1] J. Schirmer, L.S. Cederbaum, *J. Phys. B* 11 (1978) 1889.
- [2] J. Schirmer, *Phys. Rev. A* 26 (1982) 2935.
- [3] J. Schirmer, L.S. Cederbaum, O. Walter, *Phys. Rev. A* 28 (1983) 1237.
- [4] J. Schirmer, *Phys. Rev. A* 43 (1991) 4647.
- [5] H. Nakatsuji, K. Hirao, *J. Chem. Phys.* 68 (1978) 2053.
- [6] H. Nakatsuji, *Chem. Phys. Lett.* 59 (1978) 362.
- [7] H. Nakatsuji, *Chem. Phys. Lett.* 67 (1979) 329.
- [8] H. Nakatsuji, in: *Computational Chemistry. Review of Current Trends*, Vol. 2, pp. 62–124.
- [9] H. Nakatsuji, *Acta Chim. Hung.* 129 (1992) 719.
- [10] H. Nakatsuji, *Chem. Phys.* 75 (1983) 425.
- [11] H. Nakatsuji, *Chem. Phys.* 76 (1983) 283.
- [12] H. Nakatsuji, *J. Chem. Phys.* 80 (1984) 3703.
- [13] H. Nakatsuji, O. Kitao, T. Yonezawa, *J. Chem. Phys.* 83 (1985) 723.
- [14] H. Nakatsuji, S. Saito, *J. Chem. Phys.* 91 (1989) 6205.
- [15] H. Nakatsuji, M. Ehara, M.H. Palmer, M.F. Guest, *J. Chem. Phys.* 97 (1992) 2561.
- [16] H. Nakatsuji, M. Ehara, *J. Chem. Phys.* 101 (1994) 7658.
- [17] H. Nakatsuji, *Chem. Phys. Lett.* 177 (1991) 331.
- [18] H. Nakatsuji, *J. Chem. Phys.* 83 (1985) 731–743.
- [19] H. Nakatsuji, *J. Chem. Phys.* 94 (1991) 6716.
- [20] K. Siegbahn, C. Nordling, G. Johansson, J. Hedman, P.F. Heden, K. Hamrin, U. Gelius, T. Bergmark, L.O. Werme, R. Manne, Y. Baer, *ESCA Applied to Free Molecules* (North-Holland, Amsterdam, 1971).
- [21] D.W. Turner, C. Baker, A.D. Baker, C.R. Brundle, *Molecular Photoelectron Spectroscopy* (Wiley-Interscience, New York, 1970).

- [22] L. Asbrink, C. Fridh, *Phys. Scripta* 9 (1974) 338.
- [23] L. Asbrink, C. Fridh, E. Lindholm, C. Codling, *Phys. Scripta* 10 (1974) 183.
- [24] S. Krummacher, V. Schmidt, F. Wuilleumier, *J. Phys. B13* (1980) 3993.
- [25] N. Kosugi, H. Kuroda, S. Iwata, *Chem. Phys.* 39 (1979) 337.
- [26] W.C. Ermler, A.D. Mclean, *J. Chem. Phys.* 73 (1980) 2297.
- [27] P.W. Langhoff, S.R. Langhoff, T.N. Rescigno, J. Schirmer, L.S. Cederbaum, W. Domcke, W. von Niessen, *Chem. Phys.* 58 (1981) 71.
- [28] J. Schirmer, O. Walter, *Chem. Phys.* 78 (1983) 201.
- [29] S. Huzinaga, *J. Chem. Phys.* 42 (1965) 1293.
- [30] T.H. Dunning Jr., *J. Chem. Phys.* 53 (1970) 2823.
- [31] S. Huzinaga, J. Andzelm, M. Klobukowski, E. Radzio-Andzelm, Y. Sakai, H. Tatewaki, *Gaussian Basis Sets for Molecular Calculations* (Elsevier, Amsterdam, 1984).
- [32] M. Dupuis, A. Farazdel, Program System HONDO8, A. MOTECC-91, Center for Scientific and Engineering Computations, IBM Corp., 1991.
- [33] J. Hasegawa, H. Nakatsuji, private communication.
- [34] 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.