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Cluster Expansion of the Wave Function. Electron Correlations in Singlet and Triplet Excited States, Ionized States, and Electron Attached States by SAC and SAC-CI Theories*

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Abstract

The symmetry-adapted-cluster (SAC) and SAC-CI theories reported previously have been applied to the study of electron correlations in ground state, singlet and triplet excited states, ionized state, and electron attached state. Formulas for calculations of one-electron properties and transition properties from the SAC and SAC-CI wave functions are given. Calculations were carried out for the ground and Rydberg excited states of water and its positive and negative ions, with the use of the simpler computational scheme than the previous one. The results compare well with experiments.

1. Introduction

Cluster expansion theory is one of the most promising approaches for studies of accurate wave functions (electron correlations) [1–3]. In this series of studies, we are developing cluster expansion theories which cover not only closed- and open-shell ground states but also various types of excited states. Such studies are topics in current development of cluster expansion theory [4–9]. Previously, we have proposed symmetry-adapted-cluster (SAC) expansion theory for closed- and open-shell systems [8]. In a nonlinear expansion of the wave function, symmetry adaptation of the excitation generator is necessary. Otherwise, different symmetry spaces may mix each other through unlinked terms. Applications of this expansion to relatively small systems were reported previously [9]. When only one-electron cluster generators are included, the SAC expansion gives a new orbital theory, called pseudo-orbital theory, as the conventional cluster expansion gives (unrestricted) Hartree–Fock theory (the Thouless theorem [10]). The pseudo-orbital theory has been applied to the studies of spin correlations in open-shell atoms and organic and inorganic radicals [8, 11].

For excited states, we have proposed SAC-CI theory [9]. It utilizes the fact that the functions in the complementary space of the SAC wave function of the ground state form an adequate basis set for the excited states. Physically, this

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corresponds to studying the correlations in the excited states starting from the correlations in the ground state [5, 7]. These facts have led us to believe that the SAC–CI expansion converges more rapidly than ordinary CI expansion. We have shown two methods of solutions, i.e., variational and nonvariational solutions, for both of the SAC and SAC–CI theories [9]. We have discussed the features of these solutions and applied them to singlet ground and excited states of relatively small systems [9]. The results seemed to show a promising future of these theories. Recently, the SAC theory has also been applied to excited states with a slight modification of the original theory [12].

In this paper we show applications of the SAC–CI theory to not only singlet excited states but also triplet excited states, ionized states, and electron attached states. We have used a simpler computational scheme than the previous one with dropping off some small and negligible terms. Such modification was shown useful from computational point of view. We have summarized the formulas for calculations of one electron properties and transition properties from the SAC and SAC–CI wavefunctions. The calculation was carried out for the ground and Rydberg excited states of water and its positive and negative ions.

2. Solution of the SAC and SAC–CI Theories

Theories for the SAC and SAC–CI expansions of the wave functions have been given in detail previously [8, 9]. The formulas for computations were reported in a previous paper [9]. Here, we briefly summarize the theoretical background pertinent to the present calculations.

The ground state was calculated by the SAC expansion around the Hartree–Fock reference state $|0\rangle$,

$$\Psi_g = \exp\left(\sum_I C_I S_I^\dagger\right)|0\rangle, \tag{1}$$

where $S_I^\dagger$ is a symmetry-adapted excitation operator. The expansion was terminated at second order in the coefficients

$$\Psi_g \simeq \left(1 + \sum_I C_I S_I^\dagger + \frac{1}{2}\sum_{IJ} C_I C_J S_I^\dagger S_J^\dagger\right)|0\rangle. \tag{2}$$

As linked configurations $S_I^\dagger|0\rangle$, we have included all single and double excitations from the reference $|0\rangle$. In the unlinked configurations $S_I^\dagger S_J^\dagger|0\rangle$, we have included only quadruple excitations as products of double excitations. For closed shell ground state, double and triple excitations in the unlinked terms can be neglected [2], though they were included in the previous calculations [9]. We have confirmed this point for H_2O using the previous basis set.

The SAC wave function was solved by two methods: variational (SAC–V) and nonvariational (SAC–NV or SAC–MET) methods. Formulas for these solutions were given previously [9]. Of the two methods, the variational one includes some approximations in the matrix elements between unlinked terms. The nonvariational one does not include such approximation since such terms do not

occur. In both cases, the basic equations can be written in simultaneous linear equations. They were solved iteratively by the Gauss method with an accelerating ω parameter [13]. The method for eigenvalues and eigenvectors for large non-symmetric matrices described below were also useful.

The excited states (singlet and triplet), ionized states, and electron attached states are described by the SAC-CI theory [9]. Let $\{R_K^\dagger\}$ be a set of symmetry adapted excitation operators for these excitation processes. It is shown that the functions Φ_K defined by

$$\Phi_K = \mathcal{P} R_K^\dagger \Psi_g, \tag{3}$$

where $\mathcal{P}$ is a projector, $\mathcal{P} = 1 - |\Psi_g\rangle\langle\Psi_g|$, and Ψ_g is the SAC variational wave function for the ground state, span the basis for these excited states; i.e., they satisfy the necessary conditions for the excited states

$$\langle\Phi_K|\Psi_g\rangle = 0, \tag{4}$$

$$\langle\Phi_K|H|\Psi_g\rangle = 0. \tag{5}$$

Then, in the SAC-CI theory, we represent the wave function for the excited state Ψ_e by a linear combination of the excited functions $\{\Phi_K\}$,

$$\Psi_e = \sum_K d_K \Phi_K. \tag{6}$$

Since the excited functions $\{\Phi_K\}$ are formed from the correlated ground state Ψ_g as Eq. (3), the SAC-CI expansion (6) has only to describe a difference in electron correlation from that of the ground state. Because of these features, the SAC-CI expansion for the excited state is more rapidly convergent than the ordinary CI expansion.

In this calculation, we have truncated the SAC-CI expansion at the second order in the coefficients

$$\Psi_e = \sum_K d_K \left(R_K^\dagger + R_K^\dagger \sum_I C_I S_I^\dagger - \mathcal{S}_{Kg} \right) |0\rangle, \tag{7}$$

where $\mathcal{S}_{Kg} = \langle\Psi_g|R_K^\dagger\Psi_g\rangle$ and is nonzero only for totally symmetric singlet excited states. As linked operators $R_K^\dagger$, we have included all single and double excitations from the reference configuration $|0\rangle$. For singlet excited states, the single excitation operator is given by

$$S_i^a = (a_{a\alpha}^\dagger a_{i\alpha} + a_{a\beta}^\dagger a_{i\beta})/\sqrt{2} \tag{8}$$

and the double excitation operator is expressed by the products $S_i^a S_j^b$, etc., where i, j denote occupied orbitals and a, b denote virtual orbitals. For triplet excited states, the single excitation operator is given by

$$T_i^a = a_{a\alpha}^\dagger a_{i\beta} \tag{9}$$

and the double excitation operator is expressed by the products $T_i^a S_j^b$, etc. For ionized states, the single excitation operator is given by a destruction operator

$$I_i = a_{i\beta} \tag{10}$$

and the double excitation operator is given by the products $I_i S_j^a$, etc. For electron attached states, the single excitation operator is given by a creation operator

$$A^a = a_{a\alpha}^{\dagger} \tag{11}$$

and the double excitation operator is given by the products $A^a S_i^b$, etc. For the unlinked configurations $R_K^{\dagger} S_I^{\dagger}|0\rangle$ of Eq. (7), we have used the following simplifications. Since the operators $S_I^{\dagger}$ represent the correlations in the ground state, only the double excitations were included for $S_I^{\dagger}$. This approximation is consistent to that used for the unlinked terms of Eq. (2) for the ground state. Since the excited states studied here are primarily of single excitation in nature, we have included only single excitation operators for the $R_K^{\dagger}$'s in the unlinked terms. Therefore, the unlinked configurations in Eq. (7) are triply excited configurations alone from the reference $|0\rangle$. This is a large simplification in comparison with the previous calculations [9] in which quadruply excited (double × double) and other unlinked configurations were included. We have confirmed that this simplification results in a considerable saving in computational time with a very little change in excitation energies (examined for H_2O with the previous basis set). However, for excitations in which double excitations from the reference $|0\rangle$ are of importance (e.g., shake up and satellite bands in ionization spectra), we should also include double excitations for $R_K^{\dagger}$'s in the unlinked terms.

The SAC-CI wave function was also solved by the two methods, i.e., variational (SAC-CI-V) and nonvariational (SAC-CI-NV) methods. Formulas for these methods were given previously [9]. In the SAC-CI-V method, we have neglected the terms which are second order in the SAC coefficients C_I [see Eq. (36) of Ref. 9]. We have used the Davidson algorithm for diagonalization of large symmetric matrices [14]. In the SAC-CI-NV method, the matrix to be diagonalized is nonsymmetric. We have shown that the Davidson algorithm can be extended to such cases and used it for the present calculations. Details of the method will be published elsewhere. We note that in the present approximation the formula of the matrix of the SAC-CI-V method is just a symmetrized one of the SAC-CI-NV matrix.

3. Density and Transition Density for SAC and SAC-CI Wave Functions

For calculations of one-electron properties of ground and excited states and of the transition properties between them, we summarize here the formulas for calculations of density and transition density from the SAC and SAC-CI wavefunctions.

Let Q be a spin-independent one-electron operator

$$Q = \sum_{\nu} q(\nu). \tag{12}$$

For density, we have $q(\nu) = \delta(\mathbf{r} - \mathbf{r}_\nu)$. From the SAC wave function given by Eq. (2), we have calculated the one-electron property by

$$\langle Q \rangle_g = \langle \Psi_g | Q | \Psi_g \rangle / \langle \Psi_g | \Psi_g \rangle, \tag{13}$$

$$\langle\Psi_g|Q|\Psi_g\rangle \simeq \langle 0|Q|0\rangle + 2\sum_I C_I\langle 0|QS_I^\dagger|0\rangle + \sum_{IJ} C_IC_J\langle 0|S_IQS_J^\dagger|0\rangle, \tag{14}$$

$$\langle\Psi_g|\Psi_g\rangle \simeq 1 + \sum_{IJ} C_IC_J\langle 0|S_I \cdot S_J^\dagger|0\rangle. \tag{15}$$

These equations are correct to third order in the coefficients, since the matrices between linked and unlinked terms $\langle 0|S_IQS_J^\dagger S_K^\dagger|0\rangle$ vanish identically ($S_J^\dagger S_K^\dagger$ includes only quadruple excitations). The matrices between unlinked terms (fourth order in the coefficients) were neglected.

The density and one-electron property of the excited state are calculated from the SAC-CI wave function given by Eq. (7) as

$$\langle Q\rangle_e = \langle\Psi_e|Q|\Psi_e\rangle/\langle\Psi_e|\Psi_e\rangle, \tag{16}$$

$$\begin{aligned}\langle\Psi_e|Q|\Psi_e\rangle = {} & \Big(\sum_K d_K\mathscr{S}_{Kg}\Big)^2\langle 0|Q|0\rangle - 2\Big(\sum_K d_K\mathscr{S}_{Kg}\Big)\Big(\sum_L d_L\langle 0|QR_L^\dagger|0\rangle\Big) \\ & + \sum_{KL} d_Kd_L\langle 0|R_KQR_L^\dagger|0\rangle \\ & + 2\sum_K\sum_L\sum_I d_Kd_LC_I\langle 0|R_KQR_L^\dagger S_I^\dagger|0\rangle \\ & + \sum_{KL}\sum_{IJ} d_Kd_LC_IC_J\langle 0|R_KS_IQR_L^\dagger S_J^\dagger|0\rangle,\end{aligned} \tag{17}$$

$$\langle\Psi_e|\Psi_e\rangle = \Big(\sum_K d_K\mathscr{S}_{Kg}\Big)^2 + \sum_{KL} d_Kd_L\langle 0|R_K \cdot R_L^\dagger|0\rangle + \sum_{KL}\sum_{IJ} d_Kd_LC_IC_J\langle 0|R_KS_I \cdot R_L^\dagger S_J^\dagger|0\rangle. \tag{18}$$

The first and second terms of Eq. (17) are nonzero only for states of the same spin and space symmetry as the ground state. In the last two terms of Eq. (17), large contributions arise mainly from terms which have large values in the coefficients $\{d_K\}$. Since calculations of the last two terms are time consuming, we have included only such unlinked terms whose d_K's are larger than 0.1. It should be noted that in the SAC-CI theory, the unlinked terms appear directly in the expressions of density and one-electron property, though they do not in the SAC theory in the present formalism [Eqs. (14) and (15)].

Natural orbitals for the ground and excited states are obtained by diagonalizing the first-order density matrix as

$$\rho(1|1') = \sum_i n_i\eta_i(1)\eta_i(1'), \tag{19}$$

where n_i is the occupation number for the natural orbital η_i.

Transition property between ground and singlet excited state is calculated from Eqs. (2) and (7) as

$$\langle Q\rangle_{ge} = \langle\Psi_g|Q|\Psi_e\rangle/(\langle\Psi_g|\Psi_g\rangle\langle\Psi_e|\Psi_e\rangle)^{1/2}, \tag{20}$$

$$\begin{aligned}\langle\Psi_g|Q|\Psi_e\rangle \simeq -\Big(\sum_K d_K \mathcal{S}_{Kg}\Big)\Big(\langle 0|Q|0\rangle + \sum_I C_I\langle 0|S_I Q|0\rangle\Big) \\ + \sum_K d_K\langle 0|QR_K^\dagger|0\rangle + \sum_K\sum_I C_I d_K\langle 0|S_I QR_K^\dagger|0\rangle \\ + \sum_I\sum_K\sum_J C_I d_K C_J\langle 0|S_I QR_K^\dagger S_J^\dagger|0\rangle,\end{aligned} \tag{21}$$

where we have neglected the term between unlinked terms. Note that the overlap between ground and excited states vanish to a good approximation since $\mathcal{S}_{Kg} \simeq \sum_I C_I\langle 0|S_I \cdot R_K^\dagger|0\rangle$.

4. Application to Water

We have applied here the SAC and SAC-CI theories to the ground and Rydberg excited states of water and its cations and anions. We have used the following two kinds of basis set. Basis I includes $(9s6p/4s)$ GTO's [15] contracted to a $[3s2p/2s]$ set [16], diffuse s and p GTO's on oxygen with $\zeta_s = 0.032$ and $\zeta_p = 0.028$ as Rydberg AO's, and further diffuse p ($\zeta = 0.059$) GTO's on oxygen as basis for electron attached states [16]. Basis II includes Bases I and d-polarization functions on oxygen with $\zeta = 0.85$ [16]. The calculation was carried out for the equilibrium geometry (OH = 1.8111 a.u., $\angle$HOH = 104.45°). The molecule is on the yz plane with the z axis being the C_2 axis.

In the linked terms of Eqs. (2) and (7), we have included all single and double excitations from the reference $|0\rangle$, though the $1s$ AO of oxygen was treated as frozen. The number of linked terms (size of the matrices involved in the calculation) are summarized in Table I. In the unlinked terms, we have included only such double excitation operators $S_I^\dagger$ that have the CI coefficients larger than 0.1×10^{-2} for the ground state. This selects 472 operators from 533 possible ones for Basis I and 835 from 1010 possible ones for Basis II. If the basic assumption in the cluster expansion is accurate, the present results for the singlet A_1 states may be compared roughly with the CI calculations of the order of $556 + (472)^2 = 223{,}340$ configurations for the ground state and $555 + 22\times 472 = 10{,}939$ configurations for the $^1A_1$ excited states, where we have 22 single excitation operators. Similar estimates also hold for other states. Though this is an overestimate since it includes repetitions and vanishing configurations, this roughly shows the merit of the present approach since one of the difficulties in the conventional CI lies in the diagonalization and treatment of very large Hamiltonian matrices.

Table II shows the correlation energy for the ground state of water. It includes the CI results of Winter, Goddard, and Bobrowicz [17], whose basis set is close to Basis I, and of Buenker and Peyerimhoff [18] whose basis set is close to Basis

TABLE I. Number of independent variables for the calculation of water.[a]

State	Basis I			Basis II		
	SE	DE	Total	SE	DE	Total
ground(SAC)						
$^1A_1$	22	533	556	30	1009	1040
excited(SAC-CI)						
$^1A_1$	22	533	555	30	1009	1039
$^3A_1$	22	634	656	30	1245	1275
$^1A_2$	8	397	405	12	797	809
$^3A_2$	8	558	566	12	1117	1129
$^1B_1$	13	422	435	19	846	865
$^3B_1$	13	576	589	19	1156	1175
$^1B_2$	17	478	495	23	918	941
$^3B_2$	17	632	649	23	1228	1251
cation(SAC-CI)						
$^2A_1$	2	74	76			
$^2B_1$	1	56	57			
$^2B_2$	1	64	65			
anion(SAC-CI)						
$^2A_1$	7	278	285			
$^2B_1$	3	197	200			
$^2B_2$	5	253	258			

[a] SE: single excitation; DE: double excitation.

TABLE II. Correlation energy for ground state of water.

Method	Present		Winter Goddard Bobrowicz[a]	Buenker Peyerimhoff[b]	Bartlett Purvis[c]
	Basis I	Basis II			
Hartree-Fock	-76.01195	-76.03731	-76.01114	-76.03107	-76.04784
(1+2) CI	-0.12840	-0.18799	-0.12755	-0.1575	-0.24111
SAC-V	-0.13285	-0.19412			
SAC-MET	-0.13422	-0.19619			-0.24666
DQ-MBPT(4)[c]					-0.24651

[a] Reference 17.
[b] Reference 18.
[c] Reference 20. In Ref. 20, the details of the calculational methods are different from the present ones.

II. The energy lowering due to the inclusion of unlinked terms is 0.006 a.u. for Basis I and 0.008 a.u. for Basis II. A detailed comparison of the SAC results of water with the CI results including single, double, triple, and quadruple excitations reported by Hosteny et al. [19] was given previously [9]. There, we have used the common basis set. Recently, Bartlett and Purvis [20] gave a comparison between the results of the coupled cluster and many-body perturbation theories [CCD and DQ-MBPT(4), respectively] for the ground state of water. Table II includes some of their results. Though the basis set and the details of the calculational method are different from the present ones, similar improvements were obtained by both CCD and DQ-MBPT(4) calculations.

Table III shows the vertical excitation energies of water for various Rydberg excitations. It compares the present results with the experimental values and

TABLE III. Vertical excitation energy of water (eV).

State	Orbital picture	Winter Goddard Bobrowicz[a] CI	Buenker Peyerimhoff[b] CI	Yeager McKoy Segal[c] EOM	SAC-CI-V Basis I	SAC-CI-V Basis II	SAC-CI-NV Basis I	SAC-CI-NV Basis II	Exptl.[a]
$1\,^3B_1$	$1b_1 \rightarrow 3s\ a_1$	7.26	6.90	6.89	6.48	6.59	6.80	6.91	7.0, 7.2
$1\,^1B_1$		7.61	7.30	7.22	6.93	7.03	7.25	7.49	7.4, 7.49 $\tilde{A}$
$1\,^3A_2$	$1b_1 \rightarrow 3p_y b_2$	9.34	9.04	8.97	8.71	8.73	9.02	8.84	8.9, 9.1, 9.2
$1\,^1A_2$		9.46	9.20	9.02	8.89	8.90	9.21	9.37	9.1
$2\,^3B_1$	$1b_1 \rightarrow 3p_z a_1$	9.99	9.84	9.47	9.53	9.47	9.86	9.58	9.98
$2\,^1B_1$		10.06	9.90	9.48	9.60	9.54	9.93	10.02	10.01, 9.996 $\tilde{C}$
$3\,^3A_1$	$1b_1 \rightarrow 3p_x b_1$	9.74	9.65	9.39	9.23	9.24	9.56	9.35	9.81, 9.80
$3\,^1A_1$	d	10.16	10.32	9.61	9.64	9.72	9.98	10.20	10.17,10.14 $\tilde{D}$
$2\,^3A_1$	$3a_1 \rightarrow 3s\ a_1$	9.44	9.01	9.34	8.67	9.00	8.99	9.10	9.3
$2\,^1A_1$	e	9.82	9.80	9.54	9.09	9.40	9.41	9.86	9.67, 9.73 $\tilde{B}$
$1\,^3B_2$	$3a_1 \rightarrow 3p_y b_2$	11.11	10.99	11.47	10.69	11.02	11.01	11.12	
$1\,^1B_2$		11.47	11.21	11.40	10.99	11.31	11.31	11.78	
$3\,^3B_1$	$3a_1 \rightarrow 3p_x b_1$[f]	11.87	11.68	---	11.40	11.69	11.73	11.80	
$3\,^1B_1$		11.92	11.72	---	11.47	11.82	11.80	12.29	11.91
$4\,^3A_1$	$3a_1 \rightarrow 3p_z a_1$	11.77	11.53	11.69	11.27	11.58	11.61	11.69	
$4\,^1A_1$		12.08	---	11.82	11.58	11.89	11.91	---	

[a] Reference 17.
[b] Reference 18.
[c] Reference 21.
[d] Leading configurations are $0.73(1b_1 \rightarrow 3p_x b_1) - 0.51(3a_1 \rightarrow 3sa_1)$.
[e] Leading configurations are $0.62(3a_1 \rightarrow 3sa_1) + 0.59(1b_1 \rightarrow 3p_x b_1)$.
[f] Leading configurations are $0.60(3a_1 \rightarrow 3p_x b_1) + 0.50(1b_1 \rightarrow ap_z a_1) + 0.44[1b_1 \rightarrow \sigma^*(\mathrm{OH})]$.

those obtained by the CI methods [17, 18] and equation-of-motion method [21]. Though the numbers of the independent variables included in the SAC-CI methods are smaller than those in the CI calculations, the present results show good agreement with experiments. Between the SAC-CI-V and SAC-CI-NV methods, the latter consistently gives better agreement with experiments. The former results are lower than the latter and the experimental values. Between Basis I and Basis II, the latter gives higher excitation energies than the former except for the $1\,^3A_2$, $2\,^3B_1$, and $3\,^3A_1$ states. This is due to the fact that with the

inclusion of the d-polarization functions (Basis II), the ground state is lowered more than the excited states, as expected.

The orbital picture given in the second column of Table III shows a leading configuration for the excited state. However, for the $2\,^1A_1$ and $3\,^1A_1$ states ($\tilde{B}$ and $\tilde{D}$ bands) and for the $3\,^3B_1$ state, the leading configurations are not unique but a mixture of different single excitations. The main configurations are shown in footnotes d–f of Table III. Interestingly, however, the corresponding triplet ($2\,^3A_1$ and $3\,^3A_1$) and singlet ($3\,^1B_1$) states are represented well by a single leading configuration as shown in Table III. Therefore, for these states the singlet and triplet pairs may have very different properties and geometries.

TABLE IV. Oscillator strength for singlet excitations of water (a.u.).

State	Orbital Picture	Buenker Peyerimhoff[a] CI	Yeager McKoy[b] Segal EOM	SAC-CI[c] V	SAC-CI[c] NV	Exptl.[a]
$1\,^1B_1$	$1b_1 \rightarrow 3s\ a_1$	0.0592	0.05	0.0601	0.0600	0.060 ± 0.006
$1\,^1A_2$	$1b_1 \rightarrow 3p_y b_2$	0.0	0.0	0.0	0.0	
$2\,^1B_1$	$1b_1 \rightarrow 3p_z a_1$	0.0120	0.006	0.0120	0.0116	
$3\,^1A_1$	$(1b_1 \rightarrow 3p_x b_1)$	0.0130	0.02	0.0353	0.0346	
$2\,^1A_1$	$(3a_1 \rightarrow 3s\ a_1)$	0.0689	0.06	0.0704	0.0680	0.05
$1\,^1B_2$	$3a_1 \rightarrow 3p_y b_2$	0.0035	---	0.0132	0.0194	
$3\,^1B_1$	$3a_1 \rightarrow 3p_x b_1$	0.0002	---	2.3×10^{-6}	5.5×10^{-6}	

[a] Reference 18.
[b] Reference 21.
[c] Calculated with Basis II.
[d] See footnotes d–f of Table III.

Table IV shows the oscillator strength for the singlet excitations of water. They were obtained from transition moment by

$$\mathbf{f} = \tfrac{2}{3}\Delta E |\langle \mathbf{r} \rangle_{ge}|^2. \tag{22}$$

For the lowest $^1B_1$ and $^1A_1$ transitions, the experimental values are known. The present results agree well with them.

Table V shows dipole moments and second moments for the ground and excited states of water. The calculated dipole moment for the ground state (−0.897 a.u.) is larger than the experimental value (−0.7296 a.u.). By excitations the dipole moments vary largely: the excitation to $3s$ AO shifts electron density towards hydrogens and the excitation to $3p_z$ AO shifts electron density outside of oxygen. The diffuse nature of the excited state is seen from the second moments centered at oxygen. Generally speaking, the diffuseness increases with increasing excitation energy. Between the singlet and triplet pairs, the singlet state is more

TABLE V. Dipole moment and second moment of water (a.u.).[a]

State	Orbital picture	Dipole moment $\langle z \rangle$	Second moment (electronic)[b] $\langle x^2 \rangle$	$\langle y^2 \rangle$	$\langle z^2 \rangle$
1^1A_1	ground state	-0.897[c]	6.0	7.5	7.0
1^3B_1	$1b_1 \rightarrow 3sa_1$	0.482	9.8	13.3	13.3
1^1B_1		0.615	10.4	13.7	14.1
1^3A_2	$1b_1 \rightarrow 3p_yb_2$	-0.664	10.4	26.4	12.9
1^1A_2		-0.757	11.2	28.5	13.5
2^3B_1	$1b_1 \rightarrow 3p_za_1$	-3.045	9.3	13.4	27.9
2^1B_1		-3.115	13.5	15.8	31.7
3^3A_1	$1b_1 \rightarrow 3p_xb_1$	-1.066	29.2	14.8	14.3
3^1A_1	d	-0.552	25.6	15.6	14.9
2^3A_1	$3a_1 \rightarrow 3sa_1$	0.596	10.9	13.1	12.3
2^1A_1	d	-0.046	20.0	14.5	14.0
1^3B_2	$3a_1 \rightarrow 3p_yb_2$	-0.339	11.0	25.1	11.8
1^1B_2		-0.619	12.6	29.5	12.9
3^3B_1	$3a_1 \rightarrow 3p_xb_1$[d]	0.163	21.1	15.4	18.7
3^1B_1		-0.870	32.7	15.5	14.3
4^3A_1	$3a_1 \rightarrow 3p_za_1$	-2.899	14.1	14.8	27.5
4^1A_1		-2.489	15.0	16.0	32.5

[a] Results of SAC and SAC-CI-V calculations with Basis II.
[b] Centered at oxygen.
[c] Experimental value −0.7296 a.u.
[d] Leading configurations are not single but mixtures of different single excitations (see footnotes d–f of Table III).

diffuse than triplet. For the excitation into $3p_\alpha$ orbital, the second moment increases especially in α direction. Interestingly, these properties for the $2\,^1A_1$, $3\,^1A_1$, and $3\,^3B_1$ states cannot be understood without the knowledge that the leading configurations of these states are not unique but mixtures of different single excitations (see the footnotes of Table III). For these states, the singlet and triplet pairs have very different values for dipole moment and second moment.

Table VI shows the ionization potentials of water obtained by various methods. The best theoretical result in Table VI is the extensive CI result of Meyer with the basis set including even f-polarization functions [22]. The present SAC-CI result was obtained with Basis I. Though the numbers of the independent variables are very small for cations as shown in Table I, the present result compares relatively well with experiment. In comparison with the ΔSCF values, an inclusion of electron correlation certainly improves the agreement. Between the SAC-CI-V and SAC-CI-NV methods, the former gives lower values as for the

TABLE VI. Ionization potential of water (eV).

State	Orbital picture	Koopmans	ΔSCF[a]	Meyer[a] Extensive CI	Buenker Peyerimhoff[b] CI	SAC-CI-V	SAC-CI-NV	Exptl.[a]
$^2B_1$	$b_1(\pi) \to \infty$	13.94	11.10	12.34	12.13	11.84	12.17	12.61
$^2A_1$	$a_1(n) \to \infty$	15.60	13.32	14.54	14.06	13.84	14.17	14.73
$^2B_2$	$b_2(b) \to \infty$	19.70	17.59	18.73	---	18.73	19.07	18.55
$^2A_1$	$a_1(2s) \to \infty$ [c]	37.25	34.22	32.25	---	33.29	33.48	32.19

[a] Reference 22.
[b] Reference 18.
[c] This configuration is strongly mixed with the doubly excited configurations which represent an ionization of a $b_1(\pi)$ electron with a simultaneous excitation of the other $b_1(\pi)$ electron (see text).

excitation energies shown in Table III. The ionization from $2s$ orbital ($^2A_1$) is found to mix strongly with the double excitation (shake-up) process which is an ionization of a $b_1(\pi)$ electron with a simultaneous excitation of the other $b_1(\pi)$ electron. This mixing accounts for the satellite bands for the ESCA spectrum [23]. However, the present result is not accurate enough for these double excitation processes because we did not include in the unlinked terms double excitations from such shake up configurations (quadruple excitations from the reference $|0\rangle$). This seems to be a reason for the relatively worse result for the ionization from the $a_1(2s)$ orbital.

Table VII shows the results for the electron affinity of water. The experimental values seem not to exist to the best of our knowledges, but it is certain that the electron affinity of water is negative [24]. In the electron transmission spectroscopy by Sanche and Schulz [24], no resonant structure was found in the range 0–7 eV. However, the present results predict electron attached states at 1–2 eV higher than the ground state if an electron is trapped in the $3s$ or $3p$ Rydberg AO's and at 5–7 eV if an electron is trapped in the anionic AO's around oxygen.

TABLE VII. Electron affinity of water (eV).

State	Orbital picture	Koopmans	ΔSCF	SAC-CI-V	SAC-CI-NV
$^2A_1$	$\infty \to a_1(3s)$	-1.23	-1.21	-0.59	-1.13
$^2B_2$	$\infty \to b_2(3p_y)$	-1.57	-1.57	-1.00	-1.55
$^2B_1$	$\infty \to b_1(3p_\pi)$	-1.75	-1.75	-1.21	-1.76
$^2A_1$	$\infty \to a_1(3p_z)$	-2.03		-1.42	-1.97
$^2B_2$	$\infty \to b_2(ap_y)$	-6.51		-5.78	-6.29
$^2A_1$	$\infty \to a_1(ap_z)$	-6.81		-6.16	-6.66
$^2B_1$	$\infty \to b_1(ap_\pi)$	-7.09		-6.59	-7.10

(In the second column showing the orbital picture, the notation ap_y, etc., show the MO's the main components of which are the diffuse anionic p AO's with the exponent $\zeta = 0.059$.) The experiment seems to suggest that these electron attached states are too short-lived to be detected.

The electron correlations in these electron attached states are very similar to that in the ground state. The SAC-CI-NV results are very close to the ΔSCF results and even to the Koopmans values. This is expected since the attached electron lies in a very diffuse orbital and has very little chance to collide with the valence electrons.

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