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Feature Article

ELECTRONIC STRUCTURES OF GROUND, EXCITED, IONIZED AND ANION STATES STUDIED BY THE SAC/SAC-CI THEORY

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The SAC (symmetry adapted cluster) and SAC-CI theories and their applications for studying electronic structures and spectroscopic properties of the ground, excited, ionized, and anion states of molecules are reviewed, and the usefulness of the SAC/SAC-CI method is confirmed in a wide field of excited-state chemistry. The SAC theory is based on the symmetry adapted formalism of the cluster expansion of the wave function. It gives not only an accurate correlated ground state, but also a functional space which spans excited, ionized and anion states. The SAC-CI theory uses this functional space for describing these states. Program system SAC85 is coded for the SAC/SAC-CI calculations of singlet (closed shell) ground states, singlet and triplet excited states, and doublet ionized and electron attached states. Extensions to higher spin-multiplet states have recently been done. When Hartree–Fock dominant state is missing, the SAC theory is not applicable, and then, the exponentially generated wave function (EGWF) theory is useful.

Applications of the SAC/SAC-CI method are reviewed. First, its results are compared with the full CI results, the exact solutions, and shown to be quite accurate, though the solution is much easier than those in the full CI and conventional CI methods. After giving some typical results for the valence and Rydberg excited states, we show the results for the excited states of conjugated molecules; butadiene and benzene, in particular. We have overcome the difficulty in describing the ionic V states of conjugated molecules. For *trans*-butadiene, for example, the error has been reduced from 1.75 eV to 0.47 eV. For ionizations, the SAC/SAC-CI method is useful not only for ordinary outer valence ionizations, which are one-electron processes, but also for inner valence shake-up ionizations, which are two-electron processes relative to the Hartree–Fock configuration. Neutral doublet radicals are described as ionized (or electron attached) states of closed-shell anion (or cation). We can also calculate excited states, ionized and shake-up states of doublet radicals. Fermi-contact hyperfine splitting constants of doublet radicals, which strongly depend on the quality of the wave function, are shown to be well reproduced by the SAC-CI method. Potential energy curves of the ground and excited states are calculated by the SAC/SAC-CI method. Van der Waals complexes are good subjects since the Hartree–Fock configuration is dominant throughout the ground state interactions. The SAC/SAC-CI method is also useful for studying surface-molecule interactions, since on the surface there are many lower electronic states and the catalytically active state is not necessarily the ground state. Further, electron transfer between surface and admolecule is sometimes of crucial importance and this is expressed by ionic and/or electron attached state. Needless to say, electron correlation is quite important for systems involving transition metals, bond fissions and formations. Finally, concluding remarks are given.

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Introduction

Every molecule has a large number of electronically excited states, and they show behaviors entirely different from those of the ground state [1 – 4]. Differences in thermal and photochemical reactions are one such example. This implies an existencee of a broad plain of chemistry to be cultivated. Recently, chemistry and physics of excited states have been much advanced, as laser and synchrotron orbital radiation techniques are developed. Multi-photon absorption spectroscopy has extended observable regions of excited and ionized states [5]. Since excited states are very short-lived species, it is difficult to elucidate their properties and dynamics only by experimental means. Reliable theories for excited states are quite useful not only for understanding what are observed experimentally [6], but also for designing experiments which cleverly utilize the characteristic aspects of excited states. However, until recently, *ab initio* theories could not even explain quantitatively the valence $\pi - \pi^*$ excitations of conjugated molecules, such as butadiene, benzene, etc. We have to overcome this difficulty for developing reliable theories of excited states [7].

Ionized states are produced by light or electron beam bombardment. Ionization spectra thus obtained give information on both ground and excited states of ionized molecules [8 – 10]. Geometries and molecular vibrations are, for example, elucidated from such spectra. In a deeper region of ionizations, we sometimes observe a larger number of peaks than expected from the number of occupied molecular orbitals. Satellite peaks, or shake-up peaks are such examples. Obviously, electron correlations are essentially important for theoretically describing such ionizations [11].

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Radicals, which have open-shell ground states, show remarkable properties and reactivities mainly due to an existence of unpaired electrons. Recent advances in experiments have made it possible to observe excited and ionized states of these short-lived radicals. Shake-up ionization spectra of radicals are particularly interesting [12], because ionization-excitation processes in neutrals radical may produce two electron excited states of closed-shell cations [13], which are seldom observed for ordinary molecules. Magnetic properties also originate from the existence of unpaired electrons. Fermi-contact hyperfine splitting constants observed by ESR and microwave spectroscopies are the properties which require a good theory for reliable calculations [14].

Potential energy curves of molecules in ground, excited, and ionized states give basic and useful information for investigating geometries, vibrations, absorptions, emissions, reactions, energy transfers, relaxations, etc. Recently, much spectroscopic attention has been paid for the dynamics of Van der Waals complexes. They give models for investigating solute-solvent interactions to be studied in the same accuracy as that for isolated molecules. Potential energy curves for molecules on metal clusters and surfaces are valuable for elucidating electronic processes and mechanisms involved in catalytic processes.

The purpose of the theory described here is to give reliable theoretical means for investigating these phenomena. We first describe ground states in a considerable accuracy, and then calculate excited states, ionized states, and anion states in the same accuracy. If unbalanced, we can not expect a reliability in difference properties such as excitation energy. A necessary condition for the consistency between the ground and excited states is given by the quantum theory as [15]

$$<\Psi_g|\Psi_e> = 0, \quad <\Psi_g|H|\Psi_e> = 0\,, \tag{1}$$

where Ψ_g and Ψ_e denote the wave functions of the ground and excited states, respectively, and H the Hamiltonian of the system. The theory we review here satisfies this condition.

The reliability of a theory is most easily checked by comparing with the exact solutions. Within a limited space of a basis set, such solutions are given by the full CI method. A problem of the full CI method is that the solutions are possible only for small molecules, so that this method is impractical for most chemical problems.

We review here the symmetry adapted cluster (SAC) expansion theory [16,17] for the ground state and the SAC-CI theory [17,18] for the excited, ionized, and electron attached states. The theoretical relation of these two theories has some resemblance with that between Hartree–Fock and single excitation (SE) CI theories [13]. The SAC/SAC-CI theories has been applied to spectroscopies of various kinds of excited and ionized states, doublet radicals, and surface electronic processes, some of which are reviewed in this article.

Hartree – Fock and SECI theories as reference theories

We first summarize, for comparison, some theoretical aspects of the Hartree – Fock (HF) and single excitation (SE) CI theories for ground and excited states, respectively. The Brillouin theorem is a key theorem, which interconnects these two theories. We consider, for a while, a closed-shell ground state with $2n$ electron, and the excited and ionized states produced therefrom.

The HF molecular orbital theory is a good starting approximation for the ground state. It assumes single determinant wave function,

$$\Psi_g^{HF} = ||\varphi_1\alpha\varphi_1\beta \ldots \varphi_i\alpha\varphi_i\beta \ldots \varphi_n\alpha\varphi_n\beta||\,, \tag{2}$$

where molecular orbitals φ_i are the solutions of the Fock equation,

$$F\varphi_i = \varepsilon_i\varphi_i \tag{3}$$

with ε_i being orbital energies. Generally speaking, the HF model is appropriate for molecules near equilibrium geometry.

An important property of the HF wave function is described by the Brillouin theorem,

$$<\Psi_g^{HF}|H|\Phi_i^a> = 0\,, \tag{4a}$$

and the orthogonality,

$$<\Psi_g^{HF}|\Phi_i^a> = 0\,, \tag{4b}$$

where Φ_i^a is a singly excited configuration given by

$$\Phi_i^a = ||\varphi_1\alpha\varphi_1\beta \ldots \varphi_i\varphi_a(\alpha\beta - \beta\alpha)/2^{1/2} \ldots \varphi_n\alpha\varphi_n\beta||\,. \tag{5}$$

It is easy to show that the Brillouin theorem is theoretically equivalent with the HF equation given by Eq. (3).

The meaning of Eq. (4) is that if Ψ^{HF} is a good approximation of the ground state Ψ_g, the singly excited configurations $\{\Psi_i^a\}$ span a good basis for excited states Ψ_e. So, we describe excited state by a linear combination of Φ_i^a, i.e.,

$$\Psi_e^{SECI} = \Sigma_i\Sigma_a\, C_i^a\Phi_i^a\,, \tag{6}$$

which is the SECI method. The coefficients C_i^a are determined as a solution of the Schrödinger equation within the space of $\{\Phi_i^a\}$, i.e.,

$$<\Phi_i^a|\,H-E\,|\,\Psi_e^{SECI}> = 0\,, \tag{7}$$

which is a secular equation. The solution automatically satisfies

$$<\Psi_g^{HF}\,|\,\Psi_e^{SECI}> = 0\,, \qquad <\Psi_g^{HF}\,|H|\,\Psi_e^{SECI}> = 0\,, \tag{8}$$

as a result of the Brillouin theorem. Different solutions of Eq. (7) also satisfy

$$<\Psi_e^{SECI}|\Psi_f^{SECI}> = 0\,, \quad <\Psi_e^{SECI}\,|H|\,\Psi_f^{SECI}> = 0\,. \tag{9}$$

Eq. (8) shows that the HF and SECI wave functions satisfy mutually correct relations given by Eq. (1), so that we expect that the SECI method may describe the excited states as well as the HF method does the ground state.

Similar relations hold for ionized states. In the HF model, the ionization energy from the orbital φ_i is written by the Koopmans' relation,

$$Ip(i) = -\,\varepsilon_i\,. \tag{10}$$

The corresponding ionized state is written by

$$\Psi_i = ||\varphi_1\alpha\varphi_1\beta \ldots \varphi_i\alpha \ldots \varphi_n\alpha\varphi_n\beta||\,. \tag{11}$$

It is easy to show the relations,

$$<\Psi_i\,|\,\Psi_g^{HF}> = 0\,, \quad <\Psi_i\,|H|\,\Psi_g^{HF}> = 0, \tag{12}$$

and the relations,

$$<\Psi_i\,|\,\Psi_j> = \delta_{ij}\,, \quad <\Psi_i\,|H|\,\Psi_j> = E_i\delta_{ij}\,. \tag{13}$$

Eq. (12) corresponds to Eq. (4), and Eq. (13) means that the secular equation, Eq. (7) is already diagonal for the ionized configurations Ψ_i. Thus, the Koopmans' relation is valid up to SECI. Similar relations hold for electron attached states.

Theoretical simplicity and beauty of the HF and SECI theories are valuable, but this does not necessarily mean that these methods give quantitatively reliable results for the ground, excited, and ionized states. Later, in Tables XI and XV, we will compare the excitation and ionization energies of CO_2 calculated by various methods with experiments. The agreements are poor for the SECI and Koopmans methods. Thus, eletron correlations are important for describing excitation and ionization properties.

We note that the theoretical consistency of the HF/SECI method is valid only up to single excitations. The Brillouin theorem means that the first correction to the HF wave function is an inclusion of doubly excited configurations. When such configurations are included (e.g., as in singles and doubles (SD) CI), the Brillouin theorem is no longer satisfied. It is hoped to extend the simplicity and beauty of the HF/SECI theories up to the levels including electron correlations. We will show that these merits are kept, in the SAC/SAC-CI theories, at any stage up to the exact limit.

SAC theory for ground state

SAC is an abbreviation for the symmetry adapted cluster, the meaning of which will become clear later. This theory belongs to the cluster expansion approach for the exact wave function. The idea originates from the statistical theory for interacting systems [19]. It was developed, among others, by Coester [20], Kümmel [21], Sinanoglu [22], Primas [23], Cizek [24], and Paldus [25].

Electron correlation is defined on the basis of the HF theory as

$$E^{\mathrm{corr}} = E^{\mathrm{exact}} - E^{\mathrm{HF}}, \tag{14a}$$

$$\mathrm{X}^{\mathrm{corr}} = \Psi^{\mathrm{exact}} - \Psi^{\mathrm{HF}}, \tag{14b}$$

where 'exact' stands for the exact solution of the non-relativistic Schrödinger equation. Since the HF model is an independent particle model, electron correlations represent mainly the collisions of electrons scattering into unoccupied orbitals. We introduce an excitation operator $T_I{}^\dagger$ which represents such a scattering. For example, a collision of two electrons belonging to the occupied orbital φ_i, resulting in the scattering into the unoccupied orbital φ_a, is represented by the excitation operator $T_{ii}{}^{aa}$,

$$T_{ii}{}^{aa} = a_{a\alpha}{}^\dagger \, a_{a\beta}{}^\dagger \, a_{i\alpha} \, a_{i\beta}\,, \tag{15}$$

$$T_{ii}{}^{aa} \mid 0> = \mid\mid \varphi_1\alpha\varphi_1\beta \ldots \varphi_a\alpha\varphi_a\beta \ldots \varphi_n\alpha\varphi_n\beta \mid\mid, \tag{16}$$

where $\mid 0 > \; = \Psi_g{}^{\mathrm{HF}}$ given by Eq. (2).

Configuration interaction (CI) method is one of the most popular methods for including electron correlations. This method is based on the expansion theorem [26], and the correlated wave function is written by

$$\Psi^{\mathrm{CI}} = B_0 \mid 0 > + \Sigma_I B_I T_I{}^\dagger \mid 0 >, \tag{17}$$

where B_I are expansion coefficients. This method is simple and exact, but is usually slowly converging, especially for excited states. The dimension of configurations easily reaches to the order of $10^5 \approx 10^8$, though many efficient algorithms for handling such large matrices are proposed [27–29]. Further, it is difficult to extract a physical meaning from such a large number of configurations. It is also difficult to solve many lower solutions of such a large matrix [30].

The main factor of electron correlations is a collision of two electrons. In many electron systems, however, there is a chance for three, four and more electrons to collide each other. However, the probability for four electrons, for example, to actually collide at the same time and place is very small. Four electron collisions actually important are the products of pair collisions occuring at different places of a molecule. This is because the fluctuation potential for the electron correlation is very short range in nature, as Sinanoglu has pointed out very clearly [22]. When we introduce a sum of the excitation operators as

$$T = \Sigma_I C_I T_I^\dagger , \tag{18}$$

the wave function including higher-order collisional effects is written as

$$\Psi_g = (1 + T + (1/2) T^2 + (1/6) T^3 + \ldots) |0> , \tag{19}$$

where the terms T^2, T^3, etc., represent two pair collisions, three pair collisions, etc., and the factors 1/2, 1/6, etc., are due to the indistinguishability of pair collisions. Eq. (19) is more compactly written as

$$\Psi_g = \exp (T) |0> , \tag{20}$$

which is the cluster expansion. The suffix g again stands for the ground state. The theory based on this expansion is called coupled cluster (CC) theory [24]. Hereafter, we call the term, $(1+T)|0>)$ as linked term and the term, $((1/2)T^2+(1/6)T^3+\ldots)|0>)$ as unlinked term.

In the above formulation, we have introduced the operators $T_I^\dagger$ as representing two electron excitations (pair collisions). However, generally speaking, this is just an example, and we may take any operators physically important. An important example is to choose T as the sum of all single excitation operators.

$$T_{(1)} = \Sigma_i^{\mathrm{occ}} \Sigma_a^{\mathrm{unocc}} C_i^a a_a^\dagger a_i , \tag{21}$$

Then, we get Thouless theorem [31], i.e.,

$$\Psi^{SD} = \mathfrak{R} \exp(T^{(1)}) \Phi^{SD} , \tag{22}$$

where Φ^{SD} and Ψ^{SD} are different single determinants, $\mathfrak{R}$ a renormalization constant. This theorem states that the transformation of a single determinant to another one is expressed by the operator $\mathfrak{R}$ $\exp(T^{(1)})$: the cluster expansion includes the self-consistency of orbitals.

We note that for open-shell systems, the single determinant Ψ^{SD} on the left hand side of Eq. (22) is not a restricted determinant [32], but an unrestricted one which is not an eigen function of the spin-squared operator S^2. This implies that generally the wave function of the CC theory given by Eq. (20) is not spin-adapted. In a linear expansion like CI, the solution of the secular equation is always symmetry-adapted, irrespective of the choice of the excited configurations, because the Hamiltonian is totally symmetric. However, this is not the case for non-linear expansions like the cluster expansion. Further, as explained below, the coupled cluster expansion may involve a larger number of variables than that necessary for describing the state [16].

These difficulties are circumbented by choosing the excitation operators to be symmetry adapted. We define an excitation operator $S_I^\dagger$ to be symmetry adapted when the configuration $S_I^\dagger\ |0>$ is symmetry adapted. For totally symmetric singlet states, the symmetry adapted cluster (SAC) expansion is defined by [16,17]

$$\Psi_g^{SAC} = \exp(S)\ |0> , \tag{23}$$

where
$$S = \Sigma_I C_I S_I^\dagger . \tag{24}$$

Since $S_I^\dagger$ is totally symmetric, the unlinked terms of Eq. (23) are also totally symmetric. For higher symmetries, we need a symmetry projector (Q) as

$$\Psi_g^{SAC} = Q \exp(S)\ |0> = [1 + S + Q((1/2)S^2 + (1/6)S^3 + ...)]\ |0>, \tag{25}$$

where $|0>$ is a restricted determinant and Q applies only to the unlinked terms, since the linked term is already symmetry adapted.

The SAC expansion defined by Eq. (23) is different from the CC expansion given by Eq. (20). Table I shows a schematic summary. Generally speaking, the number of unknown variables necessary for describing a state is the number of the symmetry adapted configurations belonging to this symmetry. The SAC expansion involves just such number of variables, since the unknown variables C_I are associated with the symmetry-adapted operators, $S_I^\dagger$ (Eq. (24)). In the expansion (20), on the other hand, the operator T is symmetry non-adapted so that it generally involves larger number of variables than necessary. For example, the particle-hole operators include singlet, triplet, etc., operators, though the state under consideration is singlet. Since the products of two triplet operators may give singlet ones, the unlinked terms may involve the unknown variables originating from the triplet space, and they are not projected out by the symmetry projector Q as applied in Eq. (25). Thus, the conventional cluster expansion may involve a larger number of variables than that necessary for describing the state. This may cause a difficulty in solution. In Table I, we have sketched the differences between the CC expansion given by Eq. (20) and the SAC expansion given by Eq. (23) or (25).

The Thouless' theorem suggests an existence of a new orbital theory based on the SAC expansion. We construct the wave function,

$$\Psi^{PO} = Q \exp(S^{(1)})\ \Phi^{RHF} , \tag{26}$$

using only single excitation SAC operator $S^{(1)}$. This is called pseudo-orbital theory [33,34]. Though the unrestricted HF (UHF) theory and the spin-extended HF (SEHF) theory are shown to be inadequate for the description of spin density distributions [35,36], the pseudo-orbital theory gives the spin densities which are free from such deficiencies [34,37]. However, later, it has been shown that electron correlations are very important for calculating reliable spin densities [38–40].

Table I

Schematic summary for the difference of the SAC expansion from the conventional cluster expansions[a]

Expansion	Linked term	Unlinked term [b]	Number of independent variables [c]	Symmetry [d]	With $T^{(1)}$ or $S^{(1)}$ alone [e]
$\exp(T)\Phi_0$	$T\Phi_0$	$T_I T_J \Phi_0$	Larger	Mixed	UHF
$Q\exp(T)\Phi_0$	$QT\Phi_0 \rightarrow S\Phi_0$	$QT_I T_J \Phi_0$	Larger!	Pure	SEHF
$Q\exp(S)\Phi_0$	$S\Phi_0$	$QS_I S_J \Phi_0$	Just as required	Pure	Pseudo-orbital

[a] The operators T_I are not symmetry-adapted, but the operators S_I are symmetry-adapted

[b] Only the second-order unlinked terms are given

[c] The number of the independent variables included in each expansion is compared with that necessary for the description of the system under consideration

[d] Symmetry of the total wavefunction

[e] This column gives the orbital theory which is *equivalent* with each cluster expansion including $T^{(1)}$ or $S^{(1)}$ alone. We assume that these cluster expansions are solved with the variational principle. SEHF stands for spin extended Hartree-Fock

We now consider the solution of the SAC theory. In the SAC expansion the unknown variables C_I are associated to the linked excitation operators $S_I^\dagger$, so that we require Schrödinger equation, $(H-E_g)\ |\Psi_g^{SAC}> = 0$, within the space of the linked configurations as

$$<0|H-E_g|\Psi_g^{SAC}> = 0\,, \tag{27a}$$

$$<0|S_I(H-E_g)\ |\Psi_g^{SAC}> = 0\,. \tag{27b}$$

We have the same number of equations as the number of the unknown variables. This solution is called non-variational solution [17].

The variational solution is obtained by applying the variational principle to the SAC wave function as [16,17]

$$<\Psi_g^{SAC}\ |\ H-E_g\ |\ \Psi_g^{SAC}> = 0\,, \tag{28a}$$

$$<\Psi_g^{SAC}\ |\ (H-E_g)\,S_I^\dagger\ |\ \Psi_g^{SAC}> = 0\,. \tag{28b}$$

This equation is valid only for the SAC expansion, but not for the CC expansion, because of the reasons summarized in Table I. Generally speaking, the variational solution is more difficult than the non-variational one, because the former involves the integrals between unlinked terms, but the latter does not. As long as the wave function itself is accurate, the difference between the variational and non-variational solutions should be small.

We note that Eq. (28b) is the generalized Brillouin theorem. In comparison with Eq. (4a), Ψ_g^{SAC} corresponds to Ψ_g^{HF} and $S_I^{\dagger}\ \Psi_g^{SAC}$ does to Φ_i^a. As the Brillouin theorem is a key equation in the HF/SECI theory, the generalized Brillouin theorem given by Eq. (28b) is a key equation in the theoretical framework of the SAC/SAC-CI theory. We will show this in the next section.

The SAC theory has the following properties. The first three are common to the CC theory.

(1) It effectively involves higher-order effects of electron collisions.

(2) It is size consistent [41] or size extensive [42], so that it correctly describes energy changes in dissociation processes such as $X_n \rightarrow nX$. This property is a direct consequence of the exponential ansatz, since

$$\exp(A)\,\exp(B) = \exp(A+B)\,, \tag{29}$$

when the operators A and B are commutable. This equation also implies that the correlations included in the cluster expansion is *separable* in the sense of Primas [23].

(3) It includes self-consistency. This property is best represented by the Thouless' theorem given by Eq. (22). It guarantees that the cluster expansion is independent of a choice of the reference orbitals, when we include all the single excitation operators.

(4) The SAC theory defines two spaces, one is the SAC wave function itself for the ground state Ψ_g^{SAC}, and the other is the functional space which spans the basis for excited states [18]. This property, which is explained in the next section, is valid only for the SAC theory, and is probably the most important property among others. The SAC-CI theory is based on this property as explained in the next section.

SAC-CI theory for excited, ionized and electron attached states

It is thought that the description of electron correlations in excited states is much more difficult than that in the ground state. Excited states are generally open shells and are not represented by a single Slater determinant. Many different states of many different symmetries are involved in excited states, which makes it difficult to suppose a single general theory in a useful framework. However, these are not the case in the SAC-CI theory. By using the SAC-CI method, we can easily calculate the correlated wave functions of the excited, ionized and anion states, as shown in this section.

We describe the electron correlations in the excited state on the basis of those in the ground state. Approximately speaking, excitations and ionizations involve only one or two electrons, and most other electrons lie in the same orbitals as in the ground state. Therefore, the electron correlations in the excited state should be compactly described by only adding some modifications to the ground-state electron correlations. We define excited functions $\{\Phi_K\}$ by

$$\Phi_K = \mathcal{P}\, S_K{}^{\dagger}\, \Psi_g{}^{SAC}\,, \tag{30}$$

where $\mathcal{P}$ is the operator which projects out the ground state wave function,

$$\mathcal{P} = 1 - |\,\Psi_g{}^{SAC}\!><\!\Psi_g{}^{SAC}\,|\,, \tag{31}$$

and $\{S_K{}^{\dagger}\}$ a set of excitation operators involving the excitations under consideration. From the generalized Brillouin theorem of the SAC theory, Eq. (28b), it is easily shown that the functions $\{\Phi_K\}$ satisfy

$$<\!\Phi_K|\Psi_g{}^{SAC}\!> = 0\,, \quad <\!\Phi_K\,|H|\,\Psi_g{}^{SAC}\!> = 0\,. \tag{32}$$

These equations imply, as Eq. (1) shows, that the set of the functions $\{\Phi_K\}$ spans the space for excited states. We therefore describe the excited state by a linear combination of the functions $\{\Phi_K\}$,

$$\Psi_e{}^{SAC\text{-}CI} = \Sigma_K\, d_K\, \Phi_K\,, \tag{33}$$

which is the SAC-CI theory [18].

Applying the variational principle for solving the unknown variables $\{d_K\}$, we obtain

$$<\!\Phi_K\,|H-E_e|\,\Psi_e{}^{SAC\text{-}CI}\!> = 0\,. \tag{34}$$

The SAC-CI wave function automatically satisfies the correct relations with the ground state,

$$\begin{gathered}<\!\Psi_g{}^{SAC}\,|\,\Psi_e{}^{SAC\text{-}CI}\!> = 0,\\ <\!\Psi_g{}^{SAC}\,|H|\,\Psi_e{}^{SAC\text{-}CI}\!> = 0\,,\end{gathered} \tag{35a}$$

and also with different excited states,

$$\begin{gathered}<\!\Psi_e{}^{SAC\text{-}CI}\,|\,\Psi_f{}^{SAC\text{-}CI}\!> = 0,\\ <\!\Psi_e{}^{SAC\text{-}CI}\,|H|\,\Psi_f{}^{SAC\text{-}CI}\!> = 0\,,\end{gathered} \tag{35b}$$

as the solutions of the common secular equation. Thus, the SAC-CI wave function satisfies the correct relations with the ground state and with the other excited states. This is very important when we consider the properties, like transitions, which interconnect different states.

In the above formulation, we have implicitly considered the excited states having the same symmetry as the ground state. However, the SAC-CI theory is also valid for the excited states having different symmetries (e.g., triplet), and for ionized and electron attached states [17]. We generalize Eq. (30) as

$$\Phi_K = \mathcal{P}\, R_K{}^{\dagger}\, \Psi_g{}^{SAC}\,, \tag{36}$$

where $\{R_K^\dagger\}$ represents a set of excitation, ionization, and/or electron attachment operators. In any cases, Eqs (32) - (35) are valid.

Though the above formulation of the SAC-CI theory is variational, non-variational formulation is also possible and has been given in Ref. [43]. The non-variational SAC-CI solution is obtained by projecting the Schrödinger equation onto the space of the linked configurations,

$$<0\ |R_K(H-E_e)|\ \Psi_e^{\text{SAC-CI}}> = 0\,. \tag{37}$$

Practically speaking, the non-variational solution is easier than the variational one by the reason similar to that stated for the SAC solution, but we have to diagonalize non-symmetric matrices. For calculations of large dimensions, we have prepared the algorithm of iterative diagonalization of non-symmetric matrices [44]. It is an extension of the Davidson's algorithm [45].

The SAC-CI wave function has the following structure. With a neglect of the projection operator in Eq. (30), the SAC-CI wave function is written as

$$\Psi_e^{\text{SAC-CI}} \cong \exp(\Sigma_I\, C_I S_I^\dagger)\ \Sigma_K\, d_K R_K^\dagger\ |\ 0>\ . \tag{38}$$

which has the structure of the multi-reference CI. The configurations $R_K^\dagger\ |0>$ represent the reference configurations and $\exp(\Sigma_I\ C_I S_I^\dagger)$ represents the excitations from these reference configurations. In the latter, we use the coefficients $\{C_I\}$ determined for the ground state, which is based on the transferability of electron correlations between the ground and excited states. In the SAC-CI method, the dimension is the number of the reference configurations which may be of the order of $10^3 - 10^4$. Therefore, in the SAC-CI method, there are almost no ambiguity in the choice of the 'main reference' configurations in contrast to the multi-reference CI method.

The SAC-CI theory has the following properties.

(1) It describes many different excited, ionized, and electron attached states, at the same time, in a similar accuracy.

(2) It is more rapidly convergent than an ordinary CI. It gives very accurate results, as shown below, with much smaller computational labors than CI.

(3) It is insensitive to the choice of the external parameters, like main reference configurations, configuration selection thresholds, etc.

These properties make the SAC-CI method very widely applicable and useful. Physically, they are due to the approximate transferability of electron correlations between ground and excited states.

There exists a beautiful theoretical similarity between the SAC/SAC-CI theory and the HF/SECI theory explained in the earlier section [13]. This is summarized schematically in Table II. For the ground state, the HF equation is just equivalent with the Brillouin theorem with respect to the *single* excitation operators $s_i^\dagger$, while the generalized Brillouin theorem of the SAC theory is valid for any excitation operators $S_I^\dagger$. In the HF/SECI method, the excited state is described by a linear combination of the singly excited configurations, $\psi_k = s_k^\dagger \Psi^{HF}$, which are orthogonal and Hamiltonian orthogonal to the HF ground state. In the SAC-CI theory, the excited state is described by a linear combinations of $\{\Phi_K\}$, which are orthogonal and Hamiltonian orthogonal to the SAC ground state. In the HF/SECI theory, the theoretical consistency is valid *only within single* excitations, but in the SAC-CI theory it is valid, in principle, *at any stage up to the exact limit.*

Table II

Analogy in the theoretical framework between HF/SECI theory and SAC/SAC-CI theory

	HF/SECI	SAC/SAC-CI
GROUND	HF HF eq. = Brillouin Theorem $< \Psi_g^{HF} \| H s_i^\dagger \| \Psi_g^{HF} > = 0$ $s_i^\dagger$; single excitation operator	SAC Generalized Brillouin Theorem $< \Psi_g^{SAC} \| (H-E_g) S_I^\dagger \| \Psi_g^{SAC} > = 0$ $S_I^\dagger$; general excitation operator
EXCITED	SECI $\psi_k = s_k^\dagger \Psi_g^{HF}$ $< \psi_k \| \Psi_g^{HF} > = 0$ $< \psi_k \| H \| \Psi_g^{HF} > = 0$ $\Psi_e^{SECI} = \Sigma_k d_k \psi_k$ theoretically consistent *only within single* excitations	SAC-CI $\Phi_K = P S_K^\dagger \Psi_g^{SAC}$ $< \Phi_K \| \Psi_g^{SAC} > = 0$ $< \Phi_K \| H \| \Psi_g^{SAC} > = 0$ $\Psi_e^{SAC\text{-}CI} = \Sigma_K d_K \Phi_K$ theoretically consistent *at any stage up to exact* limit
	$\Psi_e \cong$ single ψ_k "frozen-orbital approximation"	$\Psi_e \cong$ single Φ_K "frozen-correlation approximation"

In the framework of the HF theory, one often adopts a frozen-orbital approximation, in which an excited state is represented by a single function ψ_k. Similarly, we may approximate an excited state by a single function Φ_K. This approximation may be called 'frozen-orbital, frozen-correlation' approximation, in which a complete transferability of electron correlations between ground and excited states is further assumed.

As the HF theory for open-shells and excited states exists, the SAC theory is also applicable to open-shells [38] and excited states [46] and some applications have actually been reported. We expect accurate results, though the calculation is more time-consuming than the SAC-CI one.

As theories related to the SAC-CI theory, we refer to the theories presented independently by Paldus et al. [47], by Ohmine et al. [48] and by Mukherjee et al. [49]. Although the renormalized CI method of Ohmine et al. is not a cluster expansion theory and the linear responce approach of Mukherjee et al. is the theory for difference properties, these theories have some physical idea in common, namely, transferability of electron correlations between ground and excited states. However, these theories do not satisfy Eq. (32), which is a key formula for the SAC-CI theory as a theory for excited states. Therefore, they do not have a beautiful relations as those of the SAC/SAC-CI theory summarized in Table II. Furthermore, we have coded a general *ab initio* program for the SAC/SAC-CI calculations, called later as SAC85, and applied this method for solving many chemically interesting problems of the excited and ionized states.

Program system SAC85

Program system SAC85 is the program for calculating correlated closed-shell ground state by the SAC theory and the singlet and triplet excited states and doublet ionized and electron attached states by the SAC-CI theory [50]. We explain here the algorithms of calculations and the approximations introduced for making the calculations efficient [17,51–53]. Recently, we have extended the propgram to higher spin-multiplet states such as quartet, quintet, sixtet and septet states [54].

The program SAC85 is written in FORTRAN and run on the Fujitsu (Amdahl) MSP system and Hitachi VOS system, which are close to the IBM MVS system, and also on the UNIX system [50]. This program is released worldwide to any scientist.

SAC method

We include in the linked terms totally symmetric single and double excitation operators of the forms

single excitation, $$S_i^a = (a_{a\alpha}^\dagger a_{i\alpha} + a_{a\beta}^\dagger a_{i\beta})\, 2^{-1/2} \tag{39}$$

double excitation, $$S_{ij}^{ab} = S_i^a S_j^b\,, \tag{40}$$

and in the unlinked terms the products of only the double excitation operators, which are quadruple excitation operators,

quadruple excitation $$S_i^a\, S_j^b\, S_k^c\, S_l^d\,. \tag{41}$$

Triple excitations are known to be less important than quadruple excitations which represent simultaneous occurrences of two pair collisions. We use the suffices, *i, j, k, l* for occupied orbitals and *a, b, c, d* for unoccupied orbitals in the reference single determinant (usually HF one). We adopt non-variational solution, for simplicity, so that we need integrals only up to linked × unlinked, and we need not to consider the unlinked terms higher than the third order.

The number of the linked operators is reduced by the configuration selection technique [51] which is popular in the CI calculations [27]. This is effective for saving computer time. Namely,

(a) all single excitation operators are included.

(b) Double excitation operator $S_i^a S_j^b$ is included when its second-order contribution to the energy is larger than a given threshold λ_g; i.e.,

$$| \Delta E_s | > \lambda_g , \tag{42}$$

where $$\Delta E_s = | <0|H|\Phi_{ij}^{ab} > |^2 / (<\Phi_{ij}^{ab}|H|\Phi_{ij}^{ab}> - <0|H|0>) , \tag{43}$$

with $$\Phi_{ij}^{ab} = S_i^a S_j^b \ | 0> . \tag{44}$$

For the unlinked terms, we include the products of such linked operators whose coefficients in the SDCI are larger than a given threshold, ζ_g, which is usually $10^{-3} \sim 10^{-2}$. This approximation is effective in reducing the time necessary for integral evaluations.

The SAC solution is carried out by the non-variational procedure, though a code is given for an approximate variational procedure [50] which was less satisfactory than the non-variational one.

SAC-CI method

Expanding the SAC-CI wave function given by Eq. (33), we obtain

$$\Psi_e^{\text{SAC-CI}} = (\Sigma_K \, d_K R_K^\dagger + \Sigma_K \, \Sigma_I \, d_K C_I R_K^\dagger S_I^\dagger) \ |0> - \Sigma_K d_K \, \mathcal{S}_{Kg} \Psi_g^{\text{SAC}} + .. \tag{45}$$

where $$\mathcal{S}_{Kg} = <\Psi_g^{\text{SAC}} \, |R_K^\dagger \, \Psi_g^{\text{SAC}} > . \tag{46}$$

The expansion is terminated at the second order for the coefficients d_K and C_I. Since the integrals in the non-variational procedure are up to linked × unlinked, this is not an approximation. The operators $\{S_I^\dagger\}$ and their coefficients $\{C_I\}$ are transferred from the SAC calculation for the ground state. The SAC-CI operators $R_K^\dagger$ involve single and double excitation operators shown in Table III. Generally speaking, the excitation order of the operators $R_I^\dagger$ should be higher by one than the order of the real excitations to be described. For ordinary single excitation and ionization processes, this choice of the SAC-CI operators is sufficient. For multiple excitation processes, like shake-up ionizations, the inclusion of triple and/or quadruple excitations in the linked term is very effective [55].

Table III

Single and double excitation operators for singlet and triplet excitations, ionizations and electron attachment [a]

Type of excitation	Single excitation operator	Double excitation operator
Singlet excitation	$S_i^a = (a^\dagger_{a\alpha} a_{i\alpha} + a^\dagger_{a\beta} a_{i\beta}) / 2^{1/2}$	$S_i^a S_j^b$
Triplet excitation	$T_i^a = a^\dagger_{a\alpha} a_{i\beta}$	$T_i^a S_j^b$
Ionization	$I_i = a_{i\beta}$	$I_i S_j^a$
Electron attachment	$A^a = a^\dagger_{a\alpha}$	$A^a S_i^b$

[a] i, j and a, b denote occupied and unoccupied orbitals, respectively, in the reference Hartree-Fock configuration

For the unlinked terms, we include the terms

$$\text{single } R_K^\dagger \times \text{double } S_I^\dagger = \text{triple excitation} \tag{47}$$

for single electron processes such as ordinary excitations and ionizations, and further the terms

$$\text{double } R_K^\dagger \times \text{double } S_I^\dagger = \text{quadruple excitation} \tag{48}$$

for more accurate calculations and for two electron processes such as shake-up ionizations. The operators $S_I^\dagger$ are restricted to doubles since electron collisions are the main origin of electron correlations.

The configuration selection technique is also introduced for saving computer time [51]. For the linked $R_K^\dagger$ operators,

(a) all single excitation operators are included.

(b) Double excitation operators are selected in the following way.

Let $\Psi^{(p)}$ be a primary configuration

$$\Psi^{(p)} = \Sigma_i\, \alpha_i^{(p)}\, \Phi_i^{(p)}, \quad (p=1,\ldots,N)\,, \tag{49}$$

which is the sum of single-excitation or ionization configurations $\Phi_i^{(p)}$. N is the number of the states under consideration. We denote the doubly excited configuration to be selected as Φ_s and define

$$\Delta E_{si}^{(p)} = |H_{si}^{(p)}|^2 / (H_{ii}^{(p)} - H_{ss})\,, \tag{50}$$

where $H_{si}^{(p)} = <\Phi_s|H|\Phi_i^{(p)}>$, $H_{ii}^{(p)} = <\Phi_i^{(p)}|H|\Phi_i^{(p)}>$, and $H_{ss} = <\Phi_s|H|\Phi_s>$. We include only such Φ_s which satisfies

$$|\Delta E_{si}^{(p)}| > \lambda_e\,, \tag{51}$$

with at least one of the configurations $\Phi_i^{(p)}$. As the configuration $\Phi_i^{(p)}$ in Eq. (49) we include all single-excitations whose coefficients are larger than 0.1 in an ordinary single-excitation CI.

In the unlinked term $\Sigma\, d_K C_I R_K^\dagger S_I^\dagger|0>$, we include only such double-excitation operators $S_I^\dagger$ whose coefficients in the ground-state CI are larger than 1×10^{-3}. As for the $R_K^\dagger$ operators in the unlinked term, two types of selections are possible. For single-electron processes, we include only single-excitation operators whose coefficients in the CI including only linked operators are larger than 0.1. The unlinked term then represents triple excitations. For two-electron processes like shake-up ionizations, we include single- *and* double-excitation operators whose coefficients in the CI including only linked operators are larger than 0.1. The unlinked term then includes triple *and* quadruple excitations. We refer to the former calculations as '3-excited' calculations and the latter as "3,4-excited" calculations.

The unlinked terms in the SAC-CI theory represent a spirit of multi-reference CI; namely, double excitations from important reference configurations. The double excitations and their coefficients are transferred from the SAC calculation for the ground state (transferability). The reference configurations are singly excited configurations for one-electron processes and doubly excited configurations for two-electron processes. A sufficient number of reference configurations are selected automatically in our scheme because it does not result in an increase of the dimension of the matrices to be diagonalized. The size of the matrices to be diagonalized is the size of the *linked* terms.

The SAC-CI solution is carried out by the non-variational method. We have also given an approximate variational procedure [17] in which the final matrices to be diagonalized are just the symmetrized ones of the non-variational ones. This method also gives satisfactory results.

Densities and properties of the SAC/SAC-CI wave functions

The formulas for the density and transition density are calculated from the SAC and SAC-CI wave functions [52]. They are necessary for calculating one-electron properties of the ground and excited states and the transition properties between them.

Let $\mathfrak{Q}$ be a spin-independent one-electron operator

$$\mathfrak{Q} = \Sigma_\nu\, q(\nu)\,. \tag{52}$$

For density, we have $q(\nu) = \delta(r-r_\nu)$. From the SAC wave function given by Eq. (23), we calculate the one-electron property as

$$<\mathcal{Q}>_g = <\Psi_g\,|\mathcal{Q}|\,\Psi_g> / <\Psi_g|\Psi_g>\,, \tag{53}$$

$$\begin{aligned}<\Psi_g|\mathcal{Q}|\Psi_g> = {} & <0|\mathcal{Q}|0> + 2\Sigma_I\, C_I <0|\mathcal{Q}\, S_I{}^\dagger|0> \\ & + \Sigma_{IJ}\, C_I C_J <0|S_I \mathcal{Q} S_J{}^\dagger|0>,\end{aligned} \tag{54}$$

$$<\Psi_g|\Psi_g> = 1 + \Sigma_{IJ}\, C_I C_J <0\,|S_I\, S_J{}^\dagger\,|\,0>\,, \tag{55}$$

These equations are correct to third order in the coefficients, since the matrices between the linked and unlinked terms $<0\ |S_I\ \mathcal{Q}\ S_J{}^\dagger\ S_K{}^\dagger\ |\ 0>$ vanish identically ($S_J{}^\dagger\, S_K{}^\dagger$ includes only quadruple excitations). The matrices between unlinked terms (fourth order in the coefficients) are neglected.

The densities for excited, ionized, and electron attached states, and the transition densities are similarly calculated from the SAC/SAC-CI wave functions and summarized in Ref. [52].

Program guide

The program system SAC85 deals with

1. the SAC wave function for a closed-shell system (usually ground state), and
2. the SAC-CI wave functions for singlet and triplet excited states, and doublet ionized and electron attached states;
3. neutral doublet radical calculated by the SAC-CI method as an ionized state of a closed-shell anion or as an electron attached state of a closed-shell cation;
4. the density matrices and the one-electron properties for the above states;
5. the transition density and the transition properties between the SAC and SAC-CI wave functions.

Integrals between configurations are evaluated using the projective reduction formalism for bonded functions developed by Reeves and others [56]. The subroutine for the projective reduction is a modified one of the program due to Gilson [57].

Algorithms for the integral transformation from AO bases to MO ones are due to LINK 901 of the Gaussian 70 program of Pople et al. [58] The Bender's algorithm [59] for vector processors is useful and coded for larger calculations [60].

Eigenvalues and eigenvectors of matrices are solved by the QL method for symmetric ones and by the QR method for non-symmetric ones [61], if the dimensions are relatively small. We use the program-package 'NUMPAC' due to Ninomiya and Hatano [62]. For matrices of large dimensions, we use Davidson's algorithm [45] for symmetric matrices and our algorithm for non-symmetric matrices

[44]. One electron properties are calculated by modifying the subprogram PA60 of the POLYATOM program [63].

The program system SAC85 consists of several main steps and sub-steps summarized in Tables IV and V, respectively [49,53,54]. The main steps involve the steps necessary for calculating the SAC/SAC-CI wave functions and the one-electron properties therefrom. The sub-steps involve integral transformation program, dimension set-up program, interface programs, supplemental programs, etc.

The detailed accounts on how to use the program are given in the step, GUIDE [49], which also involves input manual and JCL (job control language) examples. Most calculations are easily done by just changing some variable inputs of the sample JCL as appropriate for the system under consideration.

Limitations of the program SAC85

First, the program can deal with the spin symmetries, singlet, doublet and triplet, only. For space symmetries, any symmetry is alright, and the reduction is automatically done for non-degenerate symmetries. The extensions to higher spin-multiplicity [54] and to higher multiple excitation processes [55] are not included in SAC85.

Second, the SAC method is applicable only to the HF dominant state. Otherwise, more elaborate theory as described in the next section is necessary.

Third, in the program SAC85, molecular repulsion integrals are stored in the main memory of the computer, so that the maximum number of active orbitals is dependent on the size of the main memory of the computer used. This makes, however, the program free from the I/O bound.

Exponentially generated wave functions

The cluster expansion ansatz is valid when the state is primarily described by the HF method. However, when the state is not well approximated by a single determinant, the cluster expansion ansatz fails down [64]. When the SAC theory fails down, we can not define the SAC-CI wave function.

Extensions of the cluster expansion ansatz to more general cases like quasi-degenerate situations have been proposed by several authors [64–67]. They are generally called multi-reference (MR) cluster expansion. We have considered such extensions by generalizing the exponential operator [68,69]. We call such methods as exponentially generated wave function (EGWF) method [68]. It involves the MR-SAC method [64] and the exponentially generated CI method [68,70].

Table IV

Main steps in the SAC/SAC-CI program

Step	Main job	Main input	Main output
PRES	1 Generate labels of all the linked operators 2 Classify linked operators by their symmetries	1 Number of active MO's 2 MO symmetry	1 Labels of linked operators
CIMX	1 Selection of linked operators 2 Integrals between linked configurations 3 Singly excited CI as initial vectors	1 Molecular integrals	1 Linked operators after selection 2 Integrals between linked configurations
CID	1 Diagonalization of CI matrix within linked operators (Iterative procedure) • For small dimension, use direct procedure #DAS#.		1 CI eigenvalues and eigenvectors
ULINT1	1 Integrals for unlinked terms in the SAC calculation	1 Molecular integrals	1 Unlinked integrals for the SAC calculation
SAC	1 Solve SAC equation (Recommend non-variational method - SACMET-) • For small dimension, direct method #DSAC# may be used.		1 Solution of the SAC method
ULINT2	1 Integrals for unlinked terms in the SAC-CI calculation (Program is the same as in the step #UNLINT1#.)	1 Molecular integrals	1 Unlinked integrals for SAC-CI
SCIV	1 Solve SAC-CI equation --Variational method-- (Iterative procedure) • For small dimension, use direct procedure #DAS#.		1 Eigenvalues and eigenvectors of the SAC-CI-V method
SCINV	1 Solve SAC-CI equation -- Non-variational method -- (Iterative procedure) • For small dimension, use direct procedure #DNAS#.		1 Eigenvalues and eigenvectors of the SAC-CI-NV method
DENS	1 Density matrix and natural orbitals for the SAC and SAC-CI wave functions 2 Transition density between the SAC and SAC-CI wave functions 3 Spin density matrix		1 Natural orbitals 2 Transition density 3 Spin density matrix
PROP	1 One-electron properties 2 Transition properties		1 One electron properties 2 Transition properties
SPIND	1 Spin density		1 Spin density

Footnotes
(1) Steps are given in the order of job stream.
(2) The step below uses the outputs of the steps above as inputs
These informations are transferred through files

Table V

Sub-steps in the SAC/SAC-CI program

Step		Main Job
GUIDE	1	Explanation of the program
	2	JCL guide
	3	JCL example
SET	1	Definition of the dimensions of the program Dimensions of the variables in the program are fixed before calculations using the sub-step #SET#. For optimal use of main memory, we recommend to determine the optimal dimension for each set of calculations.
ERI (ERIH, ERIG, ERIP)	1	Transformation of integrals from AO to MO (AO integrals from HONDO, GAMESS, GAUSSIAN 70, and POLYATOM are adaptable.)
ISORT	1	Integral sorting in canonical order (Suitable for vector processors in large scale calculations)
----		---- (ISORT and ERIB are used in pair.) ----
ERIB	1	Transformation of integrals from AO to MO in Bender's algorithm (Suitable for vector processors in large scale calculations)
FOCK	1	Fock matrix based on non-canonical orbitals
FILE	1	Adjust file interface of the outputs of #DAS# and #DNAS# for #CID#, #SCIV#, and #SCINV#.
GSUM	1	Group sum of linked operators for different geometries
SATEI	1	Intensity of ionization peaks including shake-up process
ANALY	1	Analysis of the SAC and SAC-CI wave functions
COMCG	1	Rewrite the information in the common file
IRDC	1	Integral reducing
NPAC	1	Mathematical subroutine package for private library (Modified from NUMPAC due originally to I. Ninomiya, Nagoya University)
OUT	1	Example of output list (Outlist statement)

Recently, we have developed a method of describing excited, ionized and electron attached states on the basis of the EGWF's [70,71]. This method includes a generalization of the SAC/SAC-CI method [71]. We call such methods as excited (EX-)EGWF method [70,71]. Details of the EGWF/EX-EGWF methods are outside of this review, so that we only refer to the original papers [64,68–71].

The theoretical basis to extend the SAC/SAC-CI method to more general cases is thus already completed, and the results of the test calculations for small molecules are promising. The remaining problem is to develop an algorithm for rapid evaluations of the integrals involved.

Accuracy of the SAC/SAC-CI method as compared with full-CI

When the theory and the first version of the program of the SAC/SAC-CI method had been completed, the first calculations were for confirming the accuracy of the method by comparing the results with the already existed very accurate calculations [50]. For Be and H_2O, the results agreed well with the accurate results for ground and excited states. For BH_3 and H_2O, the merit of the cluster expansion method was confirmed.

More recently, full CI calculations have become available and the comparison of the SAC/SAC-CI results with the full CI ones has been published [72]. Tables VI – IX show the results for H_2O. For the ground state, Handy et al. [73,74] reported the full CI calculations for the [4s2p/2s] basis [75]. Table VI shows the comparison for the singlet states. The SAC result reproduces 98.9% of the exact correlation energy, though the dimension of the unknown variables are much smaller. The excitation energy calculated by the SAC-CI method agrees quite well with the full CI result: the error is less than 0.9%. The dimension of the calculation is remarkably smaller than that of the full CI. Table VII shows the comparison for the triplet excitation energy. The SAC-CI result agrees quite well with the full CI result, though the dimension of the calculation is much smaller than that of the full CI.

Table VI

Singlet ground and excited states of H_2O calculated by the SAC-CI and full CI method

State	Orbital picture	Method	Dimension	Total energy (au)	Excitation energy (eV)	Error from full CI (%)
$^1A_1$	ground state	SAC	361	−76.156254	0.0	0.002
		Full CI	256474	−76.157866	0.0	
	$3a_1(n) \to 4a_1$	SAC-CI	360	−75.754848	10.923	0.8
		Full CI	256474	−75.759512	10.840	
	$1b_2(\sigma) \to 2b_2$	SAC-CI	360	−75.450371	19.208	0.8
		Full CI	256474	−75.457584	19.056	
$^1A_2$	$1b_1(\pi) \to 2b_2$	SAC-CI	192	−75.756082	10.889	0.8
		Full CI	245000	−75.761050	10.798	
$^1B_1$	$1b_1(\pi) \to 4a_1$	SAC-CI	216	−75.833910	8.772	0.9
		Full CI	245776	−75.838288	8.696	
$^1B_2$	$3a_1(n) \to 2b_2$	SAC-CI	312	−75.664680	13.377	0.8
		Full CI	254752	−75.670141	13.272	
	$1b_2(\sigma) \to 4a_1$	SAC-CI	312	−75.564611	16.100	0.9
		Full CI	254752	−75.571512	15.956	

Table VII

Triplet excited states of H_2O calculated by the SAC-CI and full CI methods

State	Orbital picture	Method	Dimension	Total energy (au)	Excitation energy (eV)	Error from full CI (%)
$^3A_1$	$3a_1(n)\rightarrow 4a_1$	SAC-CI	417	-75.794396	9.847	0.3
		Full CI	440475	-75.797174	9.815	
	$1b_2(\sigma)\rightarrow 2b_2$	SAC-CI	417	-75.566185	16.057	0.3
		Full CI	440475	-75.569523	16.010	
$^3A_2$	$1b_1(\pi)\rightarrow 2b_2$	SAC-CI	274	-75.775095	10.372	0.9
		Full CI	437640	-75.779926	10.284	
$^3B_1$	$1b_1(\pi)\rightarrow 4a_1$	SAC-CI	294	-75.864292	7.945	0.6
		Full CI	437520	-75.867507	7.901	
$^3B_2$	$3a_1(n)\rightarrow 2b_2$	SAC-CI	410	-75.718219	11.920	0.4
		Full CI	441120	-75.721626	11.871	
	$1b_2(\sigma)\rightarrow 4a_1$	SAC-CI	410	-75.631970	14.267	0.4
		Full CI	441120	-75.635841	14.215	

The effectiveness of the SAC-CI method is prominent for the ionized states summarized in Table VIII. Though the dimensions of the matrices handled in the SAC-CI calculations are less than a hundred, the accuracy is quite comparable with the full CI results of the dimension 230,000. The ΔSCF result is the difference of the independent SCF results for the ground and ionized states. It is about 1.0 eV smaller than the exact result. This is because the correlation correction is larger for the ground state than for the excited state, since the number of the paired electrons is larger for the ground state. The Koopmans values are, on a contrary, about 1 eV larger. With this basis set, the calculated ionization potentials are different from experiment by 0.4 – 1.1 eV. Table IX shows a similar result for the electron attached states.

Similar comparisons for H_2O with the use of larger basis set including polarization functions are given by Hirao [76]. The agreement with the full-CI results became worse than the above results. Nevertheless, it is safe to conclude that the SAC/SAC-CI method is very accurate and reproduces well the full-CI results.

Excited states

The SAC-CI theory has been applied to various kinds of excited states of various molecules. They include singlet and triplet, valence and Rydberg excited states of organic and inorganic compounds, metal complexes and clusters. They are H_2O [50,52,71], CH_2 [46], H_2CO [77], CO_2, N_2O [51], NO radical [13], Li_2 [78], CO [43], NH_4^+ [79], π-conjugated molecules, ethylene (C_2H_4) [7,80], glyoxal ($C_2H_2O_2$)

[81], butadiene [82], pyrrole (C_4H_5N), furan (C_4H_4O), cyclopentadiene (C_5H_6) [83], benzene (C_6H_6) [7,69,84], pyridine (C_5H_5N) [85], naphthalene ($C_{10}H_8$) [86], metal complexes, RuO_4, OsO_4 [87], $MoO_{4-n}S_n$ (n= 0,1,2,3), $MoSe_4$ [88], MnO_4^- [89], TiX_4 (X= Cl, Br, I) [90], van der Waals complexes, Ar_2 [91], CsXe [92], model chemisorption systems, PdH_2, Pd_2H_2 [93], PtH_2 [94], Ag_2O_2, Ag_4O_2 [95], ZnO [96], etc. The ground and excited states of ions and anions have also been calculated, but they are reviewed in the next section.

Table VIII

Ionization potential of H_2O calculated by full CI and SAC-CI methods

State	Orbital picture	Method	Dimension	Ionization potentials (eV)	Error from full CI (%)
$^2B_1$	$1b_1(\pi)\rightarrow\infty$	Koopmans	1	13.673	14.3
		ΔSCF	1	10.952	−8.0
		SAC CI	48	11.895	−0.1
		Full CI	223282	11.909	
		exptl.		12.61	
$^2A_1$	$3a_1(n)\rightarrow\infty$	Koopmans	1	15.047	10.1
		ΔSCF	1	12.613	−7.7
		SAC CI	82	13.645	−0.1
		Full CI	232968	13.666	
		exptl.		14.73	
$^2B_2$	$1b_2(\sigma)\rightarrow\infty$	Koopmans	1	19.517	2.8
		ΔSCF	1	17.909	−5.7
		SAC CI	66	18.976	−0.1
		Full CI	232068	18.988	
		exptl.		18.55	

Table IX

Electron affinities of H_2O calculated by full CI and SAC-CI methods

State	Orbital picture	Method	Dimension	Electron affinity (eV)	Error from full CI (%)
$^2A_1$	$\infty\rightarrow 4a_1$	Koopmans	1	−5.8229	9.2
		ΔSCF	1	−5.5881	4.8
		SAC CI	150	−5.3507	0.4
		Full CI	651720	−5.3309	
$^2B_2$	$\infty\rightarrow 2b_2$	Koopmans	1	−8.3289	7.7
		ΔSCF	1	−8.0401	4.0
		SAC CI	132	−7.7726	0.5
		Full CI	650724	−7.7343	

Valence and Rydberg excitations

We show here the SAC/SAC-CI results for the CO_2 molecule [51]. We used the GTO bases of Dunning and Hay [97]. The HF orbital sequence is

$$(\text{core})^6 (3\sigma_g)^2 (2\sigma_u)^2 (4\sigma_g)^2 (3\sigma_u)^2 (1\pi_u)^4 (1\pi_g)^4 . \tag{56}$$

Table X shows the energy of the ground state. We see that the polarization functions are very important. Our SAC correlation energy is larger than those of the CI methods of Winter, Bender and Goddard (WBG) [98] and of England and Ermler (EE) [99].

Table X

Hartree-Fock energy and correlation energy of the ground state of CO_2 (au)

Method	Valence plus Rydberg basis [a]	Valence plus polarization basis [a]	CI [b]	MC-CI [c]
Hartree-Fock	-187.55521	-187.67466	-187.5561	-187.7226
SDCI	-0.28401	-0.39869	-0.1307	-0.2570
SAC	-0.30317	-0.41457		

[a] See Ref. [51]; [b] See Ref. [98]; [c] See Ref. [99]

Table XI shows the vertical excitation energies for CO_2. Note that the 3s Rydberg state is lower than the lowest valence excited states. This is not described by the SECI method and the CI calculations of WBG: the ordering of the states is the same between these two calculations. However, the SAC-CI results and the MC-CI results of EE are much different from these two ones. For the valence excitations and higher Rydberg excitations to the 3p states, our SAC-CI results agree quite well with the experimental values.

For the 3s Rydberg states,$^3\Pi_g$ and $^1\Pi_g$, our results are about 0.4 eV higher than the experimental values. This is understood as being due to the geometrical relaxation effect in the excited state. Fig. 1 shows a schematic potential curves of the ground and excited states of CO_2 against the OCO angle [99]. At the vertical excited states $<OCO = 180°$, the Rydberg 3s state $^1\Pi_g$ is lower than the valence $^1\Sigma_u$ and $^1\Delta_u$ states. When CO_2 is bent, an avoided crossing occurs between these valence and Rydberg states and the valence states soon becomes lower than the Rydberg state. Considering this effect and the fact that the transition intensity is larger for the valence transitions than for the Rydberg one, we understand why the experimental 3s transition energies are smaller than our theoretical values.

Table XI

Valence and Rydberg excitation energies of CO_2 (eV)

State [a]	Orbital picture	SECI	CI [b]	MC-CI [c]	SAC-CI	Exptl.
$^3\Sigma_u{}^+$	$1\pi \rightarrow 4\pi_u$	7.24	7.35	8.65	8.15	8.1
$^3\Pi_g$(R)	$1\pi \rightarrow 5\sigma_g$(s)	9.31	8.95	8.86	8.73	8.3
$^3\Delta_u$	$1\pi \rightarrow 4\pi_u$	8.02	7.83	9.02	8.80	8.8
$^1\Pi_g$(R)	$1\pi \rightarrow 5\sigma_g$(s)	9.83	9.23	9.10	8.93	8.4-8.6
$^3\Sigma_u$	$1\pi \rightarrow 4\pi_u$	8.66	8.24	9.42	9.19	
$^1\Sigma_u{}^-$	$1\pi \rightarrow 4\pi_u$	8.66	8.27	9.42	9.27	
$^1\Delta_u$	$1\pi \rightarrow 4\pi_u$	8.99	8.38	9.43	9.32	9.3-9.4
$^1\Sigma_u{}^+$(R)	$1\pi \rightarrow 2\pi_u$(pπ)	12.19	11.07	11.20	11.00	11.08-11.20
$^3\Pi_u$(R)	$1\pi \rightarrow 4\sigma_u$(p$\sigma$)	12.28	11.49	11.43	11.31	
$^1\Pi_u$(R)	$1\pi \rightarrow 4\sigma_u$(p$\sigma$)	12.46	11.53	11.45	11.39	11.4-11.6
$^3\Sigma_g$	$1\pi \rightarrow 4\pi_u$	11.04		12.13	11.79	
$^3\Delta_g$	$1\pi \rightarrow 4\pi_u$	12.22		12.91	12.44	12.4

[a] (R) denotes Rydberg excited state; [b] See Ref. [98]; [c] See Ref. [99]

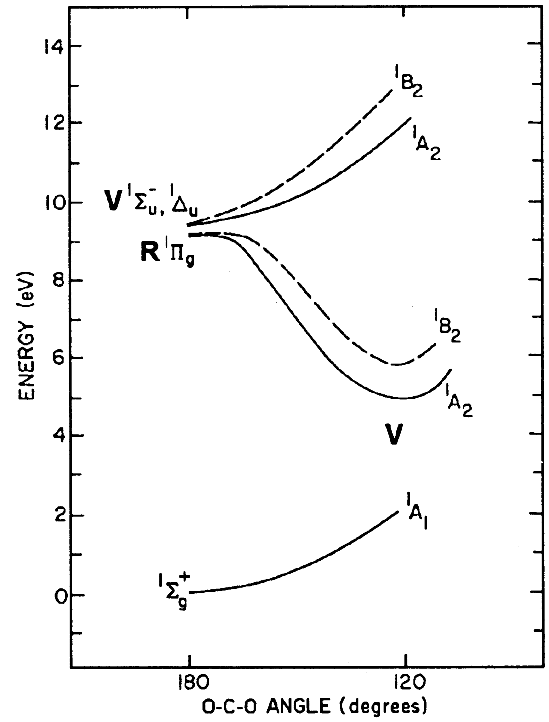


Fig. 1. Schematic potential energy curves for the ground and excited states of CO_2 as a function of bending angle [99]

Excited states of conjugated molecules

For *ab initio* studies of excited states of conjugated hydrocarbons, there was a serious difficulty in reproducing the excitation energies of the so-called V states (ionic valence excited states), though fairly reliable results were obtained for the other valence and Rydberg excitations.

For ethylene, modern quantum chemistry is able to reproduce the $\pi \rightarrow \pi^*$ transition energy to within 0.5 eV of the experimental value [80,100]. For butadiene, however, the earlier reliable CI calculations due to Buenker et al. [101] gave the valence $^1B_{1u}$ state at 7.67 eV above the ground state in comparison with the experimental value of 5.92 eV [102]: the discrepancy was as large as 1.75 eV, though their results for the covalent valence and Rydberg excited states were satisfactory. Similarly for benzene, the earlier reliable π-CI results of Hay and Shavitt [103] for the excitation energies of the V states were 7.00, 7.64, and 8.34 eV for the 1^3B_{2u}, 1^1B_{1u}, and 1^1E_{1u} states, respectively, in comparison with the experimental values of 5.60, 6.20, and 6.95 eV. The discrepancy is about 1.4 eV, again very large, though their results for the other excited states agreed well with the experimental values.

Thus, we have to conceive that something is wrong or missing in the existing descriptions of the valence V excited states of conjugated molecules. This problem has caused a serious suspicion on the reliability of the quantum chemistry of excited states, and thereby has hindered a fruitful interplay between theory and experiment.

For ethylene, the SAC-CI method has reproduced well both valence and Rydberg excitations, including the V-state [7,80]. We review here the results for *trans*-butadiene and benzene. The excited states of pyridine, a key heteroaromatics, are understood from those of benzene plus $n \rightarrow \pi^*$ transitions [85].

Trans-butadiene

Many theoretical studies have been reported for butadiene, but the results for the V(^1B_u) state were pessimistic. Two possibilities have been suggested as a solution of this situation.

(1) Inclusion of a large amount of σ electron correlations.

(2) The peak maximum may not correspond to the vertical transition. The geometry deformation after the electronic transition may be important.

The UV-IR double resonance experiment [104], however, suggested the planarity of the V state and questioned on the second possibility.

We have performed the SAC-CI calculations for the *trans*- and *cis*-butadiene using fairly flexible basis set. The active space consists of 36π plus 64σ MO's. We have also performed 36π MO calculation, as a reference, for examining the effect of σ-election correlations.

The $\pi \rightarrow \pi^*$ excitation energies of *trans*-butadiene are summarized in Table XII and Fig. 2. The study of Buenker, Shih, and Peyerimhoff (BSP) [101], recent extensive CI calculations of Cave and Davidson (CD) [105] and our SAC-CI results [81] are displayed. The experimental data corresponds to the peak maxima of the electron energy-loss spectra of Flicker et al [102].

Table XII

$\pi \rightarrow \pi^*$ *excitation energies of* trans-*butadiene (eV)*

State	Exptl. [a]	SAC-CI 36π(Δ [c])	 $36\pi+64\sigma$(Δ)	CI(BSP) [d] $12\pi+34\sigma$ (Δ)	CI(CD) [c,e]
2^1A_g (V)	7.08	6.93 (−0.15)	7.05 (−0.03)	7.02 (−0.06)	6.24 (−0.84), 6.77(−0.31)
3^1A_g ($3d_\pi$)	7.48	7.73 (0.25)	7.38 (−0.10)	7.53 (0.05)	
4^1A_g ($3d_\delta$)	7.80	7.69 (−0.11)	7.86 (0.06)	7.78 (−0.02)	
1^1B_u (V)	5.92[b]	7.71 (1.79)	6.43 (0.51)	7.67 (1.75)	6.08 (0.16), 6.23 (0.31)
2^1B_u ($3p_\pi$)	6.64	6.84 (0.20)	7.08 (0.44)	6.67 (0.03)	6.76 (0.12), 7.16 (0.52)
3^1B_u ($4p_\pi$)	8.00	8.24 (0.24)	7.91 (−0.09)	7.96 (−0.04)	7.64 (−0.36)
1^3A_g (V)	4.91	5.14 (0.23)	5.15 (0.24)	4.92 (0.01)	
2^3A_g ($3d_\delta$)		7.61	7.22		
3^3A_g ($3d_\pi$)		7.64	7.26		
1^3B_u (V)	3.22	3.44 (0.22)	3.48 (0.26)	3.31 (0.09)	
2^3B_u ($3p_\pi$)		6.99	6.65		
3^3B_u ($4p_\pi$)		8.17	7.83		
average deviation		0.40	0.22	0.26	0.37, 0.38

[a] See Ref. [102]; [b] This is a broad intense band from 5.7 to 6.3 eV with three peaks at 5.76, 5.92, and 6.05 eV (maximum occuring at 5.92 eV)[a]

[c] Δ shows the difference from the experimental value; [d] See Ref. [101]; [e] See Ref. [105]

The σ electron correlations play a crucial role in the description of the 1^1B_u(V) state. The effect is as large as 1.28 eV, though the effect is much smaller for the other valence and Rydberg excited states. The excitation energy for the 1^1B_u state is calculated at 6.43 eV which differ from the experiment by 0.51 eV, much smaller than the BSP result of 1.75 eV. The extensive CI calculations of CD [105], who also included the σ-reorganization effect, reproduce it to within 0.12−0.52 eV. The SAC-CI method gives reasonable results for the other valence $\pi \rightarrow \pi^*$ and Rydberg excitations. The average deviation is about 0.2 eV.

It is well known that the wave function of the ionic V state of the π conjugated system expands like a Rydberg state when only the π-electron correlation is included, but shrinks to like a quasi-valence state when both σ and π correlations are included [106]. This characteristic behaviour is very clearly seen from the second moment

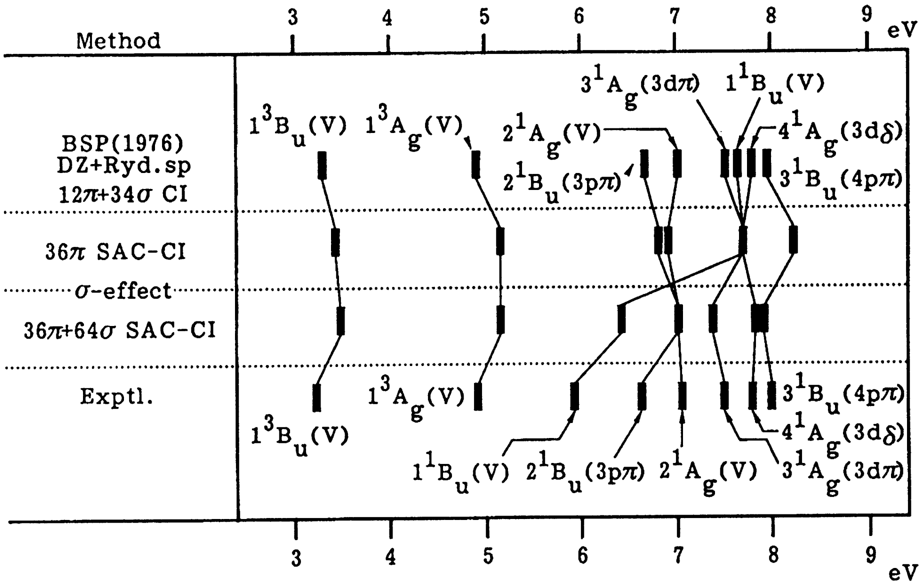


Fig. 2. Comparison of the theoretical and experimental excitation energies of trans-butadiene. BSP refers to the results reported in Ref. [101]

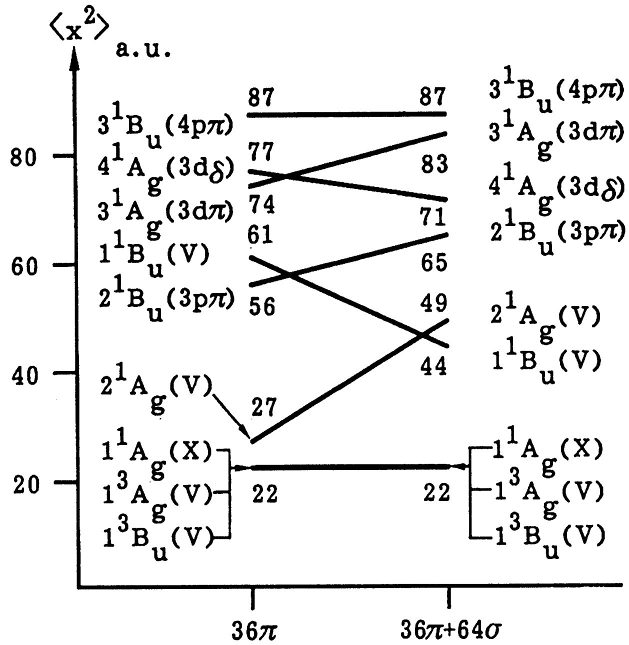


Fig. 3. Electronic part of the second moment of trans-butadiene obtained by the $36\pi + 64\sigma$ SAC-CI calculations. The x axis is perpendicular to the molecular plane

shown in Fig. 3. By including the σ correlations, the mixing between the first and second ^1B_u states is resolved. The second moment of the 1^1B_u state thus decreases from 61 au to 44 au, while that of the 2^1B_u state increases from 56 au to 71 au. The calculated oscillator strength of the 1^1B_u state is 0.466, in good agreement with the experimental value, ~0.417. The calculated value for the 2^1B_u state is 0.234.

Another remarkable changes are seen in Fig. 3 for the $2^1A_g(V)$ and $4^1A_g(3d_\delta)$ states. A large mixing of the π^* and $3d_\delta$ natures is observed for these states after including the σ electron correlations. This is reflected on the electronic part of the second moment.

Benzene

Benzene is a key aromatic molecule, and has played a historical role in the development of electronic structure theories. It is enough to remind the names of the pioneers, Kekulé [107], Hückel [108], Pauling [109], Goeppart-Mayer, Sklar [110], Pariser, Parr [111], and Pople [112].

We studied lower six excited states of benzene [84]. They are produced by the excitations from the highest occupied π MO's to the lowest unoccupied π^* MO's. We call the $^1B_{2u}$, $^1B_{1u}$ and $^1E_{1u}$ states as S_1 S_2 and S_3 states, respectively, and the $^3B_{1u}$, $^3E_{1u}$ and $^3B_{2u}$ states as T_1, T_2 and T_3 states, respectively. The T_3, S_2, and S_3 states are the so-called ionic V states [106]. We used fairly flexible basis set and performed the SAC-CI calculations within 35π and $35\pi+45\sigma$ active MO's.

Table XIII shows the experimental results [113], π-CI results of HS [103], and our 35π and $35\pi+45\sigma$ SAC-CI results [84]. The values in parentheses show the deviations from experiment. Fig. 4 shows these results schematically. The uppermost row of Fig. 4 shows the result of the π-CI of HS. The average error from the experimental values shown in the bottom row is 0.77 eV. The second row shows the result of the SAC-CI calculation within only π MO's including d-polarization functions. The d polarization function improves T_3 and S_2 states by 0.48 eV and 0.39 eV, respectively. The average error decreases to 0.65 eV. When we further relax the σ-electron space, the T_3, S_2, and S_3 states are much improved. The improvement is 0.63 eV for T_3, 0.71 eV for S_2 and 0.78 eV for S_3. The average error reduces to 0.34 eV. The remaining error still existing is in maximum 0.52 eV for the S_3 state. A substantial improvement was also reported by the CI calculations of Matos et al. [114].

We thus conclude:

1. The T_1, T_2, and S_1 states are explainable within π-CI.
2. For the T_3 and S_2 states, the polarization d_π function reduces the error by 0.4–0.5 eV and the σ-reorganization effect reduces the error by 0.6–0.7 eV.
3. For the S_3 state the effect of the d_π polarization function is small, but the σ-correlation effect is as large as 0.78 eV.

Table XIII

Valence $\pi \rightarrow \pi^*$ excitation energy of benzene (eV) [a]

State	SDT π-CI [b]	SAC-CI		Exptl.[c]	Oscillator strength	
	23π	35π	$35\pi+45\sigma$		35π	$35\pi+45\sigma$
$^1B_{2u}$ (S_1)	5.00 (0.10)	5.25 (0.35)	5.25 (0.35)	4.90	0.0	0.0
$^1B_{1u}$ (S_2)	7.64 (1.44)	7.31 (1.11)	6.60 (0.40)	6.20	0.0	0.0
$^1E_{1u}$ (S_3)	8.34 (1.39)	8.25 (1.30)	7.47 (0.52)	6.95	0.61	1.03
$^3B_{1u}$ (T_1)	3.83 (−0.12)	3.80 (−0.15)	4.06 (0.11)	3.95		
$^3E_{1u}$ (T_2)	4.98 (0.23)	5.05 (0.30)	5.02 (0.27)	4.75		
$^3B_{2u}$ (T_3)	7.00 (1.40)	6.65 (1.05)	6.02 (0.42)	5.60		

[a] Values in parentheses show the deviations from the experimental values
[b] See Ref. [103]; [c] See Ref. [113]

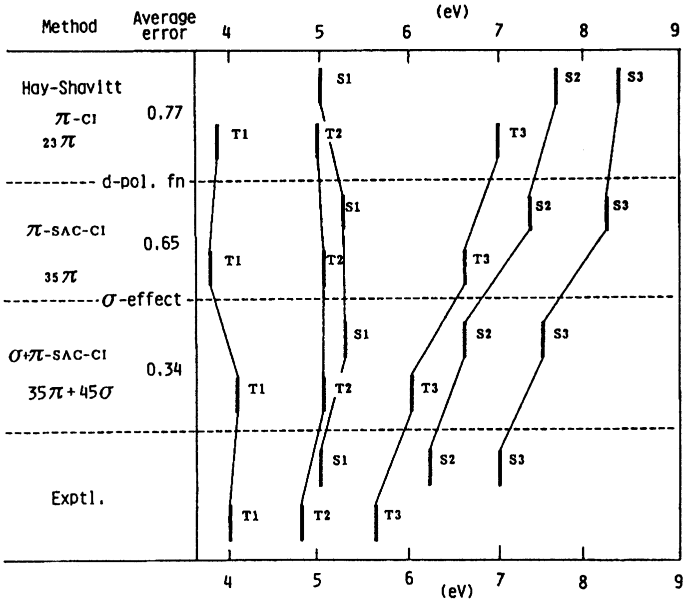


Fig. 4. Comparison of various levels of theoretical results with experiments for the valence $\pi \rightarrow \pi^*$ excitation energies of benzene

The electronic part of the second moment is displayed in Fig. 5. Before the σ-correlation effect is included, the S_3 state looks almost like Rydberg from the $<x^2>$ value. However, when it is included, the electron cloud considerably shrinks and the state becomes essentially valence in nature. Accordingly, the oscillator strength increases from 0.61 (35π) to 1.03 ($35\pi+45\sigma$). This behaviour is common to the valence excited V states of conjugated polyenes.

We have also performed systematic calculations for the Rydberg excited states of benzene involving both π and σ states. We show the results for the singlet states in Table XIV together with the experimental values [115–118]. The SAC–CI method excellently reproduces the experimental values. The average error is 0.1 eV. The effects of the σ correlation on the Rydberg transitions are about 0.3 eV, which is smaller than those for the valence excited states.

Table XIV

Excitation energies of the singlet Rydberg excited states of benzene (eV)

Orbital picture	State	Exptl.	SAC-CI		SDT-CI [b]
			$29\pi+51\sigma$	Δ [a]	23π
Ground	1^1A_{1g}	0.0	0.0	0.0	0.0
Excited					
$\pi\rightarrow 3s$	1^1E_{1g}	6.33	6.31	0.02	
$\pi\rightarrow 3p_\sigma$	1^1A_{1u}		7.10		
	1^1A_{2u}	6.93	6.88	0.05	
	1^1E_{2u}	6.95	6.99	0.04	
$\pi\rightarrow 3p_\pi$	1^1E_{1u}	7.19, 7.41	6.91		7.26
			7.02	0.28	
$\pi\rightarrow 3d_\sigma$	1^1B_{1g}	7.46	7.42	0.04	
	1^1B_{2g}	7.46	7.42	0.04	
	2^1E_{1g}		7.44		
$\pi\rightarrow 3d_\delta$	3^1E_{1g}	7.54	7.35	0.19	
$\pi\rightarrow 3d_\pi$	2^1A_{1g}	7.80	7.64	0.16	7.92
	1^1A_{2g}		7.57		7.94
	1^1E_{2g}	7.81	7.64	0.17	7.90
$\pi\rightarrow 4s$	4^1E_{1g}	7.95	7.90	0.05	
$\pi\rightarrow 4p_\pi$	2^1E_{1u}	8.37	8.13	0.24	9.25
$\pi\rightarrow 4d_\pi$	3^1A_{1g}	8.44	8.53	0.09	9.71
	2^1A_{2g}		8.44		9.62
	2^1E_{2g}	8.44	8.52	0.08	9.56
$\pi\rightarrow 4f_\pi$	1^1B_{1u}		8.17		8.58
	1^1B_{2u}		8.16		8.52
	3^1E_{1u}	8.38	8.33	0.05	8.74

[a] Δ shows the difference from the experimental value; [b] See Ref. [103]

$\sigma\pi$ correlations

We conclude that the difficulty in describing the ionic V states of conjugated molecules is essentially solved by including a large amount of σ-electron correlations with the use of relatively large basis sets. The SAC-CI method has been proven to be very useful for making such a large-scale calculations tractable. The discrepancy still remain would be due to the insufficiencies in including the $\sigma\pi$ correlations and in the basis set, and also due to the vibronic coupling effect in the excited states, since a large change in geometry is expected in the V excited states. For the other valence and Rydberg excitations, the SAC-CI results agree well with experiments.

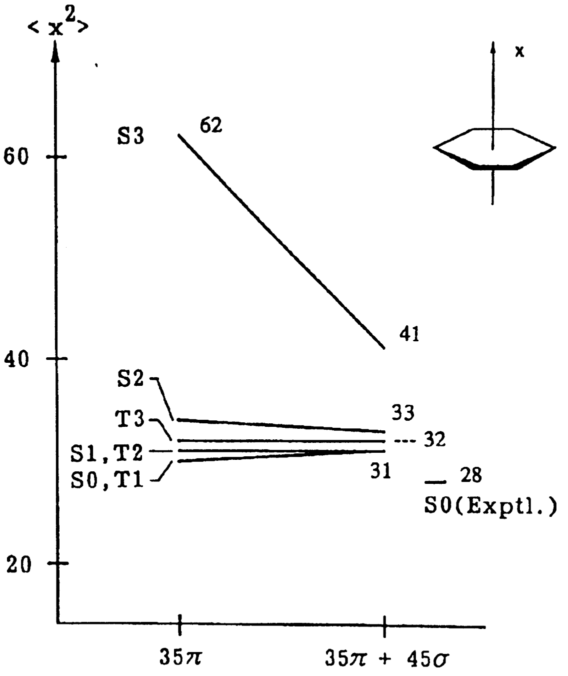


Fig. 5. Electronic part of the second moment of benzene

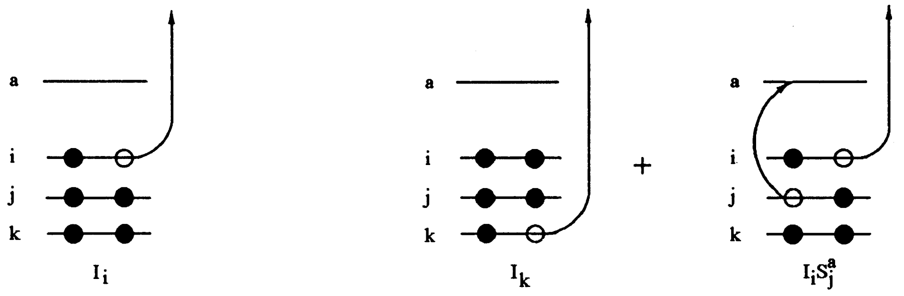
The physical reason of a large σ reorganization effect in the V type excited state is well known at least conceptually [106]. Because these states involve the ionic structures in the VB sense, the possibility of two electrons coming close is large and so the electron correlation is very important. Further, in these states, electron correlations take place in a relatively large space and cause large polarizations of the π and σ electron clouds. This is why a large basis set and a large active space are necessary for properly describing the effects. (This is the reason why the previous moderate scale calculations were unable to describe these states.) The physical picture is that a large bias of the π electron cloud on the *outer*-side is compensated by the net polarization of the σ electron cloud on the *inner*-side. We call this $\sigma\pi$ interaction as ***molecular in-out correlation*** as a generalization of the left-right correlation previously considered for ethylene [106]. As a consequence, the π-electron cloud of the V state shrinks considerably through the $\sigma\pi$ correlations.

Ionizations and shake-up ionizations

In the HF model, ionizations are described by the Koopmans model which is depicted in Fig. 6a. However, when we examine experimental ionization spectra, we often find a larger number of peaks than the number of MO's. For example, Fig. 7 shows the experimental photoelectron spectra of CO_2 [119] and N_2O [120], isoelectronic molecules. The occupied MO's of CO_2 are given in Eq. (56) and those of N_2O are

$$(\mathrm{core})^6\,(4\sigma)^2\,(5\sigma)^2\,(6\sigma)^2\,(1\pi)^4\,(7\sigma)^2\,(2\pi)^4\,. \tag{57}$$

For N_2O, we can count about 10 peaks, but the number of the MO levels in this energy region is 6. We will show that the peaks in 25–45 eV region (inner-valence region) are due to the two electron processes as depicted in Fig. 6b, namely, a mixing of the simultaneous ionization excitation process ($I_iS_j{}^a$) with the one-electron process (I_i). This process can not be described by a single electron model and therefore, electron correlations are essential.



(a)
Valence ionization

(b)
mixing with ionization-excitation
(inner-valence ionization)

Fig. 6. (a) One-electron and (b) two-electron ionization processes

The ionization potentials of CO_2 are shown in Table XV. The peak intensity is calculated by the monopole approximation [121]. The Koopmans' model is qualitatively valid for the ionizations in 10–25 eV region (outer-valence region), as the intensity is close to unity. For the inner-valence region, the intensity is small (0.67 and 0.47) so that the mixing of the shake-up process is large for these ionizations. The SAC-CI results agree well with the experimental values. The CI result of Iwata et al. [10] and Green's function result of von Niessen et al. [122] and Domcke et al. [123] are also given. In the Green's function method, OVT (over-valence type) method is for valence ionizations and TDA (Tamm-Dancoff approximation) for inner valence ionizations: two different methods must be used. The Koopmans' method itself is quantitatively unreliable.

Table XV

Ionization potential of CO_2 (eV)

	Orbital		SAC-CI			CI [a]	Green's function	
State	picture	Koopmans	Ip	Intensity	Exptl. [a]	Iwata	OVT [b]	TDA [c]
$^2\Pi_g$	$1\pi_g \rightarrow \infty$	14.77	13.42	0.92	13.78	13.01	13.66	12.65
$^2\Pi_u$	$1\pi_g \rightarrow \infty$	19.47	17.60	0.89	17.59	17.69	17.87	17.08
$^2\Sigma_u$	$3\sigma_u \rightarrow \infty$	20.17	17.69	0.90	18.08	17.84	18.30	16.56
$^2\Sigma_g$	$4\sigma_g \rightarrow \infty$	21.75	19.03	0.89	19.40	19.21	19.65	17.51
$^2\Sigma_u$	$2\sigma_u \rightarrow \infty$	40.25	35.61	0.67				35.30
$^2\Sigma_g$	$3\sigma_g \rightarrow \infty$	41.76	36.52	0.47				36.84

[a] See Ref. [10]; [b] See Ref. [122]; [c] See Ref. [123]

The ionization spectra of CO_2 and N_2O are calculated by the SAC-CI method for both valence and inner-valence regions and are displayed in Fig. 8. The theoretical spectra reproduce the general features of the experimental photoelectron spectra shown in Fig. 7. In the inner-valence region, the observed spectrum of CO_2 is composed of a single broad peak ranging from 30 to 43 eV with a flat shoulder in the 30–35 eV region. On the other hand, for N_2O, the main spectrum ranging from 30 to 43 eV is composed of several (at least four) split but overlapping peaks, and there are at least two distinct peaks in the 22–30 eV region. The theoretical spectra reproduce these general features and also the differences between the CO_2 and N_2O spectra. The main peaks in the 30–43 eV region are due to the superposition of many peaks of inner-valence ionizations and their satellites. The small peaks of N_2O in the 22–30 eV region seem to be due to the satellites of the ionizations from the 1π, 6σ and 5σ orbitals.

As origins of the shake-up peaks, the excitations from the $4\sigma_g$, $3\sigma_u$, $1\pi_u$, and $1\pi_g$ MO's to the $5\sigma_g$, $2\pi_u$, and $3\pi_u$ MO's are important for CO_2 and the excitations from the 6σ, 1π, 2π, and 7σ MO's to the 8σ and 3π MO's are important for N_2O. These occupied orbitals are bonding and non-bonding MO's and the unoccupied ones are antibonding MO's, so that in the shake-up states, a considerable elongation in the bond length should occur. This effect should also be a reason of the broadness of the peaks. (This effect tends to shift the overall shape of the spectrum to the lower-energy region.) Further, we see from Fig. 8 that many weak peaks are embedded between the relatively strong peaks. This is also an origin of the broadness of the peaks in the inner-valence region.

Similar calculations are also reported for H_2O [124], COS, CS_2 [125], ethylene [80], benzene [84] and NO radical [13].

Fig. 9 and Table XVI show experimental [126] and theoretical ionization spectra of naphthalene. The assignments of the peaks in 7–13 eV region are the same as those given previously [126], but those in 13–20 eV are firstly done by the SAC-CI method. The experimental peak at 16.0 eV may be assigned either to the theoretical peak at 15.1 eV or to the small shake-up peak at 16.0 eV. In the latter assignment, the theoretical peak at 15.1 eV would be assigned to the shoulder at 14.8 eV. Though the calculated intensity of the shake-up peak at 16.0 eV is small, we prefer the latter assignment, since generally speaking, the monopole approximation tends to underestimate the intensity, when it is combined with the SAC-CI method. The average discrepancy is 0.16 eV. Further, the broad experimental peak at 15–20 eV is explained as a composite of the shake-up peaks having B_{1g}, B_{3u}, and B_{2u} symmetries.

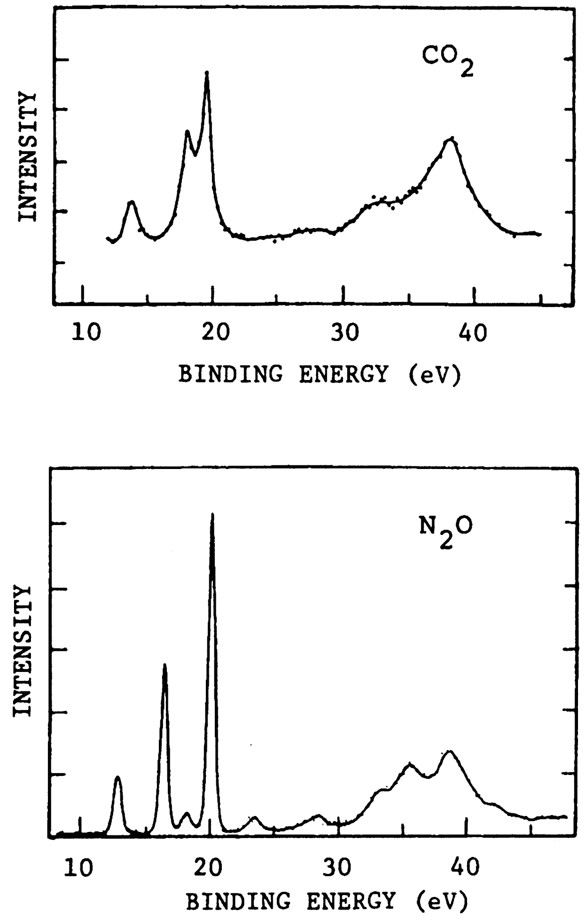


Fig. 7. Experimental photoelectron spectra of CO_2 [119] and N_2O [120]

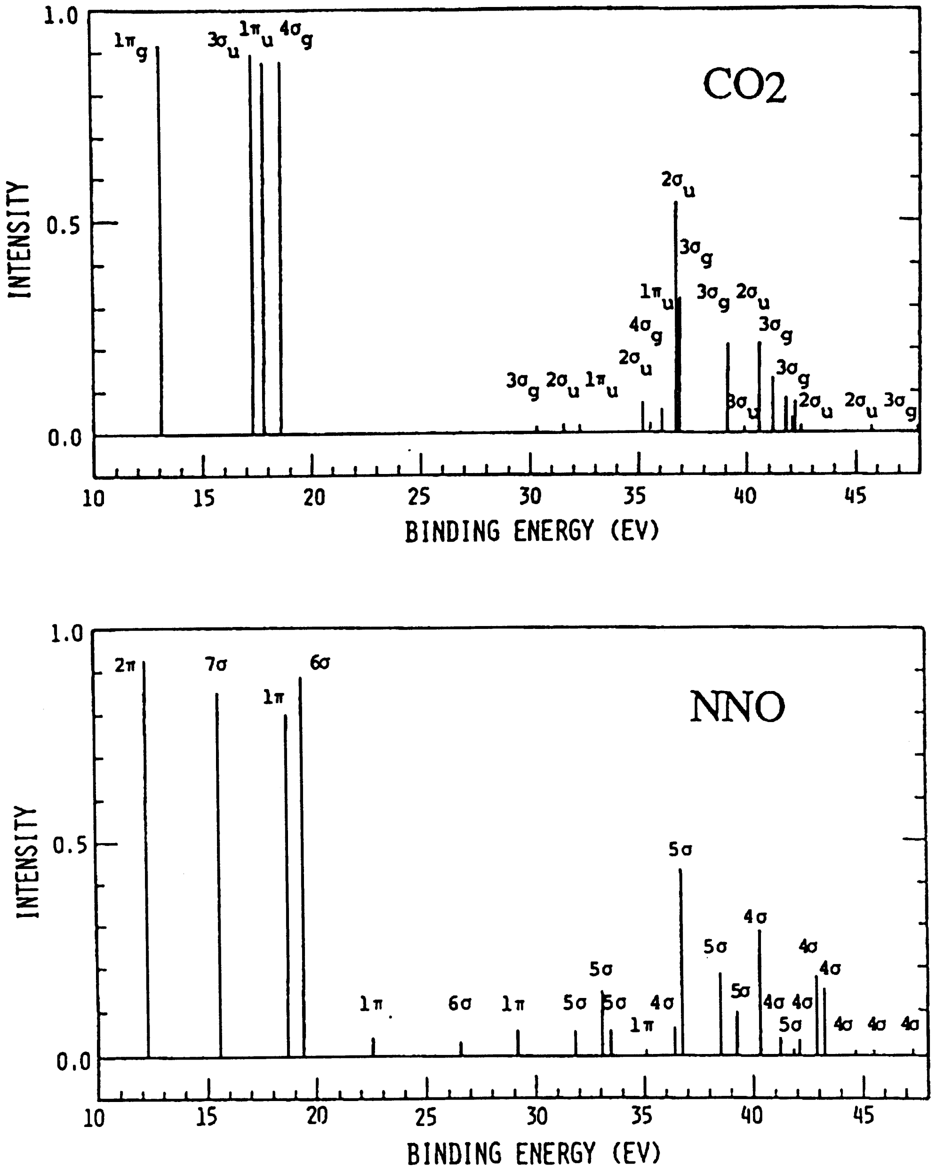


Fig. 8. Theoretical ionization spectra of CO_2 and N_2O calculated by the SAC-CI method

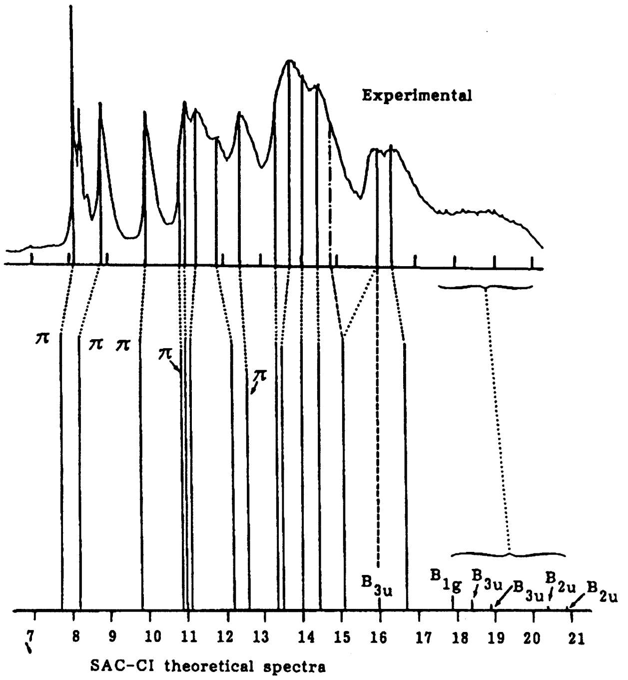


Fig. 9. Experimental (above) and theoretical (below) ionization spectra of naphthalene. The experimental spectrum is due to Brundle et al. [126]

Doublet radicals

The SAC method is applicable not only to closed shell molecules but also to open shell radicals [38,46]. The excited states of the radicals are calculated by the SAC-CI method. Another method of calculating doublet radicals is to calculate first closed-shell singlet state (anion or cation) by the SAC method and then to calculate doublet ground and excited states by the SAC-CI method by applying ionization or electron-attachment operators. These two methods are schematically explained in Fig. 10. In Method 2, the orbitals of the closed-shell reference are not necessarily the RHF orbitals of cation or anion, but may be the open-shell RHF orbitals of the doublet radical under consideration. In our laboratory, most calculations have been done with Method 2, since it is easier and less time consuming. We have shown that the final results are rather independent of the choice of the starting closed-shell state, i.e., cation or anion [38]. The ionized states explained in the preceding section are the ground and excited states of the doublet radicals calculated by Method 2 with the SAC-CI method.

Table XVI

Ionization potential of naphthalene (eV)

				Exptl. [b]
MO	Koopmans	SAC-CI [a]	BRK [b]	Present assignment [c]
$5\pi a_u$	8.12	7.68 (−0.45)	8.13	
$4\pi b_{3u}$	8.86	8.22 (−0.66)	8.88	
$3\pi b_{2g}$	10.63	9.75 (−0.26)	10.01	
$2\pi b_{1g}$	12.38	10.94 (0.04)	10.90	
$29\sigma a_g$	13.02	10.97 (−0.11)	11.08	
$28\sigma b_{3g}$	13.15	11.06 (−0.31)	11.37	
$27\sigma b_{2u}$	14.32	12.22 (0.33)	11.89	
$1\pi b_{3u}$	14.70	12.59 (0.09)	12.50	
$26\sigma b_{1u}$	15.54	13.38 (−0.1)		13.5
$25\sigma b_{2u}$	15.89	13.47 (−0.3)		13.8
$24\sigma b_{3g}$	16.09	13.98 (−0.2)		14.2
$23\sigma a_g$	16.85	14.47 (0.0)		14.5
$22\sigma b_{1u}$	17.12	15.10 (−0.9,03)		16.0, 14.8 [d]
shake-up	−	16.00 (0.0)		16.0 [d]
$21\sigma a_g$	18.54	16.69 (0.2)		16.5
average deviation	1.31	0.28, 0.22		

[a] Values in parentheses show deviations from the experimental values
[b] See Ref. [126]; [c] Peak maxima of the experimental spectrum of Brundle et al. are assigned using the present SAC-CI calculations; [d] For this assignment, see text

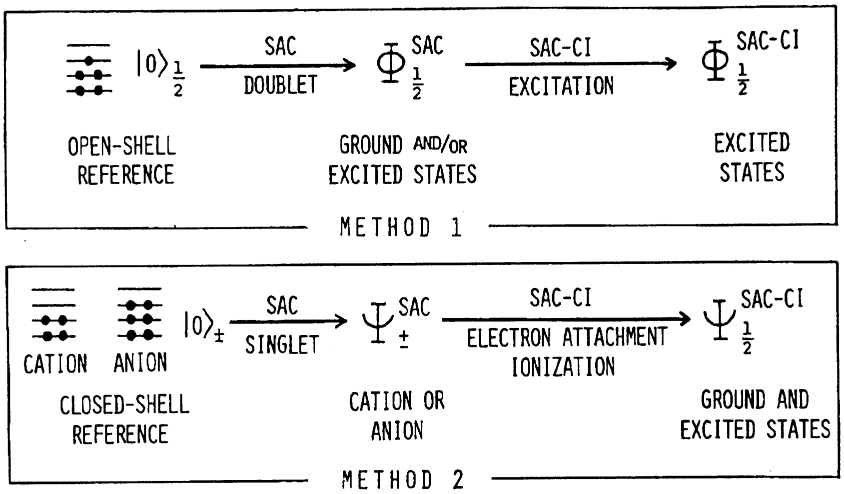


Fig. 10. Schematic explanation of Method 1 and Method 2 which are two ways of constructing doublet wave functions in the SAC/SAC-CI formalism

Ground and excited states

We show here an application of Method 2 to NO radical [13]. The HF configuration is

$$(\text{core})^4\,(1\sigma)^2\,(2\sigma)^2\,(3\sigma)^2\,(1\pi)^4\,(2\pi)^1\,. \tag{58}$$

We calculate the closed-shell ground state of the NO cation by the SAC method and the ground and excited states of the NO radical by the SAC-CI method using electron attachment operators.

Table XVII shows the vertical excitation energies of the NO radical. They correspond to the excitations from the singly occupied 2π MO to the unoccupied Rydberg orbitals. The SAC-CI results agree well with the experimental values [4]. However, note that even Koopmans' relation gives a satisfactory agreement with experiment. This is probably due to a cancellation of the orbital reorganization effect and the difference in electron correlations between the initial and final states.

Table XVII

Vertical excitation energy of NO radical (eV) [a]

State	Orbital picture	Koopmans	SAC-CI [b]	Exptl.	CI [c]
A $^2\Sigma^+$	$2\pi\rightarrow 3s\sigma$	5.41	5.31	5.45	5.38
C $^2\Pi$	$2\pi\rightarrow 3p\pi$	6.40	6.39	6.46	6.50
D $^2\Sigma^+$	$2\pi\rightarrow 3p\sigma$	6.41	6.40	6.58	6.56
E $^2\Sigma^+$	$2\pi\rightarrow 4s\sigma$	7.58	7.62	7.52	
H $^2\Pi$	$2\pi\rightarrow 3d\pi$	7.80	7.83	7.75	

[a] See Ref. [13]; [b] Relative to the $X^2\Pi$ ground state, -129.55479 au; [c] See Ref. [139]

Ionizations and shake-up ionizations

The ionized states of the NO radical are calculated by the SAC/SAC-CI method. They are singlet ground state and singlet and triplet excited states. Table XVIII shows the outer-valence ionization potential of the NO radical. The SAC/SAC-CI results are compared with the experimental results [10] and the CI results of Iwata et al. [10]. We note that an ionization from the 1π orbital produces six different states. The present SAC-CI results agree well with the experimental values. The assignments are different, however, from the CI results for the $^3\Sigma^-$ and $^1\Pi$ states.

Brion and Tan [12] observed the ionization spectra of the NO radical shown in Fig. 11 by the dipole (e, 2e) spectroscopy. The peaks in 9–20 eV region are well assigned as shown in Table XVIII. Brion and Tan noted that the three peaks arrowed in Fig. 11 (called here α, β, and γ peaks) are not explained by the single electron ionization picture. They may be explained by the shake-up ionizations, but the shake-up correlations in open-shell radicals should be different from those in closed-shell molecules.

Table XVIII

Outer-valence ionization potential of NO radical

Peak no.	Ionizing state	Orbital [a]	SAC/SAC-CI	Exptl. [b]	CI[b]
1	$^1\Sigma^+$	2π	9.02	9.54	9.22
2	$^3\Sigma^+$	1π	15.87	16.11	15.65
3	$^3\Pi$	3σ	16.35	16.56	15.87
4	$^3\Delta$	1π	17.31	17.34	17.25
5	$^3\Sigma^-$	1π	18.25	18.05	18.22
6	$^1\Pi$	3σ	18.40	18.27	17.67
7	$^1\Sigma^+$	1π	18.55	18.32	18.56
8	$^1\Delta$	1π	18.96	18.51	18.97
9	$^3\Pi$	2σ	21.85	21.7	
10	$^1\Pi$	2σ	24.62	23.3	
11	$^1\Sigma$	1π	24.81	≈24	

[a] Hartree-Fock configuration of NO radical is $(\text{core})^4\,(1\sigma)^2\,(2\sigma)^2\,(3\sigma)^2\,(1\pi)^4\,(2\pi)^1$

[b] See Ref. [10]

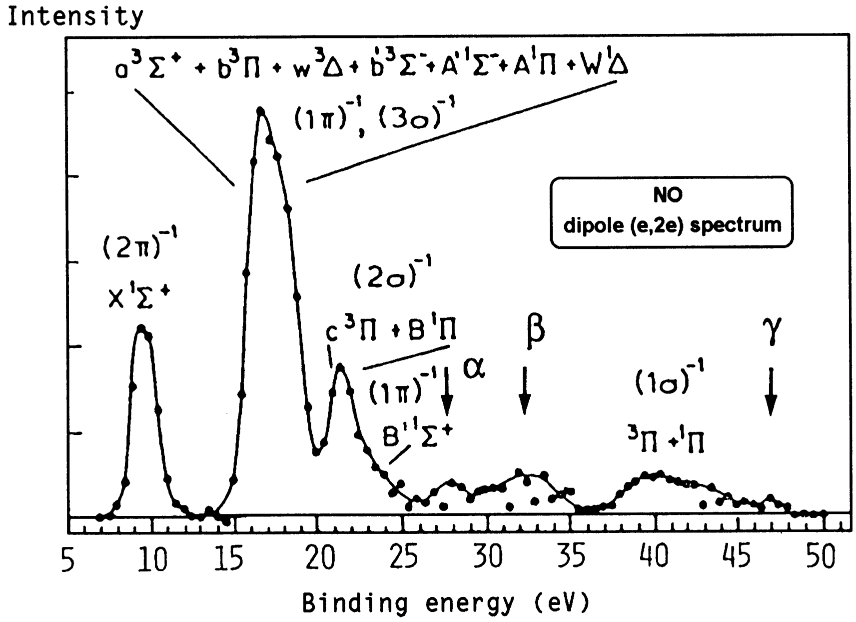
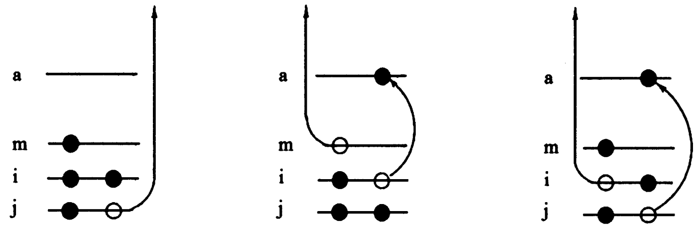


Fig. 11. Experimental ionization spectra of NO radical observed by the dipole (e, 2e) spectroscopy [12]

Figure 12 shows schematic pictures for the one and two-electron processes in the ionizations of open-shell radicals. Φ_1 represents a single electron process, and Φ_2 and Φ_3 two electron processes. When these configurations are constructed from the closed-shell cation ground state, Φ_1 and Φ_2 are produced by single electron excitations, but Φ_3 by a two-electron excitation. Though the observation of the two-electron excited state of a closed-shell molecule is very limited, the three peaks in Fig. 11 may correspond to this state if Φ_3 is the main configuration of these states.



	Φ_1	Φ_2	Φ_3
From radical	One	Two	Two
From cation	One	One	Two

Fig. 12. One and two-electron processes for the ionizations of open-shell radicals

The theoretical ionization spectrum calculated by the SAC-CI method is shown in Fig. 13. The peaks are composed of the singlet and triplet ionizations, but most of the stronger satellite peaks appear in the singlet manifold. The theoretical spectrum reproduces well the experimental one shown in Fig. 11. The assignments in the outer valence region are already seen in more detail in Table XVIII. In the inner valence region, the theoretical spectrum reproduces the three unassigned arrowed peaks observed by Brion and Tan. The peak α is assigned to the satellite of the singlet ionization from the 2σ MO ($^1\Pi$). Its principal nature is a simultaneous ionization-excitation from the 3σ and 1π MO's to the 2π MO. Similarly, the peak β is assigned to the satellite of the singlet ionization from the 1σ MO ($^1\Pi$) accompanied by the simultaneous ionization-excitation from the 2σ and 1π MO's to the 2π MO. Brion and Tan further pointed out the existence of a small peak at ca. 47 eV. Certainly, in the theoretical spectrum a group of small peaks exist at 48–49 eV. They are singlet peaks and the strongest one is at 48.8 eV. We then assign the peak γ to the satellite of the singlet ionization from the 1σ MO($^1\Pi$) accompanied by the simultaneous ionization from the 2σ and 1π MO's to the 2π MO.

Between the two types of the shake-up configurations, Φ_2 and Φ_3 shown in Fig. 12, the configurations of the type Φ_3 are much more important than the type Φ_2. Thus, the peaks observed by Brion and Tan corresponds to the genuine doubly excited configurations of the closed shell molecule which are seldom observed by ordinary spectroscopic techniques.

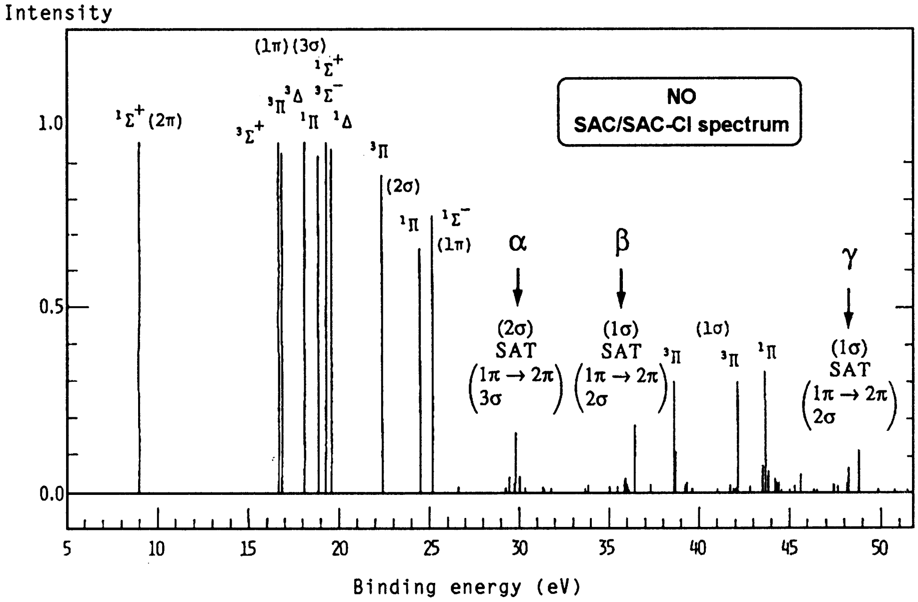


Fig. 13. Theoretical ionization spectrum of the NO radical calculated by the SAC/SAC-CI method

In the theoretical ionization spectrum, we see many peaks of relatively small intensities. This should be a reason for the broadness of the observed peaks in the inner-valence region. Further, all of the shake-up configurations involve the ionization-excitations from bonding or nonbonding MO's to antibonding MO's. Therefore, the geometries of the shake-up states should largely differ from that of the ground state. This should also be a reason for the broadness of the spectrum.

Hyperfine splitting constants

Hyperfine splitting constant (hfsc) is an important property of a doublet radical. The isotropic hfsc is represented by the Fermi contact interaction which is proportional to the spin density at the nucleus. Since this is a very local property, *ab initio* calculations of the hfsc's are more difficult than those of the other electronic properties such as dipole moment, polarizability, etc. It has been clarified that the following factors are important for adequate descriptions of the hfsc's.

(a) spin-polarization corrections [35,36]
(b) electron correlation corrections [38,39,127]
(c) cusp condition at the positions of nuclei [14].

Table XIX

Hyperfine splitting constants of some doublet radicals

Molecule	Nucleus	UHF	SAC-CI		Experiment ^{a,b}
			GTO	STO	
H_2^+	H	330.1	330.1	327.4	333.7
H_2O^+	O	-48.2	-23.1	-26.2	(-)29.7
	H	-49.2	-26.2	-24.1	(-)26.1
CH_3	C	71.3	28.4	25.6	28.7
	H	-40.6	-21.9	-29.6	-24.7
CH_3CH_2	Cβ	-28.4	-12.2	-12.1	-13.6
	Hβ	24.6	23.9	24.5	26.9
	Cα	76.4	22.2	24.0	29.5
	Hα	-39.6	-23.1	-25.9	-24.5
CH_3NH	C	-27.0	-11.9	-12.3	
	Hβ	28.4	29.0	29.6	34
	N	22.2	6.7	7.8	13
	Hα	-47.3	-21.5	-21.2	(-)22
CH_3O	C	-28.4	-13.9	-13.7	-15.6
	H	32.4	-37.7	39.4	43.7
	O	-36.7	-9.0	-18.3	
$CH_3OCH_3^+$	C	-17.8	-9.3	-8.5	
	H	30.8	39.4	39.8	43
	O	-61.4	-16.9	-23.9	
H_2CO^+	C	-64.8	-28.8	-29.8	-38.8
	H	98.3	117.1	119.4	132.7, 90.3
	O	-51.6	-13.3	-19.9	
CH_2CH	Cβ	-65.7	-7.4	-1.1	-8.6
	H*trans*	66.4	47.5	51.4	68.5
	H*cis*	49.6	29.3	34.1	34.2
	Cα	206.3	113.4	102.2	107.6
	Hα	-17.2	17.4	12.1	13.3
HCO	C	167.6	134.3	119.0	131.0
	H	114.8	115.3	119.0	127.0
	O	-14.8	-9.3	-16.3	

^{a} The sign(-) is based on the present theoretical result; ^{b} See Ref. [14]

The spin-polarization and electron correlation corrections are adequately described by the SAC-CI method, and the cusp condition at the positions of nuclei is reasonably well described when Slater-type orbitals (STO's) are used instead of Gaussian-type orbitals (GTO's). We have proposed a convenient STO calculation of hfsc's [14], using MO programs which can deal with only GTO's. Namely, the STO's are Gaussian expanded and all the integrals except for the Fermi contact integrals and the cusp values are calculated by the Gaussian expansion method. We have also shown that the Huzinaga-Dunning [4s2p/2s] GTO bases [75] are fairly useful for the calculations of hfsc's [38,39], though this basis does not satisfy the cusp condition.

We note that in the calculations of hfsc's, we should not do ordinary configuration selections in the SAC-CI step of Method 2 of Figure 10, because the spin density is sensitive to this procedure [38,39]. Since the dimension of the matrices to be diagonalized in the SAC-CI method is usually much smaller than those in a conventional CI, we can handle the matrices without doing configuration selection. Otherwise, we should do configuration selections using both energy and spin-density criteria.

We show in Table XIX the hfsc's of some doublet radicals calculated by the SAC-CI method with using the GTO and STO bases [14]. In fine examinations, we notice that the STO calculations are consistently better than the GTO calculations. The differences between the STO and GTO results are, however, small at least for the radicals including only H, C, N, and O atoms. The agreement between theory and experiment is satisfactory, so that the present method is useful for assignments of unknown radical species.

Table XIX also shows the results of the unrestricted HF (UHF) calculations using the GTO basis. We see that the UHF method is totally unreliable for the calculations of hfsc's. This is because both spin-polarization and electron-correlation corrections are very poorly included in the UHF method [35,36].

We give here the hfsc's only for the ground states of doublet radicals. However, in the present SAC/SAC-CI method, it is very easy to calculate the hfsc's of the excited states of doublet radicals. We have performed such calculations for the excited state of the NH_2 radical [128]. We encourage experimentalists to observe the hfsc's of the excited states, since it is expected that they will open a new field for investigating electronic structures of excited states.

Potential energy curves

Potential energy curves of molecules in ground, excited and ionized states have information very valuable for understanding and designing dynamics of molecular excited states. However, since the SAC theory is a single reference theory, it can not be applicable to quasi-degenerate electronic states which often appear in the dissociation of homolytic bonds. In order that the SAC theory is safely applicable, the HF configuration should be dominant throughout the process. In such case, we can calculate the potential energy curves of the ground, excited, ionized, and anion states by the SAC/SAC-CI method. The potential curves of doublet radicals are calculated by Method 2 of Fig. 10. The SAC/SAC-CI method would be applied to the calculations of the potential energy curves of the ground, excited and ionized states for

1. molecular vibrations,
2. isomerization processes,
3. ionic dissociation processes,
4. van der Waals interactions, and
5. surface interactions and chemisorptions.

We have also applied this method for calculating the potential curves of Li_2 [78] and CO [43]. We here review briefly the calculations for van der Waals molecules and chemisorption processes.

Van der Waals molecules

Recently, much attension has been paid for the spectroscopy of van der Waals molecules, since they are important as laser sources and since they offer good models for investigating solvent-solute interactions [129]. The potential curves of the ground, excited, ionized, and anion states of the van der Waals molecules would be good subjects of the SAC/SAC-CI method, since the HF configuration is dominant throughout the ground state interactions.

As an example, we show the SAC/SAC-CI calculations of the potential energy curves of Ar_2 [89]. It works as a laser source, and a detailed knowledge on the potential curves of the ground and excited states is a basis for understanding the dynamics of this system. Fig. 14 shows the potential curves of the ground state, 4s and 4p Rydberg excited states, and ionized states of Ar_2 calculated by the SAC/SAC-CI method. The spin-orbit coupling is included by the semi-empirical method [130]. The ground state is essentially repulsive, but has a very shallow minimum at about 8 bohr (experimentally at 7.1 bohr [131]). The spectroscopic properties of the 4s Rydberg states are summarized in Table XX. Values in parentheses are the experimental ones [131,132], which are mostly known for the A and C states. The agreement between theory and experiment is reasonable except for the binding energy D_e of the A state which is considerably smaller than the experimental value.

Table XXI is a summary of the spectroscopic constants for the ionized states of Ar_2 [89]. Both of the vertical and adiabatic ionization potentials agree well with the experimental values [133]. We have given some new assignments of the spectra based on the potential curves given in Fig. 14.

Another interesting application of the SAC-CI theory is an analysis of the collision induced absorption of Cs-Xe system [91], an open-shell van der Waals system. Though the 6s→5d and 6s→7s transitions of the Cs atom are forbidden, new absorption profiles appear near the forbidden lines when Xe gas is injected into the Cs vapour [134]. These profiles have been reproduced by the SAC-CI calculations of the potential energy curves and the transition moments for the Ce-Xe system with the use of the quasi-static model [135] for the interactions.

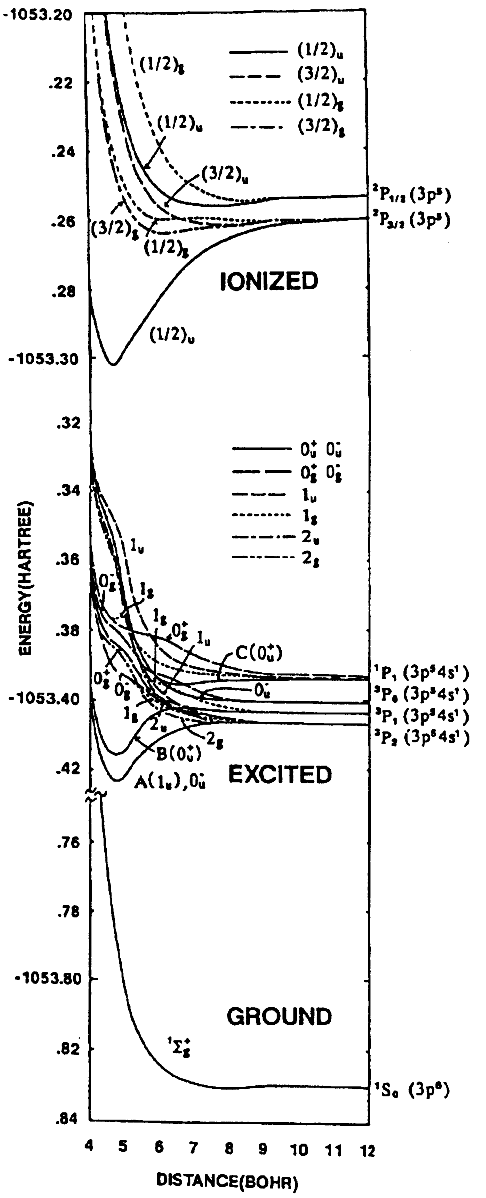


Fig. 14. Potential energy curves of the ground, excited and ionized states of Ar_2 calculated by the SAC/SAC-CI method

Table XX

Spectroscopic constants of the 4s Rydberg excited states of Ar_2 with spin-orbit interactions

State		T_e [a] (cm^{-1})	Emission [b] (cm^{-1})	R_{min} [c] (bohr)	R_{hump} [d] or R_{shoul} [e] (bohr)	ω_e [f] (cm^{-1})	$\omega_e x_e$ [g] (cm^{-1})	D_e [h] (cm^{-1})
$A1_u(^3P_2)$	calc.	89625	79620	4.66		273.5	4.10	3504,4194[i]
	exptl.	~87458[j]	79400[k]	(4.69[i])		297.2[l]	3.3[l]	6130[l],5643[l]
$BO_u^+(^3P_1)$	calc.	91307	81170	4.65	6.63(h)[m]	231.3	3.03	2499,3629[i]
	exptl.	~88210[j]	80000[k]	(4.67[i])				
$CO_u^+(^1P_1)$	calc.	95557		6.50	4.60(s)[m]	69.8	6.05	423
	exptl.	95033.6[j]		6.80[j]		68.16[j]	4.631[j]	465.8[j]

[a] Adiabatic excitation energy; [b] Emission energy; [c] Distance at the potential minimum;
[d] Distance at the hump; [e] Distance at the shoulder; [f] Vibrational frequency; [g] Anharmonicity constant
[h] Dissociation energy; [i] (theoretical value) see Ref. [140]; [j] See Ref. [131];
[k] See Ref. [141]; [l] See Ref. [132]; [m] h and s in parentheses mean hump and shoulder, respectively

Table XXI

Spectroscopic constants of the ionized states of Ar_2

State		R_{min} [a] (bohr)	Vertical IP(eV)	Adiabatic IP(eV)	ω_e [b] (cm^{-1})	$\omega_e x_e$ [c] (cm^{-1})	D_e [d] (eV)
$I(1/2)_u(^2P_{3/2})$	calc.	4.64	15.20	14.36	269.8	2.13	1.11
	exptl.		15.55[e]	14.44[e]			1.33[e]
$I(3/2)_g(^2P_{3/2})$	calc.	6.0	15.42	15.39			0.099
	exptl.		15.67[e]	15.63[e]			0.14[e]
$I(3/2)_u(^2P_{3/2})$	calc.		15.48				
$I(1/2)_g(^2P_{3/2})$	calc.		15.50				
$II(1/2)_u(^2P_{1/2})$	calc.	8.0	15.62	15.60			0.64
	exptl.		15.87[e]	15.84[e]			0. 10[e]
$II(1/2)_g(^2P_{1/2})$	calc.		15.76				
	exptl.		15.99[e]				

[a] Distance at the potential minimum; [b] Vibrational frequency; [c] Anharmonicity constant
[d] Dissociation energy; [e] See Ref. [133]

Surface interactions and chemisorptions

In our laboratory, we are also interested in surface-molecule interaction systems, catalytic reaction systems in particular. We have experienced that the SAC/SAC-CI method is very useful for studying such systems, since the catalytically active state is not necessarily the lowest surface state. Excited states may often be lowered significantly by interacting with admolecules and lead to dissociative chemisorptions [94].

Another reason of the usefulness of the SAC/SAC-CI method is that electron correlations are substantially important for describing surface electronic processes: transition metal is often involved in a surface and a bond formation and breaking occur on a surface of catalyst. The HF model alone is almost useless even for deducing qualitative conclusions [93].

Furthermore, the electron transfer between admolecule and a metal surface is sometimes of crucial importance for some surface-molecule interaction systems. There, the SAC-CI method gives a useful model of describing electron transfer from a bulk metal. The energetic consistency of the SAC-CI method between cation, neutral and electron attached states is very important in such applications. For details, we refer to the dipped adcluster model [136] and its application to the molecular and dissociative adsorptions of an oxygen molecule on a silver surface [95].

We explain here two examples of applications. Namely, hydrogen chemisorptions on Pt [94] and Pd [93] surfaces. We use the cluster model since an electron transfer from a metal surface to the admolecule is small in these systems.

Let an H_2 molecule approach to the Pt atom in a side-on, on-top mode, as shown in Fig. 15 from #1 to #7. Fig. 16 shows the potential curves of the $Pt-H_2$ system calculated by the SAC/SAC-CI method [94]. This potential does not include the spin-orbit coupling effect, which has been shown to be relatively small [94]. A notable point in Fig. 16 is that the catalytically active state is not the ground state but the excited state of the Pt atom. When an H_2 molecule approaches, the excited ^1S state of the Pt atom is much stabilized by the interaction, but the ground ^3D states are all repulsive. At the minimum ~#6 of this system, the H−H distance is 2.05 Å which is almost three times larger than the equilibrium H−H distance of the free H_2 molecule 0.741 Å. This means that a single Pt atom can dissociate H_2 with almost no barrier; the $^1A_1$ state at #6 is connected with the ground state of the separated system, $Pt(^3D) + H_2$ by the spin-orbit interaction. At the dissociated geometry, the HPtH angle is about 90°: two hydrogen atoms are captured by the d orbital of the Pt atom. The stabilization energy is calculated to be ~40 kcal/mol. The experimental adsorption energy is 24 kcal/mole. When we use Pt_3 cluster instead of the Pt atom, the adsorption energy is calculated to be 31.3 kcal/mol. The model for chemisorption is more natural in the Pt_3-H_2 system than in the $Pt-H_2$ system [94].

Next example is a hydrogen chemisorption on a Pd surface [93]. We first calculated $Pd-H_2$ system, but we could not obtain a dissociative state, differently from the $Pt-H_2$ system. The most stable geometry corresponds to a molecular adsorption state, the optimized H−H distance for the $Pd-H_2$ system being 0.768 Å which is close to 0.741 Å of a free H_2 molecule.

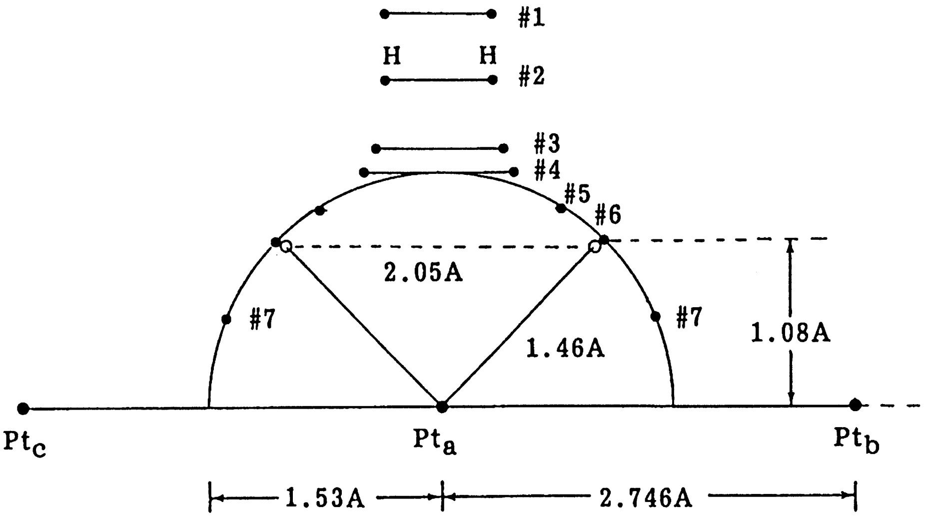


Fig. 15. Side-on, on-top reaction path for the Pt-H_2 system. Open circle indicates the most stable geometry

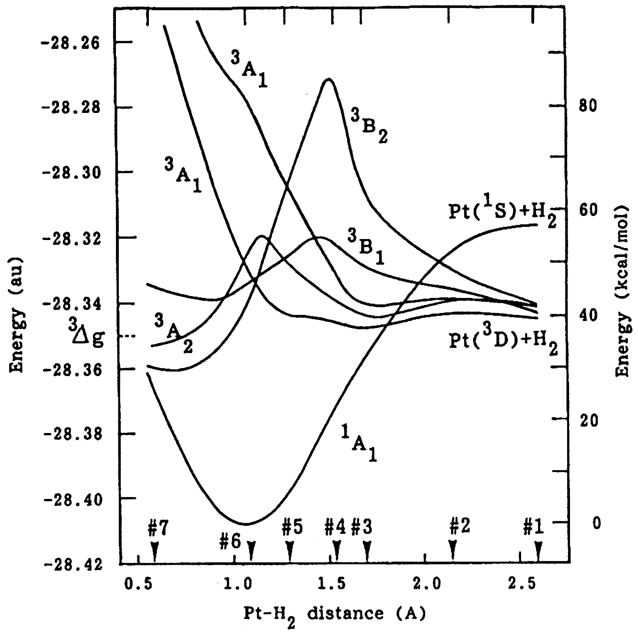


Fig. 16. Potential energy curves for the ground and excited states of Pt-H_2 calculated by the SAC/SAC-CI method without including spin-orbit coupling. The $^3\Delta_g$ state shown on the left-hand side is the lowest state for the linear geometry

We then considered a side-on bridge site approach of H_2 on Pd_2. The geometry of the interaction is shown in Fig. 17. It shows the potential curves of H_2 interacting at several distances with Pd_2. It was calculated by the modified CAS-SCF method [137]. When the Pd_2-H_2 distance R is larger than 2.0 Å, the potential of H_2 is very sharp, but when R approaches 1.6 Å, the potential suddenly becomes very flat for an elongation of the H–H distance. At R = 1.5 Å, a second minimum appears at about 1.8 Å. The heat of adsorption is calculated to be about 15 kcal/mol in comparison with the experimental value, 25–29 kcal/mol.

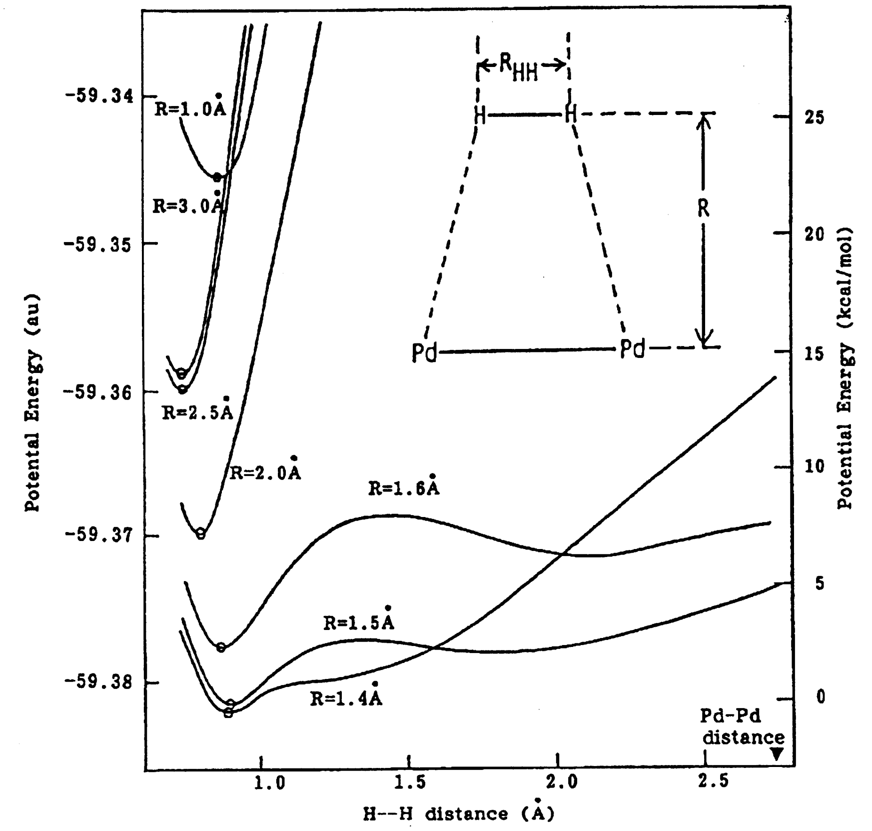


Fig. 17. Potential curves for the H-H stretching of the Pd_2-H_2 system at different Pd_2–H_2 separations (CAS-SCF method)

In order to obtain more reliable result, we have performed the SAC/SAC-CI calculations for the dissociation processes of H_2 on Pd_2 at R = 1.5 Å. Fig. 18 shows the result. The ground state curve calculated by the SAC method is well separated from the excited state curves, showing no participation of the excited states to this process. The ground state shows two potential minima: the minimum at $R_{HH}=0.90$ Å corresponds to molecular adsorption and the one at $R_{HH}=2.1$ Å to dissociative adsorption. The latter is more stable than the former by 2.2 kcal/mol in agreement with the experimental fact.

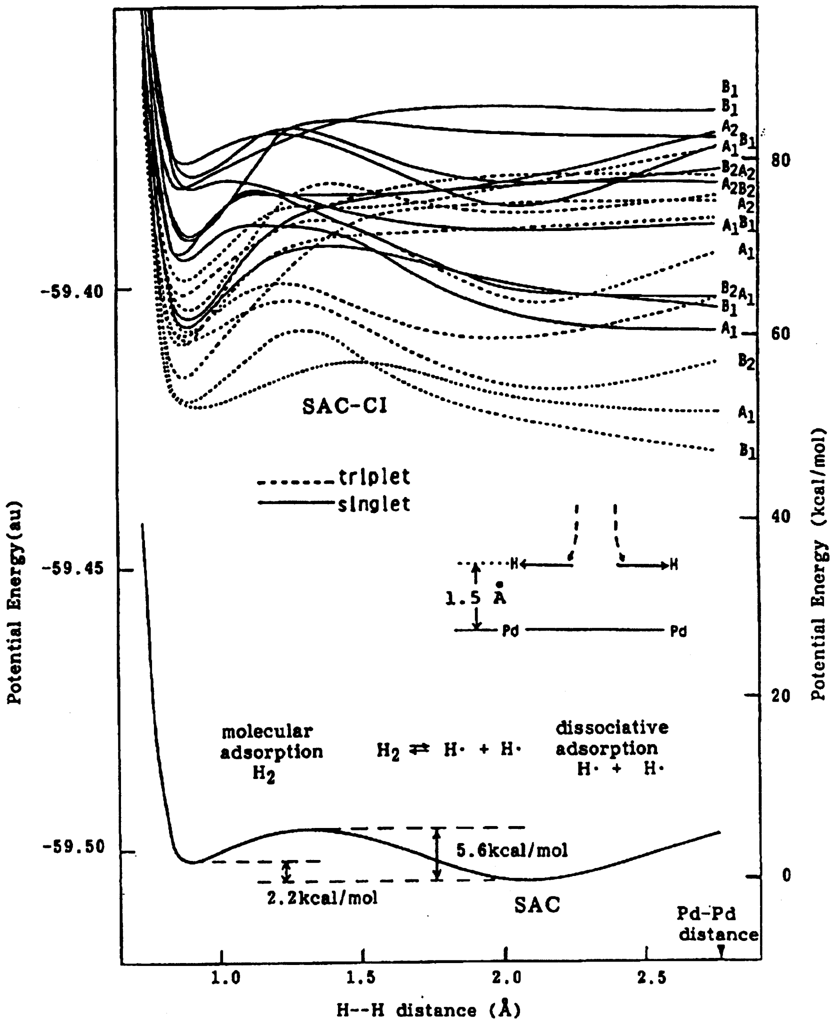


Fig. 18. Potential energy curves of the ground and excited states of the Pd_2-H_2 system as a function of the H-H distance of the H_2 molecule at 1.5 Å apart from the Pd_2 fragment (SAC/SAC-CI method)

We note that the dissociative adsorption is describable only when electron correlations are sufficiently included. The HF model does not give the second minimum of the dissociative adsorption [93]. In the CAS-SCF curve shown in Fig. 17, the molecular adsorption state is more stable than the dissociative state, but in the SAC curve shown in Fig. 18, the dissociative state is more stable in agreement with experiment.

The existence of molecular and dissociative surface states seems to explain an irreversibility of the photoelectron spectra of H_2 adsorbed on a palladium surface [138]. A detailed argument is given in Ref. [93]. We note that the molecular adsorption was not calculated for the Pt surface [94].

Concluding remarks

We have shown that the applicability of the SAC/SAC-CI theory covers a wide field of chemistry involving molecular ground, excited, ionized, and electron attached states. The theoretical structure of the SAC/SAC-CI theory is simple and yet accurate up to the exact limit. It has been proved to give reliable energies and properties. We conclude that the SAC/SAC-CI method is simple enough to be useful and accurate enough to be useful.

All the results shown in this review are calculated by the program SAC85 [50]. As the author of the theory and the program, the present author wishes that this method is widely utilized for solving many different scientific problems and thereby contributes to the progress of science. The program SAC85 is offered worldwide from the author, by request, for scientific studies with peacefull purposes [50].

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