Introduction to SAC-CI method

part II

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preface

Symmetry Adapted Cluster /Configuration Interaction

The SAC-CI method is based on the cluster expansion approach and is an accurate electronic-structure theory for ground, excited, ionized and electron-attached states of molecules. The energy gradient method has also implemented and therefore, we can calculate the energy gradient (force) acting on nuclei for all of these electronic states. We can study molecular structures and chemical reaction dynamics involving these different electronic states

preface

SAC/SAC-CI program

Accurate correlation theory for ground and excited states

(H. Nakatsuji, 1978)

SAC singlet closed-shell state (ground state)

SAC-CI

- singlet excited states
- triplet ground & excited states
- ionized states (doublet ground & excited states)
- electron-attached states (doublet ground & excited states)
- quartet to septet ground & excited states

Energy Gradient (Force acting on nuclei)

Dynamics involving ground and excited states

Subject: Chemistry and Physics involving these states

Released through Gaussian03

SAC theory

For the totally symmetric singlet closed-shell state, we define symmetry adapted cluster (SAC) expansion as:

$$\left|\Psi_g\right\rangle = \exp\left(\sum_I C_I S_I\right)\left|0\right\rangle \qquad (1)$$

$$= \left(1 + \sum_I C_I S_I + \tfrac{1}{2}\sum_{I,J} C_I C_J S_I S_J + \ldots\right)\left|0\right\rangle$$

Where |*0*> is Hartree-Fock and $\boldsymbol{S_I}$ is symmetry adapted excitation operator.

SAC theory

S_I denotes symmetry-adapted excitation operator which produces a symmetry-adapted configuration on applying the reference wavefunction Φ_0, which is chosen as restricted HF wavefunction:

$$\Phi_0 = \left|0\right\rangle = \left\| \varphi_1 \overline{\varphi}_1 \ldots \varphi_k \overline{\varphi}_k \ldots \varphi_q \overline{\varphi}_q \varphi_{q+1} \ldots \varphi_p \overline{\varphi}_p \right\| (2)$$

SAC theory

A single excitation from occupied orbital *i* to virtual orbital *a* is given by

$$S_i^a = \frac{1}{\sqrt{2}}\left(a^{\dagger}_{\mathrm{a}\alpha} a_{\mathrm{i}\alpha} + a^{\dagger}_{\mathrm{a}\beta} a_{\mathrm{i}\beta}\right) \qquad (3)$$

Double, triple and quadruple excitations are written as products of single excitation operators as

$S_i^a S_j^b, S_i^a S_j^b S_k^c$ *and* $S_i^a S_j^b S_k^c S_l^d$ respectively.

SAC theory

1. non-variational solution.

If the SAC wavefunction were the exact wavefunction the function $(H\text{-}E_g)|\Psi_g>$ would be identically zero. We require the conditoin in the space of the linked configurations $|0>$ and $S_K^+|0>$, that is

$$\langle 0 | H - E_g | \Psi_g \rangle = 0 \qquad (4)$$

$$\langle 0 | S_I (H - E_g) | \Psi_g \rangle = 0 \qquad (5)$$

These equations are sufficient to determine the unknowns $\{C_I\}$ and E_g.

SAC theory

1. non-variational solution.

Non-variational solution is also called as SAC MET.

The features of that method are as follows.

Its energy doesn’t have an upper bound nature.

The concept of self-consistency seems not apply to the non-variational solution. However, a remarkable merit of this solution over the variational one is that the former doesn’t include matrix elements between unlinked terms but **include at most elements between linked and unlinked terms.**

SAC theory

2. variational solution

As in the original paper, the variational solution is obtained by applying the variational principle to the SAC wave function and the equations are:

$$\left\langle \Psi_g \middle| H - E_g \middle| \Psi_g \right\rangle = 0 \qquad (6)$$

$$\left\langle \Psi_g \middle| (H - E_g) S_I^\dagger \middle| \Psi_g \right\rangle = 0 \qquad (7)$$

Eqs. (6) and (7) suffice to determine all the unknowns $\{C_I\}$ and E_g.

SAC theory

2. variational solution

The features of the variational solution are as follows. **It gives an upper bound to the exact energy.** It gives a basis for an analysis and extension of various variational model theories, since formally it includes completely the self-consistency in an expansion form. On the other hand, a computational **problem of this procedure is that it includes matrix elements between unlinked terms.** This make a complete solution of eqs. (6) and (7) almost prohibitive. In applications we shall introduce some approximations which express high-order terms in terms of the lower-order ones.

SAC-CI theory

The SAC theory defines not only the SAC wave function for the ground state, but also the excited functions which span the basis of high quality for the excited states. We define the excited functions (***Φ***Φ_K) by using the SAC wave function as

$$\Phi_K = P S_K^{\dagger} \left| \Psi_g \right\rangle \qquad (8)$$

where *P* is an operator which projects out the ground state

$$P = 1 - \left| \Psi_g \right\rangle \left\langle \Psi_g \right| \qquad (9)$$

SAC-CI theory

It is easily shown that the functions satisfy the important relation of the basis for excited states:

$$\left\langle \Phi_K \middle| \Psi_g \right\rangle = 0, \qquad (10)$$

$$\left\langle \Phi_K \middle| H \middle| \Psi_g \right\rangle = 0 \qquad (11)$$

This relation means that the function $\{\Phi_K\}$ form a basis for *excited states*. Then we may express the excited states in CI form as

$$\Psi_e^{SAC-CI} = \sum_K d_K \Phi_K \qquad (12)$$

$$= \Big(\sum_K d_K R_K + \sum_{K,I} d_K C_I R_K S_I + \ldots\Big)\left|0\right\rangle - \sum_K d_K S_{gK} \left|\Psi_g\right\rangle$$

SAC-CI theory

where $$S_{gK} = \left\langle \Psi_g \middle| R_K \middle| \Psi_g \right\rangle \tag{12}$$

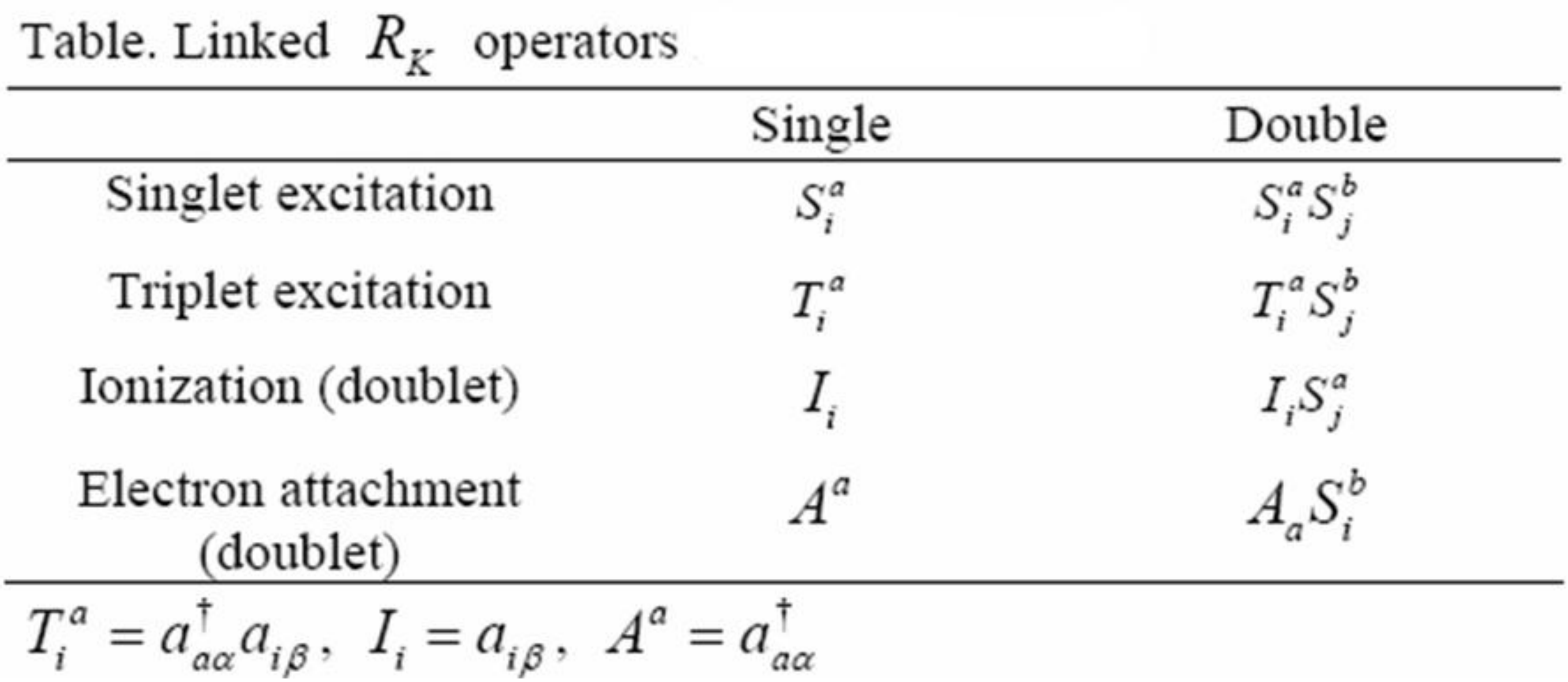

Table. Linked R_K operators

	Single	Double
Singlet excitation	S_i^a	$S_i^a S_j^b$
Triplet excitation	T_i^a	$T_i^a S_j^b$
Ionization (doublet)	I_i	$I_i S_j^a$
Electron attachment (doublet)	A^a	$A_a S_i^b$

$T_i^a = a_{a\alpha}^\dagger a_{i\beta}$, $I_i = a_{i\beta}$, $A^a = a_{a\alpha}^\dagger$

where ($\boldsymbol{R_K}$) represent a set of excitation, ionization, and/or electron attachment operators.

SAC-CI theory

For the unlinked operators, $R_K S_I$, we include

single R_K* double S_I= triple excitation

and

double R_K * double S_I= quadruple excitation.

SAC-CI theory

1. variational solution

Applying the variational principle for solving the unknown variables (***d****_K*), we obtain

$$\left\langle \Phi_K \middle| H - E_e \middle| \Psi_e^{SAC-CI} \right\rangle = 0 \qquad (13)$$

The SAC-CI wave function automatically satisfies the orthogonality and Hamiltonian orthogonality with the ground state and also with different excited states.

SAC-CI theory

2. non-variational solution

Though the formulation of the SAC-CI theory is variational, non-variational formulation is also possible. The non-variational SAC-CI solution is obtained by projecting the Schrödinger equation onto the space of the linked configurations

$$\left\langle 0 \middle| R_K (H - E_e) \middle| \Psi_e^{SAC-CI} \right\rangle = 0 \qquad (14)$$

SAC-CI theory

non-variational vs. variational solution

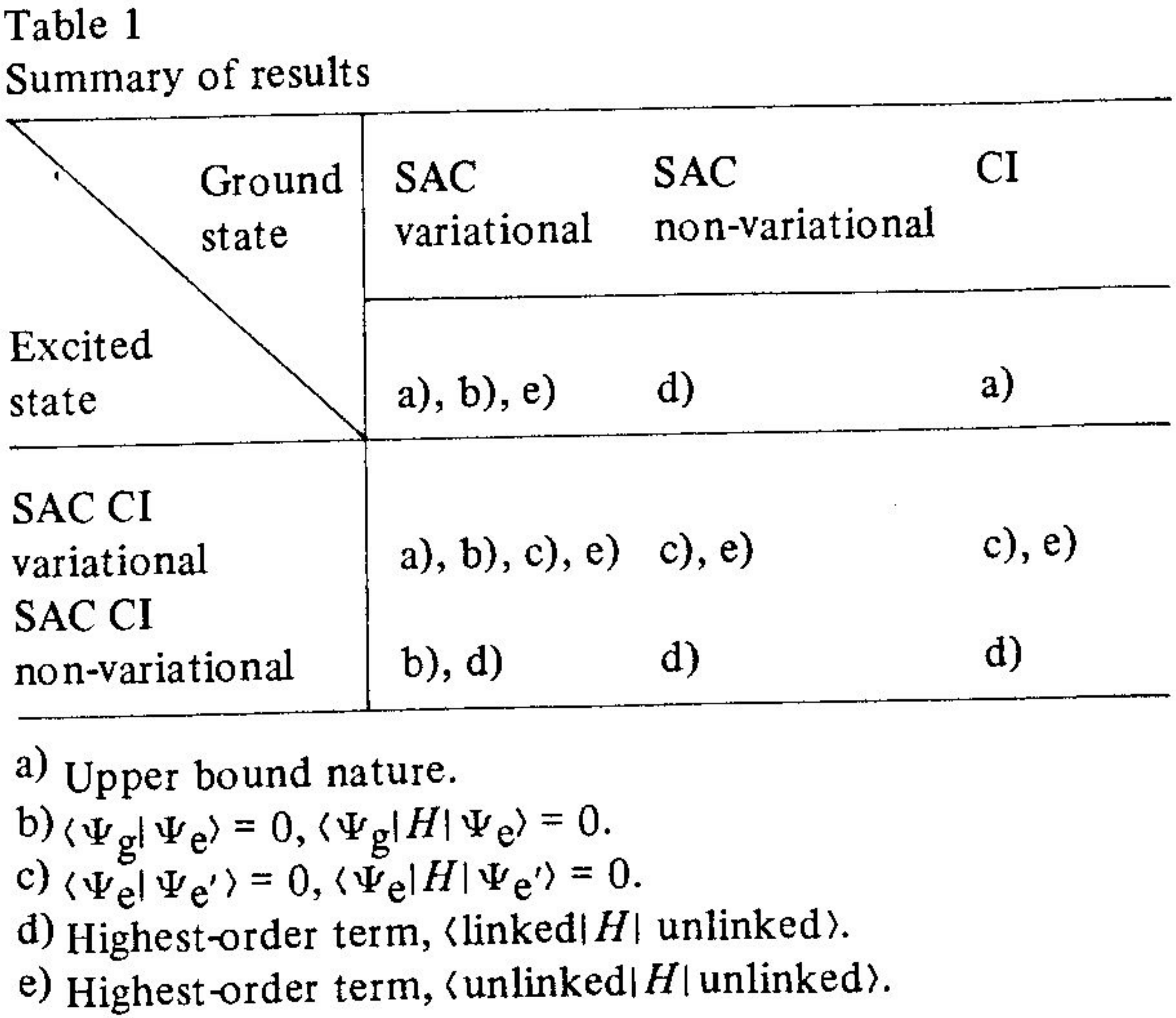

Table 1
Summary of results

Ground state Excited state	SAC variational	SAC non-variational	CI
	a), b), e)	d)	a)
SAC CI variational	a), b), c), e)	c), e)	c), e)
SAC CI non-variational	b), d)	d)	d)

a) Upper bound nature.
b) $\langle \Psi_g | \Psi_e \rangle = 0$, $\langle \Psi_g | H | \Psi_e \rangle = 0$.
c) $\langle \Psi_e | \Psi_{e'} \rangle = 0$, $\langle \Psi_e | H | \Psi_{e'} \rangle = 0$.
d) Highest-order term, ⟨linked| H | unlinked⟩.
e) Highest-order term, ⟨unlinked| H | unlinked⟩.

The END

Thank You
for
Your Attention