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CLUSTER EXPANSION METHODS FOR THE STUDY OF CORRELATIONS IN

OPEN SHELL AND EXCITED STATES

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Because of its linear variational nature, the CI expansion gives a consistent method for ground and excited states. The solutions for both states are mutually orthogonal and hamiltonian-orthogonal, and they constitute upper bounds for both states. However, another feature lies in its slow convergence. This becomes severe especially for excited states, though a stride has been made in recent years in efficient solutions of the CI expansion.[1]

The cluster expansion gives, on the other hand, a rapidly convergent method for ground states with inclusion of higher-order unlinked terms.[2,3] It also shows a correct dependence on the number of particles involved, in contrast to a standard (1+2)CI.[4] Though the applications are still very limited, the results seem to show a promising utility of the theory.[5]

We consider an extension of this approach to open-shell systems, introducing symmetry-adapted-cluster (SAC) expansion.[6] Variational and non-variational solutions are considered. In a single excitation

case, this expansion gives pseudo-orbital theory. It is applied to the study of spin-correlations in open-shell atoms and molecules. We next consider the SAC-CI theory for excited states.[7] The SAC theory combined with the variational principle gives a basis for the excited states. Variational and non-variational solutions are considered. Then, the SAC and SAC-CI theories are applied to the study of electron correlations in the ground and excited states of relatively small molecules. So far, the results have shown excellent agreements with the full CI and close-to-full CI results, with much smaller numbers of variables (sizes of the matrices) involved. This seems to show a utility of the SAC and especially of the SAC-CI theory, since the slow convergence of the CI expansion is much more critical for excited states than for ground states.

1. SAC Expansion for Ground States

We expand the ground state of a given spin-space symmetry by

$$\Psi_g = O \exp(\hat{S})\Phi_0 = [1 + \hat{S} + O\,(\frac{1}{2}\hat{S}^2 + \frac{1}{6}\hat{S}^3 + \,\cdots\,\,)\,]\Phi_0$$

$$= O \exp(\sum_I C_I S_I^+)\,\Phi_0 \tag{1}$$

$$\hat{S} = \hat{S}_{(1)} + \hat{S}_{(2)} + \hat{S}_{(3)} + \cdots + \hat{S}_{(N)} = \sum_I C_I S_I^+ \tag{2}$$

where $\hat{S}$ is a sum of the essentially $\underline{i}$-ple excitation operator $\hat{S}_{(i)}$. S_I^+ denotes a symmetry-adapted excitation operator which produces symmetry-adapted configuration on applying the reference wavefunction (wf) $\Phi_0 = |0\rangle$, which is chosen as restricted HF wf. The symmetry adaptation of the excitation operator is necessary because of the non-linear nature of the expansion. Otherwise, a mixing of different symmetry spaces may occur as discussed in detail previously.[6] We note

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that for totally symmetric singlet states, the projection operator O is unnecessary.

A. Variational solution (SAC-V); Application of the variational principle to the SAC wf given by eq.(1) leads to an equation

$$\langle \Psi_g | (H - E_g) S_K^+ | \Psi_g' \rangle = 0 \tag{3}$$

where $\Psi_g' = \exp(\sum_I C_I S_I^+) \Phi_0$. The energy may be calculated from

$$\langle \Psi_g | H - E_g | \Psi_g \rangle = 0 . \tag{4}$$

B. Non-variational solution (SAC-MET); If the SAC wf were the exact wf, the function $(H - E_g) | \Psi_g \rangle$ would be identically zero. Requiring this condition in the space $|0\rangle$ and $S_K^+ |0\rangle$, we obtain

$$\langle 0 | H - E_g | \Psi_g \rangle = 0 \tag{5}$$

$$\langle 0 | S_K (H - E_g) | \Psi_g \rangle = 0 . \tag{6}$$

For closed shell, the solution of eqs.(5) and (6) seems to be equivalent to that of the coupled-cluster many-electron theory (CC-MET) by Cizek and Puldus, though the latter was derived in diagrammatic form.[3,5]

The variational solution gives an upper bound to the exact energy. It also gives a basis for an analysis and extension of various model theories, since formally it includes completely the self-consistency in an expansion form. In a single excitation case, it gives a new orbital theory, called pseudo-orbital theory, as the conventional cluster expansion leads to a conventional (UHF) orbital theory (Thouless theorem[8]). Including only spin-polarization excitation and its self-consistency to first order, we have calculated spin densities of atoms and molecules (Table 1). On the other hand, the non-variational method is simpler computationally than the variational one, since the former

does not include the matrix element between unlinked terms.

2. SAC-CI Theory for Excited States

We define a set of functions $\{\Phi_K\}$ on the basis of the SAC ground state Ψ_g as

$$\Phi_K = N_K P O^{(R)} R_K^+ \Psi_g ' \tag{7}$$

where P is a projector $P = 1 - |\Psi_g><\Psi_g|$ and R_K^+ is a symmetry-adapted excitation operator for the symmetry of the excited state under consideration. $O^{(R)}$ is the projector for that symmetry. We note that when the ground state is a totally symmetric singlet state, the projector $O^{(R)}$ is unnecessary.

When the SAC wf Ψ_g for the ground state satisfies the variational equation (eq.(3)), the functions $\{\Phi_K\}$ satisfy the relations

$$<\Phi_K|\Psi_g> = 0 , \qquad <\Phi_K|H|\Psi_g> = 0 \tag{8}$$

which are the Brillouin theorem in a generalized sense. This relation means that the functions $\{\Phi_K\}$ form a basis _for excited states_. Then, we may express the excited states in a form

$$\Psi_e = \sum_K d_K \Phi_K \tag{9}$$

This is the SAC-CI wf for the excited states.[7]

The SAC-CI theory for excited states seems to converge more rapidly than the conventional CI expansion. (a) Theoretically the basis functions $\{\Phi_K\}$ already satisfy the necessary condition (8) for the excited state. (b) Since the basis Φ_K includes the electron correlation in the ground state through $\Psi_g '$, the SAC-CI method has only to express the reorganization in electron correlation in the excited state. The similar the two correlations are, the more rapid would be the convergenc

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A. Variational solution (SAC-CI-V); Application of the variational principle leads to a seqular equation

$$\sum_L \langle \Phi_K | H - E_e | \Phi_L \rangle \, d_L = 0 \; . \tag{10}$$

Recently, Paldus, Cizek, and coworkers[9] have considered in a diagrammatic form a similar variational theory for open shell-systems using the non-variational CP-MET solution for closed-shell ground state. In their formulation the relation (8) which is a key in the SAC-CI formalism does not arise.

B. Non-variational solution (SAC-CI-NV); If the SAC-CI wf were the exact wf, it would satisfy the Schrödinger equation $(H - E_e) | \Psi_e \rangle = 0$. Requiring this condition in the space of the linked configurations $R_K^+ | 0 \rangle$, we obtain

$$\sum_L \langle 0 | R_K (H - E_e) | \Phi_L \rangle \, d_L = 0 \; . \tag{11}$$

This equation suffices to determine all of the unknowns in the SAC-CI wf.

When the basis functions $\{\Phi_K\}$ satisfy eq.(3), the nth solution of the variational eq.(10) gives an upper bound of the energy of the nth excited state. The excited states obtained from eq.(10) show correct relations to each other. However, a merit of the non-variational solution is that it includes at most the element between linked and unlinked terms.

3. Applications

In Table 1, we have summarized the results of the pseudo-orbital theory applied to the calculations of the spin densities of first-row atoms. Further, the SAC and SAC-CI theories have been applied to the calculations of the electron correlations in the ground and excited

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states of relatively small molecules. Approximations were considered

for the variational solutions since time-consuming terms are involved.

The results for the ground and Rydberg excited states of H_2O are given

in Table 2 and compared with the very accurate CI results of Hausman,

Bloom, and Bender.[10] The present results show excellent agreement

with the accurate results with much smaller numbers of variables (sizes

of the matrices) involved.

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Table 1. Spin densities for first-row atoms

	UHF	SEHF	SOHF	FOCI	Present	Experiment
Li ^{2}S	0.2248	0.2406	0.2265	0.2065	0.2243	0.2313
^{2}P	−0.01747	−0.02304	−0.0169	−0.02222	−0.0168	−0.01693
Be$^+$ ^{2}S		1.008	0.9938		0.9694	
B^{2+} ^{2}S		2.521	2.516		2.484	
B ^{2}P	0.0192	0.0361	0.0022	0.0041	0.0147	0.0081
C ^{3}P	0.0753	0.0733	0.0423	0.0288	0.0487	
N ^{4}S	0.1853	0.1579	0.1200	0.0714	0.1176	0.09705
O ^{3}P	0.1944	0.2137		0.0628	0.0712	0.11398
F ^{2}P	0.1298	0.2455		0.0496	0.0305	0.071835

Table 2. Ground and Rydberg excited states of H_2O compared with accurate wavefunctions [a,b]

State		HF-SECI	(1+2)CI	SAC-V SAC-CI-NV	SAC-V SAC-CI-V	Hausman-Bloom-Bender[c] wf 2	wf 4
$^1A_1$	1(G)	(6)[d] 0.0	(59) −0.04225	(59 for G, 58 for E) −0.04257	−0.04257	(1051)[d] −0.04225	(11149) −0.04461
	2(E)	0.32171	0.24296	0.22509	0.22096	0.22090	0.21978
	3	0.35063	0.26323	0.24403	0.23908	0.23918	0.23816
	4	0.42588	0.34275	0.32657	0.32065	0.32090	0.31958
$^1A_2$	1	(3) 0.32060	(41) 0.22874	(41) 0.20932	(41) 0.20405	(516) 0.20266	(10952) 0.20162
$^1B_1$	1	(4) 0.24959	(43) 0.15946	(43) 0.13920	(43) 0.13534	(1088) 0.13505	(11001) 0.13396
	2	0.33066	0.24661	0.22505	0.21981	0.21844	0.21754
	3	0.39446	0.32494	0.30792	0.30424	0.30369	0.30306
$^1B_2$	1	(5) 0.39093	(47) 0.31496	(47) 0.30005	(47) 0.29452	(468) 0.29419	(11101) 0.29342

a) The present results are relative to the HF energy, −75.52590 au.

b) SAC-MET energy for the ground state is −0.04236 au.

c) The values for wf 2 and wf 4 were calculated from the results of ref. 10.
wf 2 = (multi-ref) + (excitations through doubles)
wf 4 = (multi-ref) + (excitations through sextuples)

d) The integers in parentheses show the numbers of the independent variables (sizes of the matrices) involved in the present calculation and the numbers of the Slater determinants involved in wf 2 and wf 4.