COMPOSITE NATURAL ORBITALS FOR CONFIGURATION INTERACTION METHOD

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Dedicated to Dr R. Zahradnik on the occasion of his 60th birthday.

A new method of constructing approximate natural orbitals (NO's) is proposed. A system can usually be regarded as consisting of fragments. The approximate NO's of the entire system are constructed from the NO's of fragments in their ground states. These orbitals are expected to be useful in configuration interaction (CI) calculations of a large system where orbital truncation is necessary. The usefulness of these approximate NO's, which are called composite NO's (CNO's), is demonstrated on C_4H_6. This molecule may be regarded as a combination of two fragments i.e., C_2H_4's. Excitation energies calculated by single and double excitation CI with the truncated CNO's (14σ, 7π correlating orbitals) agree reasonably well with those calculated with a full orbital set (37σ, 12π correlating orbitals), while the truncated SCFMO's of the same size give disastrous excitation energies.

The method of configuration interaction (CI) has been widely used in quantum chemistry because of its conceptional simplicity and its flexibility. The method, however, suffers from slow convergence in its expansion. Even with an orbital basis of moderate size, a full CI calculation is virtually impossible and one has to truncate the expansion at a certain point. The bigger the system under treatment, the shorter the expansion.

It is well known that the convergence of truncated CI depends also on an orbital set from which configuration state functions (CSF's) are constructed. Although the canonical self consistent field molecular orbitals (SCFMO's) are frequently used in CI, they are not appropriate for describing electron correlation. The canonical SCF virtual orbitals are determined under the influence of $N + 1$ electron potential, so that they have only small amplitude in the region of space covered by the occupied orbitals and thus they are not effective in describing electronic correlation. The latter shortcoming can be circumvented by using the natural orbitals (NO's). It was proved that the NO's give the fastest convergence in two-electron systems[1]. It is generally believed that the NO's are also the most suitable orbitals for describing electron correlation in many-electron systems. A drawback about the NO's is that they cannot be obtained before the CI calculation.

There are several attempts to prepare orbitals which approximate the NO's without actually carrying out the CI of a target system. Meyer et al. developed the pseudo-natural orbital (PNO) method, where NO's for all possible electron pairs are generated and are used in construction of CSF's[2]. Although they showed excellent convergence in CI expansion, the transformation of two-electron integrals would become very time consuming for large systems. Cooper and Pounder have proposed the modified virtual orbitals, which are a solution of a modified Fock equation with extra Coulomb attraction from nuclei and has large amplitude in the valence region[3]. Davidson analyzed features of NO's and found that NO's have maximal exchange integrals with occupied orbitals[4]. Thus, Feller and Davidson developed the K-orbital method, in which the K-orbitals are determined to satisfy the above criterion[5]. These orbital sets show definitely better convergence than the ordinary canonical SCFMO's.

In this paper, we propose another way of preparing approximate NO's from a rather different point of view. A molecule can usually be regarded as consisting of fragments. The electronic correlation of the total system is related naturally with those of fragments. Therefore, the NO sets obtained for fragments would be a suitable component from which approximate NO's are constructed. A way of constructing these approximate NO's from NO's of fragments is proposed in this paper. The resulting orbitals are called composite natural orbitals (CNO's). Furthermore, if the same CNO's can be used for both the ground and excited states, only the NO set of one particular state e.g. the ground state of the fragments would be enough in constructing CNO's. In the first section of this paper, we examine C_2H_4 and show that this is indeed the case, namely the ground state NO's are acceptable substitute for the excited state NO's in C_2H_4. In the following section we construct CNO's for C_4H_6 from the ground state NO's of C_2H_4 and show that they yield reasonable excitation energies even when orbitals are grossly truncated. In all calculations with CNO's reported in this paper, the occupied orbitals are determined for each state by the SCF procedure or by making NO's from single excitation CI.

In the last section conclusions as to the effectiveness of CNO's are given.

RESULTS AND DISCUSSION

Ethylene Molecule

Ethylene is a natural fragment of linear polyenes. First, a CI calculation of the ground state is performed. Then CI calculations of several excited states are carried out by using the NO set of the ground state as virtual orbitals or correlating orbitals. The results show that these ground state NO's are acceptable substitute of the NO's for the excited states.

The orbital basis used in the calculation consists of a split valence contracted Gaussian-type orbitals (CGTO) prepared by Tatewaki and Huzinaga[6] and two diffuse p functions on each C with the exponents of 0·03477 and 0·01074. These exponents were determined for butadiene by Hosteny et al.[7]. The geometry of C_2H_4 is taken from the experimental equilibrium geometry of s-*trans*-butadiene[8]. The X and Y-axis are chosen to be the C—C axis and perpendicular to the molecular plane, respectively.

Single and double excitation CI calculations (SD-CI) are carried out on the ground state $^1A_g(1b_{3u}^2)$ and the following excited states; $^{3,1}B_{1u}(1b_{3u}1b_{2g})$, $^3A_g(1b_{3u}2b_{3u})$, and $2\,^1A_g\,(1b_{3u}2b_{3u})$, where the π-electron configurations are shown in parenthesis.

Occupied orbitals are determined by SCF calculations for the three states $1\,^1A_g$, $^3B_{1u}$, and ^3A_g and by single excitation CI(S-CI) for the $^1B_{1u}$ and $2\,^1A_g$ states, where our SCF program package does not work. The results of SCF(S-CI) calculations are summarized in Table I.

Two kinds of correlating orbitals are used in the following CI calculation. The first set is SCFMO's or NO's from S-CI. The second set is the NO's obtained from SD-CI of the ground state. Since the second set is not orthogonal to the occupied orbitals for the excited states, it is orthogonalized by the Schmidt procedure. Hereafter, we denote the first set plus the occupied orbitals determined by SCF or S-CI as "SCFMO" and the second set plus the occupied orbitals as "GNO".

In the SD-CI calculation, the $1s$ cores of C are frozen and two electron excitations from the σ orbitals are excluded. When no orbital truncation is made, the results are the same for "SCF" and "GNO" and these are given in Table II. They agree reasonably well with the results obtained by more extensive CI calculations of Buenker et al.[8].

The main purpose of the calculation in this section is to examine how much we can truncate the correlating orbitals without sacrificing too much accuracy. The full

TABLE I

Result of SCF and S-CI calculations of ethylene. Ground state energies are given as E/E_h, $E_h = 2·6255 . 10^6$ J mol^{-1} and transition energies are in eV

State	This work	BPK (ref.[8])
^1A_g	−77·91135	−78·0019
$^3B_{1u}$	3·510	3·289
$^1B_{1u}$	7·404	7·414
^3A_g	6·915	6·778
$2\,^1A_g$	6·908	

set of correlating orbitals contained 22σ and 6 (7 for the ground state) π orbitals. Various orbital truncations are tried; namely the 22σ correlating orbitals are truncated to 15 and 7, while the 6π correlating orbitals are truncated to 3, 2, and 1 (for the ground state 4, 3, and 2). The SD-CI calculation with truncated orbitals is carried out for two kinds of basis mentioned above i.e. "SCF" and "GNO". The results are shown in Tables III – VII.

TABLE II

Result of SD-CI calculation of ethylene. Energies are given in the same manner as in Table I

State	Number of CSF's	This work	BPK^a	Expt.
^1A_g	2 037	−77·99711	−78·0376	
$^3B_{1u}$	3 449	4·568	4·255	4·6[b]
$^1B_{1u}$	3 369	8·606	8·323	7·66[c]
^3A_g	3 449	8·105	7·732	
$2\,^1A_g$	3 369	8·284	8·035	8·257[d]

[a] Ref.[8]; [b] ref.[9]; [c] ref.[10]; [d] ref.[11].

TABLE III

Truncated SD-CI results for the ground state of ethylene. The difference in energy between the untruncated (22/7) and the truncated SD-CI energy. All energies are given in eV

$N_\sigma/N_\pi{}^a$	Number of CSF's	$\Delta E(SCF)^b$	$\Delta E(GNO)^b$
(22/7)	2 037	0·0	0·0
(15/7)	1 281	0·806	0·0
(7/7)	589	1·407	0·051
(22/4)	1 326	1·798	0·0
(15/4)	810	2·059	0·001
(7/4)	358	2·245	0·052
(22/3)	1 091	1·920	0·006
(15/3)	655	2·136	0·006
(7/3)	283	2·261	0·056
(22/2)	857	2·270	0·111
(15/2)	501	2·321	0·111
(7/2)	209	2·333	0·157

[a] The numbers (N_σ/N_π) in the first column mean that N_σ and N_π correlating orbitals are used for σ and π orbitals, respectively; [b] $\Delta E(SCF) = E(\text{truncated SCF}) - E(\text{untruncated SCF})$, and similarly for $\Delta E(GNO)$.

TABLE IV
Truncated SD-CI results for the $^3B_{1u}$ state of ethylene. The difference in energy between the untruncated (22/6) and the truncated SD-CI energy. All energies are given in eV

N_σ/N_π	Number of CSF's	$\Delta E(\text{SCF})^a$	$\Delta E(\text{GNO})^a$	$\Delta EE(\text{SCF})^b$	$\Delta EE(\text{GNO})^b$
(22/6)	3 449	0·0	0·0	0·0	0·0
(15/6)	2 308	0·689	0·001	0·117	0·0
(7/6)	1 064	1·203	0·097	0·204	−0·045
(22/3)	2 111	0·857	0·011	0·940	−0·010
(15/3)	1 390	1·135	0·012	0·924	−0·011
(7/3)	626	1·264	0·107	0·981	−0·055
(22/2)	1 667	0·923	0·036	0·997	−0·030
(15/2)	1 496	1·170	0·036	0·966	−0·030
(7/2)	482	1·268	0·127	0·992	−0·071
(22/1)	1 224	0·927	0·431	1·343	−0·320
(15/1)	783	1·172	0·432	1·148	−0·320
(7/1)	339	1·268	0·510	1·064	−0·353

^{a} $\Delta E(\text{SCF})$ and $\Delta E(\text{GNO})$ are the same as in Table III; ^{b} $\Delta EE(\text{SCF}) = EE$(excitation energy by untruncated SCF) − EE(excitation energy by truncated SCF), and similarly for $\Delta EE(\text{GNO})$.

TABLE V
Truncated SD-CI results for the ^3A_g state of ethylene. The difference in energy between the untruncated (22/6) and the truncated SD-CI energy. All energies are given in eV

N_σ/N_π	Number of CSF's	$\Delta E(\text{SCF})^a$	$\Delta E(\text{GNO})^a$	$\Delta EE(\text{SCF})^b$	$\Delta EE(\text{GNO})^b$
(22/6)	3 449	0·0	0·0	0·0	0·0
(15/6)	2 308	0·526	0·005	0·280	−0·005
(7/6)	1 064	1·036	0·046	0·371	0·005
(22/3)	2 111	0·493	0 021	1·305	−0·021
(15/3)	1 390	0·812	0·025	1·247	−0·025
(7/3)	626	1·093	0·064	1·151	−0·013
(22/2)	1 667	0·542	0·094	1·378	−0·089
(15/2)	1 086	0·829	0·098	1·307	−0·092
(7/2)	482	1·097	0·132	1·163	−0·077
(22/1)	1 224	0·570	0·300	1·699	−0·189
(15/1)	783	0·844	0·303	1·476	−0·193
(7/1)	339	1·102	0·327	1·230	−0·212

^{a} $\Delta E(\text{SCF})$ and $\Delta E(\text{GNO})$ are the same as in Table III; ^{b} $\Delta EE(\text{SCF}) = EE$(excitation energy by untruncated SCF) − EE(excitation energy by truncated SCF), and similarly for $\Delta EE(\text{GNO})$.

TABLE VI

Truncated SD-CI results for the $^1B_{1u}$ state of ethylene. The difference in energy between the untruncated (22/6) and the truncated SD-CI energy. All energies are given in eV

N_σ/N_π	Number of CSF's	$\Delta E(\text{SCF})^a$	$\Delta E(\text{GNO})^a$	$\Delta EE(\text{SCF})^b$	$\Delta EE(\text{GNO})^b$
(23/6)	3 369	0·0	0·0	0·0	0·0
(15/6)	2 256	0·030	0·009	0·776	−0·009
(7/6)	1 044	0·435	0·081	0·972	−0·029
(22/3)	2 028	0·830	0·140	0·968	−0·140
(15/3)	1 335	0·845	0·146	1·214	−0·146
(7/3)	603	0·958	0·208	1·287	−0·157
(22/2)	1 583	0·831	0·251	1·090	−0·245
(15/2)	1 030	0·846	0·255	1·291	−0·249
(7/2)	458	0·958	0·301	1·303	−0·245
(22/1)	1 139	0·978	0·475	1·292	−0·364
(15/1)	726	0·987	0·480	1·334	−0·369
(7/1)	314	1·096	0·510	1·237	−0·353

[a] $\Delta E(\text{SCF})$ and $\Delta E(\text{GNO})$ are the same as in Table III. [b] $\Delta EE(\text{SCF}) = EE$(excitation energy by untruncated SCF) − EE(excitation energy by truncated SCF), and similarly for $\Delta EE(\text{GNO})$.

TABLE VII

Truncated SD-CI results for the $2\,^1A_g$ state of ethylene. The difference in energy between the untruncated (22/6) and the truncated SD-CI energy. All energies are given in eV

N_σ/N_π	Number of CSF's	$\Delta E(\text{SCF})^a$	$\Delta E(\text{GNO})^a$	$\Delta EE(\text{SCF})^b$	$\Delta EE(\text{GNO})^b$
(22/6)	3 369	0·0	0·0	0·0	0·0
(15/6)	2 256	0·028	0·004	0·778	−0·004
(7/6)	1 044	0·354	0·049	1·053	0·002
(22/3)	2 028	0·807	0·072	0·991	−0·072
(15/3)	1 335	0·823	0 075	1·236	−0·075
(7/3)	603	0·846	0·114	1·399	−0·063
(22/2)	1 583	0·811	0·135	1·110	−0·129
(15/2)	1 030	0·827	0·138	1·310	−0·132
(7/2)	458	0·848	0·173	1·413	−0·118
(22/1)	1 139	0·978	0·349	1·292	−0·238
(15/1)	726	0·985	0·352	1·336	−0·241
(7/1)	314	0·999	0·375	1·334	−0·219

[a] $\Delta E(\text{SCF})$ and $\Delta E(\text{GNO})$ are the same as in Table III. [b] $\Delta EE(\text{SCF}) = EE$(excitation energy by untruncated SCF) − EE(excitation energy by truncated SCF), and similarly for $\Delta EE(\text{GNO})$.

It is immediately clear from the ΔE column of all these tables that we could truncate correlating orbitals much more safely in the "GNO" set than in "SCF" set. In other words, the convergence with respect to the orbital basis is much better if we use the "GNO" set rather than the "SCF" set. For example, when we use 15σ and 3π correlating orbitals in the "GNO" set, the error is less than 0. 15 eV* for all the states considered. The error becomes 0·8 to 2·1 eV for the "SCF" set. From ΔEE column, we can see the effect of orbital truncation on the excitation energy. Again, when the 15σ and 3π correlating orbitals are used with the "GNO" set, the largest error is 0·146 eV (overestimate) for the $^1B_{1u}$ state and the second largest is 0·075 eV (overestimate) for the $2\,^1A_g$ state. If the "SCF" set is used, the biggest error is 1·247 eV (underestimate) for the ^3A_g state and the second largest is 1·236 eV (underestimate) for the $2\,^1A_g$ state.

The ground state NO's are used for excited states in the calculations with the "GNO" basis. We feel that the overall performance of the "GNO" basis is satisfactory when the excitation energies are to be calculated within a few tenth of eV. In this sense, we may conclude that the ground state NO's are acceptable substitute for the excited state NO's.

Butadiene Molecule

In this section, the butadiene molecule (C_4H_6) is examined by the use of composite natural orbitals (CNO's). We refer the orbital set as to "CNO" when

1) occupied orbitals are determined by SCF or S-CI for each state,

2) correlating or virtual orbitals are constructed from the NO's of a fragment in its ground state.

The procedure to construct correlating orbitals is as follows:

1) Carry out the CI calculation on a fragment in its ground state and produce the NO set.

2) Arrange the NO's in the order of their occupation numbers.

3) Delete the NO's corresponding to the occupied orbitals.

4) From the remaining NO's of a fragment in its ground state, the correlating orbitals are constructed, e.g. by the use of symmetry operation. Details on this step are given in Appendix.

5) Project the resulting correlating orbitals onto a virtual orbital space of the entire system. By this step, redundant atomic orbitals, such as orbitals on two extra H atoms in C_4H_6, are discarded.

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*   1 eV $= 96\cdot4868$ kJ mol^{-1}.

6) Subject the correlating orbitals to Schmidt orthogonalization with respect to the occupied orbitals and among themselves in the order of the occupation numbers in a fragment.

When C_4H_6 is taken as two C_2H_4 units, step 4) is very simple: we can just add and subtract two corresponding NO's of C_2H_4.

The SD-CI calculations were carried out on the ground state $1\,^1A_g(1a_u^2 1b_g^2)$ and the four $\pi \to \pi^*$ excited states — namely $^3B_u(1a_u^2 1b_g 2a_u)$, $^3A_g(1a_u^2 1b_g 2b_g)$, $^1B_u(1a_u^2 1b_g 2a_u)$, and $2\,^1A_g(1a_u^2 1b_g^2)$. The same orbital basis set was used as for C_2H_4. The numbers of σ (a_g and b_u) and π (a_u and b_g) orbitals were 56 and 16, respectively. Six σ and one π orbitals were deleted due to a near linear dependence. The geometry assumed was the experimental geometry of s-trans-butadiene[8].

The SCF results for ^1A_g and $B_u^{1,3}$ and S-CI results for ^3A_g and $2\,^1A_g$ are collected in Table VIII. In the S-CI calculation, two reference configurations ($1a_u^2 1b_g 2b_g$ and $1a_u 1b_g^2 2a_u$) for ^3A_g and three reference configurations ($1a_u^2 2a_u^2$, $1a_u^2 2b_g^2$, and $1a_u^2 1b_g 2b_g$) for 2^1A_g are employed.

When the untruncated orbital set is used, the SD-CI dimension becomes 10,000 – 30,000. In order to save computational load, important CSF's are selected by the second-order perturbation theory. The energy threshold for the selection is chosen to be $5\,\mu H$, i.e. $5 . 10^{-3}E_h$ in SI units. The effect of configurations state functions (CSF's) thrown away is estimated by the formula,

$$\Delta E = \sum_i^{b\text{-space}} \frac{\left| \displaystyle\sum_k^{a\text{-space}} H_{ik}C_k \right|^2}{(E_{CI} - H_{ii})},$$

TABLE VIII

Result of SCF and S-CI calculations of butadiene. Ground state energies are given as E/E_h, E_h $2\cdot6255 . 10^6$ J mol^{-1} and transition energies are in eV

State	This work	BSP[a]
^1A_g	−154·68093	−154·8579
^3B_u	3·127	3·11
^1B_u	6·419	6·07
^3A_g	6·341	6·41
$2\,^1A_g$	6·240	

[a] Ref.[12].

where a- and b-spaces are spanned by the reference configurations and the CSF's thrown away, respectively, and C_k and E_{CI} are the eigenvector and eigenvalue of the Hamiltonian within the selected space. In Table IX, we list the total energy of the selected CI and estimated values for the "SCF" and "CNO" sets. The numbers of selected CSF's for "CNO" is clearly smaller than those for "SCF". Thus the "CNO" has apparent advantage over "SCF" for truncation of CI expansion.

TABLE IX

SD-CI calculations by the perturbation selection of butadiene. All energies are given as E/E_h, $E_h = 2\cdot6255 \cdot 10^6$ J mol^{-1}

State	Orbital basis	Total number of CSF's	Selected number of CSF's	Total energies	
				CI1[a]	CI2[a]
^1A_g	"SCF"	10 427	3 023	−154·842035	−154·847197
	"CNO"		1 673	−154·847523	−154·850983
^3B_u	"SCF"	15 834	3 883	−154·708820	−154·717172
	"CNO"		1 583	−154·715973	−154·721107
^3A_g	"SCF"	30 967	4 964	−154·651263	−154·662227
	"CNO"		4 024	−154·656233	−154·664730
^1B_u	"SCF"	15 662	3 434	−154·592807	−154·601060
	"CNO"		2 067	−154·599400	−154·604359
$2\,^1A_g$	"SCF"	24 488	4 930	−154·574967	−154·583010
	"CNO"		3 806	−154·579409	−154·585018

[a] CI1 are the energies by selected CSF's and CI2 are the estimated energies.

TABLE X

Result of SD-CI calculation of butadiene. Ground state energies are given as E/E_h, $E_h = 2\cdot6255 \cdot 10^6$ J mol^{-1} and transition energies are in eV

State	This work[a]	BSP[b]	Expt.[c]
^1A_g	−154·85098	−155·1900	
^3B_u	3·534	3·31	3·22
^3A_g	5·068	4·92	4·91
^1B_u	6·711	6·67	5·92
2^1A_g	7·237	7·02	

[a] The energies used here are the estimated values; [b] ref.[12]; [c] ref.[13].

TABLE XI

Truncated SD-CI results of butadiene. The difference in energy and excitation energy between the untruncated and the truncated SD-CI energy. All energies are given in eV

N_σ/N_π	Number of CSF's	$\Delta E(SCF)^a$	$\Delta E(GNO)^a$	$\Delta EE(SCF)^b$	$\Delta EE(GNO)^b$
ground state					
(37/13)	10 427	0·0	0·0		
(14/10)	2 977	2·755	0·163		
(14/8)	2 455	3·139	0·165		
(14/6)	1 925	3·491	0·175		
(14/4)	1 387	3·681	0·353		
^3B_u state					
(37/12)	15 834	0·0	0·0	0·0	0·0
(14/9)	4 532	2·562	0·205	0·193	−0·042
(14/7)	3 751	2·666	0·212	0·473	−0·047
(14/5)	2 959	2·690	0·228	0·800	−0·053
(14/3)	2 153	2·728	0·628	0·953	−0·275
^1B_u state					
(37/12)	15 662	0·0	0·0	0·0	0·0
(14/9)	4 495	2·608	0·181	0·147	−0·018
(14/7)	3 709	2·692	0·193	0·447	−0·028
(14/5)	2 909	2·882	0·275	0·609	−0·100
(14/3)	2 008	2·902	0·568	0·779	−0·215
^3A_g state					
(37/12)	30 697	0·0	0·0	0·0	0·0
(14/9)	8 779	0·436	0·256	2·319	−0·093
(14/7)	7 213	0·536	0·269	2·603	−0·104
(14/5)	5 623	0·701	0·303	3·790	−0·128
(14/3)	4 012	1·129	0·960	2·552	−0·607
$2\,^1A_g$ state					
(37/12)	24 489	0·0	0·0	0·0	0·0
(14/9)	6 974	0·779	0·189	1·976	−0·027
(14/7)	5 670	0·952	0·196	2·187	−0·031
(14/5)	4 350	1·041	0·267	2·450	−0·092
(14/3)	3 014	2·086	0·559	1·595	−0·206

[a] $\Delta E(SCF)$, $\Delta E(GNO)$, $\Delta EE(SCF)$, and $\Delta EE(GNO)$ are same as in Table III. [b] The untruncated energies are the estimated values.

In Table X, the result of SD-CI calculation of C_4H_6 is given. Our energy is much higher than that of Buenker et al.[12], because our orbital basis set is smaller and CI is less extensive. However, excitation energies of the two calculations agree within about 0·2 eV.

Now we examine how much we can truncate the orbital basis while retaining reasonable accuracy. The number of σ correlating orbitals we kept from the total number of 37 was fixed to be 14 and the number of π correlating orbitals was reduced from 12 to 9, 7, 5, and 3 (13, 10, 8, 6, and 4 for the ground state). The results are shown in Table XI. When 14σ and 7π correlating orbitals are used, the error from the full correlating set is at most 0·27 eV (^3A_g) with "CNO", while the corresponding value can be as big as 2·69 eV (^1B_u) with "SCF". A similar result for excitation energy is seen from the column ΔEE. By using the 14σ and 7π correlating orbitals, the largest error is 0·104 eV (underestimate) for ^3A_g with "CNO", while it is 2·6 eV (^3A_g) with "SCF". The superiority of "CNO" over "SCF" becomes evident in Table XII, where we compare the truncated SD-CI results (14σ and 7π) with those of the untruncated (37σ and 12π) SD-CI for the "CNO" and "SCF" sets.

CONCLUSION

The results of the present calculations can be summarized as follows: (i) The natural orbitals determined for the ground state can be used as acceptable approximate NO's for excited states. (ii) Approximate NO's of a composite system (CNO) can be constructed from the ground state NO's of a fragment. (iii) The CI calculation using CNO's gives rapid convergence. The error due to the truncation of a set of correlating orbitals is small in both the total energies and excitation energies. (iv) In butadiene, the error in energies caused by the "CNO" orbital truncation from $(37\sigma/12\pi)$ to $(14\sigma/7\pi)$ is 0·16 − 0·27 eV. We may expect that by using "CNO" the CI

TABLE XII

Excitation energy of butadiene calculated by SD-CI with two truncated (14/7) orbital bases "CNO" and "SCF". All energies are given in eV

State	Full basis (37/12)	CNO (14/7)	SCF (14/7)
$2\ ^1A_g$	7·24	7·27	5·00
^1B_u	6·71	6·74	6·25
^3A_g	5·07	5·17	2·43
^3B_u	3·53	3·58	3·07
^1A_g	0·00	0·00	0·00

calculation of a composite system has roughly the same quality as that of a fragment system.

These results show that the "CNO" is useful in CI of a large system where orbital truncation is necessary.

APPENDIX

Here details of the step 4) in constructing CNO's from fragment NO's are given.

Let $\varphi_i^{(\kappa)}$ be a NO of a fragment, where the superscript κ denotes an irreducible representation of the fragment. The fragment NO is expressed as

$$\varphi_i^{(\kappa)} = \sum_{a,p} c_{i,a,p}^{(\kappa)} \chi_p^a ,$$

where χ_p^a is a p-th atomic orbital on atomic site a and $c_{i,a,p}^{(\kappa)}$ is a known coefficient. Suppose $P^{(\gamma)}$ is an operator which projects out the part belonging to the representation γ from an arbitrary function. Any fragment NO can be symmetrized by the projection.

$$P^{(\gamma)}\varphi_i^{(\kappa)} = \sum_R P^{(\gamma)}(R) \, P_R \varphi_i^{(\kappa)} = \sum_{a,p} c_{i,a,p}^{(\gamma)} \sum_R P^{(\gamma)}(R) \, P_R \chi_p^a . \qquad (2)$$

Note that P_R is a symmetric operation in the composite system and $P^{(\gamma)}(R)$ denotes the γ-th irreducible representation.

As an example, let us consider the projection of $2s_a + 2s_b$ to construct CNO's for the benzene molecule C_6H_6. The a_{1g} orbital is created by operating the symmetrizer as follows:

$$\phi(a_{1g}) = \sum_R P^{(a)_{1g}}(R) \, P_R(a + b) = E(a + b) + C_2(a + b) + \sum C_3(a + b) +$$

$$+ \sum C_6(a + b) + \sum C_2'(a + b) + \sum C_2''(a + b) = 2(a + b + c + d + e + f), \qquad (3)$$

where E, C_2, C_3 ... are the symmetric operations of D_{6h} and a, b, c, ..., f are $2s$ orbitals of carbon atoms in C_6H_6. Similar projections to other irreducible representations give b_{2g}, e_{1g}, and e_{2g} orbitals. From the antisymmetric orbital $2s_a - 2s_b$, a_{2g}, b_{1g}, e_{1g}, and e_{2g} orbitals are generated. This operation yields twelve symmetric orbitals from six $2s$ orbitals, this means that the orbitals are linearly dependent.

This redundancy stems from the multidimensional representation of a group and there is no unique method to remove it. In actual calculation with a larger basis, however, the difficulty is not as bad as it first appears. The reason is that we do not usually construct CNO's from all NO's of the fragment and secondly each NO does not have a simple form as in the above noted example. When we orthogonalize these CNO's against occupied orbitals we should remove orbitals whose norm is small to avoid the linear dependency problem. Thus, a little attention needs to be paid in case of non-Abelian group.

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