The Application of an MC-SCF Theory to Organic Chemical Reactions

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MC-SCF equations have been derived with the help of Segal's partition-basis-set technique; these equations can be used for the calculation of the potential curves of many organic reactions. They were applied to two typical organic reactions, and the results were compared with those obtained by CI methods. The corrections of the SCF-CI energies by the MC-SCF procedure were small for the present system.

The Hartree-Fock(HF) wavefunction describes the ground state of a normal molecule passably well, and its mixing with the excited configurations is generally small. However, the HF wavefunction is unreliable for a molecular system in which the interaction between the HF wavefunction and some excited configuration functions is very large. Such a breakdown of the HF method[1] occurs in the study of a thermally-"forbidden" reaction, during which an occupied MO crosses a vacant MO. The part of a potential curve in this region is much more unreliable than the other parts of the potential curve. Multi-configuration(MC) wavefunctions, thus, should be used so as to obtain reliable potential curves for these types of reactions. Here, the criterion of a reliable potential curve is that the potential curve has an equal reliability at all of its points.

Configuration interaction(CI) methods are easy to use, and many potential curves of these types of reactions have been obtained by CI methods.[2] MC-SCF methods have also been applied to some reactions by Basch.[3] In MC-SCF methods, the configurations to be included vary with the type of reaction and with the electronic state under consideration. The SCF equations, thus, must be derived separately for each state of each reaction. As a matter of practical convenience, it would be desirable to have MC-SCF equations which could be used for many types of reactions and many types of states. In this paper, we will consider the configurations which give the most reliable potential curves of many types of reactions, and an MC-wavefunction will be set up. Using Segal's "partition-basis-set" technique,[4] Fock-type equations will be derived for the wavefunction. These equations will then be applied to two reactions, and the results will be compared with those obtained by the CI method.

Theory

First, let us consider the configurations which give the lowest singlet potential curve whose reliability is the same at all of its points. The configurations to be included are determined from the MO correlation diagram of the reaction under consideration. Figure 1 shows two typical features of MO correlation diagrams: in the first case, (a), the crossing of an occupied MO and a vacant MO occurs during the reaction process, while in the second case, (b), the difference between their MO energies becomes small (or two MO's are degenerate) on one side of the diagram. Examples of these cases are: (a) the disrotatory process of the cycloaddition reaction of *cis*-butadiene and (b) the dimerization of the methyl radical to form ethane. In the case of (a), the lowest closed-shell configuration changes near the crossing region. In this region, the mixing of the lower configurations, $(\cdots\phi_i^2\phi_k^0)$ and $(\cdots\phi_k^2\phi_i^0)$, is very large, and neither one of them separately, but a linear combination of them, can be a good approximation to the wavefunction of the lowest state. For the reaction whose MO correlation diagram has the feature (a) or (b) of Fig. 1, the lowest singlet potential curve should be described by the MC-wavefunction including the $\phi=(\cdots\phi_i^2\phi_k^0)$ and $\phi=(\cdots\phi_k^2\phi_i^0)$ configurations, and $\phi=(\cdots\phi_i^1\phi_k^1)$ one, if nescessary.

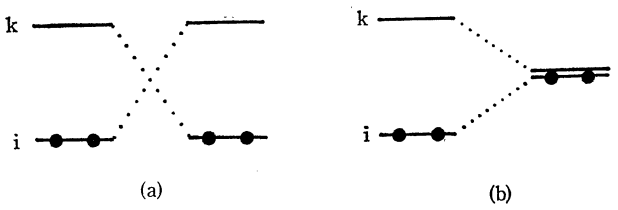

Fig. 1. Typical features appearing in MO correlation diagrams.
(a): Reaction process during which the crossing of an occupied MO and a vacant MO occurs.
(b): Reaction process at one side of which the difference between an occupied MO energy and a vacant MO energy becomes small.

There are actually many chemical processes whose MO correlation diagrams are more complex. In order to obtain MC-SCF equations which can be used for many reactions, two occupied MO's (i and j) and two vacant MO's (k and l) were selected, and all the singly- and doubly-excited singlet configurations derived from these four orbitals were taken into account. The lowest and some excited singlet potential curves of many chemical reactions can be described by this wavefunction. Thus, the MC-wavefunction was written as:

$$\begin{aligned}{}^1\Phi = {} & C_0\Psi_0 + C_1\Psi_i^k + C_2\Psi_i^l + C_3\Psi_j^k + C_4\Psi_j^l + C_5\Psi_{ii}^{kk} \\ & + C_6\Psi_{ii}^{ll} + C_7\Psi_{jj}^{kk} + C_8\Psi_{jj}^{ll} + C_9\Psi_{ii}^{kl} + C_{10}\Psi_{jj}^{kl} \\ & + C_{11}\Psi_{ij}^{kk} + C_{12}\Psi_{ij}^{ll} + C_{13}\Psi_{ij}^{kl}(1) + C_{14}\Psi_{ij}^{kl}(2) \end{aligned} \quad [1]$$

with

$$\sum_i C_i^2 = 1$$

where the configuration functions are:

$$\Psi_0 = |\ldots i\bar{i}j\bar{j}|$$

$$\Psi_i^k = \frac{1}{\sqrt{2}}\{|\ldots i\bar{k}j\bar{j}| + |\ldots k\bar{i}j\bar{j}|\}$$

$$\Psi_{tt}^{kk} = |\ldots k\bar{k}j\bar{j}|$$

$$\Psi_{tt}^{kl} = \frac{1}{\sqrt{2}}\{|\ldots k\bar{l}j\bar{j}| + |\ldots l\bar{k}j\bar{j}|\}$$

$$\Psi_{tj}^{kk} = \frac{1}{\sqrt{2}}\{|\ldots i\bar{k}k\bar{j}| + |\ldots k\bar{i}j\bar{k}|\}$$

$$\Psi_{tj}^{kl}(1) = \frac{1}{2}\{|\ldots i\bar{k}l\bar{j}| + |\ldots k\bar{i}j\bar{l}| + |\ldots\bar{i}\bar{k}jl| + |\ldots ik\bar{j}\bar{l}|\}$$

$$\Psi_{tj}^{kl}(2) = \frac{1}{2\sqrt{3}}\{2|\ldots i\bar{k}j\bar{l}| + |i\bar{k}l\bar{j}| + |\ldots k\bar{i}j\bar{l}| + 2|\ldots k\bar{i}l\bar{j}| - |\ldots\bar{i}\bar{k}jl| - |\ldots ik\bar{j}\bar{l}|\}$$

and where the others are obtained by changing the indices, i and j or/and k and l, in these configuration functions. The electronic energy of [1] is written as:

$$E_{\text{elec}} = E_g + \sum_{p,q} A_{pq}L_{pq} + \sum_{p,q,r,s} B_{pqrs}\langle pq|rs\rangle$$

where p, q, r, and s run over four orbitals, i, j, k, and l; where A_{pq} and B_{pqrs} are expressed by the configuration expansion coefficients (they are given in the Appendix). Also,

$$E_g = \sum_{t}^{\text{occ}} 2I_{tt} + \sum_{t,u}^{\text{occ}} \{2\langle tt|uu\rangle - \langle tu|ut\rangle\}$$

$$L_{rs} = I_{rs} + \sum_{t}^{\text{occ}} \{2\langle tt|rs\rangle - \langle ts|rt\rangle\}$$

$$I_{rs} = \int \phi_r^*(1)H_{\text{core}}(1)\phi_s(1)d\tau$$

$$\langle rs|tu\rangle = \int \phi_r^*(1)\phi_s(1)\frac{e^2}{r_{12}}\phi_t^*(2)\phi_u(2)d\tau$$

where t and u in the first two equations run over the doubly-occupied and i and j orbitals.

A troublesome aspect of implementing the MC-SCF formalism involves the handling of the off-diagonal Lagrangian multipliers, which insure orthonormality between open- and closed-shell orbitals of the same symmetry.[5] Segal has put forward the "partition-basis-set" technique, which simplifies the calculation of the wavefunctions of the excited states of molecules.[4] His method corresponds to a partial variational method, in which the variations of open-shell orbitals are expanded by virtual orbitals. Thus, the MO's obtained by this method are not the optimum ones.[6] However, its simplicity makes it possible to obtain many types of MC-SCF wavefunctions easily. This technique, which has been applied to the calculation of MC-SCF wavefunctions by Basch,[3] was used in the present study. The Fock-type equations obtained are:

$$F_\lambda|\phi_\lambda\rangle = \varepsilon_\lambda|\phi_\lambda\rangle \qquad (\lambda=1, 2, \ldots\ldots, i-1)$$

$$F_p|\phi_p\rangle + \sum_{q\neq p} F_{pq}|\phi_q\rangle = \varepsilon_p|\phi_p\rangle \qquad (p=i, j, k, l)$$

The second equations were converted to eigenvalue forms by rewriting the equations using the operators defined by:

$$F'_{pq} = F_{pq}|\phi_q\rangle\langle\phi_p|$$

and by adding the following quantity to both sides of the equation:

$$\sum_{q\neq p} F'^{\dagger}_{pq}|\phi_p\rangle = \sum_{q\neq p}|\phi_p\rangle\langle\phi_q|F_{qp}|\phi_p\rangle$$

The final eigenvalue forms are:

$$F_\lambda|\phi_\lambda\rangle = \varepsilon_\lambda|\phi_\lambda\rangle \qquad (\lambda=1, 2, \ldots\ldots, i-1) \qquad [3\text{-}1]$$

$$F_p|\phi_p\rangle = \varepsilon_{p'}|\phi_p\rangle \qquad (p=i, j, k, l) \qquad [3\text{-}2]$$

The operators F_λ and F_p are given by:

$$F_\lambda = H_{\text{core}} + \sum_t (2J_t - K_t) + \sum_{r,s}\frac{1}{2}A_{rs}(2f_{rs} - g_{rs})$$

$$F_p = F_{pp} + \sum_{r(\neq p)}\{F_{pr}|\phi_r\rangle\langle\phi_p| + |\phi_p\rangle\langle\phi_r|F_{rp}\}$$

$$F_{pp} = (\delta_{pt}+\delta_{pj})F_\lambda + \frac{1}{2}A_{pp}\{H_{\text{core}} + \sum_t(2J_t - K_t)\} + \sum_{r,s}(B_{pprs}f_{rs} + B_{psrp}g_{rs}) - \sum_r B_{pprp}f_{rp}$$

$$F_{pq} = \frac{1}{2}A_{pq}\{H_{\text{core}} + \sum_t(2J_t - K_t)\} + \sum_{\substack{r(\neq p,q)\\ s(\neq p,q)}} B_{pqrs}f_{rs} + \sum_{r(\neq p,q)}\{B_{pqpr}f_{pr} + B_{pqrq}f_{rq} + B_{prrq}g_{rr}\} + B_{pqqq}f_{qq} + B_{pqpq}f_{pq} \qquad (p\neq q)$$

where t runs over orbitals which are doubly occupied in the Ψ_0 configuration, and where r and s run over four orbitals, i, j, k, and l. The J_t, K_t, and H_{core} operators have their usual meanings, and the f and g operators are defined by:

$$f_{rs}(1)\phi_t(1) = \left(\int \frac{e^2}{r_{12}}\phi_r^*(2)\phi_s(2)d\tau_2\right)\phi_t(1)$$

$$g_{rs}(1)\phi_t(1) = \left(\int \frac{e^2}{r_{12}}\phi_r^*(2)\phi_t(2)d\tau_2\right)\phi_s(1)$$

$_{p}'$ is connected with the Lagrangian multiplier, ε_p, by:

$$\varepsilon_{p'} = \varepsilon_p + \sum_{r(\neq p)}\langle r|F_{rp}|p\rangle.$$

If the variation method is applied so as to minimize the E_{elec} with respect to the LCAO coefficients, $\mathbf{c}$, of

$$\phi_r = \chi\mathbf{c}_r$$

equations equivalent to [3-1] and [3-2] are obtained.

$$\mathbf{F}_\lambda\mathbf{c}_\lambda = \mathbf{c}_\lambda\varepsilon_\lambda \qquad (\lambda=\text{inner MO's}) \qquad [4\text{-}1]$$

$$\mathbf{F}_p\mathbf{c}_p = \mathbf{c}_p\varepsilon_{p'} \qquad (p=i, j, k, l) \qquad [4\text{-}2]$$

where the matrices, $\mathbf{F}_\lambda$ and $\mathbf{F}_p$, are evaluated with the corresponding operator and the set of AO's.

The configuration expansion coefficients and the orbital expansion coefficients are determined by the following process.[3a]

(1) From an initial LCAO-MO set, the CI matrix elements, H_{ab}, are calculated, while the configuration expansion coefficients are determined from the lowest-energy solution of the secular determinant:

$$|H_{ab} - E\delta_{ab}| = 0$$

(2) From the above set of orbitals and the newly-obtained configuration expansion coefficients, the Hermitian matrices, $\mathbf{F}_\lambda$ and $\mathbf{F}_p$, of Eqs. [4] are calculated.

(3) Eq. [4-1] is solved in the usual manner to obtain the set of occupied MO's, ϕ_λ, and the set of orthogonal virtual MO's.

(4) The MO's ϕ_i, ϕ_j, ϕ_k, and ϕ_l, are successively determined by Segal's technique[4] from the virtual MO's obtained in (3).

(5) The procedure reverts to (1), and the process

is continued until the convergency of the total energy and AO bond populations is achieved.

While the excited states, as well as the ground state, can be evaluated by means of this procedure, the wavefunctions obtained by this procedure are not the optimum ones and are not correct to the first-order; that is, Brillouin's theorem does not hold for these wavefunctions.[4,6] First-order accuracy may be achieved by a CI calculation in which all the wave-functions formed by single excitations from the present MC-SCF function are included. This problem was not, however, examined in this paper.

Examples

The present MC-SCF method can be used for the calculations of the potential curves which are described by the wavefunction [1]. It was applied here to two reactions, the cycloaddition of *cis*-butadiene to form cyclobutene, and the dimerization of methylene to form ethylene. The lowest (ground-state) potential curves obtained were compared with those obtained by the CI method, in which the same approximation as in the MC-SCF method was used. The CI method is easy to use for the calculation of the potential curves of forbidden reactions. It is, thus, worth comparing the results obtained by the MC-SCF and CI methods. Semi-empirical method were used in the present applications because they are easily applicable to organic chemical reactions including rather large molecules. The INDO approximation,[7] which is one of the most widely accepted semi-empirical approximations, was used in the second example. In the first example, the MINDO/2 approximation[8] was used, since the MINDO /2-CI calculation for this reaction has already been performed.[9]

The Disrotatory Process of Cycloaddition of cis-*Butadiene to Form Cyclobutene.* The lowest singlet potential curve of this process was calculated for the ideal path, in which the molecule has C_s symmetry. The wavefunction can be described by two configurations, as was pointed out in the previous section:

$$^1\Phi = C|\ldots(5a'')^2| + C'|\ldots(7a')^2|$$

where $5a''$ and $7a'$, which correspond to the i and k orbitals in Fig. 1-(a) respectively, are anti-symmetric and symmetric with respect to the symmetry plane, which bisects the C_2-C_3 bond and is perpendicular to the carbon skeleton. The rotation angle of the CH_2 group was varied from 0°(*cis*-butadiene) to 90°(cyclobutene) in steps of 15°. The other geometrical parameters were gradually varied from those of *cis*-butadiene to those of cyclobutene. At each rotation angle, the SCF MO's of the all-valence electrons were obtained by means of the MINDO/2 method; these values were then used as the initial MO's of the MC-SCF procedure and as the basic MO's in the CI calculation. The total energy is the sum of the electronic energy and the core-repulsion energy, as calculated by means of the MINDO/2 approximation.[8]

The orbital expansion coefficients of $7a'$ and $5a''$ orbitals at $\theta=45°$ are shown in Table 1. The differences between the orbital expansion coefficients obtained by the MC-SCF method and the CI method are small. This was also observed for the orbitals at other points in the reaction process. The differences in configuration expansion coefficients between the two methods are also small (Table 2). Thus, no remarkable difference in the total energy between the two methods was observed during the process (<0.2 eV, Table 3). The overall shapes of both potential curves were similar to that obtained by a larger CI calculation in which 20 configuration functions were included.[9] Thus, a small MC-wavefunction is passable in the semi-empirical study of the present process.

The deviation of the energy obtained by the single-configuration wavefunction from that obtained by two configuration wavefunction largely depends on the rotation angle of the CH_2 group. At $\theta=45°$, the difference is 1.36 eV, which is much larger than those of normal molecules: 0.19 eV for *cis*-butadiene and 0.42 eV for cyclobutene. Thus, MC-wavefunctions should be used in the study of the forbidden reaction so as to obtain a reliable potential curve.

Dimerization of Triplet Methylene to Form Ethylene. The least-motion approach of two triplet ($^3B_1$) methylenes, or the least-motion dissociation of ethylene, was considered. It may be seen in Fig. 2 that the lowest closed-shell configuration changes from $(\text{core})^8\sigma^2\pi^2$ to $(\text{core})^8\sigma^2\sigma^{*2}$ during the dissociation of ethylene to methylenes. The lowest state(ground state) of methylene dimer is sufficiently described by the following configurations:[10]

$(\text{core})^8\sigma^2\pi^2$ at $R_{cc}\sim R_0$, the value of normal ethylene,
$(\text{core})^8\sigma^2\pi^2$ and $(\text{core})^8\sigma^2\pi^{*2}$ at $R_{cc}\sim 2.0$ Å,
$(\text{core})^8\sigma^2\pi^2$, $(\text{core})^8\sigma^2\pi^{*2}$, $(\text{core})^8\sigma^{*2}\pi^2$, $(\text{core})^8\sigma^{*2}\pi^{*2}$, and $(\text{core})^8\sigma\sigma^*\pi\pi^*$ at $R_{cc}>3.0$ Å,

where σ, σ^*, π, and π^* are the MO's of the D_{2h} methylene dimer. The wavefunction of the lowest state of the methylene dimer, whose C–C separation varies from R_0 to ∞, was written as:

$$^1\Phi = C_0\Psi_0 + C_5\Psi_{ii}^{kk} + C_6\Psi_{ii}^{ll} + C_7\Psi_{jj}^{kk} + C_8\Psi_{jj}^{ll} + C_{13}\Psi_{ij}^{kl}(1) + C_{14}\Psi_{ij}^{kl}(2)$$

so that the wavefunction always involves the above configurations whether the lowest closed-shell configuration is $(\text{core})^8\sigma^2\pi^2$ or $(\text{core})^8\sigma^2\sigma^{*2}$. The dissociation of ethylene has been studied by Basch.[3a] In his MC-SCF treatment, the first five configurations in the above wavefunction were taken into account. Thus, his wavefunction does not correctly represent the two $^3B_1$ methylenes at $R_{cc}\rightarrow\infty$.[10]

Calculations were also carried out for several C–C separations with a fixed CH_2 unit in an ideal geometry: CH=1.10 Å and ∠HCH=120°. The INDO approximation[7] was used for this process. The total energy of the lowest singlet state of the methylene dimer is shown in Table 3. The overall shape of the lowest potential curve was similar to that obtained by Basch.[3a] It may be seen from Table 3 that the difference between the single-configuration energy and the MC-SCF energy depends largely on the C-C separation. This was observed between the single-configuration energy and the CI energy calculated with 40 configuration

TABLE 1. ORBITAL EXPANSION COEFFICIENTS OF $5a''$ AND $7a'$ MO'S AT THREE TYPICAL ROTATION ANGLES OF CH_2 GROUPS[a]

AO[d]		$5a''$ MO[b]			$7a'$ MO[c]		
		0°	45°	90°	0°	45°	90°
C_1	2s	0.0000	0.1857	0.0000	0.0000	0.1602	0.0000
		(0.0000)	(0.1936)	(0.0000)	(0.0000)	(0.1455)	(0.0000)
	$2p_x$	0.0000	−0.4586	0.0000	0.0000	−0.3598	0.0000
		(0.0000)	(−0.4309)	(0.0000)	(0.0000)	(−0.3900)	(0.0000)
	$2p_y$	0.0000	−0.2382	0.0000	0.0000	−0.1888	0.0000
		(0.0000)	(−0.2298)	(0.0000)	(0.0000)	(−0.1800)	(0.0000)
	$2p_z$	0.5712	0.3487	−0.0418	0.5592	0.3455	0.1401
		(0.5616)	(0.3509)	(0.0404)	(0.5574)	(0.3455)	(0.1407)
C_2	2s	0.0000	0.0239	0.0000	0.0000	−0.0765	0.0000
		(0.0000)	(−0.0005)	(0.0000)	(0.0000)	(−0.0922)	(0.0000)
	$2p_x$	0.0000	−0.0478	0.0000	0.0000	0.0629	0.0000
		(0.0000)	(−0.0447)	(0.0000)	(0.0000)	(0·0665)	(0.0000)
	$2p_y$	0.0000	0.0402	0.0000	0.0000	0.0737	0.0000
		(0.0000)	(0.0314)	(0.0000)	(0.0000)	(0.0665)	(0.0000)
	$2p_z$	0.4169	0.2070	0.6987	−0.4327	−0.3527	−0.6553
		(0.4297)	(0.2363)	(0.6851)	(−0.4351)	(−0.3216)	(−0.6530)
H_1	1s	0.0000	0.0424	0.0709	0.0000	−0.1827	−0.1596
		(0.0000)	(0.0518)	(0.1204)	(0.0000)	(−0.1640)	(−0.1640)
H_2	1s	0.0000	−0.1507	−0.0709	0.0000	−0.0430	0.1596
		(0.0000)	(−0.1747)	(−0.1204)	(0.0000)	(−0.0428)	(0.1640)
H_3	1s	0.0000	0.0704	0.0000	0.0000	0.1226	0.0000
		(0.0000)	(0.0944)	(0.0000)	(0.0000)	(0.1596)	(0.0000)

a) SCF-MO's are also shown in parentheses. b) Add the other half part which is asymmetric with respect to the symmetry plane. c) Add the other half part which is symmetric with respect to the symmetry plane. d) C_1, terminal carbon; H_1 and H_2 methylene protons; x axis, parallel to C_2-C_3 bond; z axis, parpendicular to the carbon skeleton.

TABLE 2. TOTAL ENERGY AND CONFIGURATION EXPANSION COEFFICIENTS OF THE LOWEST SINGLET STATE ALONG THE CYCLOADDITION OF *cis*-BUTADIENE TO CYCLOBUTENE

θ[b]	MC-SCF			SCF-CI			SD[a]
	E (eV)	C	C'	E (eV)	C	C'	E (eV)
0°	−607.14	0.9859	−0.1672	−607.14	0.9869	−0.1612	−606.95
15°	−606.69	0.9796	−0.2011	−606.67	0.9820	−0.1887	−606.47
30°	−605.76	0.9463	−0.3233	−605.70	0.9581	−0.2864	−605.39
45°	−605.14	0.6546	−0.7559	−605.14	0.6410	−0.7676	−603.78
60°	−605.95	0.2658	−0.9640	−605.77	0.2635	−0.9646	−605.44
75°	−607.28	0.1748	−0.9846	−607.07	0.0875	−0.9962	−607.01
90°	−608.29	0.2302	−0.9731	−608.26	0.2218	−0.9751	−607.87

a) Obtained by single-configuration SCF method. b) $\theta=0°$ corresponds to *cis*-butadiene and $\theta=90°$ to cyclobutene.

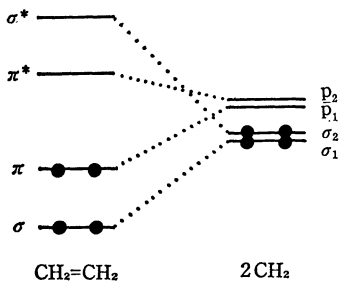

Fig. 2. MO correlation diagram connecting four MO's of ethylene and two methylenes.

TABLE 3. THE LOWEST SINGLET ENERGY (eV) OF D_{2h} METHYLENE DIMER

R_{cc}(Å)	MC-SCF	SCF-CI	SD[a]
1.30	−451.35	−451.12	−450.62
1.50	−449.93	−449.59	−448.66
2.00	−438.91	−438.68	−435.36
2.50	−431.42	−431.32	−427.42
3.00	−429.02	−429.00	−427.32

a) Energies obtained by single-configuration SCF method. The lowest closed-shell configuration at large C-C separation is $(\cdots\sigma^2\sigma^{*2})$ which does not contribute to the lowest singlet state of D_{2h} methylene dimer.

functions. Thus, the breakdown of the HF method in the intermediate region of the process gives a largely unreliable potential curve. The correction of the SCF-CI energy by the MC-SCF procedure was small (Table 3) in the present case, as in the previous example. This may be a result of the limited AO basis in the semi-empirical methods.

As a result, in semi-empirical all-valence electron calculations, the MC-SCF method or a rather large CI method may be sufficient to produce potential curves which remove the error originating from the HF method and which have a reliability comparable to that of the HF molecular ground state of a usual molecule.

The authors wish to express their thanks to Professor Keizo Suzuki for his helpful suggestions. The calculations were carried out by a HITAC 8800 computer at The University of Tokyo.

Appendix

A_{pq} and B_{pqrs} in Eq. (2) are expressed by the configuration expansion coefficients as follows. The others are obtained from the relations, $A_{pq}=A_{qp}$ and $B_{pqrs}=B_{qpsr}=B_{srqp}=B_{rspq}$.

$$A_{ii} = -(C_1^2 + C_2^2 + 2C_5^2 + 2C_6^2 + 2C_9^2 + C_{11}^2 + C_{12}^2 + C_{13}^2 + C_{14}^2)$$

$$A_{jj} = -(C_3^2 + C_4^2 + 2C_7^2 + 2C_8^2 + 2C_{10}^2 + C_{11}^2 + C_{12}^2 + C_{13}^2 + C_{14}^2)$$

$$A_{kk} = C_1^2 + C_3^2 + 2C_5^2 + 2C_7^2 + C_9^2 + C_{10}^2 + 2C_{11}^2 + C_{13}^2 + C_{14}^2$$

$$A_{ll} = C_2^2 + C_4^2 + 2C_6^2 + 2C_8^2 + C_9^2 + C_{10}^2 + 2C_{12}^2 + C_{13}^2 + C_{14}^2$$

$$A_{ij} = -(C_1C_3+C_2C_4+\sqrt{2}\{C_5C_{11}+C_6C_{12}+C_7C_{11}+C_8C_{12} + C_9C_{13}+C_{10}C_{13}\})$$

$$A_{kl} = C_1C_2 + C_3C_4 + \sqrt{2}\{C_5C_9+C_6C_9+C_7C_{10}+C_8C_{10} + C_{11}C_{13}+C_{12}C_{13}\}$$

$$A_{ik} = \sqrt{2}C_0C_1 + \sqrt{2}C_1C_5 + C_2C_9 + C_3C_{11} + \frac{\sqrt{2}}{2}C_4C_{13} + \frac{\sqrt{6}}{2}C_4C_{14}$$

$$A_{il} = \sqrt{2}C_0C_2 + \sqrt{2}C_2C_6 + C_1C_9 + C_4C_{12} + \frac{\sqrt{2}}{2}C_3C_{13} - \frac{\sqrt{6}}{2}C_3C_{14}$$

$$A_{jk} = \sqrt{2}C_0C_3 + \sqrt{2}C_3C_7 + C_1C_{11} + C_4C_{10} + \frac{\sqrt{2}}{2}C_2C_{13} - \frac{\sqrt{6}}{2}C_2C_{14}$$

$$A_{jl} = \sqrt{2}C_0C_4 + \sqrt{2}C_4C_8 + C_2C_{12} + C_3C_{10} + \frac{\sqrt{2}}{2}C_1C_{13} + \frac{\sqrt{6}}{2}C_1C_{14}$$

$$B_{iiii} = C_5^2 + C_6^2 + C_9^2$$

$$B_{jjjj} = C_7^2 + C_8^2 + C_{10}^2$$

$$B_{kkkk} = C_5^2 + C_7^2 + C_{11}^2$$

$$B_{llll} = C_6^2 + C_8^2 + C_{12}^2$$

$$B_{iikk} = -\frac{1}{2}(C_1^2+4C_5^2+2C_9^2+2C_{11}^2+C_{13}^2+C_{14}^2)$$

$$B_{iill} = -\frac{1}{2}(C_2^2+4C_6^2+2C_9^2+2C_{12}^2+C_{13}^2+C_{14}^2)$$

$$B_{jjkk} = -\frac{1}{2}(C_3^2+4C_7^2+2C_{10}^2+2C_{11}^2+C_{13}^2+C_{14}^2)$$

$$B_{jjll} = -\frac{1}{2}(C_4^2+4C_8^2+2C_{10}^2+2C_{12}^2+C_{13}^2+C_{14}^2)$$

$$B_{ikki} = C_1^2 + C_5^2 + \frac{1}{2}(C_9^2+C_{11}^2) + \frac{1}{4}(C_{13}^2+3C_{14}^2+2\sqrt{3}C_{13}C_{14})$$

$$B_{illi} = C_2^2 + C_6^2 + \frac{1}{2}(C_9^2+C_{12}^2) + \frac{1}{4}(C_{13}^2+3C_{14}^2-2\sqrt{3}C_{13}C_{14})$$

$$B_{jkkj} = C_3^2 + C_7^2 + \frac{1}{2}(C_{10}^2+C_{11}) + \frac{1}{4}(C_{13}^2+3C_{14}^2-2\sqrt{3}C_{13}C_{14})$$

$$B_{jllj} = C_4^2 + C_8^2 + \frac{1}{2}(C_{10}^2+C_{12}^2) + \frac{1}{4}(C_{13}^2+3C_{14}^2+2\sqrt{3}C_{13}C_{14})$$

$$B_{iijj} = \frac{1}{2}(C_{11}^2+C_{12}^2+C_{13}^2+C_{14}^2)$$

$$B_{kkll} = \frac{1}{2}(C_9^2+C_{10}^2+C_{13}^2+C_{14}^2)$$

$$B_{ijji} = \frac{1}{2}(C_{11}^2+C_{12}^2+C_{13}^2-C_{14}^2)$$

$$B_{kllk} = \frac{1}{2}(C_9^2+C_{10}^2+C_{13}^2-C_{14}^2)$$

$$B_{iiij} = \frac{\sqrt{2}}{2}(C_5C_{11}+C_6C_{12}+C_9C_{13})$$

$$B_{ijjj} = \frac{\sqrt{2}}{2}(C_7C_{11}+C_8C_{12}+C_{10}C_{13})$$

$$B_{kkkl} = \frac{\sqrt{2}}{2}(C_5C_9+C_7C_{10}+C_{11}C_{13})$$

$$B_{klll} = \frac{\sqrt{2}}{2}(C_6C_9+C_8C_{10}+C_{12}C_{13})$$

$$B_{iiik} = -\frac{1}{2}(\sqrt{2}C_1C_5+C_2C_9)$$

$$B_{iiil} = -\frac{1}{2}(\sqrt{2}C_2C_6+C_1C_9)$$

$$B_{jjjk} = -\frac{1}{2}(\sqrt{2}C_3C_7+C_4C_{10})$$

$$B_{jjjl} = -\frac{1}{2}(\sqrt{2}C_4C_8+C_3C_{10})$$

$$B_{ikkk} = \frac{1}{2}(\sqrt{2}C_1C_5+C_3C_{11})$$

$$B_{illl} = \frac{1}{2}(\sqrt{2}C_2C_6+C_4C_{12})$$

$$B_{jkkk} = \frac{1}{2}(\sqrt{2}C_3C_7+C_1C_{11})$$

$$B_{jlll} = \frac{1}{2}(\sqrt{2}C_4C_8+C_2C_{12})$$

$$B_{ijij} = C_5C_7 + C_6C_8 + C_9C_{10}$$
$$B_{klkl} = C_5C_6 + C_7C_8 + C_{11}C_{12}$$
$$B_{ikik} = C_0C_5$$
$$B_{ilil} = C_0C_6$$
$$B_{jkjk} = C_0C_7$$
$$B_{jljl} = C_0C_8$$
$$B_{ijik} = -\frac{1}{2}C_1C_{11} - \frac{\sqrt{2}}{4}C_2C_{13} + \frac{\sqrt{6}}{4}C_2C_{14}$$
$$B_{ijil} = -\frac{1}{2}C_2C_{12} - \frac{\sqrt{2}}{4}C_1C_{13} - \frac{\sqrt{6}}{4}C_1C_{14}$$
$$B_{jjik} = -\frac{1}{2}C_3C_{11} - \frac{\sqrt{2}}{4}C_4C_{13} - \frac{\sqrt{6}}{4}C_4C_{14}$$
$$B_{jjil} = -\frac{1}{2}C_4C_{12} - \frac{\sqrt{2}}{4}C_3C_{13} + \frac{\sqrt{6}}{4}C_3C_{14}$$
$$B_{kkil} = \frac{1}{2}C_1C_9 + \frac{\sqrt{2}}{4}C_3C_{14} - \frac{\sqrt{6}}{4}C_3C_{14}$$
$$B_{kkjl} = \frac{1}{2}C_3C_{10} + \frac{\sqrt{2}}{4}C_1C_{13} + \frac{\sqrt{6}}{4}C_1C_{14}$$
$$B_{llik} = \frac{1}{2}C_2C_9 + \frac{\sqrt{2}}{4}C_4C_{13} + \frac{\sqrt{6}}{4}C_4C_{14}$$
$$B_{lljk} = \frac{1}{2}C_4C_{10} + \frac{\sqrt{2}}{4}C_2C_{13} - \frac{\sqrt{6}}{4}C_2C_{14}$$
$$B_{ijki} = -\frac{\sqrt{2}}{4}C_2C_{13} - \frac{\sqrt{6}}{4}C_2C_{14} - \frac{1}{2}C_1C_{11}$$
$$B_{ijli} = -\frac{\sqrt{2}}{4}C_1C_{13} + \frac{\sqrt{6}}{4}C_1C_{14} - \frac{1}{2}C_2C_{12}$$
$$B_{jikj} = -\frac{\sqrt{2}}{4}C_4C_{13} + \frac{\sqrt{6}}{4}C_4C_{14} - \frac{1}{2}C_3C_{11}$$
$$B_{jilj} = -\frac{\sqrt{2}}{4}C_3C_{13} - \frac{\sqrt{6}}{4}C_3C_{14} - \frac{1}{2}C_4C_{12}$$
$$B_{klik} = \frac{\sqrt{2}}{4}C_3C_{13} + \frac{\sqrt{6}}{4}C_3C_{14} + \frac{1}{2}C_1C_9$$
$$B_{kljk} = \frac{\sqrt{2}}{4}C_1C_{13} - \frac{\sqrt{6}}{4}C_1C_{14} + \frac{1}{2}C_3C_{10}$$
$$B_{likl} = \frac{\sqrt{2}}{4}C_4C_{13} - \frac{\sqrt{6}}{4}C_4C_{14} + \frac{1}{2}C_2C_9$$
$$B_{lkjl} = \frac{\sqrt{2}}{4}C_2C_{13} + \frac{\sqrt{6}}{4}C_2C_{14} + \frac{1}{2}C_4C_{10}$$
$$B_{ikkl} = -\sqrt{2}\,(C_5C_9 + C_6C_9) - \frac{\sqrt{2}}{2}(C_{11}C_{13} + C_{12}C_{13}) - \frac{1}{2}C_1C_2$$
$$B_{jjkl} = -\sqrt{2}\,(C_7C_{10} + C_8C_{10}) - \frac{\sqrt{2}}{2}(C_{11}C_{13} + C_{12}C_{13}) - \frac{1}{2}C_3C_4$$
$$B_{kkij} = -\sqrt{2}\,(C_5C_{11} + C_7C_{11}) - \frac{\sqrt{2}}{2}(C_9C_{13} + C_{10}C_{13}) - \frac{1}{2}C_1C_3$$
$$B_{llij} = -\sqrt{2}\,(C_6C_{12} + C_8C_{12}) - \frac{\sqrt{2}}{2}(C_9C_{13} + C_{10}C_{13}) - \frac{1}{2}C_2C_4$$
$$B_{ikli} = C_1C_2 + \frac{\sqrt{2}}{2}(C_5C_9 + C_6C_9) + \frac{\sqrt{2}}{4}(C_{11}C_{13} + C_{12}C_{13}) - \frac{\sqrt{6}}{4}(C_{11}C_{14} - C_{12}C_{14})$$
$$B_{jklj} = C_3C_4 + \frac{\sqrt{2}}{2}(C_7C_{10} + C_8C_{10}) + \frac{\sqrt{2}}{4}(C_{11}C_{13} + C_{12}C_{13}) + \frac{\sqrt{6}}{4}(C_{11}C_{14} - C_{12}C_{14})$$
$$B_{kijk} = C_1C_3 + \frac{\sqrt{2}}{2}(C_5C_{11} + C_7C_{11}) + \frac{\sqrt{2}}{4}(C_9C_{13} + C_{10}C_{13}) - \frac{\sqrt{6}}{4}(C_9C_{14} - C_{10}C_{14})$$
$$B_{lijl} = C_2C_4 + \frac{\sqrt{2}}{2}(C_6C_{12} + C_8C_{12}) + \frac{\sqrt{2}}{4}(C_9C_{13} + C_{10}C_{13}) + \frac{\sqrt{6}}{4}(C_9C_{14} - C_{10}C_{14})$$
$$B_{ijik} = -\frac{1}{2}(\sqrt{2}\,C_3C_5 + C_4C_9)$$
$$B_{ijil} = -\frac{1}{2}(\sqrt{2}\,C_4C_6 + C_3C_9)$$
$$B_{jijk} = -\frac{1}{2}(\sqrt{2}\,C_1C_7 + C_2C_{10})$$
$$B_{jijl} = -\frac{1}{2}(\sqrt{2}\,C_2C_8 + C_1C_{10})$$
$$B_{kikl} = \frac{1}{2}(\sqrt{2}\,C_2C_5 + C_4C_{11})$$
$$B_{kjkl} = \frac{1}{2}(\sqrt{2}\,C_4C_7 + C_2C_{11})$$
$$B_{likl} = \frac{1}{2}(\sqrt{2}\,C_1C_6 + C_3C_{12})$$
$$B_{ljlk} = \frac{1}{2}(\sqrt{2}\,C_3C_8 + C_1C_{12})$$
$$B_{ikil} = \frac{\sqrt{2}}{2}C_0C_9$$
$$B_{jkjl} = \frac{\sqrt{2}}{2}C_0C_{10}$$
$$B_{kikj} = \frac{\sqrt{2}}{2}C_0C_{11}$$
$$B_{likj} = \frac{\sqrt{2}}{2}C_0C_{12}$$
$$B_{ikjl} = \frac{1}{2}(C_0C_{13} + \sqrt{3}\,C_0C_{14})$$
$$B_{iljk} = \frac{1}{2}(C_0C_{13} - \sqrt{3}\,C_0C_{14})$$
$$B_{iklj} = C_1C_4 + \frac{1}{2}(C_5C_{13} + C_8C_{13} + C_9C_{12} + C_{10}C_{11}) + \frac{\sqrt{3}}{2}(C_5C_{14} + C_8C_{14})$$
$$B_{ilkj} = C_2C_3 + \frac{1}{2}(C_6C_{13} + C_7C_{13} + C_9C_{11} + C_{10}C_{12}) - \frac{\sqrt{3}}{2}(C_6C_{14} + C_7C_{14})$$
$$B_{ijkl} = -(C_6C_{13} + C_7C_{13} + C_9C_{11} + C_{10}C_{12}) - \frac{1}{2}C_2C_3$$

$$B_{ijlk} = -(C_5C_{13}+C_8C_{13}+C_9C_{12}+C_{10}C_{11}) - \frac{1}{2}C_1C_4$$

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