

## FROZEN CORE AND VIRTUAL ORBITALS IN THE MC SCF THEORY

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An efficient approximation in the multiconfigurational self-consistent field (MC SCF) method is presented for calculations on large systems. In this method, the orbitals are spanned by adequate orthonormal orbitals, such as Hartree-Fock orbitals, instead of by the entire set of basis functions, and certain of these are not included in the orbital optimization. These include the core orbitals and high-energy virtual orbitals selected from the Hartree-Fock manifold. The computational time for MC SCF calculations dramatically decreases without significant loss of accuracy. This saving in computer time is primarily due to the reduction in the size of the integral transformation. Test calculations are performed for  $\text{Sc}_2$ , CO, and acetylene, and the accuracy of the energy and the Hellmann-Feynman force are checked.

### 1. Introduction

In electronic structure calculations, MC SCF (multiconfigurational self-consistent field) [1,2] theory is often used when single-determinant Hartree-Fock theory is not a good approximation; for example, in the description of the quasi-degenerate state appearing in a bond-breaking process. MC SCF orbitals are also used as reference orbitals for CI (configuration interaction) calculations [3], since the orbitals are optimized for reference configurations composed of several determinants. The CAS (complete active space) MC SCF method [4,5] is a useful addition to the MC SCF approach. As the MC SCF wavefunction satisfies the Hellmann-Feynman (HF) theorem, it is useful for developing the force and density concepts in chemical reaction processes [6-9]. We have previously presented a practical method of calculating reliable Hellmann-Feynman forces by simply adding the derivative bases to the basis set already used [10-12].

In spite of the special virtues of MC SCF theory, applications to large molecular systems are rather

limited, although recent technical improvements have been made [13-18] in MC SCF algorithms. This is probably due to the fact that MC SCF calculations are rather time consuming, particularly when applied to large molecular systems. The key step is the integral transformation appearing in every SCF iteration cycle.

In this paper we propose an approximate method of calculating the MC SCF wavefunction. It considerably reduces the computational effort, while essentially maintaining all the virtues of MC SCF theory. It is based on the following practical observations in MC SCF calculations. First, the transformation of the two-electron repulsion integrals is the most time-consuming step. Second, orbitals which are always doubly occupied and low-lying energetically, such as core orbitals, scarcely differ in form from simple HF SCF orbitals. These "inner orbitals" may be frozen throughout the MC SCF calculation [19]. Similarly, some unoccupied orbitals which have high orbital energies or which are unimportant from symmetry considerations may be excluded from the variational space spanning the MC SCF orbitals. If

the size of the variational space can be reduced, significant savings in time and storage space for the integral transformation step could result, without much affecting the accuracy of the final answer.

In the following sections, we first describe the method we propose and then apply it to MC SCF calculations on  $\text{Sc}_2$ , CO, and acetylene. The efficiency and the accuracy of the present method are also examined. Although the test molecules studied here may be too small to prove the utility of the method, we have already applied it to somewhat larger systems involving the reactions of palladium and platinum metal clusters with a hydrogen molecule and acetylene [20–23].

## 2. Orbital classification in MC SCF theory

A general MC SCF wavefunction may be written as

$$\Psi = \sum_k A_k \Phi_k, \quad (1)$$

where  $\Phi_k$  is a Slater determinant composed of MC SCF orbitals  $\{\psi_i\}$ , which are expanded in a set of basis functions  $\chi_r$ ,

$$\psi_i = \sum_r c_{ir} \chi_r. \quad (2)$$

The coefficients  $A_k$  and  $c_{ir}$  satisfy

$$\sum_k A_k^2 = 1, \quad \mathbf{c}^\dagger \mathbf{S} \mathbf{c} = \mathbf{1}, \quad (3)$$

where  $\mathbf{S}$  is an overlap integral matrix. Usually MC SCF calculations are manipulated using the basis functions  $\{\chi_r\}$ . Alternatively, we may expand the MC SCF orbitals  $\{\psi_i\}$  in a set of orthonormal orbitals  $\{\phi_j\}$  as

$$\psi_i = \sum_j t_{ij} \phi_j \quad (4)$$

with

$$\mathbf{t}^\dagger \mathbf{t} = \mathbf{1}. \quad (5)$$

Practically, the orbitals  $\{\phi_j\}$  are usually Hartree-Fock SCF MOs. They can be expanded in the same basis set  $\{\chi_r\}$  as

$$\phi_j = \sum_r d_{jr} \chi_r \quad (6)$$

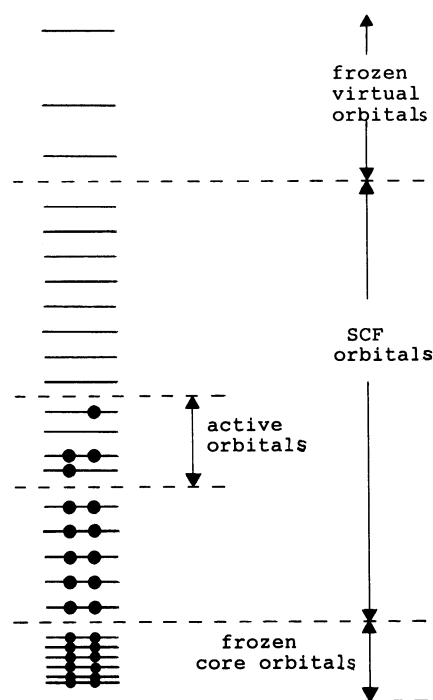


Fig. 1. Schematic picture of the orbital diagram showing the orbital classification scheme. Occupied orbitals and unoccupied orbitals are shown by --- and —, respectively.

with

$$\mathbf{d}^\dagger \mathbf{S} \mathbf{d} = \mathbf{1}. \quad (7)$$

Let us consider the MC SCF calculation using the MOs  $\{\phi_j\}$  as an initial guess. These orbitals may be classified into three types. A schematic picture is shown in fig. 1. The first type may be denoted frozen-core orbitals. They are doubly occupied and remain unchanged throughout the MC SCF calculation. The second type may be called SCF orbitals. The MC SCF orbitals are spanned by these orbitals. In the CAS MC SCF method, the so-called active orbitals and inactive doubly occupied orbitals, which constitute the primary orbital space, and the secondary orbitals, which are unoccupied, are included within this space. The last type may be denoted frozen virtual orbitals. They are selected, for example, from the unoccupied SCF orbitals of high orbital energy, and are excluded from the variational space for the MC SCF orbitals. Based on this classification of the orbitals,

we assume that the transformation matrix  $\mathbf{t}$  in eq. (4) takes the following form

$$\mathbf{t} = \begin{pmatrix} \mathbf{1} & \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \mathbf{t}' & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & \mathbf{1} \end{pmatrix}, \quad (8)$$

where  $\mathbf{1}$  and  $\mathbf{0}$  are unit and zero matrices, respectively. The first unit matrix corresponds to the frozen-core orbital part, the second matrix  $\mathbf{t}'$  to the SCF orbital part, and the last unit matrix corresponds to the frozen virtual orbital part. Thus the variational space for the MC SCF calculation is limited to the SCF orbital space and the frozen core and virtual orbitals are left unchanged. Variational theorems, such as the Hellmann–Feynman theorem, are not satisfied by this approximate MC SCF wavefunction. When the SCF space includes all the orbitals, the results are obviously identical to those of the ordinary MC SCF method.

The energy expression is modified to distinguish between frozen core and SCF orbitals,

$$\begin{aligned} E &= \sum_{ij}^{\text{SCF}} \gamma_{ij} (h_{ij} + U_{ij}^{\text{core}}) + \sum_{ijkl}^{\text{SCF}} \Gamma_{ijkl}(ij:kl) + H^{\text{core}} \\ &= \sum_{ij}^{\text{SCF}} \gamma_{ij} \sum_{ab}^{\text{SCF}} t'_i a'_j b (h_{ab} + U_{ab}^{\text{core}}) \\ &\quad + \sum_{ijkl}^{\text{SCF}} \Gamma_{ijkl} \sum_{abcd}^{\text{SCF}} t'_i a'_j b'_k c'_l d (ab:cd) + H^{\text{core}}, \quad (9) \end{aligned}$$

$$H^{\text{core}} = 2 \sum_m^{\text{core}} h_{mm} + \sum_{mn} [2(mm:nn) - (mn:mn)], \quad (10)$$

$$U_{ij}^{\text{core}} = \sum_{mn}^{\text{core}} [2(ij:mn) - (im:jn)], \quad (11)$$

where  $h_{ij}$  and  $(ij:kl)$  represent core Hamiltonian and electron repulsion integrals, respectively.  $\gamma_{ij}$  and  $\Gamma_{ijkl}$  are one- and two-electron coupling constants defined by

$$\gamma_{ij} = \langle \Psi | a_i^\dagger a_j | \Psi \rangle, \quad \Gamma_{ijkl} = \langle \Psi | a_i^\dagger a_k^\dagger a_l a_j | \Psi \rangle, \quad (12)$$

respectively. In eq. (12),  $a_i^\dagger$  and  $a_j$  are creation and annihilation operators associated with orbitals  $\phi_i$  and  $\phi_j$ , respectively. The symbols “SCF” and “core” used in the summation imply that the summations are limited to the SCF orbitals and the frozen-core orbitals, respectively. As the frozen-core orbitals are

fixed,  $H^{\text{core}}$  in eq. (11) is a constant which should be added to the total SCF energy.  $U^{\text{core}}$  in eq. (11) represents the integrals for Coulomb and exchange repulsions between the electrons in the core and SCF orbitals.

The variational parameters  $\{A_k\}$  and  $\{t_{ij}\}$  are determined under the conditions expressed by eq. (5). Details of the variational procedure are described in the literature [1]. In the present method the variational space is automatically limited to that of the SCF orbitals by using  $\{t'_{ij}\}$  given by eq. (8). Integral transformations are limited to within this SCF orbital space, which leads to a significant decrease in computational time and storage space. If the same calculation is performed using the basis set  $\{\chi_r\}$ , we need the projection operators which exclude the frozen core and frozen virtual orbitals. The computational time may scarcely decrease, because the integrals in eq. (9) are transformed by  $c_{ir}$  in which  $r$  runs over all the basis functions. As  $\{t'_{ij}\}$  are non-linear parameters in MC SCF theory, they are calculated iteratively. The integral transformations required in the present method are carried out via the coefficients  $\{t'_{ij}\}$ , which has the same dimension as the SCF orbital space. When we start from the Hartree–Fock SCF orbitals, the transformation into the space of the basis functions  $\{\chi_r\}$  needs to be done once only when the MC SCF procedure has converged.

### 3. Successive MC SCF calculations in small SCF spaces

The MC SCF wavefunction may be obtained in the following way:

(i) Carry out the MC SCF procedure within the selected set of SCF orbitals.

(ii) After the convergence of step (i), select a new SCF orbital set from the resultant MC SCF orbitals and the frozen orbitals fixed in step (i). The active orbitals must always be included in the SCF orbital space. The dimension of the SCF orbital space in step (ii) is usually larger than that in step (i), but can be equal to or even smaller than it. The integral transformation required in each iteration only involves the SCF orbitals.

(iii) Execute steps (i) and (ii) until the required

accuracy is obtained. The orthonormality condition between the SCF and fixed orbital sets is always satisfied. When the SCF orbital space includes all the orbitals, the resultant MC SCF wavefunction is equivalent to the conventional one expanded in the set  $\{\chi_r\}$ .

#### 4. Test calculations

Test calculations were performed for  $\text{Sc}_2$ , CO, and acetylene. We carried out CAS MC SCF calculations using the Newton–Raphson method [17] for determining  $\{t_{ij}\}$  in eq. (8). We have modified the program “GAMESS” [24] for the present purpose. The basis sets used were MIDI-4 [25] for the Sc atom and 4-31G [26] for C, O, and H atoms. The derivative bases of the 4-31G set were added to the C, O, and H atoms so that the Hellmann–Feynman (H–F) theorem is approximately satisfied for the Hartree–Fock and MC SCF wavefunctions (10)–(12). As frozen virtual orbitals we took all orbitals which have  $\Delta$  symmetry and those orbitals which are highest in orbital energy. The electronic states of  $\text{Sc}_2$  and CO have been reported previously [27,28].

In the calculations on  $\text{Sc}_2$ , the configurations taken involve all possible distributions of six electrons within the two  $4s\sigma_g$  MOs, the  $4s\sigma_u$  MO, and the  $3d\pi_u$  MO of  $\text{Sc}_2$ . We calculated the lowest singlet state at  $R=2.5$  Å. The reference HF SCF orbitals were taken from the  $^1\Sigma^+$  state with configuration  $(4s\sigma_g)^2(3d\pi_u)^4$ . Although this is not the main configuration of the lowest singlet state [27], we used these Hartree–Fock orbitals as starting orbitals because the resulting large orbital reorganization provides a stringent test of our method. Table 1 gives the energies calculated by the HF SCF, CI, and MC SCF methods at the various levels of approximation and the CPU time for each MC SCF iteration. As can be seen from the table, freezing the core orbitals has a negligible effect on the energy. The difference in energy between IV and VI and between V and VI is less than 0.000001 au. This means that the core orbitals of the MC SCF wavefunction are essentially the same as those of the HF SCF wavefunction. On the other hand, the effect of excluding eight virtual orbitals from the SCF space is more marked. The difference

between III and VI is about 0.0004 au. Nevertheless, these differences are sufficiently small to allow us to use methods IV or I with considerable savings in computer time without a significant loss in accuracy. The total CPU time needed falls to  $\frac{1}{8}$ – $\frac{1}{4}$  of that of the full MC SCF (VI) calculation even in this small example.

For the CO molecule, configurations are generated from all possible distributions of six electrons within six orbitals;  $5\sigma$ ,  $6\sigma$ ,  $1\pi$ , and  $2\pi$ . We took CO bond lengths of 1.3 and 1.0 Å, which are longer and shorter than the equilibrium value (1.128 Å). The energy and the Hellmann–Feynman (H–F) forces acting on C and O are shown in tables 2 and 3. The effect of excluding fourteen virtual orbitals is less than 0.00001 au in energy. The effect of freezing the two core orbitals is greater than this and also greater than in the case of  $\text{Sc}_2$ . The CPU time of calculation I is about  $\frac{1}{3}$  of the full MC SCF calculation (III). Table 3 shows the H–F force and the energy gradient (EG) calculated for these MC SCF wavefunctions. When the two core orbitals are frozen to the HF SCF orbitals, the H–F force acting on oxygen at  $R=1.3$  Å becomes worse. Hence for the H–F force, freezing the core orbitals does not seem to be a good approximation. However, when only the fourteen virtual orbitals are frozen, the H–F force is close to that of the full MC SCF wavefunction. Although the error is larger for the oxygen atom (about 6%), it is much smaller than the error in the EG (16%) obtained without including the derivative basis. This shows the importance of the derivative basis for the EG and the H–F force.

Table 4 shows the results for acetylene. We used the 4-31G plus the derivative basis and the geometry was somewhat distorted as shown in the footnote of table 4. CAS MC SCF calculations were performed with  $\pi$  and  $\pi^*$  MOs as active orbitals. Again we see that by freezing core and virtual orbitals, considerable savings in computer time can be achieved without affecting significantly the energy or the H–F force. However, note that when 38 virtual MOs are frozen and the MC SCF calculation carried out within this 34 MO space (calculation IV), the error becomes considerable.

We next show the results of successive improvement of the MC SF wavefunction, keeping an SCF space of 29 MOs. We first calculate the MC SCF en-

Table 1

Total energies of  $\text{Sc}_2$  at  $R=2.5 \text{ \AA}$  calculated by the HF SCF, CI, and MC SCF methods at several levels of approximation and the CPU time for each MC SCF iteration

Method	Number of orbitals			Energy (au)	CPU time <sup>a)</sup> (s)
	SCF	frozen core	frozen virtual		
I	34	10	8	-1516.357370	37
II	42	2	8	-1516.357371	144
III	44	0	8	-1516.357371	201
IV	42	10	0	-1516.358791	69
V	50	2	0	-1516.358792	230
VI <sup>b)</sup> (full)	52	0	0	-1516.358792	302
configuration interaction <sup>c)</sup>				-1516.335559	-
Hartree-Fock SCF				-1516.305830 <sup>d)</sup>	-
				(-1516.233137) <sup>e)</sup>	-

<sup>a)</sup> Timing on the HITAC M280H computer. Overhead time before the MC SCF calculations is not included.

<sup>b)</sup> The total number of basis functions for  $\text{Sc}_2$  is 52.

<sup>c)</sup> The reference orbitals and configurations used in this CI are the same as those used in the MC SCF calculations.

<sup>d)</sup> This HF configuration is  $(4s\sigma_g)^2(4s\sigma_u)^2(3d\sigma_g)^2$ .

<sup>e)</sup> This HF configuration is  $(4s\sigma_g)^2(3d\pi_u)^4$ . This orbital set was used as the starting orbitals of the MC SCF calculation.

Table 2

MC SCF total energy and CPU time for CO at  $R=1.3$  and  $1.0 \text{ \AA}$  calculated using the 4-31G set plus derivative bases <sup>a)</sup>

MC SCF method	Number of orbitals			Total energy (au)		CPU time (s)
	SCF	frozen core	frozen virtual	$R=1.3 \text{ \AA}$	$R=1.0 \text{ \AA}$	
I	40	2	14	-112.710084	-112.692724	47
II	42	0	14	-112.710091	-112.692749	58
III (full)	56	0	0	-112.710095	-112.692755	121

<sup>a)</sup> The MC SCF energies calculated without including the derivative bases are -112.657282 and -112.610284 au for  $R=1.0$  and  $1.3 \text{ \AA}$ , respectively.

Table 3

Energy gradient (EG) and Hellmann-Feynman (H-F) force for CO at  $R=1.3 \text{ \AA}$  and  $R=2.0 \text{ \AA}$  calculated by the MC SCF method <sup>a)</sup>

MC SCF method <sup>b)</sup>	$R=1.3 \text{ \AA}$			$R=1.0 \text{ \AA}$		
	EG	H-F force		EG	H-F force	
		C	O		C	O
I	0.2093	0.2013	0.2509	-0.5125	-0.5364	-0.5276
II	0.2094	0.2042	0.2132	-0.5126	-0.5241	-0.5311
III (full)	0.2098	0.2016	0.1971	-0.5119	-0.5224	-0.5286
parent basis <sup>c)</sup>	0.1753	-	-	-0.5924	-	-

<sup>a)</sup> Definition of the force is  $\text{C} \rightarrow - \leftarrow \text{O}$ .

<sup>b)</sup> Definitions of the MC SCF methods are as shown in table 2.

<sup>c)</sup> Calculation without including the derivative bases.

Table 4

MC SCF total energy, CPU time, energy gradient (EG) and Hellmann–Feynman (H–F) force for acetylene calculated using the 4-31G set plus derivative bases

MC SCF method	Number of orbitals			Energy (au)	CPU time (s)	Carbon		Hydrogen	
	SCF	frozen orbital				EG (au)	H–F (au)	EG (au)	H–F (au)
		virtual	core						
I	52	18	2	-76.723561	112.4	-0.0533	-0.0587	0.1012	0.0996
II	54	18	0	-76.723563	138.6	-0.0534	-0.0511	0.1012	0.1004
III	44	28	0	-76.723298	53.7	-0.0529	-0.0566	0.1009	0.0984
IV	34	38	0	-76.721660	16.2	-0.0505	-0.0601	0.1002	0.1028
V (full)	72	0	0	-76.723565	427.3	-0.0534	-0.0539	0.1012	0.1005

a) Geometry of acetylene and definition of force are  $\text{H}-\text{C}-\text{C}-\text{H}$ .  
 $\text{1.06\AA} \quad \text{1.203\AA} \quad \text{1.36\AA}$

b) The energy gradient obtained from the MC SCF calculation without including the derivative bases is  $-0.0792$  au for carbon and  $0.0989$  au for hydrogen.

Table 5

Total energy of CO at  $R=1.3$  Å as calculated by the MC SCF method in which SCF orbitals are successively replaced by frozen virtual orbitals<sup>a)</sup>

Step	Energy (au)	H–F force (au) <sup>b)</sup>	
		C	O
1	-112.709130	0.2108	0.3161
2	-112.710016	0.2019	0.2073
3	-112.710094	0.2037	0.2061
full	-112.710095	0.2016	0.1971

a) The numbers of SCF and frozen virtual orbitals are 29 and 27, respectively. In each step, 19 SCF orbitals are replaced by 19 frozen virtual orbitals.

b) The energy gradient of the full MC SCF wave function is 0.2098.

ergy within the lowest 29 SCF MO space (No. 1) and then replace 19 SCF orbitals with 19 frozen orbitals and recalculate the MC SCF energy within the new 29 SCF orbital space (No. 2). We repeat a similar step once again (No. 3) and present the results in table 5. After two steps of this procedure, the energy is already very close to the full MC SCF value. The H–F force also shows good convergence.

## 5. Concluding remarks

A practically useful method for calculating MC SCF wavefunctions is described. By fixing some of

the core and virtual orbitals to the HF SCF MOs, we could dramatically reduce the computational time for the MC SCF calculation without much loss of accuracy. This is primarily due to savings in the integral transformation step which is necessary in every iteration of the SCF procedure. The Hellmann–Feynman force is also shown to be fairly reliable even in this approximate MC SCF method, if the basis set includes the first derivative bases and the core MOs are included in the SCF space. The present results can be improved by doing full MC SCF calculations in the first few iterations, and then fixing some of the MOs and performing succeeding in the reduced MO space. We have already utilized the procedure proposed here for several years for calculating MC SCF wavefunctions in studies of the catalytic reactions of small palladium and platinum clusters with hydrogen and acetylene [20–23]. Without this method, it would have been difficult to perform MC SCF calculations for such large systems.

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