A quasi-complete active space self-consistent field method

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Abstract

A multi-configuration self-consistent field method is proposed in which a quasi-complete active space, which is the product space of complete active spaces, is used as a variational space. The computational effort for wavefunctions is significantly reduced compared with the complete active space self-consistent field (CAS-SCF) method. Efficient formulae with segmented alpha and beta strings are derived. The scheme is tested on the spectroscopic constants and a potential energy curve of CO, the transition state barrier height of the reaction, $H_2CO \rightarrow H_2 + CO$, and the energy difference between *trans*- and *cis*-butadiene. The results are in good agreement with the corresponding CAS-SCF results. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

In the study of chemical reaction mechanisms, the multi-configuration self-consistent field (MC-SCF) method is a useful approach and hence frequently used, especially in the form of the complete active space self-consistent field (CAS-SCF) method [1–5]. However, CAS-SCF often generates far too many configurations, and the size of the active space outgrows the capacity of present technology. Even today, the size of the configuration interaction (CI) space that can be routinely used has a dimension of about one million at most, which roughly corresponds to 12–14 active orbitals.

Several methods have been proposed to overcome the problem of the CI dimension. One is the restricted active space (RAS) SCF method of Olsen et al. [6]. In RAS-SCF, the active orbitals are divided into three subsets RAS1, RAS2, and RAS3. RAS1 is restricted to a minimum number of occupied spin orbitals, and RAS3 is restricted to a maximum number of such orbitals whilst RAS2 is unrestricted. RAS is an extension of the usual CI spaces such as single and double excitation CI (SDCI) spaces as well as being an extension of CAS.

Another method for overcoming the CI dimension problem is the generalized valence bond with a complete active space (GVB-CAS) method of Clifford et al. [7], which is a hybrid method of the GVB and CAS-SCF methods. In GVB-CAS, the active orbitals are divided into some pairs of orbitals for GVB spaces and a set of orbitals for CAS. The GVB-type excitations are allowed for a set of GVB orbitals, and CAS-CI is performed among the remaining active orbitals.

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Before the RAS-SCF method, Walch et al. [8] used a 'constrained CAS (CCAS)' as an MC-SCF variational space to study the electronic states of Cr_2 and V_2. CCAS [9] is defined as a space that contains all configurations that can be formed by distributing the active electrons within certain groups of active orbitals with a given occupation number in each group.

In this Letter, we propose an MC-SCF method with a quasi-complete active space (QCAS), i.e., a QCAS-SCF method.

QCAS is defined as a product space of complete active spaces constructed by active electrons and orbitals within each group. This space is similar to CCAS, but differs in the spin-coupling scheme between the groups and construction scheme of CI basis functions. CCAS includes all spin couplings constructed from singly occupied orbitals, while QCAS includes only spin couplings generated as a product of spin functions of each group. Furthermore, CI basis functions in CCAS are constructed with configuration state functions (CSF) by limiting some routes [9] in the distinct row table in the graphical unitary group approach, while functions in QCAS are constructed from the product of (segmented) alpha and beta strings (or as the product of CSF). This construction scheme of QCAS allows us to take a string in a group independently of strings in the other groups, making the computational scheme simple.

Note that an MC-SCF space yielded by valence-bond-like construction can be a sort of QCAS. For example, McLean et al. [10] used such a space (space E in Ref. [10]) to approach a symmetry breaking problem in molecular calculations.

QCAS-SCF is a natural extension of CAS-SCF, and therefore retains the advantages of CAS-SCF. Furthermore, since the dimension of QCAS is generally much smaller than that of CAS, the computational effort of QCAS-SCF is much less than that of CAS-SCF.

2. Method

In the MC-SCF method, we partition orbitals into core, active, and virtual, and then construct the CI space by distributing active electrons among the active orbitals. Let us further divide the active electron and orbital sets into N sub-sets and fix the number of active electrons, m_i, and orbitals, n_i, in each sub-set,

$$m_{\mathrm{act}} = \sum_i^N m_i, \; n_{\mathrm{act}} = \sum_i^N n_i, \tag{1}$$

where m_{act} and n_{act} denote the number of active electrons and orbitals, respectively. We define the quasi-complete space as the product space of CAS spanned by the determinants or CSF as follows:

$$\mathrm{QCAS}(\{m_i\}, \{n_i\}) = \mathrm{CAS}(m_1, n_1) \times \mathrm{CAS}(m_2, n_2) \times \cdots \times \mathrm{CAS}(m_N, n_N), \tag{2}$$

such that the number of electrons in each orbital group satisfies the restriction in Eq. (1).

The dimension of QCAS is much smaller than that of CAS for the same set of active electrons and orbitals. For example, the dimension of CAS(16,16) spanned by the determinants with $M = 0$ is 165 636 900 (throughout this Letter, the dimension of an active space is expressed by the number of determinants with $M = 0$ and no symmetry). If we divide the active electrons and orbitals into five groups: (4e,4o) + (4e,4o) + (4e,4o) + (2e,2o) + (2e,2o), where 4e and 4o denote 4 electrons and 4 orbitals in the group, respectively, the dimension of QCAS is 746 496 ($= 36^3 \cdot 4^2$).

One of the most time-consuming steps in the MC-SCF procedure is the solution of the CI eigenvalue problem. In particular, the computation of the σ-vector,

$$\sigma = \sum_J H_{IJ} c_J = \sum_J \left\{ \sum_{ij} h_{ij} \langle I | E_{ij} | J \rangle + \frac{1}{2} \sum_{ijkl} (ij|kl) \langle I | E_{ij} E_{kl} - \delta_{jk} E_{il} | J \rangle \right\} c_J, \tag{3}$$

is an essential part of the problem. Here, H_{IJ} and c_J are the elements of the CI Hamiltonian and CI vector, respectively, h_{ij} and $(ij|kl)$ are the core Hamiltonian and electron repulsion integrals, respectively, and $|I\rangle$ and E_{ij} are the CI basis functions (Slater determinants or CSF) and the unitary group generators, respectively.

We adopt here Slater determinants as the basis functions of CI space rather than CSF. Furthermore, we split a determinant into an alpha and beta string of each group,

$$|I\rangle = |I_\alpha^1 \cdots I_\alpha^N; I_\beta^1 \cdots I_\beta^N\rangle = |I_\alpha^1\rangle \cdots |I_\alpha^N\rangle |I_\beta^1\rangle \cdots |I_\beta^N\rangle , \tag{4}$$

where $|I\rangle$ are now determinants and $|I_\alpha^G\rangle$ and $|I_\beta^G\rangle$ are segmented alpha and beta strings of group G, respectively. We can specify a string in a group independently of those in the other groups.

Let us consider the case where the numbers of alpha and beta electrons are equal in each group, and the case where the unpaired alpha electrons take the highest spin coupling ($S = M \neq 0$). In these cases, the number of alpha and beta electrons, as well as the total number of electrons, in each group may be fixed. Then we can decompose one-body alpha coupling constants $\langle I|E_{ij}^\alpha|J\rangle$ and beta coupling constants $\langle I|E_{ij}^\beta|J\rangle$ in Eq. (3) into the coupling constants for the strings of the groups as

$$\langle I|E_{ij}|J\rangle = \langle I|E_{ij}^\alpha|J\rangle + \langle I|E_{ij}^\beta|J\rangle$$

$$= \begin{cases} \langle I_\alpha^G|E_{ij}^\alpha|J_\alpha^G\rangle \displaystyle\prod_{H \neq G} \delta_{I_\alpha^H J_\alpha^H} \prod_H \delta_{I_\beta^H J_\beta^H} + \langle I_\beta^G|E_{ij}^\beta|J_\beta^G\rangle \prod_H \delta_{I_\alpha^H J_\alpha^H} \prod_{H \neq G} \delta_{I_\beta^H J_\beta^H} \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad (i,j \in G) \\ 0 \qquad (\text{otherwise}) \end{cases} \tag{5}$$

Using this relation, we obtain a σ-vector formula,

$$\sigma\left(I_\alpha^1 \cdots I_\alpha^N; I_\beta^1 \cdots I_\beta^N\right) = \sigma_\alpha^{[1]} + \sigma_\beta^{[1]} + \sigma_{\alpha\alpha}^{[2]} + \sigma_{\beta\beta}^{[2]} + \sigma_{\alpha\beta}^{[2]} , \tag{6}$$

where the first, third, and last terms of the right hand side are given by

$$\sigma_\alpha^{[1]}\left(I_\alpha^1 \cdots I_\alpha^N; I_\beta^1 \cdots I_\beta^N\right)$$

$$= \sum_G \sum_{J_\alpha^G} \sum_{ij \in G} \left[h_{ij} - \frac{1}{2}\sum_{k \in G}(ik|kj)\right]\langle I_\alpha^G|E_{ij}^\alpha|J_\alpha^G\rangle c\left(I_\alpha^1 \cdots J_\alpha^G I_\alpha^{G+1} \cdots; I_\beta^1 \cdots\right), \tag{7}$$

$$\sigma_{\alpha\alpha}^{[2]}\left(I_\alpha^1 \cdots I_\alpha^N; I_\beta^1 \cdots I_\beta^N\right)$$

$$= \frac{1}{2}\sum_G \sum_{J_\alpha^G} \sum_{K_\alpha^G} \sum_{ijkl \in G}(ij|kl)\langle I_\alpha^G|E_{ij}^\alpha|K_\alpha^G\rangle\langle K_\alpha^G|E_{kl}^\alpha|J_\alpha^G\rangle c\left(I_\alpha^1 \cdots J_\alpha^G I_\alpha^{G+1} \cdots; I_\beta^1 \cdots\right)$$

$$+ \sum_{G>H} \sum_{J_\alpha^G J_\alpha^H} \sum_{ij \in G} \sum_{kl \in H}\left[(ij|kl) - (il|kj)\right]\langle I_\alpha^G|E_{ij}^\alpha|J_\alpha^G\rangle\langle I_\alpha^H|E_{kl}^\alpha|J_\alpha^H\rangle$$

$$\times c\left(I_\alpha^1 \cdots J_\alpha^G I_\alpha^{G+1} \cdots J_\alpha^H I_\alpha^{H+1} \cdots; I_\beta^1 \cdots\right), \tag{8}$$

and

$$\sigma_{\alpha\beta}^{[2]}\left(I_\alpha^1 \cdots I_\alpha^N; I_\beta^1 \cdots I_\beta^N\right) = \sum_{GH} \sum_{J_\alpha^G J_\beta^H} \sum_{ij \in G} \sum_{kl \in H}(ij|kl)\langle I_\alpha^G|E_{ij}^\alpha|J_\alpha^G\rangle\langle I_\beta^H|E_{kl}^\beta|J_\beta^H\rangle$$

$$\times c\left(I_\alpha^1 \cdots J_\alpha^G I_\alpha^{G+1} \cdots; I_\beta^1 \cdots J_\beta^H I_\beta^{H+1} \cdots\right), \tag{9}$$

respectively. The other terms, $\sigma_\beta^{[1]}$ and $\sigma_{\beta\beta}^{[2]}$, are obtained by exchanging α and β in Eqs. (7) and (8), respectively. Similarly, the one- and two-particle density matrices used in orbital optimization in the MC-SCF procedure are written by the coupling constants for the strings of the groups.

Table 1
Bond length, vibrational frequency, and dissociation energy for CO molecule. (The experimental values are taken from Ref. [12])

	Dimension	r_e (Å)	ω_e (cm^{-1})	D_e $(kcal\ mol^{-1})$
CAS(12,12)	48 200	1.1325	2175	247.2
QCAS$[(4,4)^3]$	4 096	1.1324	2175	248.0
Exptl.	–	1.128323	2169.8	255.8

The characteristic feature to be noted here is that both the σ-vector and density formulae are written only with one-electron coupling constants between *strings in a group*, and no intergroup coupling constants appear. This fact makes the QCAS-CI eigenvector computation efficient. Note that by using CSF we cannot reach a similar decoupling.

Let us consider the case where there are unpaired alpha electrons in a group and beta-electrons in another group. To treat this case, we need to extend the definition Eq. (2) to the sum of the product spaces. We do not treat such a case in this Letter, although it will be presented in a future paper.

3. Test calculations

We calculated with QCAS-SCF some spectroscopic constants and a potential energy curve of CO, the transition state barrier height of the reaction $H_2CO \rightarrow H_2 + CO$, and the energy difference between *trans-* and *cis*-butadiene, and compared the results with those of CAS-SCF with corresponding active spaces.

3.1. Spectroscopic constants and ground state potential curve of CO

The basis set used is the correlation consistent polarized valence triple zeta (cc-pVTZ) basis set of Dunning [11]. The active spaces were constructed from 6 electrons and 12 (5σ–8σ, 1π–4π, and $1\pi'$–$4\pi'$) orbitals. CAS was used for comparison and was constructed by distributing these 6 electrons among all 12 orbitals. QCAS was constructed by first dividing the orbitals into three groups, $\{5\sigma–8\sigma\}$, $\{1\pi–4\pi\}$, and $\{1\pi'–4\pi'\}$, and then distributing two electrons among each group. Henceforth, we call this active space QCAS$[(2,4)^3]$. The dimension of QCAS$[(2,4)^3]$ is 4 096, while that of CAS(6,12) is 48 200.
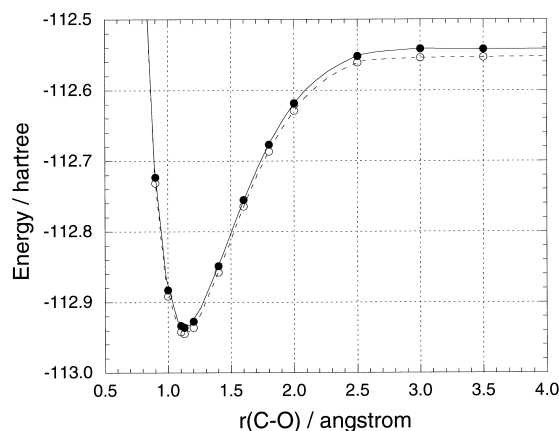

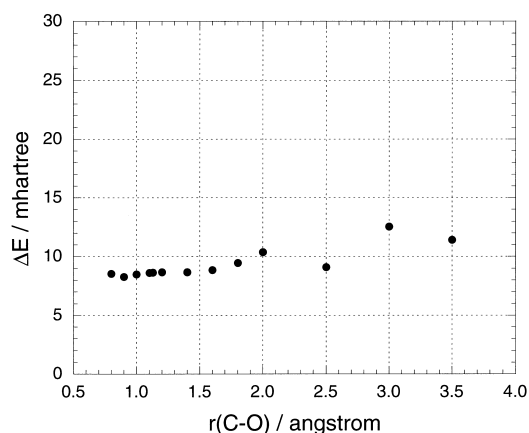Fig. 1. The QCAS-SCF (●) and CAS-SCF (○) potential curves of the ground state ($X\,^1\Sigma^+$) of CO.

Fig. 2. The energy difference between the QCAS-SCF and CAS-SCF methods in the ground state $(X^1\Sigma^+)$ of CO.

Table 1 summarizes the results of some spectroscopic constants. All the constants, r_e, ω_e, and D_e of QCAS-SCF are in good agreement with those of CAS-SCF. The differences from CAS-SCF for r_e and ω_e are less than 0.001 Å and 1 cm^{-1}, respectively, and that in D_e is only 0.8 kcal mol^{-1}. Fig. 1 shows the potential curves of the ground state, $X^1\Sigma^+$, calculated with the QCAS-SCF and CAS-SCF methods. Fig. 2 shows the difference between QCAS-SCF and CAS-SCF energies. Although the QCAS-SCF curve is about 10 millihartree above the CAS-SCF curve, QCAS-SCF reproduces the shape of the CAS-SCF potential curve well. This is indicated by the difference being almost constant (maximum deviation in energy difference is about 5 millihartree) for the entire bond length. It is the shape of potential curves that is important in chemical reaction studies, not the absolute energy. Thus, it can be said that QCAS-SCF exhibits high performance.

3.2. Transition state barrier height of reaction $H_2CO \rightarrow H_2 + CO$

The equilibrium and transition structures used are the same as in a previous paper [13]. The complete active space we used for comparison is CAS(12,10), which is a full valence active space. We split the active orbitals into $\{CO(\sigma,\sigma^*)\}$, $\{CO(\pi,\pi^*)\}$, and $\{CH(\sigma,\sigma^*),CH(\sigma',\sigma'^*),O(lp,lp)\}$, where lp denotes a lone pair orbital, and then we distributed 2, 2, and 8 electrons among the above groups, respectively, to construct $QCAS[(2,2)^2 \times (8,6)]$. The dimension of the CAS is 44 100, while that of QCAS is 3 600.

The results with cc-pVTZ and cc-pVQZ [11] are shown in Table 2. The QCAS-SCF results are very close to the corresponding CAS-SCF results. Although differences in the energy itself between QCAS-SCF and CAS-SCF are about 10 millihartree for both basis sets, the differences in the barrier height are 0.72 and 0.54 millihartree (0.4 and 0.3 kcal mol^{-1}) for cc-pVTZ and cc-pVQZ, respectively.

Table 2
Transition state barrier height for $H_2CO \rightarrow H_2 + CO$

	Dimension	Eq. (hartree)	Tr. (hartree)	ΔE (kcal mol^{-1})
cc-pVTZ				
CAS(12,10)	44 100	− 114.05837	− 113.91438	90.4
QCAS[(2,2)$^2 \times$(8,6)]	3 600	− 114.04835	− 113.90364	90.8
cc-pVQZ				
CAS(12,10)	44 100	− 114.06779	− 113.92325	90.7
QCAS[(2,2)$^2 \times$(8,6)]	3 600	− 114.05760	− 113.91252	91.0

Table 3
Energy difference between *trans*- and *cis*-butadiene

	Dimension	*trans* (hartree)	*cis* (hartree)	ΔE (kcal mol^{-1})
CAS(10,10)	63 504	−155.10398	−155.09861	3.37
QCAS[(6,6)×(4,4)]	14 400	−155.09812	−155.09270	3.40
QCAS[(2,2)^3×(4,4)]	2 304	−155.09580	−155.09026	3.47
CAS(10,14)	4 008 004	−155.12602	−155.12025	3.62
QCAS[(2,2)^3×(4,8)]	50 176	−155.10991	−155.10435	3.48

3.3. Energy difference between trans- and cis-butadiene

The basis set used was cc-pVTZ [11]. For the polarization functions, the g function on C and d function on H were omitted. The structures were determined by CAS(4,4) calculations with cc-pVDZ. The active orbitals used were six C–C $\sigma(\sigma^*)$ and four $\pi(\pi^*)$ orbitals. In the QCAS-SCF calculations, we split up the active electrons and the active orbitals as follows: (1) {6 elecs. in C–C $(\sigma,\sigma^*,\sigma',\sigma'^*,\sigma'',\sigma''^*)$ orbs.} and {4 elecs. in π,π^*,π',π'^* orbs.}, and (2) {2 elecs. in C–C (σ,σ^*) orbs.}, {2 elecs. in C–C (σ',σ'^*) orbs.}, {2 elecs. in C–C (σ'',σ''^*) orbs.} and {4 elecs. in π,π^*,π',π'^* orbs.}. The QCAS constructed with these sets are denoted by QCAS[(6,6)×(4,4)] and QCAS[(2,2)^3×(4,4)], respectively. The dimension of CAS(10,10) is 63 504, while those of QCAS[(6,6)×(4,4)] and QCAS[(2,2)^3×(4,4)] are 14 400 and 2 304, respectively. Furthermore, we carried out the calculations with QCAS constructed using the active orbitals and by adding four more diffuse π^* orbitals to the π orbital set in (2), which is denoted by QCAS[(2,2)^3×(4,8)]. The dimension of QCAS[(2,2)^3×(4,8)] is 50 176, and that of the corresponding complete active space, CAS(10,14), is 4 008 004.

The results are summarized in Table 3. The difference in the relative energy is small. The differences in ΔE from the results in CAS(10,10) are only 0.03 and 0.10 kcal mol^{-1} for QCAS[(6,6)×(4,4)] and QCAS[(2,2)^3× (4,4)], respectively. The doubled π orbitals decrease total energies by about 20 and 10 millihartree in CAS- and QCAS-SCF, respectively, but the effect on ΔE is small. Again, the agreement of the results between QCAS and the corresponding CAS is good. The difference in ΔE between QCAS[(2,2)^3×(4,8)] and CAS(10,14) is 0.14 kcal mol^{-1}.

4. Summary and conclusions

We proposed a new type of multi-configuration self-consistent field method, in which QCAS, the product space of complete active spaces, is used as a variational space. QCAS-SCF is designed to circumvent the large-scale CI problem in the CAS-SCF method. QCAS, with a physically sound partitioning of active space, can reduce the computational effort without loss of accuracy. Furthermore, since QCAS-SCF is a natural extension of CAS-SCF, it retains the advantages of CAS-SCF.

We derived efficient formulae with segmented alpha and beta strings and carried out some preliminary QCAS-SCF calculations. In all the applications, the QCAS-SCF reproduced the results of corresponding CAS-SCF quite well. The deviations from CAS-SCF were less than 1 kcal mol^{-1} in relative energy. We expect that the QCAS-SCF method is a useful approach for studying chemical reaction mechanisms.

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