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Nonorthogonal molecular orbital method: Single-determinant theory

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Using the variational principle, we have derived a variant of the Adams–Gilbert equation for nonorthogonal orbitals of a single-determinant wave function, which we name the modified Adams–Gilbert equation. If we divide the molecular system into several subsystems, such as bonds, lone pairs, and residues, we can solve the equations for the subsystems one by one. Thus, this procedure has linear scaling. We have presented a practical procedure for solving the equations that is also applicable to macromolecular calculations. The numerical examples show that the procedure yields, with reasonable effort, results comparable with those of the Hartree–Fock–Roothaan method for orthogonal orbitals. To resolve the convergence difficulty in the self-consistent-field iterations, we have found that virtual molecular-orbital shifts are very effective. © *2014 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4879059]

I. INTRODUCTION

If we attempt to carry out the standard Hartree–Fock–Roothaan (HFR)[1] calculations on macromolecules such as proteins and DNA, we must resolve two problems: the construction of a Fock matrix of very large dimensions and the solution of HFR equations of very large dimensions. These problems have been reviewed in some articles and books.[2–4] The present work is concerned with the latter problem and provides a new viewpoint on the nonorthogonality of molecular orbitals (MOs).

In the building-block approach (BBA) we divide a molecular system into several subsystems (SSs), compute the wave functions of the SSs one by one, and then collect the SS wave functions to form the wave functions of the whole system. This method has linear scaling.[2–4]

Adams[5] and Gilbert[6] presented a self-consistent-field (SCF) theory suitable for BBA. It is designed for a single-determinant wave function with nonorthogonal molecular orbitals (NOMOs) and their SCF equation is known as the Adams–Gilbert (AG) equation. Matsuoka[7] pointed out that when we adopt the basis-set expansion method[1] for the AG equation, we must use a basis set common to all SSs. Thus, for macromolecular calculations we must solve AG equations of very large dimensions and their theory has not much merit in this respect. Matsuoka[7] reformulated their theory and presented an equation named the modified Adams–Gilbert (MAG) equation. The MAG equation is similar to the AG equation and the MOs are nonorthogonal. However, we may solve SCF equations of smaller dimensions than the AG equation.

Payne,[8] Mehler,[9] and Stoll *et al.*[10] proposed other forms of the SCF equations for NOMOs. Seijo *et al.*[11,12] reformulated the AG equation and presented encouraging results based on the extended Hückel[13] and the Kohn–Sham[14] Hamiltonians.

The MAG equation[7] and other SCF equations[8–10] for NOMOs were proposed more than three decades ago. However, despite their possible applicability to macromolecular calculations, their development remains in the preliminary stages. One reason why they have not been developed seems to be the extremely slow convergence or divergence in the SCF iterative processes. In the previous MAG method,[7] the numbers of iterations were less than twice those in the HFR method.[1] However, in the other methods,[8–10] they might be very large, as seen in the study by Smits and Altona.[15] Besides, during these years we have received private correspondence that reported the convergence difficulties in the NOMO methods.[5–10]

Recently, we revisited the MAG equation to enlarge its applicability to practical macromolecular calculations. We soon encountered the convergence problem. To overcome this problem we employed the usual powerful techniques for accelerating convergence such as direct inversion in the iterative subspace (DIIS),[16] but failed. Then we reformulated the original MAG equation[7] for better convergence, but had only limited success. Finally we found an efficient method of introducing virtual-MO (VMO) shifts. Matsuoka[7] adopted VMO shifts by chance, but we now realize their importance in the SCF process. As noted by Matsuoka,[7] the MO-energy spectrum in the AG or the MAG equation differs from the one in the HFR equation. In the AG/MAG equations, without VMO shifts, the VMO energies might become lower than the occupied MO (OMO) energies and fall into the OMO space, which causes the convergence difficulty. This problem will be discussed further in Secs. II–IV.

We should mention that several other BBAs have been proposed. Among them, the divide-and-conquer method[17] and the fragment MO method[18] are still adopted for molecular calculations. In the former, the SCF equations for SSs called cells are solved numerically. In the latter, the equations for SSs called fragments are treated using the basis-set expansion method. However, the approximations introduced into the SS equations violate the variational principle and these methods appear to be algorithms for computation. We should also note

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the elongation method,[19] which is a kind of orthogonal HFR method designed for polymers. It starts the HFR calculations on the head unit of the polymer and elongates the MOs unit by unit until the tail unit is reached.

In Sec. II of this paper, we derive an SCF equation for NOMOs using the variational principle. It is essentially the MAG equation proposed by Matsuoka,[7] but takes a slightly different form in the hope of the better convergence in the SCF process. In Sec. III, we present a procedure for solving the new MAG equation, which would be applicable to macromolecular calculations. In Sec. IV, we show some numerical examples obtained by using this procedure. In Sec. V, we discuss some problems encountered during this study. In particular, we emphasize the importance of the VMO shifts to resolve the convergence difficulties that might hinder the development of the NOMO methods.[5–10]

II. MODIFIED ADAMS–GILBERT EQUATION

In this section, we derive the MAG equation in a slightly different form from that given by Matsuoka[7] and discuss its relationship to the original AG equation.[5,6]

We consider a closed-shell molecular system of $2N$ electrons having a wave function that is an antisymmetrized product of N doubly-occupied real orbitals $\{\phi_i, i = 1, \ldots, N\}$,

$$\Phi = \det|\phi_1\alpha(1)\phi_1\beta(2)\cdots\phi_N\alpha(2N-1)\phi_N\beta(2N)|, \quad (2.1)$$

each orbital being multiplied by α and β spin functions. We assume that in general the orbitals are normalized, but nonorthogonal,

$$\langle\phi_i|\phi_i\rangle = 1, \quad \langle\phi_i|\phi_j\rangle \equiv S_{ij} \neq 0 \ (i \neq j). \quad (2.2)$$

If the system Hamiltonian H consists of one- and two-electron operators, h and g,

$$H = \sum_{\mu=1}^{2N} h(\mu) + \sum_{\mu>\nu=1}^{2N} g(\mu,\nu), \quad (2.3)$$

the expectation value of the electronic energy, $E(= \langle\Phi|H|\Phi\rangle/\langle\Phi|\Phi\rangle)$, is written as[20]

$$\begin{aligned} E = {} & 2\sum_{ij=1}^{N}\langle\phi_i|h|\phi_j\rangle Z_{ij} \\ & + \sum_{ijkl=1}^{N}[2\langle\phi_i(\mu)\langle\phi_k(\nu)|g(\mu,\nu)|\phi_l(\nu)\rangle\phi_j(\mu)\rangle \\ & - \langle\phi_i(\mu)\langle\phi_k(\nu)|g(\mu,\nu)|\phi_j(\nu)\rangle\phi_l(\mu)\rangle]Z_{ij}Z_{kl}, \end{aligned} \quad (2.4)$$

where Z_{ij} is an element of the inverse of the overlap matrix $\boldsymbol{S}$ [Eq. (2.2)], $Z_{ij} = (\boldsymbol{S}^{-1})_{ij}$.

Since $\boldsymbol{SZ} = \mathbf{I}$ (the unit matrix), the variation of the inverse matrix $\boldsymbol{Z}$ is written as

$$\delta Z_{ij} = -\sum_{kl=1}^{N}\langle\delta\phi_k|\phi_l\rangle(Z_{ik}Z_{jl} + Z_{il}Z_{jk}). \quad (2.5)$$

Using Eq. (2.5) and a similar procedure for the orthogonal orbitals,[1] we obtain the variation of the energy [Eq. (2.4)]

$$\delta E = 4\sum_{ij=1}^{N}\langle\delta\phi_i|(1-\rho)F|\phi_j\rangle Z_{ij}, \quad (2.6)$$

where ρ is the system density-matrix operator,

$$\rho = \sum_{ij=1}^{N}|\phi_i\rangle Z_{ij}\langle\phi_j|, \quad (2.7)$$

and F is the Fock operator,

$$\begin{aligned} F(\mu) = {} & h(\mu) + \sum_{ij=1}^{N} Z_{ij}[2\langle\phi_i(\nu)|g(\mu,\nu)|\phi_j(\nu)\rangle_\nu \\ & - \langle\phi_i(\nu)|g(\mu,\nu)|\_\rangle_\nu\phi_j(\mu)]. \end{aligned} \quad (2.8)$$

The last term is the exchange operator, which operates on an arbitrary function ϕ as $\langle\phi_i(\nu)|g(\mu,\nu)|\phi\rangle_\nu\phi_j(\mu)$.

Thus, from the variational principle, $\delta E = 0$, we obtain

$$\sum_{k=1}^{N}(1-\rho)F|\phi_k\rangle Z_{kj} = 0. \quad (2.9)$$

Then, multiplying Eq. (2.9) by the overlap matrix S_{ij} and summing over the index j, we obtain

$$(1-\rho)F|\phi_i\rangle = 0. \quad (2.10)$$

Using the relation $\rho|\phi_i\rangle = |\phi_i\rangle$, we obtain the hermitized forms of Eq. (2.10):

$$(F - \rho F\rho)|\phi_i\rangle = 0, \quad (2.11)$$

$$[(1-\rho)F + F(1-\rho)]|\phi_i\rangle = 0. \quad (2.12)$$

Equation (2.10) is the condition that the NOMOs should satisfy. If we define the (true) VMO ϕ_v for which a relation $\rho\phi_v = 0$ holds, then Eq. (2.10) states that

$$\langle\phi_v|F|\phi_i\rangle = 0, \quad (2.13)$$

which is the Brillouin theorem for nonorthogonal orbitals corresponding to the one for orthogonal orbitals.[2–4,21]

Now we divide the closed-shell molecular system into several SSs, such as bonds, lone pairs, and residues, and denote the ith MO belonging to the Ith SS as ϕ_{Ii}. Each SS is also assumed to form a closed-shell so that the whole molecular system forms a closed shell.

We wish to transform Eqs. (2.11) and (2.12) for NOMOs into eigenvalue equations like the HFR equation for orthogonal MOs.[1] In the usual molecular calculations, we adopt the basis-set expansion method and express a set of the MOs $\{\phi_{Ii}\}$ belonging to a specified SS in terms of a specified set of basis functions. Thus, any partial orthogonal transformations among the MOs of the specified SS do not change the single-determinant wave function of the closed-shell system [Eq. (2.1)]. Using this freedom of the transformations, we adopt Gilbert's diagonalization requirement[6] and require that the Hamiltonian W_I chosen conveniently for the Ith SS should be diagonalized, within the OMO space, as

$$\rho_I W_I \rho_I|\phi_{Ii}\rangle = w_{Ii}|\phi_{Ii}\rangle, \quad (2.14)$$

where w_{Ii} is an eigenvalue and ρ_I is a density-matrix operator of the Ith SS,

$$\rho_I = \sum_{i\subset I}^{\text{occ.}} |\phi_{Ii}\rangle\langle\phi_{Ii}|. \tag{2.15}$$

For practical calculations, we may add[22,23] an arbitrary operator V_I for the VMO space $(1-\rho_I)$ to the left-hand side of Eq. (2.14) so that

$$[\rho_I W_I \rho_I + (1-\rho_I)V_I(1-\rho_I)]|\phi_{Ii}\rangle = w_{Ii}|\phi_{Ii}\rangle. \tag{2.16}$$

Then, combining Eq. (2.16) with Eq. (2.11) or Eq. (2.12), we finally obtain the eigenvalue equation,

$$G_I|\phi_{Ii}\rangle = w_{Ii}|\phi_{Ii}\rangle, \tag{2.17}$$

where

$$G_I = \rho_I W_I \rho_I + sX + (1-\rho_I)V_I(1-\rho_I), \tag{2.18}$$

with $X = F - \rho F \rho\,(\equiv X1)$ or $X = 2F - (\rho F + F\rho)$ $(\equiv X2)$. Here we have introduced an arbitrary scale factor s, since Eq. (2.11) or Eq. (2.12) holds even when multiplied by any constant. In practical calculations, a properly chosen s has been found to enhance the convergence.

Equation (2.17) is a variant of the original MAG equation,[7] where $X = X1$ and $s = 1$. We shall continue to call it the MAG equation.

In Eq. (2.14), Gilbert[6] adopted the density-matrix operator ρ [Eq. (2.7)] for the whole system, instead of the operator ρ_I defined for the Ith SS [Eq. (2.15)]. Since the whole-system density-matrix operator ρ consists of all occupied orbitals of the whole system, his diagonalization requirement means that the wave function [Eq. (2.1)] should be invariant under the transformations among all occupied orbitals, so that we must adopt the same basis set for all SSs. Therefore, when we use the basis-set expansion method, the practical merit of the AG equation is not so much. In contrast to the AG equation, the MAG equation allows us to adopt a separate basis set for each specified SS; these are expected to be much smaller than the one for the whole system.

In Eq. (2.18) we have retained two forms of the X operator, $X1$ and $X2$. Since the Fock operator contains the density matrix of the first order, $X1$ consists of the density matrix of the third order while $X2$ is of the second order. For convergence, we must estimate the small change of the density matrix in $X1$ by one order more accurately than the one in $X2$. Thus Eq. (2.17) using the $X2$ operator is expected to lead to faster SCF convergence than with $X1$, although the actual difference observed was slight.

Much more important is the introduction of the VMO-shift operator, V_I, into Eqs. (2.16) and (2.18). From Eqs. (2.17) and (2.18) we obtain the expressions for the MO energies for the OMO and VMO spaces as

$$w_{Ii} = \langle\phi_{Ii}|W_I|\phi_{Ii}\rangle, \tag{2.19}$$

$$w_{Iv} = \langle\phi_{Iv}|(sX + V_I)|\phi_{Iv}\rangle. \tag{2.20}$$

Since they are expectation values of two different operators, W_I and $(sX + V_I)$, the VMOs may fall into the OMO space. Although Matsuoka[7] pointed out the occurrence of this phenomenon, we now realize that it is the main reason for the convergence difficulties, which will be discussed further in Secs. III and IV.

III. SOLVING THE MAG EQUATION

We wish to apply the MAG equation to macromolecular calculations. We have tried several possible methods for solving it and have carried out numerous calculations on small molecular systems. In this section, we summarize one of those methods.

A. Division to subsystems

Since the whole molecular system forms a closed shell, it would be desirable for each SS to form a closed shell also. Each SS should be independent of the other SSs. Thus, in the single-determinant approximation [Eq. (2.1)], a bond, lone pair, residue, or other element could be adopted for the SS. However, we found that we actually obtained better results when we collected together several such minimum units to form a SS.

If the SS under consideration contains both core and valence electrons, the valence MOs are automatically orthogonal to the cores after we have solved the MAG equation. However, if the SS consists of only valence electrons, the valence MOs overlap the core MOs of other SSs and the valence-MO energies would happen to be lower. To eliminate this imbalance, we deal with the core and the valence SSs as separate units and assume that the core and the valence MOs are approximately orthogonal each other, using the core-shift operator[24] given below [Eq. (3.3)].

B. Basis-set expansions

In practical molecular calculations, we adopt the basis-set expansion method. For each SS we select, from the whole basis set $\{\chi_p\}$, some members of atomic orbital (AO) bases $\{\chi_{Ip}\}$ specific to the SS. Then we express the MOs of the Ith SS as

$$\phi_{Ii} = \sum_{p\subset I} \chi_{Ip} C_{Ipi}. \tag{3.1}$$

We solve the matrix eigenvalue equation iteratively, which corresponds to Eq. (2.17), to obtain the expansion coefficients $\{C_{Ipi}\}$ and MO energies $\{w_{Ii}\}$,

$$\boldsymbol{G}_I \boldsymbol{c}_{Ii} = w_{Ii} \boldsymbol{s}_I \boldsymbol{c}_{Ii}, \tag{3.2}$$

where $(\boldsymbol{G}_I)_{pq} = \langle\chi_{Ip}|G_I|\chi_{Iq}\rangle$, $(\boldsymbol{s}_I)_{pq} = \langle\chi_{Ip}|\chi_{Iq}\rangle$, and $(\boldsymbol{c}_{Ii})_p = C_{Ipi}$, G_I being the MAG operator [Eq. (2.18)].

Instead of the AO-based expansion adopted in the present study, we may employ the MO-based expansion as adopted by Matsuoka.[7] In this approach, the structure of the $\boldsymbol{G}$ matrix is more transparent and the eigenvalue equation (3.2) is simpler compared with the AO-based approach. However, in the iterative cycles we must save the OMOs as well as the VMOs in contrast to the AO-based expansion in which we save only

the OMOs. Thus, the AO-based approach is preferable in this respect.

For later convenience, we define the *reference bases* as the local AO bases on the atoms belonging to the SS under consideration and the *reference-plus bases* as the local AO bases on the neighboring atoms.

C. Subsystem Hamiltonian and MO selection

In the MAG equation, we have the freedom to choose the SS Hamiltonian W_I [Eq. (2.14)] for the OMOs. It is better to choose some localizing Hamiltonian. In the present study, we set for the valence SSs

$$W_I = P_I^{\mathrm{ref}} F P_I^{\mathrm{ref}} + \sum_c k_c |\phi_c\rangle\langle\phi_c|. \tag{3.3}$$

The first term in Eq. (3.3) is the Fock operator F projected onto the space spanned by the local reference bases $\{\chi_{Ip}\}$ and the P_I^{ref} is the projector,

$$P_I^{\mathrm{ref}} = \sum_{pq\subset I} |\chi_{Ip}\rangle \left(s_I^{-1}\right)_{pq} \langle\chi_{Iq}|, \tag{3.4}$$

where s_I^{-1} is the inverse of the overlap matrix s_I [Eq. (3.2)]. The second term in Eq. (3.3) is the core-shift operator,[24] where the summation is taken over all core MOs $\{\phi_c\}$ in the molecule and the value of the core-shift parameter, k_c, could be set around the absolute value of the core-MO energy.[24] For the core SSs we take only the first term in Eq. (3.3).

Since we have chosen the SS Hamiltonian for the OMOs as Eq. (3.3), the OMOs are like canonical MOs within the SS so that, for selecting the OMOs, we adopt the aufbau principle of choosing them in increasing order of MO energies.

We have another freedom: to choose the VMO-shift operator V_I [Eq. (2.16)] in the SS Hamiltonian. Comparing the two expressions, Eqs. (2.19) and (2.20), for the OMO and the VMO energies, we have set it as

$$V_I = W_I - sX + v_I, \tag{3.5}$$

to prevent VMOs from falling into the OMO space as explained by Matsuoka.[7] The positive constant v_I is arbitrary, but could be taken around 1.0.

Our experience has shown that the introduction of the VMO-shift operator is necessary and resolves the convergence difficulties in the SCF process.

D. Two-step SCF procedure

The MAG equation is similar to the HFR equation[1] and must be solved by an iterative procedure. However, to obtain converged solutions, we have found it effective to adopt a two-step procedure. In the first step, using only the reference bases, we perform the MAG iterations until the differences in two successive density matrices satisfy a coarse threshold (say, 0.005). Then we adopt the extended bases consisting of the reference and the reference-plus bases and perform the MAG iterations until the density matrices satisfy a finer threshold (say, 0.00001).

Each step proceeds as follows:

(1) Guess the initial density matrix $\boldsymbol{D}$ of the system, $\{\boldsymbol{D}_{pq} = \langle\chi_p|\rho|\chi_q\rangle$, ρ in Eq. (2.7)$\}$.
(2) Construct the $\boldsymbol{F}$ matrix, $\{\boldsymbol{F}_{pq} = \langle\chi_p|F|\chi_q\rangle$, F in Eq. (2.8)$\}$.
(3) For each SS in turn, compute $\boldsymbol{G}_I$ matrix [Eq. (3.2)] and solve the MAG equation [Eq. (3.2)] to find the new MOs.
(4) Compute the density matrix using the new MOs and check the convergence using the two successive density matrices; if converged, terminate the iterations and if not return to (2).

In the present study, we obtained the initial density matrix for the first step by diagonalizing the $\boldsymbol{h}$ matrix, $\{\boldsymbol{h}_{pq} = \langle\chi_p|h|\chi_q\rangle$, h in Eq. (2.3)$\}$, and for the second step we started the iterations using the final density matrix from the first step.

In the above procedure, we solve the MAG equations one by one for each SS. Thus this procedure should scale linearly if we combine it with the linear-scaling methods for the computation of the Fock matrix.[2–4]

We have introduced several convergence-control parameters (CCPs). They are the choice of the X operators, $X1/X2$ [Eq. (2.18)], a scale factor s on the X operator [Eq. (2.18)], the VMO-shift parameters v [Eq. (3.5)], and a damping factor d for the $\boldsymbol{X}$ matrix. Here the damping factor d is defined as

$$\boldsymbol{X}(\text{next iteration}) = d\boldsymbol{X}(\text{previous iteration}) + (1-d)\boldsymbol{X}(\text{new iteration}). \tag{3.6}$$

We have usually found it necessary to choose appropriate values for the core-shift parameters k_c [Eq. (3.3)] to obtain reasonable valence-MO energies.

IV. NUMERICAL EXAMPLES

Using the procedures described above, we have performed many MAG calculations on small molecules. In this section, we report some illustrative results that show the MAG method yields results comparable with those from HFR calculations.

A. Glycylglycine and $C_{12}H_{14}$

In this subsection we report the MAG calculations on α-glycylglycine (GG) and $C_{12}H_{14}$ using the basis sets of both general and segmented[2–4] contractions.

The geometry of GG is taken from the X-ray crystallographic analysis of Kvick *et al.*[25] The $C_{12}H_{14}$ is a model of dodecahexane but is a fictitious planar zigzag molecule in which all bond lengths are 1.34 Å (for C–C) and 1.08 Å (for C–H) and all bond angles are assumed 120°.

In GG, the SSs consist of the 1s cores of the C, N, and O atoms and three valence SSs, which are schematically shown in Fig. 1 with the assignment of valence electrons. In $C_{12}H_{14}$, they consist of the 1s cores of the C atoms, a π bond prevailing over the whole molecule, and the σ-bond SSs shown in the figure with σ-electron assignment. We have also tried to subdivide the valence SSs shown in Fig. 1 into smaller

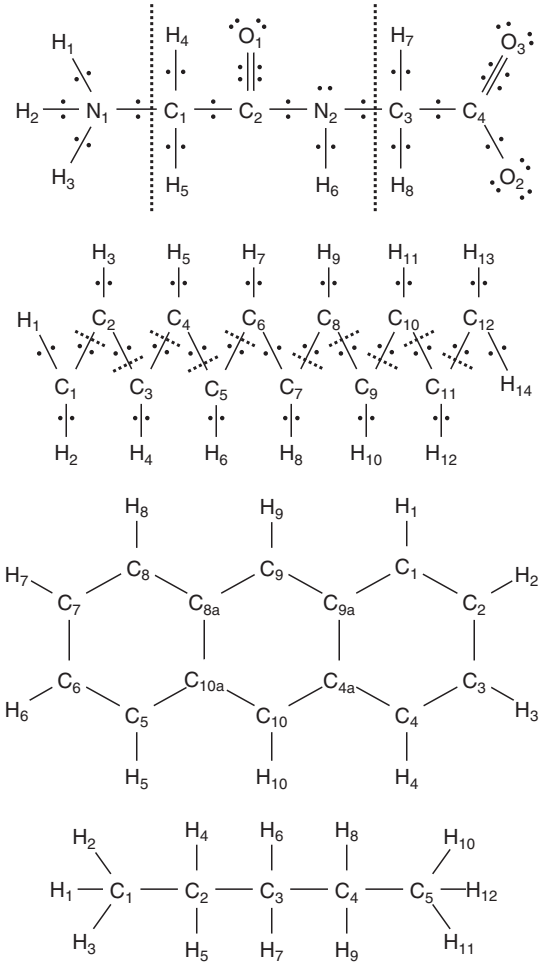

FIG. 1. Glycylglycine, $C_{12}H_{14}$, anthracene, and pentane. The partitions to valence subsystems are shown by dotted lines and the valence electrons by dots.

valence SSs. For GG, each SS consists of C–H, N–H, C–N, or C–O bonds, but the O_1–C_2–N_2 bond was treated as a separate SS. For $C_{12}H_{14}$, the valence SSs consist of a π bond and the C–C and C–H σ bonds.

For the general-contraction bases, we have adopted the Huzinaga[26] 9s5p bases of C, N, and O atoms and the Yamamoto–Matsuoka[27] 3s basis of H atoms. The core SSs consist of only the 1s AO bases of the C, N, and O atoms, while the valence SSs do not use them and adopt only the 2s and 2p AO bases. For the segmented-contraction bases, we have employed the 6-31G bases[28] contracted to [6,3,1/3,1] and used the [6,3] bases for the core SSs and the [3,1/3,1] bases for the valence SSs.

Since manual input of the reference-plus bases is cumbersome and apt to cause errors, our program has an option of generating them automatically. We assign a parameter $R_{\rm sub}$ for a given SS. The program searches the neighboring atoms that are situated within the radius $R_{\rm sub}$ of the atoms in the given SS. Then the bases on them are regarded as the reference-plus bases within the $R_{\rm sub}$.

In the illustrative calculations for GG, the reference-plus bases for the valence SSs were generated with $R_{\rm sub} = 6.0$ and 12.0 (in a.u.). For $C_{12}H_{14}$, their bases for σ bonds were generated with $R_{\rm sub} = 5.0$ and 10.0.

Using these two kinds of bases for each atom, we put $X = X1$ or $X2$ and $s = 1.0$ or 2.0. For each set of bases and the CCPs, we adopted several VMO-shift parameters v in the range [0.0–5.0] for the valence SSs and performed the MAG calculations. When the v value was larger than 0.8, the SCF iterations converged, but for v larger than 3.0, the number of iterations increased greatly.

Table I shows some MAG results and compares them with the HFRs. The MAG total energies differ from the HFRs by [0.1–3.2] mHartree, but the MAG dipole moments reproduce only three significant figures of the HFRs. The MAG results vary depending on the values of the CCPs, but have been found to be ±5 on the last digit of the numerical values in the table.

The MAG calculations using the general-contraction bases gave better total energies than those using the segmented-contraction bases. To improve the latter results, we added an s-type Gaussian to the core SSs. Thus, using the [6,3,1] bases for the core SSs and [3,1/3,1] bases for the valence SSs, we performed the MAG calculations marked by asterisks (∗) in the table. The fairly large improvement seems to imply that the mHartree discrepancies are caused by the inadequate descriptions of core electrons in the 6-31G bases.

Figure 2 depicts the convergence behavior of the total energies for the $C_{12}H_{14}$ using the general-contraction bases. It shows the importance of the VMO-shift parameter v. We particularly note that when v is small (=0.2), the total energy oscillates and becomes divergent.

Since the rate-determining step is the construction of the Fock matrix, which is renewed in every iteration, we show the numbers of iterations by the MAG method and compare them with those by the HFR. Figure 3 illustrates them for various CCPs. The convergence threshold, ΔD, of the difference of two successive density matrices was set to $\Delta D = 0.00001$. The convergence judgment in the first step of the MAG procedure was performed using $\Delta D = 0.005$. Both the MAG and the HFR iterations started from the diagonalization of the $\boldsymbol{h}$ matrix, which consists of the kinetic energy and the bare nuclear attractions. The HFR iterations were observed to diverge when the damping factors on the Fock matrix were less than 0.4. Thus these figures indicate that the MAG numbers of iterations are comparable with the HFR if we could choose proper values for the CCPs.

B. Anthracene and pentane

We also tested the MAG ability to predict the geometrical structures of molecules.

To find the most stable MAG and reference HFR structures we adopted the univariate method, which is used, for example,[29] for the optimization of exponent parameters in analytical atomic wave functions.

Table II shows two examples of anthracene and pentane. For these molecules, we obtained the HFR structures using our HFR program and the 6-31G bases[28] and the MAG structures using the same 6-31G bases contracted as those in Subsection IV A (i.e., [6,3] for the C cores and [3,1/3,1] for the valence SSs). For anthracene, D_{2h} symmetry was assumed and

TABLE I. Total energies and dipole moments (in a.u.).

HFR/MAG[a]	R_{sub}[b]	Total energy	ΔE[c]	Dipole moment	Number of iterations[d]
Glycylglycine (general contraction bases)					
HFR1		−488.599807		10.3357	55
MAG1	12.0	−488.599472	0.335	10.3416	41+60
MAG2	6.0	−488.599261	0.546	10.3564	21+31
MAG3	12.0	−488.599472	0.335	10.3415	21+22
Glycylglycine (segmented contraction bases)					
HFR2		−489.310828		10.2193	66
MAG4	12.0	−489.308500	2.328	10.2375	46+90
MAG5	6.0	−489.308172	2.656	10.2518	47+44
MAG6	12.0	−489.308503	2.325	10.2372	47+44
MAG4*	12.0	−489.309128	1.700	10.2357	46+84
MAG5*	6.0	−489.308790	2.038	10.2503	33+52
MAG6*	12.0	−489.309126	1.702	10.2351	33+39
$C_{12}H_{14}$ (general contraction bases)					
HFR3		−461.204872		0.0000	62
MAG7	10.0	−461.204814	0.058	0.0000	31+23
MAG8	5.0	−461.204597	0.275	0.0000	24+36
MAG9	10.0	−461.204815	0.057	0.0000	24+20
$C_{12}H_{14}$ (segmented contraction bases)					
HFR4		−462.234151		0.0000	55
MAG10	10.0	−462.231765	2.386	0.0000	40+24
MAG11	5.0	−462.230935	3.216	0.0000	49+53
MAG12	10.0	−462.231776	2.375	0.0000	49+23
MAG10*	10.0	−462.233082	1.069	0.0000	62+24
MAG11*	5.0	−462.232262	1.889	0.0000	55+53
MAG12*	10.0	−462.233091	1.060	0.0000	55+25

[a]MAG calculations 1, 4, 7, and 10 were performed using small SS divisions, while the other MAG calculations used larger SS divisions, as shown in Fig. 1. The MAG calculations marked by asterisks (*) were performed using basis sets in which an s-type Gaussian was added to each core SS. See text for details.
[b]Parameters (in a.u.) for generation of the reference-plus bases. See text.
[c]Deviation of MAG total energy from the HFR energy (in mHartree).
[d]See Table III for CCPs. In the MAG calculations "A+B" are the numbers of iterations needed in steps 1 and 2, respectively.

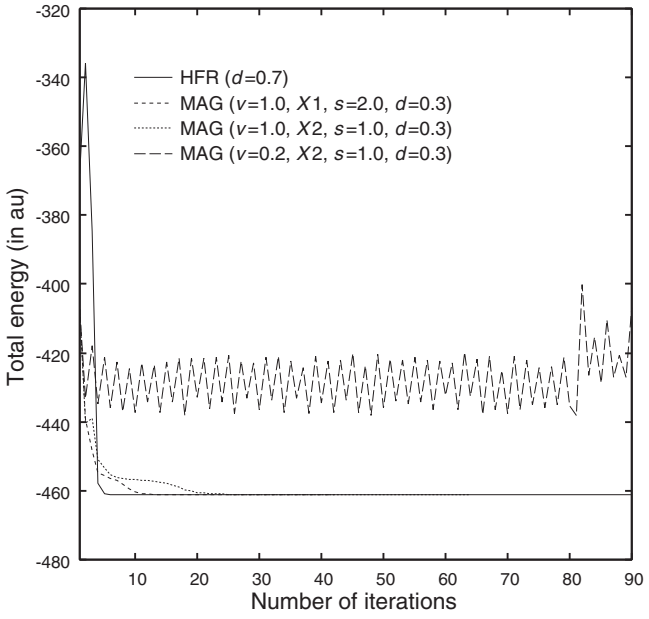

FIG. 2. Total-energy behavior in $C_{12}H_{14}$ using the general-contraction bases of Table I. Larger SS division shown in Fig. 1 and larger bases ($R_{sub} = 10.0$) in Table I are adopted for MAG calculations. See text for the CCPs.

the SSs consist of 14 C(1s) cores, a π bond ($C_1 \cdots C_{14}$), and 16 C–C σ- and ten C–H σ-bonds, as shown in Fig. 1. For pentane, C_{2v} symmetry was assumed and the SSs consist of five C(1s) cores and four C–C σ- and 12 C–H σ-bonds as shown in Fig. 1. To generate the reference-plus bases, we adopted $R_{sub} = 5.0$ (in a.u.) for both anthracene and pentane.

We usually need two or three decimal-point accuracy for the structure constants. Table II shows that the MAG calculations reproduced the HFR structures within this requirement. The mHartree discrepancies in the MAG total energies from the HFRs, as observed in Table I, do not much affect the spectroscopic constants.

The method adopted for generation of the reference-plus bases is crude, but simple and is effective, as the results in Table II show.

All MAG calculations in the tables were done using $X = X1$. Since the MAG results depend slightly on the values of the CCPs, their details are collected in Table III. See also the discussion.

V. DISCUSSION AND CONCLUSION

Using the variational principle for a single-determinant wave function, we have derived an SCF equation for NOMOs.

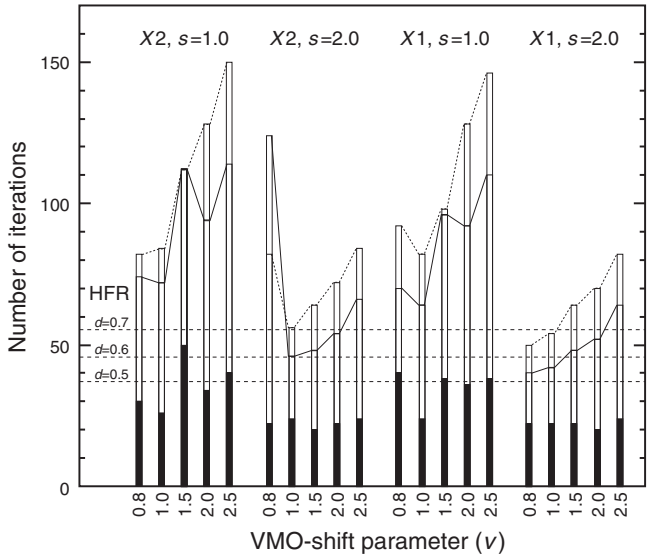

FIG. 3. Numbers of iterations for various CCPs in glycylglycine using the general-contraction bases of Table I. The larger SS division shown in Fig. 1 was adopted. The dotted horizontal lines are the numbers of iterations for the HFR calculation with $d = [0.5–0.7]$ and $\Delta D = 0.00001$; the others are those for the MAG calculations with $d = 0.3$. In the MAG calculations, the black rods show the numbers of iterations for the first step with $\Delta D = 0.005$ and the white rods are those for the second step with $\Delta D = 0.00001$. The lines connecting the tops of the white rods show the numbers of iterations required for smaller bases ($R_{sub} = 6.0$) and the connecting solid lines are those using larger bases ($R_{sub} = 12.0$). See text for the CCPs.

It is essentially the MAG equation presented by Matsuoka,[7] but takes into account the SCF convergence control. Using the basis-set expansion method and the BBA, we can treat MAG equations that have dimensions smaller than those of the standard HFR equations. Thus the method based on the MAG equations could be a linear-scaling method.[2–4]

As the illustrative examples show, the total energies, dipole moments, and geometrical structures calculated by the MAG method are comparable with those from the HFR method. The number of SCF iterations of the MAG solutions varies with the CCPs. For the small molecules we studied, it was comparable with or less than twice those required for the HFR solutions.

When we adopted the aufbau principle for the MO selection in the SCF process, we found it necessary to include the VMO-shift operator in the MAG equation. Without this operator, the VMOs might fall into the OMO space. When we select the OMOs for the next iteration by increasing order of MO energies, we might choose these fallen excited VMOs, instead of the true OMOs, so that the total energy in the next iteration would not decrease much and thus the SCF iterations slow down or diverge in most cases.

The occurrence of this phenomenon was pointed out by Matsuoka,[7] but we now understand that it is the main reason for the extremely slow or divergent behavior of the SCF iterations.

Other NOMO methods[8–10] do not seem to pay attention to this problem and might show very slow convergence.[15] However, the recent studies by Seijo *et al.*[11,12] do not adopt the VMO-shift operator, but seem to have resolved the convergence problem using the appropriate MO-localization method.

TABLE II. The most stable conformations. The total energies in a.u., the bond lengths in Å, and the bond angles in degrees.

	HFR	MAG
	Anthracene	
Total energy	− 535.812441	− 535.808050
C_1–C_2	1.3526	1.3528
C_2–C_3	1.4297	1.4297
C_1–C_{9a}	1.4343	1.4344
C_9–C_{9a}	1.3913	1.3915
C_1–H_1	1.0739	1.0738
C_2–H_2	1.0729	1.0729
C_9–H_9	1.0747	1.0745
$\angle C_{9a}C_1C_2$	120.952	120.962
$\angle C_1C_2C_3$	120.444	120.443
$\angle C_{8a}C_9C_{9a}$	121.591	121.602
$\angle H_1C_1C_2$	120.609	120.612
$\angle H_2C_2C_3$	119.152	119.150
	Pentane	
Total energy	− 196.253109	− 196.252103
C_1–C_2	1.5312	1.5312
C_2–C_3	1.5329	1.5330
C_1–H_1	1.0845	1.0845
C_1–H_2	1.0853	1.0853
C_2–H_4	1.0873	1.0873
C_3–H_6	1.0883	1.0883
$\angle C_1C_2C_3$	112.962	112.971
$\angle C_2C_3C_4$	113.314	113.322
$\angle H_1C_1C_2$	111.305	111.318
$\angle H_2C_1C_2$	111.055	111.059
$\angle H_4C_2C_3$	109.243	109.243
$\angle H_2C_1H_3$	107.723	107.722
$\angle H_4C_2H_5$	106.341	106.339
$\angle H_6C_3H_7$	106.320	106.321

We would mention that the original AG equation[5,6] for *nonorthogonal* orbitals is equivalent to the HFR equation for *orthogonal* orbitals, but would also encounter the convergence problem, which depends on the SS Hamiltonian, W_I [Eq. (2.14)]. However, by introducing the VMO-shift operator V_I [Eq. (2.16)] and the scale factor s on the X operator [Eq. (2.18)] into the AG equation, we can rewrite the equation as

$$[\rho W_I \rho + sX + (1-\rho)V_I(1-\rho)]|\phi_{Ii}\rangle = w_{Ii}|\phi_{Ii}\rangle. \quad (5.1)$$

TABLE III. Convergence-control parameters adopted for HFR and MAG calculations in Tables I and II.

	HFR/MAG	d	v	s	k(C)	k(N)	k(O)
Glycylglycine	HFR1,2	0.7					
	MAG1,2,3	0.3	1.0	2.0	11.3	15.6	20.6
	MAG4,5,6	0.3	2.0	1.8	14.3	18.6	23.6
$C_{12}H_{14}$	HFR3,4	0.7					
	MAG7,8,9	0.3	1.0	2.0	11.3	…	…
	MAG10,11,12	0.3	1.0	1.4	14.3	…	…
Anthracene		0.3	2.0	1.0	10.1	…	…
Pentane		0.3	1.0	1.0	10.1	…	…

Considering the MO-energy spectrum, if we set the VMO-shift operator as

$$V_I = W_I + v_I, \tag{5.2}$$

as in Eq. (3.5) in the MAG equation, then we could avoid the problem.

Although the proper VMO-shift operator greatly improves the SCF convergence, it may bring a small ambiguity into the results calculated by the MAG method. The VMOs are orthogonal to the OMOs of the SS under consideration, but are slightly nonorthogonal to the OMOs of *other* SSs. Thus they have a small character of OMOs, which is determined by the VMO-shift operator and other CCPs. However, the effect was found to be rather small in practice. For the examples shown in Table I, the ambiguity because of the CCPs was ±5 on the last digits if the SCF processes had converged properly. If we adopt a basis set common to all SSs, the nonorthogonality of the VMOs could be made to vanish. Thus, when we adopt larger basis sets for each SS, the ambiguity in the calculated results should decrease, as we have experienced. Of course, in the AG method, the ambiguity disappears and the OMO and the VMO spaces are mutually orthogonal.

We have made numerous MAG calculations on small molecules to find a way to approach macromolecular calculations. The procedure proposed in the present paper is one such way, although there should be others.

A referee kindly showed us several papers related to the BBAs. Among them we found that the block-localized wave function method[30,31] is equivalent to the MAG method. It does not aim to be one of the BBAs, but is designed for calculation of the delocalization energies of electrons in molecules. Like the MAG method, it assumes a single-determinant wave function consisting of the NOMOs, which are expanded in terms of local basis functions specific to the SS of interest. However, instead of solving the NOMO equations, it iterates the 2×2 Jacobi rotations among the OMOs and VMOs and searches directly for the minimum-energy point to obtain the NOMOs. Since it does not solve the eigenvalue equation as the MAG equation does, it does not need to assume the SS Hamiltonian. However, the convergence speed of the Jacobi rotations is slow and both OMOs and VMOs must be saved with every iteration.

In conclusion, although nowadays, *in the single-determinant approximation*, the methods using *orthogonal* MOs (HFR methods) are employed almost exclusively, we now have an alternative method using *nonorthogonal* MOs. This MAG method is capable of yielding the results of the orthogonal MO methods with comparable accuracy and effort and has possibilities for macromolecular calculations.

Using the MAG method, we can now obtain fairly good zeroth-order wave functions constructed from the NOMOs and thus can go a step further to estimate the electron correlations in macromolecules using them. This study is now in progress.

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