Improved Construction of Coupling Operator

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The construction of the coupling operator given by Adams is examined from the standpoint of SCF convergency. A unified, hermitian coupling operator is derived by taking into account optimum mixing for the pairs of occupied orbitals as well as the correct variational conditions.

1. Introduction

The construction of a single Fock operator for orbitals of open shell or MC wavefunctions is important not only because it simplifies the calculations but also for applications to formal problems [1]. Single Fock operators [2—5] are constructed so that variational conditions derived from the first variation of energy are satisfied at self-consistency. Recently, Colle et al. [6] showed that the diagonalization of the Fock matrix does not give the optimal variations for the orbitals in the iterative process, although the operator satisfies the correct variational conditions if the SCF converges.

Though there is no consideration how to correct the trial orbitals in the single Fock operator formalism, the open shell calculations seem to converge, if not very fast, for the cases in which there is at most one open shell of each symmetry [4, 5, 7, 8]. In our recent test calculations with the single Fock operators [5, 7], however, we have encountered convergence difficulties for the cases in which there is more than one open shell of each symmetry. We have found that, in such cases, the coupling operators [5, 7] fail to give the correct mixing among the open shell orbitals, and among the open shell and the highest closed shell orbitals. In order to obtain a smooth convergence for such cases, we need to take into account the best variations among the occupied orbitals [9]. Colle et al. [6] showed one way of doing this. Their method reduces essentially to the iterative diagonalizations of a series of matrices built from some linear combinations of "shell Hamiltonians".

In the present paper, we show how to incorporate the optimal variations for pairs of occupied orbitals into the single Fock operator proposed by Adams [5]. We refer to his open shell and natural orbital MC SCF theories at appropriate points within the text in order to facilitate our derivation.

2. The Fock Operator

Let us restrict our analysis to the cases in which the total energy can be written in terms of M occupied orbitals $\{\Phi_i\}$. All orbitals are assumed real. The extension of our analysis to a more general class of open shell systems is evident:

$$E = \sum_i^M \eta_i \langle \Phi_i | \hat{h}_1 | \Phi_i \rangle + \sum_{ij}^M (\alpha_{ij} J_{ij} - \beta_{ij} K_{ij})$$
$$= \langle \hat{h}\,\hat{p} \rangle + \tfrac{1}{2} \langle\langle \hat{v}_{12}\,\hat{P} \rangle\rangle , \qquad (1)$$

where the spinless density matrices $\hat{p}$, $\hat{P}$ are given as

$$\hat{p} = \sum_i^M \eta_i | \Phi_i \rangle \langle \Phi_i | ,$$

$$\hat{P} = \sum_{ij}^M \{ \alpha_{ij} (| \Phi_i(1)\Phi_j(2) \rangle \langle \Phi_i(1)\Phi_j(2) |$$
$$+ | \Phi_j(1)\Phi_i(2) \rangle \langle \Phi_j(1)\Phi_i(2) |)$$
$$- \beta_{ij} (| \Phi_j(1)\Phi_i(2) \rangle \langle \Phi_i(1)\Phi_j(2) |$$
$$+ | \Phi_i(1)\Phi_j(2) \rangle \langle \Phi_j(1)\Phi_i(2) |) \} . \quad (2)$$

Here the $\{\alpha_{ij}\}$ and $\{\beta_{ij}\}$ form symmetric matrices. Using the orthogonality constrained variation, the following two variational conditions can be obtained from the first variation of the energy [5]:

$$(1 - \hat{\varrho})(\hat{f}\hat{p} + \hat{q})\,\hat{\varrho} = 0 , \qquad (3\,\mathrm{a})$$
$$\hat{\varrho}(\hat{f}\hat{p} + \hat{q})\,\hat{\varrho} = \hat{\varrho}(\hat{p}\hat{f} + \hat{q}^\dagger)\,\hat{\varrho} , \qquad (3\,\mathrm{b})$$

where $\hat{\varrho}$ is the fundamental invariant;

$$\hat{\varrho} = \sum_i^M | \Phi_i \rangle \langle \Phi_i |$$

and

$$\hat{q} = \mathrm{Tr}_2(\hat{\nu}_{12}\,\hat{P}) - \hat{J}[\hat{p}]\,\hat{p} + \tfrac{1}{2}\hat{K}[\hat{p}]\,\hat{p}\,,$$
$$\hat{f} = \hat{h} + \hat{J}[\hat{p}] - \tfrac{1}{2}\hat{K}[\hat{p}]\,. \tag{4}$$

By coupling the two conditions (3a) and (3b), Adams defined a single Fock operator [5]:

$$\hat{F} = \hat{f} + \hat{G} + \hat{G}^\dagger + \hat{N}\,, \tag{5}$$

where $\hat{G} = (1 - \hat{\varrho})\,\hat{q}\sum_{i}^{M}\eta_i^{-1}\,|\Phi_i\rangle\langle\Phi_i|$. The $\hat{G}$ couples occupied orbitals to virtual orbitals. The operator $\hat{N}$ couples occupied orbitals to occupied orbitals and is defined through its matrix elements [5]:

$$\hat{N} = \sum_{i\neq j}^{M}\sum^{M}|\Phi_i\rangle\langle\Phi_i|\,\hat{N}\,|\Phi_j\rangle\langle\Phi_j|\,. \tag{6}$$

In Adams' formalism, $N_{ij} = \langle\Phi_i|\,\hat{N}\,|\Phi_j\rangle$ was determined to satisfy the condition (3b) for the orbital pair (Φ_i, Φ_j) [5]. In order to obtain a coupling operator, $\hat{N}$, which actually specifies how to correct the pair of orbitals, we must first expand the energy to the second order with respect to the mixing coefficient for the orbital pair [9]. Then we incorporate the condition for the best mixing obtained from the energy expansion into the matrix element, N_{ij}.

For the (i, j) pair of occupied orbitals, we consider the second order approximation of the orthogonal two-by-two rotation matrix

$$\begin{bmatrix}\Phi_i\\\Phi_j\end{bmatrix} \to \theta \cdot \begin{bmatrix}\Phi_i\\\Phi_j\end{bmatrix} \quad \text{where} \quad \theta = \begin{bmatrix}1 - \tfrac{1}{2}t^2 & t\\ -t & 1 - \tfrac{1}{2}t^2\end{bmatrix},$$

then, after dropping terms which are of third and higher power of t, the energy of a new state can be written as [6]

$$\begin{aligned}E = E_0 &+ 2t\langle\Phi_i|\,\hat{H}_i - \hat{H}_j\,|\Phi_j\rangle\\ &+ t^2\{\langle\Phi_j|\,\hat{H}_i - \hat{H}_j\,|\Phi_j\rangle\\ &\quad - \langle\Phi_i|\,\hat{H}_i - \hat{H}_j\,|\Phi_i\rangle\\ &\quad + 2(J_{ij} + K_{ij})(2\beta_{ij} - \beta_{ii} - \beta_{jj})\\ &\quad + 4K_{ij}(\alpha_{ii} + \alpha_{jj} - 2\alpha_{ij})\}\,, \tag{7}\end{aligned}$$

where

$$\hat{H}_i = \eta_i\hat{h} + 2\sum_{k}^{M}(\alpha_{ik}\hat{J}_k - \beta_{ik}\hat{K}_k) \quad (i \leq M)\,.$$

Differentiating E with respect to t, we find E to be stationary when [9]

$$t = A_{ij}/B_{ij}\,,$$

where

$$A_{ij} = \langle\Phi_i|\,\hat{H}_i - \hat{H}_j\,|\Phi_j\rangle \tag{8}$$

and

$$\begin{aligned}B_{ij} = &\langle\Phi_i|\,\hat{H}_i - \hat{H}_j\,|\Phi_i\rangle\\ &- \langle\Phi_j|\,\hat{H}_i - \hat{H}_j\,|\Phi_j\rangle\\ &+ 2(\beta_{ii} + \beta_{jj} - 2\beta_{ij})(J_{ij} + K_{ij})\\ &+ 4(2\alpha_{ij} - \alpha_{ii} - \alpha_{jj})K_{ij}\,.\end{aligned}$$

On the other hand, the diagonalization of the single Fock operator (5) gives the following orbital mixing for the pair in the first order perturbation approximation:

$$t = \frac{\langle\Phi_i|\,\hat{F}\,|\Phi_j\rangle}{\langle\Phi_i|\,\hat{F}\,|\Phi_i\rangle - \langle\Phi_j|\,\hat{F}\,|\Phi_j\rangle}\,.$$

Since $\langle\Phi_i|\,\hat{G} + \hat{G}^\dagger\,|\Phi_j\rangle = 0$ for all i, j $(\leq M)$, this expression reduces to

$$t = \frac{\langle\Phi_i|\,\hat{f} + \hat{N}\,|\Phi_j\rangle}{\langle\Phi_i|\,\hat{f}\,|\Phi_i\rangle - \langle\Phi_j|\,\hat{f}\,|\Phi_j\rangle}\,. \tag{9}$$

Setting (8) equal to (9), we obtain the desired (i, j) element of the coupling operator $\hat{N}$, which incorporates the optimal mixing of the occupied orbital pairs:

$$\begin{aligned}N_{ij} = &-\langle\Phi_i|\,\hat{f}\,|\Phi_j\rangle\\ &+ M_{ij}\langle\Phi_i|\,\hat{H}_i - \hat{H}_j\,|\Phi_j\rangle\,, \tag{10}\end{aligned}$$

where

$$M_{ij} = (\langle\Phi_i|\,\hat{f}\,|\Phi_i\rangle - \langle\Phi_j|\,\hat{f}\,|\Phi_j\rangle)/B_{ij}\,.$$

By (6) and (10) we define the desired form of the Hermitian coupling operator. We can easily show that the matrix $\{N_{ij}\}$ is Hermitian. From (10) we can see that N_{ij} is identically zero if the Φ_i and Φ_j are both closed shell orbitals, since $\hat{H}_i = \hat{H}_j$ for these orbitals. It reflects the fact that the wave function and the total energy are invariant to linear unitary transformations within the closed shell orbital set. Note that the method fails if

$$\langle\Phi_i|\,\hat{f}\,|\Phi_i\rangle = \langle\Phi_j|\,\hat{f}\,|\Phi_j\rangle\,.$$

But for orbitals Φ_i, Φ_j, which belong to the same sub-species of the irreducible representation, such an accidental degeneracy is rare.

With these Hermitian operators, the open shell and restricted MC SCF problems reduce to solving the pseudo-eigenvalue equation

$$\hat{F}\,|\Phi_i\rangle = \varepsilon_i\,|\Phi_i\rangle\,. \tag{11}$$

A previous approach [5] used just the condition (3b) to define the coupling operator $\hat{N}$. In our notation, N_{ij}'s determined in such a way can be written as:

For $\eta_i \neq \eta_j$

$$\begin{aligned} N_{ij} = &- \langle \Phi_i | \hat{f} | \Phi_j \rangle \\ &+ \frac{\langle \Phi_i | \hat{H}_i - \hat{H}_j | \Phi_j \rangle}{\eta_i - \eta_j} \end{aligned} \qquad (12\,a)$$

For $\eta_i = \eta_j$, if $\langle \Phi_i | \hat{H}_i - \hat{H}_j | \Phi_j \rangle \neq 0$,

$$\left.\begin{aligned} N_{ij} = &- \langle \Phi_i | \hat{f} | \Phi_j \rangle \\ &+ \langle \Phi_i | \hat{H}_i - \hat{H}_j | \Phi_j \rangle \\ N_{ji} = &- \langle \Phi_j | \hat{f} | \Phi_i \rangle \\ &+ \langle \Phi_j | \hat{H}_i - \hat{H}_j | \Phi_i \rangle \end{aligned}\right\} i > j,$$

$$\qquad (12\,b)$$

and if

$$\langle \Phi_i | \hat{H}_i - \hat{H}_j | \Phi_j \rangle = 0, \quad N_{ij} \equiv 0.$$

In contrast to (10), we need three separate equations to define $\hat{N}$. These expressions are analogous to (10), but the important factors M_{ij} are replaced by $1/(\eta_i - \eta_j)$ in (12a) and by unity in (12b).

It is only slightly more complicated to construct the N_{ij}'s in (10).

We have performed one configuration open shell SCF calculations on the second $^1A_1$ states of H_2O, O_3, CH_2 and the 2^1s state of He. We found that, for all these systems, the previous single Fock operator scheme, which uses (12a, b) for $\hat{N}$ gives an oscillatory behavior and *fails to converge*. The incorporation of the coupling operator $\hat{N}$ of (10) corrects the ill-behavior due to the neglect of optimal mixing among the occupied orbitals, and the SCF converges typically within 40 iterations. (All the calculations were done using a closed shell ground state SCF MO set as an initial guess.) Optimal mixing of the open shell orbitals effectively leads to the convergence in such cases.

Our coupling operator scheme takes into account optimal pair mixing, but a coupling among the pairs is absent so that it would not give overall quadratic convergence [10]. In the sense that the method optimizes the orbitals in pairwise mixing, our scheme is probably most closely related to the two-by-two rotation method proposed by Golebiewski et al. [11].

In the present study, the previous orthogonal Hartree theory [9] is extended to the Hartree-Fock (H-F) problem, and an improved construction of H-F coupling operator is presented. The calculations show that the new construction corrects the ill-behavior of the coupling operators previously given [2, 3, 5, 7]. Detailed studies on the convergence behavior of the present coupling operator scheme, as well as the ones [5, 7] previously given will be presented elsewhere [12].

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