Closed Shell Hartree Theory with Orthonormal Orbitals

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A natural orbital multiconfigurational SCF formalism has been applied to the closed shell Hartree theory with orthonormal orbitals. A prescription is given for constructing a single, one-electron Hamiltonian with which one can determine all the occupied orbitals. The formalism is suited to the matrix formulation of the orthogonalized Hartree theory for polyatomic systems.

1. Introduction

In recent years, there have been renewed interests in the Hartree method in relation to the orbital localization in molecules and correlation energy studies of solid-state systems [1–3].

As is well known, the Hartree method [4] approximates the wave function by a product of non-orthogonal orbitals. The method does not directly take into account the antisymmetry requirement or the electron spin. Owing to the absence of exchange terms, the evaluation of the integrals in the numerical approach is much simpler than that for the Hartree-Fock theory. However, the Hartree one-electron Hamiltonian is different for different orbitals, and this results in the eigensolutions not being mutually orthogonal and leads to some difficulties in practical applications to many electron systems.

The Hartree-Fock one determinant scheme [5, 6] antisymmetrizes the wave function with the inclusion of electron spin. The correlation is taken into account among the electrons of like spin, whereas the motion of the electrons with different spin are completely uncorrelated [7]. Though the method is more rigorous than the Hartree method, it seems to overemphasize the non-locality of the exchange contribution to the energy [1, 2b, 3]. As Harris recently argued [3], it is not really clear if the Hartree-Fock method yields the best possible zero order wave function for the molecular conformation and correlation studies.

Adams has recently applied the natural orbital multi-configurational self-consistent-field (NO MC SCF) theory [8] to the general class of open shell problems [9].

In this article, we recast the closed shell Hartree theory in terms of orthonormal orbitals [1a, b], and apply the NO MC SCF theory [8] to this class of problems. The result is a prescription for constructing a one-electron Hamiltonian with which one can determine all occupied orbitals. The present scheme is suited to the matrix formulation of the Hartree theory for polyatomic systems. The derivation of the one-electron Hamiltonian for orthonormal Hartree orbitals is related to that for open shell SCF orbitals [9], but there are some differences. Unlike the Hartree-Fock function, the energy of the Hartree product function is no longer invariant to any linear unitary transformation, and mixing among all the occupied orbitals has to be taken into account in the variational step. As Christiansen and Palke [1b] pointed out, the interorbital mixing within the occupied set is sharply restricted by the orthogonality constraints, and the conventional coupling operator scheme converges poorly. This is due partly to the fact that the conventional coupling operator method is based only on the "first order" energy variation and satisfies the variational conditions at self-consistency, but it does not take into account the optimum convergence conditions. In contrast to the previous coupling operator approaches [9, 10], our one-electron Hamiltonian is constructed so that it fulfills not only the correct variational conditions but also the best variations for all pairs of occupied orbitals.

2. Theory

Consider an N-electron system characterized by the Hamiltonian

$$\hat{\mathscr{H}} = \sum_{i}^{N} \hat{h}_i + \tfrac{1}{2} \sum_{i \neq j}^{N} \hat{v}_{ij} \,,$$

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where $\hat{h}_i$, $\hat{v}_{ij}$ are one- and two-electron operators, respectively. Suppose that the N-electron wave function for the closed shell state is approximated by a single product containing a fixed set of orthonormal orbitals, $\{\Phi_i\}$ (In the following analysis, the orbitals are assumed to be real):

$$\Psi = \Phi_1(1)\,\alpha(1)\,\Phi_1(2)\,\beta(2)\ldots\Phi_{N/2} \cdot (N-1)\,\alpha(N-1)\,\Phi_{N/2}(N)\,\beta(N)\,. \quad (1)$$

Then the electronic energy can be written as

$$E = 2\sum_i^{N/2}\langle\Phi_i|\hat{h}|\Phi_i\rangle + \sum_i^{N/2}\langle\Phi_{i\,(1)}\langle\Phi_{i\,(2)}|\hat{v}_{12}|\Phi_{i\,(2)}\rangle\Phi_{i\,(1)}\rangle + 2\sum_{i\neq j}^{N/2}\sum\langle\Phi_{i\,(1)}\langle\Phi_{j\,(2)}|\hat{v}_{12}|\Phi_{j\,(2)}\rangle\Phi_{i\,(1)}\rangle\,. \quad (2)$$

The functional E is not invariant to linear unitary transformations of occupied orbitals. The conditions for the mixing of occupied orbitals as well as for the mixing of occupied orbitals with virtual orbitals must then be taken into account in constructing the one-electron Hamiltonian. The energy is required to be stationary with respect to an arbitrary variation of the occupied orbitals subject to the orthonormality constraints [8, 9]. In terms of the projector, $\hat{\varrho} = \sum_i^{N/2}|\Phi_i\rangle\langle\Phi_i|$, this leads to the two conditions [8, 9, 10b]

$$(\hat{1}-\hat{\varrho})(\hat{h}\hat{p}+\hat{Q})\,\hat{\varrho} = 0\,, \quad (3\text{a})$$

$$\hat{\varrho}(\hat{h}\hat{p}-\hat{p}\hat{h}+\hat{Q}-\hat{Q}^\dagger)\,\hat{\varrho} = 0\,, \quad (3\text{b})$$

where $\hat{p}$ is defined as

$$\hat{p} = \sum_i^{N/2}\eta_i|\Phi_i\rangle\langle\Phi_i|\,, \quad \eta_i = 2 \quad \text{for all} \quad i\,(i = 1, \ldots, N/2)\,, \quad (4)$$

and is identical to the one electron density matrix for the closed shell Hartree-Fock one determinant approximation. $\hat{Q}$ takes the special form

$$\hat{Q} = 4\sum_i^{N/2}\sum_j^{N/2}\langle\Phi_{j\,(2)}|\hat{v}_{12}|\Phi_{j\,(2)}\rangle|\Phi_{i\,(1)}\rangle\langle\Phi_{i\,(1)}| - 2\sum_i^{N/2}\langle\Phi_{i\,(2)}|\hat{v}_{12}|\Phi_{i\,(2)}\rangle\Phi_{i\,(1)}\rangle\langle\Phi_{i\,(1)}|\,. \quad (5)$$

The conditions (3a, b) are sufficiant only to guarantee that the energy be stationary. Condition (3a) guarantees that E is stationary with respect to the mixing of occupied orbitals with virtual orbitals. (3b) must be satisfied if E is to be stationary with respect to mixing among occupied orbitals. Let us introduce necessary operators to arrive at our final equation. We introduce the Coulomb operators

$$\hat{J}[\hat{p}] = \int\hat{v}_{12}\,\hat{p}(2/2)\,\mathrm{d}\tau_2\,, \quad (6\text{a})$$

$$\hat{J}_i = \int\hat{v}_{12}|\Phi_{i\,(2)}|^2\,\mathrm{d}\tau_2\,, \quad (6\text{b})$$

and the operator $\hat{q}$ analogous to the one in the open shell SCF theory [9]:

$$\hat{q} = \hat{Q} - \hat{J}[\hat{p}]\,\hat{p}\,. \quad (6\text{c})$$

Note that there is no need to introduce the operator [9] $\hat{K}[\hat{p}]\hat{p}$ in the present Hartree problem. Using (4), (5) and (6a, b), (6c) can be rewritten as

$$\hat{q} = -2\sum_i^{N/2}\hat{J}_i|\Phi_{i\,(1)}\rangle\langle\Phi_{i\,(1)}|\,.$$

In terms of the Coulomb operators (6a, b) and $\hat{q}$, the variational conditions (3a, b) can be rewritten in the form

$$(\hat{1}-\hat{\varrho})(\hat{f}\hat{p}+\hat{q})\,\hat{\varrho} = 0\,, \quad (7\text{a})$$

$$\hat{\varrho}(\hat{f}\hat{p}-\hat{p}\hat{f})\,\hat{\varrho} = \hat{\varrho}(\hat{q}^\dagger-\hat{q})\,\hat{\varrho}\,, \quad (7\text{b})$$

where

$$\hat{f} = \hat{h} + \hat{J}[\hat{p}]\,.$$

Using (4), we easily see that the l.h.s. of (7b), $\hat{\varrho}(\hat{f}\hat{p}-\hat{p}\hat{f})\hat{\varrho}$, is identically zero. Then the condition (7b) can be restated as

$$\hat{\varrho}(\hat{q}^\dagger-\hat{q})\,\hat{\varrho} = 0\,.$$

It is useful to express this condition in terms of the occupied orbitals, $\{\Phi_i\}$:

$$\langle\Phi_i|\,\hat{J}_i-\hat{J}_j\,|\Phi_j\rangle = 0\,, \quad i, j \leqq N/2\,. \quad (7\text{c})$$

Now (7a) and (7b) (or (7a) and (7c)) are the conditions which the occupied orbitals must satisfy for an energy extremal.

In order to take the condition (7a) into account, we define an operator $\hat{G}$, which couples the occupied orbitals with the virtual orbitals, in the manner of open shell SCF theory [9]:

$$\hat{G} = (\hat{1}-\hat{\varrho})\,\hat{q}\sum_i^{N/2}\eta_i^{-1}|\Phi_i\rangle\langle\Phi_i| = -(\hat{1}-\hat{\varrho})\sum_i^{N/2}\hat{J}_i|\Phi_i\rangle\langle\Phi_i|\,. \quad (8)$$

The second operator $\hat{N}$, which couples the occupied orbitals among themselves, can be defined through its matrix elements as

$$\hat{N} = \sum_{i \neq j}^{N/2} \sum^{N/2} |\Phi_i\rangle\langle\Phi_i|\hat{N}|\Phi_j\rangle\langle\Phi_j| \, .$$

With the operators $\hat{N}$ and $\hat{G}$, we define a single, one-electron Hamiltonian [8, 9]:

$$\hat{R} = \hat{f} + \hat{G} + \hat{G}^{\dagger} + \hat{N} \, .$$

It is a Hermitian operator if the coupling operator $\hat{N}$ is constructed to be Hermitian through its elements, $\langle\Phi_i|\hat{N}|\Phi_j\rangle$.

Conventional coupling operator methods [8, 9, 10] incorporate into $\hat{N}$ the variational condition (3b) (or (7b)) derived from the first variation of E in (2). The mixing of occupied orbitals with occupied orbitals is a two electron variation which sometimes gives rise to convergence difficulties in a conventional coupling operator scheme [1b, 11].

In the present article, we determine

$$N_{ij} = \langle\Phi_i|\hat{N}|\Phi_j\rangle$$

so that $\hat{N}$ be Hermitian and takes into account not only the variational condition (7b) but also the optimal mixing for all pairs of occupied orbitals. The method is based on the second order energy variation for a two-by-two orbital rotation.

For a particular (i, j) pair of occupied orbitals, we consider the second order approximation of the orthogonal rotation matrix:

$$\begin{pmatrix}\Phi_i \\ \Phi_j\end{pmatrix} \to \theta \cdot \begin{pmatrix}\Phi_i \\ \Phi_j\end{pmatrix} \text{ where } \theta = \begin{pmatrix} 1 - \dfrac{1}{2} t^2 & t \\ -t & 1 - \frac{1}{2} t^2 \end{pmatrix} .$$

After dropping terms which are of third and higher power of t, the energy of a new state can be written as

$$\begin{aligned} E = E_0 &- 4t\{\langle\Phi_i|\hat{J}_i|\Phi_j\rangle - \langle\Phi_i|\hat{J}_j|\Phi_j\rangle\} \\ &+ 2t^2\{\langle\Phi_i|\hat{J}_i|\Phi_i\rangle + \langle\Phi_j|\hat{J}_j|\Phi_j\rangle \\ &- 2\langle\Phi_i|\hat{J}_j|\Phi_i\rangle - \\ &- 4\langle\Phi_{i\,(1)}\langle\Phi_{i\,(2)}|\hat{v}_{12}|\Phi_{j\,(2)}\rangle\Phi_{j\,(1)}\rangle\} \, , \end{aligned}$$

where E_0 is the sum of the terms which do not depend on t. By differentiation of E with respect to t we find E to be stationary if

$$t = \frac{\langle\Phi_i|\hat{J}_i - \hat{J}_j|\Phi_j\rangle}{\langle\Phi_i|\hat{J}_i - \hat{J}_j|\Phi_i\rangle - \langle\Phi_j|\hat{J}_i - \hat{J}_j|\Phi_j\rangle - 4\langle\Phi_{i\,(1)}\langle\Phi_{i\,(2)}|\hat{v}_{12}|\Phi_{j\,(2)}\rangle\Phi_{j\,(1)}\rangle} \, . \tag{9a}$$

On the other hand, the diagonalization of the one-electron Hamiltonian matrix, in a first order perturbation approximation, gives rise to the following orbital mixing for the pair:

$$\begin{aligned} t &= \frac{\langle\Phi_i|\hat{R}|\Phi_j\rangle}{\langle\Phi_i|\hat{R}|\Phi_i\rangle - \langle\Phi_j|\hat{R}|\Phi_j\rangle} \, , \\ &= \frac{\langle\Phi_i|\hat{f} + \hat{N}|\Phi_j\rangle}{\langle\Phi_i|\hat{f}|\Phi_i\rangle - \langle\Phi_j|\hat{f}|\Phi_j\rangle} \, . \end{aligned} \tag{9b}$$

Note that $\langle\Phi_i|\hat{G} + \hat{G}^{\dagger}|\Phi_j\rangle = 0$ for all $i, j (\leqq N/2)$. Setting (9a) equal to (9b), we obtain the desired (i, j) element of the coupling operator $\hat{N}$, which incorporates the optimum convergence condition for the (i, j) occupied orbital pair:

$$\begin{aligned} N_{ij} (= \langle\Phi_i|\hat{N}|\Phi_j\rangle) = &- \langle\Phi_i|\hat{f}|\Phi_j\rangle \\ &+ M_{ij}\langle\Phi_i|\hat{J}_i - \hat{J}_j|\Phi_j\rangle \end{aligned}$$

where

$$M_{ij} = \frac{\langle\Phi_i|\hat{f}|\Phi_i\rangle - \langle\Phi_j|\hat{f}|\Phi_j\rangle}{\langle\Phi_i|\hat{J}_i - \hat{J}_j|\Phi_i\rangle - \langle\Phi_j|\hat{J}_i - \hat{J}_j|\Phi_j\rangle - 4\langle\Phi_{i(1)}\langle\Phi_{i(2)}|\hat{v}_{12}|\Phi_{j(2)}\rangle\Phi_{j(1)}\rangle} \, . \tag{10}$$

We can easily see that the $\{N_{ij}\}$ form a Hermitian matrix;

$$N_{ji} = N_{ij}^{*} \, .$$

With the coupling operators $\hat{N}$ and $\hat{G}$, the orthogonalized Hartree problem reduces to solving a pseudoeigenvalue equation

$$\hat{R}|\Phi_i\rangle = \epsilon_i|\Phi_i\rangle \, . \tag{11}$$

3. Discussion

It is easy to verify that the solutions of the pseudoeigenvalue equation (11) satisfy the conditions (3a, b) [or (7a, c)]. One can easily see from (10) that the condition (7c) cannot be satisfied if there is accidental degeneracy,

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

but for the orbitals Φ_i and Φ_j which belong to the same subspecies of an irreducible representation, the accidental degeneracies are rare. If there is an accidental degeneracy, we can shift one of the energy levels by adding a level shifting operator to the diagonal element of the effective Hamiltonian.

It is also easy to show that once $\hat{R}$ is constructed from the orbitals which extremalize the energy, the eigenfunctions of $\hat{R}$ include Φ_i's used in constructing $\hat{R}$.

The matrix formulation of the pseudoeigenvalue equation is straightforward, but a little more complicated than the conventional coupling operator method due to the inclusion of the optimum convergence conditions for all pairs of occupied orbitals in constructing $\hat{N}$.

If we construct $\hat{N}$ only from the variational condition, (3b), as has been done in the previous open shell SCF scheme [9], we obtain for the **N** matrix elements:

$$\left.\begin{aligned} N_{ij} &= -\langle\Phi_i|\hat{f}|\Phi_j\rangle + 2\langle\Phi_i|\hat{J}_j - \hat{J}_i|\Phi_j\rangle \\ N_{ji} &= -\langle\Phi_j|\hat{f}|\Phi_i\rangle + 2\langle\Phi_j|\hat{J}_j - \hat{J}_i|\Phi_i\rangle \end{aligned}\right\}(i > j). \tag{12}$$

This would give slower convergence, since the optimal variations for pairs of occupied orbitals are not taken into account, although it satisfies the variational condition (3b) if the SCF converges.

A work closely related to our closed shell Hartree theory is that of Harris [3]. He gave a synthetic approach to the construction of a one-electron Hamiltonian for orthonormal Hartree orbitals. His approach is closely related to the synthetic approach of open shell SCF theories [10]. Our approach is different from his. We have arrived at the one-electron Hamiltonian by analysing and manipulating the variational conditions.

We have shown that Adams' NO MC SCF theory [8] is also applicable to the Hartree theory with orthonormal orbitals. We expect that the practical applications of our Hartree theory is essentially no more difficult than that of the open shell SCF theory [9, 11].

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