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Hamiltonian for the Orbitals of General Multiconfigurational Self Consistent Field Wave Functions

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The variational conditions for the orbitals of general multiconfigurational SCF wave functions are coupled in a unique way to construct a one-electron Hamiltonian with which one can determine all the occupied orbitals. Properties and application of the one-electron Hamiltonian in the relativistic framework are also discussed.

Key word: SCF-Theory.

1. Introduction

Since the pioneering work of Roothaan on the open shell self consistent field (SCF) theory [1], attempts have been made to construct one-electron Hamiltonians for general open shell and multiconfigurational (MC) SCF wave functions [2–10]. Construction of a single, one-electron Hamiltonian is important not only because it simplifies the calculations but also for applications to formal problems. For instance, one wants a single, one-electron Hamiltonian, if one uses the Møller–Plessett type separation of the N-electron Hamiltonian in the perturbation theory of electron correlation [11]. The one-electron Hamiltonian approach was particularly successful in single configuration closed and open shell SCF calculations. However, especially in the MC SCF case, convergence is not easily obtained, and several ways to accelerate the convergence have been proposed [3, 9, 12].

Huzinaga [5] and Hirao [6] gave a synthetic approach to the open shell and MC SCF problem. They decoupled the set of coupled Euler equations for orbital shells

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with the use of projection operators, and transformed them into a single pseudo-secular equation. In a series of papers, Adams developed an elegant orbital SCF theory and constructed a natural orbital Hamiltonian for MC SCF wave functions [8]. The theory has been extended to construct a one-electron Hamiltonian for the orbitals of the fully general class of MC SCF wave functions and has been applied to MC SCF calculations of excited states of atoms and molecules [9].

In the next section, a prescription is given for constructing a one-electron Hamiltonian with which one can determine all the occupied orbitals of general MC functions. We start with a general form of the total energy expression. It has no restrictions on the configurational form of the total wave function, and is applicable to excited states as well as ground states. In the last section, we discuss the property of our one-electron Hamiltonian in the quasi- and fully relativistic SCF framework, and compare with the one-electron Hamiltonians previously given.

2. Theory

In the MC SCF theory, the total wave function is determined by making the energy stationary with respect to the orbitals and with respect to the configuration expansion coefficients. The variation of the expansion coefficients and the variation of the orbitals are independent only in the first order. Second order coupling effects, which are important for the SCF convergence especially in excited state calculations [13], will not be discussed in this article. The variation of the expansion coefficients leads to the well-known CI equation. Here we focus on the first order variation of the orbitals and on the construction of a one-electron Hamiltonian for general MC SCF wave functions

We start with a molecular N-electron Hamiltonian which is taken as the sum of one-electron operators and two electron interaction terms. The general MC energy functional for the M (M≥N) orthonormal occupied orbitals can be expressed as:

$$\begin{aligned} E &= \sum_{i,j=1}^{M} \gamma_{ij}\langle\phi_j|\hat{h}|\phi_i\rangle + \tfrac{1}{2}\sum_{i,j,k,l}^{M} \Gamma_{ij,kl}\cdot\langle\phi_k(1)\phi_l(2)|\hat{v}_{12}|\phi_i(1)\phi_j(2)\rangle \\ &= \operatorname{tr}(\hat{h}\hat{\gamma}) + \tfrac{1}{2}\operatorname{tr}(\hat{v}_{12}\hat{\Gamma}). \end{aligned} \tag{1}$$

The $\hat{\gamma}$ and $\hat{\Gamma}$ are the one and two electron density matrices [14] and they are given as:

$$\begin{aligned} \hat{\gamma} &= \sum_{i,j}^{M} |\phi_i\rangle\gamma_{ij}\langle\phi_j|, \\ \hat{\Gamma} &= \sum_{i,j,k,l}^{M} |\phi_i(1)\phi_j(2)\rangle\Gamma_{ij,kl}\langle\phi_k(1')\phi_l(2')|. \end{aligned} \tag{2}$$

It should be understood that the averaging over sublevels or levels is incorporated in γ_{ij} and $\Gamma_{ij,kl}$.

Conditions that the orthonormal orbitals must satisfy in order to make the energy stationary, can be derived by the orthogonality constrained variation [7–9]. It is expressed in a compact form by the fundamental invariant $\hat{\rho} = \sum_i^M |\phi_i\rangle\langle\phi_i|$:

$$|\delta\phi_i\rangle = \mu \cdot \{(1-\hat{\rho})\hat{m}\hat{\rho} + \hat{\rho}\hat{m}\hat{\rho}\}|\phi_i\rangle, \tag{3}$$

where the constant μ is infinitesimally small, and $\hat{m}$ is arbitrary except for the condition $(\hat{\rho}\hat{m}\hat{\rho})^\dagger = -(\hat{\rho}\hat{m}\hat{\rho})$, which guarantees the orthonormality of the occupied orbitals.

Substitution of the above equation in the energy functional (1) gives rise to the two conditions [8, 9]

$$(1-\hat{\rho})\hat{F}\hat{\rho} = 0, \tag{4a}$$

$$\hat{\rho}(\hat{F}-\hat{F}^\dagger)\hat{\rho} = 0, \tag{4b}$$

where

$$\hat{F} = \hat{h}\hat{\gamma} + \hat{Q}, \qquad \hat{F}^\dagger = \hat{\gamma}\hat{h} + \hat{Q}^\dagger$$

with

$$\hat{Q} = \sum_{ijkl}^{M} \Gamma_{ij,kl} \cdot \langle\phi_l(2)|\hat{v}_{12}|\phi_j(2)\rangle|\phi_i(1)\rangle\langle\phi_k(1')|.$$

Conditions (4a) and (4b) may be expressed in a more familiar form:

$$\langle\chi_v|\hat{F}|\chi_0\rangle = 0, \tag{5a}$$

$$\langle\chi_{0'}|\hat{F}-\hat{F}^\dagger|\chi_0\rangle = 0, \tag{5b}$$

where χ_0, $\chi_{0'}$ are any linear combinations of occupied orbitals and χ_v is any linear combination of virtual orbitals. McWeeny [7] and Hirao [6] arrived at the correct variational conditions analogous to (5a, b), but in more restricted form.

Both (4a) and (4b) (or (5a) and (5b)) must be satisfied for the energy functional to be stationary with respect to the mixing of occupied with virtual orbitals and of occupied orbitals among themselves. We have given one prescription for translating the two conditions into a pseudoeigenvalue equation [9]. The construction of open shell and MC SCF Hamiltonians [8, 9] was guided by the following idea: The one-electron Hamiltonian is defined so, that it differs from the closed shell restricted Fock operator only as much as is essential, and that the resultant orbitals still satisfy conditions (4a) and (4b).

In the present article, we present a simpler and unique prescription:

The two conditions (4a) and (4b) can be easily coupled together to the form

$$\hat{R}_0 = (1-\hat{\rho})\hat{F}\hat{\rho} + \lambda\hat{\rho}(\hat{F}-\hat{F}^\dagger)\hat{\rho} = 0.$$

where λ is an arbitrary non-zero complex constant. This is not a desirable form of the Hamiltonian as it is not Hermitian in general. A Hermitian form of the

Hamiltonian can be derived by averaging over its Hermitian conjugate:

$$\hat{R} = \hat{R}_0 + \hat{R}_0^\dagger = (1-\hat{\rho})\hat{F}\hat{\rho} + \hat{\rho}\hat{F}^\dagger(1-\hat{\rho}) + ia\hat{\rho}(\hat{F} - \hat{F}^\dagger)\hat{\rho}, \tag{6}$$

where $a = i(\lambda^* - \lambda)$ is a nonzero real number. The third term in Eq. (6) is indeed Hermitian since $\hat{\rho}(\hat{F} - \hat{F}^\dagger)\hat{\rho}$ is antihermitian and $i \cdot a$ is purely imaginary.

One can easily show that the resultant orbitals of the equation $\hat{R} = 0$ satisfy both (5a) and (5b). Conditions (5a) and (5b), and the resultant equation $\hat{R} = 0$, in general do not provide means of distinguishing individual occupied or individual virtual orbitals [5, 6, 8]. They simply determine the occupied and virtual manifold. Individual orbitals must then be chosen by a new set of conditions. These conditions must be sufficient to guarantee that both (5a) and (5b) are satisfied, but what the conditions are is a matter of taste.

In the case of the single Slater determinant approximation the energy functional and the operators $\hat{F}$ and $\hat{R}$ are invariant to linear unitary transformations within the occupied space. In such a case, the additional condition to determine individual occupied orbitals may be given in general as [15]

$$\hat{\rho}\hat{\Omega}_0\hat{\rho}|\phi_i\rangle = \sum_j^M \omega_{ji} \cdot |\phi_j\rangle,$$

where $\hat{\Omega}_0$ is an arbitrary Hermitian one-electron operator. Similarly we can employ the Hermitian operator $(1-\hat{\rho})\hat{\Omega}_v(1-\hat{\rho})$ for selecting the virtual orbitals [16]. Then the additional conditions to determine individual occupied and virtual orbitals may be given as

$$\hat{T}_{\mathrm{SD}}|\phi_i\rangle = \sum_j^M \omega_{ji}|\phi_j\rangle, \tag{7}$$

where

$$\hat{T}_{\mathrm{SD}} = \hat{\rho}\hat{\Omega}_0\hat{\rho} + (1-\hat{\rho})\hat{\Omega}_v(1-\hat{\rho}).$$

For a general MC wave function, a full set of Slater determinants is almost never used, and E and $\hat{R}$ are invariant under *restricted* sets of orbital transformations in the occupied space. Such orbital sets can be characterized by the projectors [6]

$$\hat{\rho}_I = \sum_{i \in I} |\phi_i\rangle\langle\phi_i|.$$

The fundamental invariant $\hat{\rho}$ may then be given in terms of the $\hat{\rho}_I$'s as

$$\hat{\rho} = \sum_I \hat{\rho}_I.$$

In terms of these projectors, a new set of conditions for determining individual MC SCF orbitals can be written as

$$\hat{T}|\phi_i\rangle = \sum_{j \in I} \omega_{ji} \cdot |\phi_j\rangle, \qquad i \in I, \tag{7a}$$

where

$$\hat{T} = \sum_I \hat{\rho}_I\hat{\Omega}_0\hat{\rho}_I + (1-\hat{\rho})\hat{\Omega}_v(1-\hat{\rho}).$$

Here the Hermitian one-electron operator $\hat{\Omega}_0$ must be chosen so that it is invariant to the set of orbital transformations. The choice $\hat{\Omega}_0 = \frac{1}{2}(\hat{F} + \hat{F}^\dagger)$ provides such an example. The $\hat{\Omega}_0$ and $\hat{\Omega}_v$ operators can also be regarded as generalized forms of the level shifting operators [17], which help the SCF iteration to converge [12]. With level shifting one can in principle optimize each orbital pair mixing, but (what has often been overlooked) one can in no way take into account the coupling among different pairs nor the coupling of orbital mixing with CI-coefficient variation. These effects have to be accounted for in order to guarantee (quadratic) convergence as e.g. in the methods of Das *et al.*, Schwarz and Chang, or Dalgaard [13].

Adding the equations $\hat{R} = 0$ and (7a) together, one obtains

$$(\hat{R} + \hat{T})|\phi_i\rangle = \sum_{j \in I} \omega_{ji} |\phi_j\rangle. \tag{8}$$

Since the one-electron Hamiltonian $(\hat{R} + \hat{T})$ is invariant to unitary transformations within the set I, the Hermitian matrix ω_{ji} can be brought to diagonal form and we now arrive at the pseudoeigenvalue equation of the general MC SCF theory:

$$\boxed{(\hat{R} + \hat{T})|\phi_i\rangle = \omega_i |\phi_i\rangle.} \tag{9}$$

It is easy to verify that the resultant orbitals of Eq. (9) satisfy (5a) and (5b). Following the method suggested by Adams [9], we can also verify that the MC SCF Hamiltonian $(\hat{R} + \hat{T})$ is defined so that the orbitals, which satisfy the Eq. (9), are the ones used to construct the Hamiltonian.

Our theory is presented with no restrictions on the type of configurations in the expansion of the total wave functions and the formalism is applicable to MC SCF calculations of the general class of ground and excited states of polyatomic molecules.

3. Discussion

Our one-electron Hamiltonian is intrinsically complex (see Eq. 6) and this property will be discussed in relation to the non-relativistic and relativistic N-electron Hamiltonian.

In the non-relativistic case and in the absence of external magnetic fields, $\hat{h} = V + \hat{p}^2/2m$ and $\hat{v}_{12} = 1/r_{12}$ are employed for the one and two electron operators. The N-electron Hamiltonian is then real: $H^* = H$, or $[H, C] = 0$. C is the complex conjugation operator, which is associated with time reversal. It follows that ψ and $C\psi$ are simultaneously eigenfunctions of H to the same energy Therefore the eigenfunctions can be chosen purely real ($\psi + C\psi$, or $i \cdot (\psi - C\psi)$). This guarantees that the momentum vanishes, $\langle \hat{p} \rangle = 0$, as it must be for stationary states [19].

If we use a linear space of trial functions, which is invariant under C, the optimized variational function $\tilde{\psi}$ can be chosen purely real, too [18]. On the other hand, the energy-optimized Hartree–Fock function (whether unrestricted, spatially symmetry-restricted, or extended) is not necessarily real [19], because the space of HF-functions is nonlinear. Nevertheless it is sensible, both for computational simplicity and for symmetry reasons ($\langle \hat{p} \rangle = 0$), to introduce the real-constraint $[F, C] = 0$ in non-relativistic Hartree–Fock theory. Therefore the introduction of the operator $\hat{R}$ (Eq. 6), which is in general complex even in a real basis set, might at first seem unreasonable.

In the relativistic case, the Dirac one-electron Hamiltonian $\hat{h}_D$ in its standard representation

$$\hat{h}_D = V + c\vec{\alpha}\vec{p} + c^2\beta m,$$

and $\hat{v}_{12} = 1/r_{12}$ are usually chosen. For the quasi-relativistic case, $\hat{h}$ may be chosen to be of the Pauli form:

$$\hat{h}_P = V + \hat{\vec{p}}^2/2m + \hat{h}_{vm} + \hat{h}_D + \hat{h}_{SO},$$

where $\hat{h}_{vm}$, $\hat{h}_D$ and $\hat{h}_{SO}$ represent velocity-mass, Darwin and spin-orbit terms, respectively, or its model potential equivalents [20].

In the quasi- and full relativistic cases, time-reversal is now associated with the Kramers operator $K = -i\sigma_y C$: $[H, K] = 0$ [21]. Then eigenfunctions Ψ of H are degenerate with $K\Psi$; but one cannot form a purely real linear combination of them. The exact eigenfunctions, and also any reasonable approximations, are intrinsically complex. Instead of $[F, C] = 0$, $[F, K] = 0$ is now a reasonable constraint. The introduction of the complex operator in the one-electron Hamiltonian (6) in order to unify Eqs. (5a, 5b) represents no additional complication in the relativistic case.

Although the relativistic Hamiltonian is complex, this is not necessarily true for its matrix representation. E.g. in the basis of its own eigenfunctions, the HF-equation has a purely real representation. However, of practical importance is whether we can find a set of basis functions before any diagonalization, only by taking advantage of the symmetry properties of the system. Furthermore, this basis should yield real matrix elements for all the different terms in the Hamiltonian. Such a basis indeed exists for systems of high symmetry such as atoms [21] and linear molecules [22], the basis being given by:

$$\begin{pmatrix} f_n \cdot \chi_{ljm} \\ 0 \end{pmatrix} \quad \text{and} \quad \begin{pmatrix} 0 \\ if_n \cdot \chi_{ljm} \end{pmatrix},$$

where χ_{ljm} are two-component spinors all referring to the same coordinate system, and f_n are radial AOs. In the case of polyatomic molecules of low symmetry, however, it does not seem possible to find general basis sets, which simultaneously yield real S-, V- and $\vec{\sigma}\vec{p}$-matrix elements.

Closely related to the present formulation are the open shell and MC SCF theories by Huzinaga [5] and Hirao [6]. Test calculations [6, 23] using such a construction of the one-electron Hamiltonian have been performed within the open shell framework, and the convergence has been found satisfactory. The definition of the one-electron Hamiltonian by Hirao and Carbo et al. [6] for the case of MC SCF orbitals is quite complicated, and makes the construction of the Hamiltonian rather difficult in practical applications. The generalized MC SCF theory of Adams et al. [9] uses the orthogonality constrained variation to arrive at the conditions (4a) and (4b). The one-electron Hamiltonian is then constructed in such a manner that it differs from the closed shell Hartree–Fock Hamiltonian only as much as is essential. It also involves a more complicated construction of the one-electron Hamiltonian.

Our one-electron Hamiltonian given in the preceeding section has no practical advantage over other one-electron Hamiltonians [1–9] with regard to the convergence properties. Our operator as well as others proposed are derived solely from the "First order" variation of energy. Applications of various one-electron Hamiltonian methods have been demonstrated in the openshell and MC SCF frameworks [6, 8–10, 23]. When these one-electron Hamiltonians give convergence difficulties, then our operator would be plagued with convergence difficulties as well.

In the present article, the conditions (4a) and (4b) have been coupled to form the one-electron Hamiltonian in a unique way, keeping the structure of the Hamiltonian as simple as possible. The method we used to couple the two conditions is essentially an extension of the method due to Huzinaga [5]. The general MC SCF theory presented here may then be viewed as a generalization of his open shell and MC SCF theories [5].

Applications of the present MC SCF formalism to relativistic model potential calculations for molecular systems are under way.

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