Spin-unrestricted formalism for a partially restricted Hartree–Fock approach

V.N. Glushkov

Physics Department, National University, 49050, per. Nauchny 13, Dniepropetrovsk, Ukraine

An alternative method of building a partially restricted single Slater determinant with the number of α electrons equal to the number of β electrons has been proposed. Using a simple to implement method of taking the orthogonality constraints into account the amended unrestricted Hartree–Fock (UHF) equations for molecular orbitals have been obtained. The formalism deals as does the UHF theory with the cubic equations with respect to the LCAO coefficients whereas a partially restricted HF approach developed in [10] leads to the fifth-degree equations. The minimal extra calculations are required to implement this scheme in existing UHF codes. Unlike the known Roothaan coupling formalism the proposed approach is suitable for use with the well-established unrestricted Møller–Plesset perturbation theories in incorporating the electron correlation effects. Some peculiarities of using the method are illustrated by considering a model molecular system.

KEY WORDS: partially restricted wave function, orthogonality constraints

1. Introduction

A single Slater determinant is the simplest wave function (WF) to study both closed and open-shell systems. Conceptual simplicity of such a WF allows one to develop the cost-effective perturbation approaches for incorporating electron correlation effects [1–3]. The existing quantum chemistry calculation methods deal with the different schemes of designing a Slater determinant. A restricted Hartree–Fock (RHF) function with the doubly occupied spatial molecular orbitals (MOs) is usually applied to closed-shell systems. However, in several cases a single RHF determinant cannot even approximately describe the states of a molecular system such as those from regions of the potential energy surface which are far from equilibrium geometry or the singlet excited states. In contrast, the unrestricted HF (UHF) determinant, in which the electrons of opposite spins are assigned to spatially different MOs, is capable of correctly describing such cases. This function, however, is not a spin eigenfunction and contains contamination by higher spin states. The approaches based on the Löwdin spin projection operator [4] are usually employed to remedy the spin contamination problem (see, e.g., [4–9, and references therein]). This requires evaluation of expectation values of the Löwdin operator and presents severe computational difficulties.

A compromise WF, a so-called partially restricted HF (PRHF) function, has been introduced in [10] for describing a transition from the diradicals to the dicarbens. This function has the following form:

$$\Psi^{(0)} = \det \left| \varphi_1^\alpha \alpha \, \varphi_1^\beta \beta \, \ldots \, \varphi_q^\alpha \alpha \, \varphi_q^\beta \beta \, \varphi_{q+1}^\alpha \alpha \, \varphi_{q+1}^\beta \beta \, \ldots \varphi_{q+p}^\alpha \alpha \, \varphi_{q+p}^\beta \beta \right|. \tag{1}$$

There are q orbitals with closed-shell character, i.e., the α MOs φ_i^α, $i = 1, 2, \ldots, q$, are taken to be spatially identical to the β MOs $\varphi_i^\alpha = \varphi_i^\beta$, $i = 1, 2, \ldots, q$. These orbitals form the so-called "core" subspace. The other p orbitals have different spatial parts, i.e., $\varphi_i^\alpha \neq \varphi_i^\beta$, $i = q+1, q+2, \ldots, q+p$, and form the unrestricted part (so-called unpaired electrons).

On the one hand, such a Slater determinant as well as the UHF function as compared to the RHF WF has the freedom of being symmetry broken. For example, singlet–triplet instabilities can be described by a PRHF WF [10]. On the other hand, the advantage of this function as compared to the fully UHF one is a simple way to construct spin eigenstates. For example, this function with two electrons in the unrestricted part (i.e., $p = 1$) is just a mixture of singlet and triplet components. The application of a single Amos annihilator [6] to such a function provides the pure spin state, whereas for the UHF function this procedure can produce a WF which, in general, is still far from an eigenfunction of $\mathbf{S}^2$.

In [10] a modified coupling operator formalism has been used for the determination of molecular orbitals (MOs) which result from three coupled equations with different Fock operators: for the "core" orbitals and for the α spin and β spin orbitals of the unrestricted part. Due to the difference in the symmetry properties of closed and open shell orbitals, it is impossible to find a common Fock operator for all orbitals [10] as is the case in the open-shell coupling operator Roothaan formalism [11,12].

It is clear that the next stage in applying this attractive model is to develop many-body perturbation theories (PTs) based on a single reference PRHF WF (1). Unfortunately, the formalism proposed in [10] as well as the open-shell Roothaan method [11] does not lend itself very readily to a well-defined zeroth-order Hamiltonian $H^{(0)}$. PT calculations based on this formalism are problematic because there is no unique way to choose off-diagonal Lagrangian multipliers coupling the closed and open-shell MOs (see, e.g., [12]). In other words, arbitrariness in their definition leads to different forms of PT. Consequently, the problem of the choice of $H^{(0)}$ is open to discussion. Useful analysis and comparison of these PTs for open-shell systems can be found in [13–16, and references therein].

In [17] we have proposed an alternative way of obtaining restricted open-shell WF from which PT can be performed using the UHF formalism and, therefore, ambiguity problems do not appear. The preliminary calculation results have shown workability of such a scheme for both the ground and the excited states [18,19]. In this paper we shall show how a similar formalism can be applied to a PRHF function. Unlike [17] we shall consider even-electron systems with the number of α electrons equal to the number of β electrons. In this case we deal with some specific orthogonality constraints different from those for open-shell systems. The variational prin-

ciple for the energy and a very simple to implement method of taking the orthogonality constraints into account (TOCIA) previously developed by us [17,20,21] leads to the amended UHF equations for the MOs of the PRHF WF. They present the natural base to describe the effects of the electron correlation using the well-established spin-annihilated PTs [7,8,22]. In order to clarify some features of this work the next section gives a brief general theory of the TOCIA method. In section 3 we discuss the restrictions imposed on the UHF model and derive the equations for the MOs. Some peculiarities of using the proposed method are discussed in section 4. Finally, concluding remarks and the potential ways for the applications are given in section 5.

2. Outline of TOCIA method

Here we describe the main ideas of our TOCIA method which proved to be the useful tool for solving the eigenvalue problems with orthogonality constraints.

It is well known that many problems in physics and, in particular, quantum chemistry can be regarded as the variational problem

$$E = \min\left(\frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle}\right), \tag{2}$$

with orthogonality constraints

$$\langle \Psi | u_i \rangle = 0, \quad u_i = 1, 2, \ldots, r. \tag{3}$$

Here E and H are the energy and the Hamiltonian of a system respectively, Ψ is a trial WF approximated by expansion in a finite basis set, i.e.,

$$|\Psi\rangle = P|\Psi\rangle,$$

where P is the orthoprojector defined by the finite basis set (dimension m). $|u_i\rangle$, $i = 1, 2, \ldots, r < m$, are the *arbitrary* constraint vectors, which are not, in general, eigenvectors of the operator PHP. For example, this is a case of the excited state calculations where a basis set specifically designed for the ground state can be used to determine a ground state energy and a different basis set used in the approximation of an excited state WF [18,23]. In section 3 we shall show that such constraint vectors are assigned to be the core orbitals.

Equations (2) and (3) present the task with constraints. The conventional methods of constrained minimization (see, e.g., [24,25]) proved not to be effective enough to solve the complicated problems of quantum chemistry, especially when nonlinear basis set parameters are varied.

Below we shall show how constrained minimization (2), (3) can be reduced to an unconstrained one. For the sake of simplicity, we limit ourselves by one constrained vector $|u\rangle$. There are three possible positions of this vector with respect to a subspace M spanned by the finite basis set:

(1) $P|u\rangle = 0$, this is a trivial case;

(2) $P|u\rangle = |u\rangle$, the constraint vector lies completely within the subspace M;

(3) $P|u\rangle \neq 0$, $P|u\rangle \neq |u\rangle$, then this vector can be divided into two parts

$$|u\rangle = P|u\rangle + (I - P)|u\rangle.$$

Here after I is the identity.

Thus, we should consider only the second case, i.e., the constraint vector is $P|u\rangle$, which we take to be normalized, i.e., $\langle u|P|u\rangle = 1$. Then the condition (3) may be rewritten in the symmetrized form which is convenient to perform the variations:

$$\langle\Psi|P_u|\Psi\rangle = 0, \qquad P_u = P|u\rangle\langle u|P. \tag{4}$$

Multiplying equation (4) by an arbitrary real multiplier λ and adding it to equation (2), we get

$$L = \min\left(\frac{\langle\Psi|(H + \lambda P_u)|\Psi\rangle}{\langle\Psi|\Psi\rangle}\right). \tag{5}$$

Then the necessary condition of minimum (5) leads to the equation

$$P(H + \lambda P_u - E)P|\Psi\rangle = 0 \tag{6}$$

which is an eigenvalue problem for the modified operator

$$H_{\text{eff}} = P(H + \lambda P_u)P.$$

In this equation the multiplier λ is as yet undetermined and condition (3) is not satisfied. The key moment of the TOCIA method is the following statement:

- The constraint vector $P|u\rangle$ tends to an eigenvector of the modified operator H_{eff}, if $\lambda \to \pm\infty$.

Then the fulfillment of condition (3) will follow automatically due to the orthogonality of the eigenvectors, which correspond to different eigenvalues of a self-conjugate operator.

Indeed, let us consider an action of H_{eff} on the vector $P|u\rangle$. Let $|e_k\rangle$, $k = 1, 2, \ldots, m$, be the basis set vectors in the subspace M. Without loss of generality, we may assume that $e_1 = P|u\rangle$ and $\langle e_i|e_k\rangle = \delta_{ik}$. Then the action takes the following matrix form [20]:

$$\begin{pmatrix} H_{11} + \lambda & H_{12} & \ldots & H_{1m} \\ H_{21} & H_{22} & \ldots & H_{2m} \\ \vdots & \vdots & \ddots & \vdots \\ H_{m1} & H_{m2} & \ldots & H_{mm} \end{pmatrix} \begin{pmatrix} 1 \\ 0 \\ \vdots \\ 0 \end{pmatrix} = \lambda \begin{pmatrix} H_{11}/\lambda + 1 \\ H_{21}/\lambda \\ \vdots \\ H_{m1}/\lambda \end{pmatrix}. \tag{7}$$

Here $H_{ik} = \langle e_i|H|e_k\rangle$.

It is easy to see that equation (7) becomes the eigenvalue problem for the modified operator, if and only if $\lambda \to \pm\infty$, Q.E.D.

As one can also see from equation (7), the constraint vector $P|u\rangle$ tends to an eigenvector of the operator H_{eff} as $1/\lambda$, therefore, $\langle\Psi|u\rangle \to 0$ as $1/\lambda$. In practice, a choice of the value λ depends on the accuracy required. Another proof of the above-mentioned statement and some applications of the TOCIA method can be found in [17,21]. This result can be easily extended to a few constraint vectors. Then P_u must be substituted by the orthoprojector on the subspace determined by all the constraint vectors.

In concluding this section we shall show that the spectra of the original operator H and the modified one H_{eff} are the same on the subspace $(P - P_u)X$, where X is a Hilbert space of states. Indeed, since $P|u\rangle$ is an eigenvector of H_{eff}, $\lambda \to \pm\infty$, the subspace M can be represented by a direct sum of subspaces

$$M = (P - P_u)X \oplus P_u X$$

which are invariant for the operator H_{eff} and, therefore, equation (6) is equivalent to the eigenvalue problem on the subspace $P_u X$, for which the solution is known (the eigenvector is $P|u\rangle$ and the corresponding eigenvalue $E_\lambda \to \pm\infty$), i.e.,

$$P_u(H - E_\lambda)P_u|u\rangle = 0, \quad E_\lambda \to \pm\infty,$$

and the equation on the subspace $(P - P_u)X$

$$(P - P_u)(H - E)(P - P_u)|\Psi\rangle = 0. \tag{8}$$

Here we took into consideration that $\lambda(P - P_u)P_u(P - P_u) = 0$ for any value λ.

Equation (8) means that the spectra of the operators $(P - P_u)(H + \lambda P_u)(P - P_u)$ and $(P - P_u)H(P - P_u)$ are the same. But, from a practical point of view, equation (6) is much simpler to solve than to solve equation (8). Indeed, equation (8) requires calculations of $\langle\Psi|H|u\rangle$ and $\langle u|H|u\rangle$, whereas equation (6) does only the overlap element $\langle\Psi|u\rangle$. Thus, minimal extra calculations are required to implement this method.

It should be also stressed that the TOCIA method allows one either to remove $(\lambda \to \infty)$ the constraint vector from the spectrum of a self-conjugate operator or to include $(\lambda \to -\infty)$ it into this spectrum without changing the spectrum on the subspace $(P - P_u)X$. This method is also a general one because it is based on the general properties of self-conjugate operators and can be applied to any eigenvalue problem with orthogonality constraints.

3. Amended UHF equations for a partly restricted Slater determinant

In this section we shall show how the method in question can be applied to a PRHF model. In [10], from the very beginning, the WF (1) with the *identical* "core" α and β orbitals is used to derive the equations for MOs. Unlike [10] we start from an UHF single determinant where all the α orbitals are permitted to be spatially different from the β orbitals. It is built upon a set of spin-orbitals which can be divided into two types of spatial MOs: MO^α: $|i^\alpha\rangle$, $i^\alpha = 1, 2, \ldots, n^\alpha$, with spin-up and MO^β: $|i^\beta\rangle$, $i^\beta = 1, 2, \ldots, n^\beta$, with spin-down. For short, hereafter we use notation $|i^\gamma\rangle$, $\gamma = \alpha, \beta$, for

the spatial part of MOs. We shall consider systems with the number of α electrons equal to the number of β electrons, i.e., $n^\alpha = n^\beta = p + q$, $S = S_z = 0$ and $n^\alpha + n^\beta = N$ is the number of electrons.

Some restrictions should be imposed on MOs to obtain a PRHF function.

First, the subspaces of the closed-shell "core" determined by $|i^\alpha\rangle$, $i = 1, 2, \ldots, q$, and $|i^\beta\rangle$, $i = 1, 2, \ldots, q$, must coincide. This requirement may be written as the following orthogonality constraint:

$$\sum_i^q \langle i^\beta | (I - P_c^\alpha) | i^\beta \rangle = 0, \quad i^\beta = 1, 2, \ldots, q, \tag{9}$$

where $P_c^\alpha = \sum_i^q |i^\alpha\rangle\langle i^\alpha|$ is the orthoprojector on the "core" subspace of MO^α.

The requirement (9) means that the MOs of the α "core" set lie completely within the subspace defined by the β "core" set.

Second, orthogonality between the α set and the β set is guaranteed by spin. But for the spatial parts, in general, we have $\langle i^\alpha | j^\beta \rangle \neq 0$. However, we are always able to transform our sets into new sets $|i_1^\alpha\rangle$, $i = 1, 2, \ldots, q + p$, and $|i_1^\beta\rangle$, $i = 1, 2, \ldots, q + p$, of so-called corresponding orbitals [6]. These orbitals have the property that their spatial overlap is diagonal:

$$\langle i_1^\alpha | j_1^\beta \rangle = T_i \delta_{ij}.$$

Therefore, the conditions

$$\begin{aligned} P_c^\alpha | i^\beta \rangle &= 0, \quad i^\beta = q + 1, q + 2, \ldots, q + p, \\ P_c^\beta | i^\alpha \rangle &= 0, \quad i^\alpha = q + 1, q + 2, \ldots, q + p, \end{aligned} \tag{10}$$

may be assumed to be fulfilled. Here P_c^β is the orthoprojector on the "core" subspace of MO^β. We shall show that our formalism unlike [10] leads to the MOs satisfying equations (10) automatically. These conditions provide the orthogonality of the open-shell orbitals to the closed-shell MOs and they are useful to derive the equations.

At last, each individual set of MOs may be assumed, without loss of generality, to be orthogonal, i.e.,

$$\langle i^\alpha | j^\alpha \rangle = \delta_{ij}, \qquad \langle i^\beta | j^\beta \rangle = \delta_{ij}. \tag{11}$$

The restriction (11) can always be fulfilled by appropriate unitary transformation within each of the sets which leave the WF (1) invariant.

Thus, to obtain the equations for the MOs we require that the total energy be stationary under all variations in the MOs consistent with the condition (9), i.e.,

$$\delta L = \delta \left[E^{\text{UHF}} + \lambda \sum_i^q \langle i^\beta | (I - P_c^\alpha) | i^\beta \rangle \right] = 0, \tag{12}$$

where λ is a non-negative Lagrange multiplier. The variations in the MOs can be divided into the following independent parts, e.g., for the β set:

$$\left|\delta i^{\beta}\right\rangle = P^{\beta}\left|\delta i^{\beta}\right\rangle + \left(I - P^{\beta}\right)\left|\delta i^{\beta}\right\rangle. \tag{13}$$

Here $P^{\beta} = \sum_i^{q+p} |i^{\beta}\rangle\langle i^{\beta}|$ is the orthoprojector on the subspace of all the occupied β MOs.

The first term in (13) does not lead to changes in the total energy because it is invariant to any orthogonal transformation of the MOs of any spin among themselves. The energetically significant variations are described only by the second term in (13).

The variations in the first term in equation (12) then give the standard result:

$$\delta E^{\text{UHF}} = \sum_i^{q+p}\left\langle\delta i^{\alpha}\left|\left(I - P^{\alpha}\right)\mathbf{F}^{\alpha}\right|i^{\alpha}\right\rangle + \sum_i^{q+p}\left\langle\delta i^{\beta}\left|\left(I - P^{\beta}\right)\mathbf{F}^{\beta}\right|i^{\beta}\right\rangle + \text{complex conjugate}, \tag{14}$$

where $\mathbf{F}^{\alpha}$ and $\mathbf{F}^{\beta}$ are the standard unrestricted Fockians.

The variations in the second term of equation (12) are important to obtain the correct equations and should be considered in more detail:

$$\delta\left[\sum_i^{q}\left\langle i^{\beta}\left|\left(I - P_c^{\alpha}\right)\right|i^{\beta}\right\rangle\right]$$
$$= \sum_i^{q}\left\langle\delta i^{\beta}\left|\left(I - P_c^{\alpha}\right)\right|i^{\beta}\right\rangle + \sum_i^{q}\left\langle i^{\beta}\left|\left(I - P_c^{\alpha}\right)\right|\delta i^{\beta}\right\rangle - \sum_i^{q}\left\langle i^{\beta}\left|\delta P_c^{\alpha}\right|i^{\beta}\right\rangle. \tag{15}$$

Due to the equation (13) the first term in (15) can be rewritten in the form

$$\sum_i^{q}\left\langle\delta i^{\beta}\left|\left(I - P_c^{\alpha}\right)\right|i^{\beta}\right\rangle = \sum_i^{q}\left\langle\delta i^{\beta}\left|\left(I - P^{\beta}\right)\right|i^{\beta}\right\rangle - \sum_i^{q}\left\langle\delta i^{\beta}\left|\left(I - P^{\beta}\right)P_c^{\alpha}\right|i^{\beta}\right\rangle. \tag{16}$$

It is clear that the first term in (16) turns into zero because of $(I - P^{\beta})P^{\beta} = 0$. Then we have

$$\sum_i^{q}\left\langle\delta i^{\beta}\left|\left(I - P_c^{\alpha}\right)\right|i^{\beta}\right\rangle = -\sum_i^{q+p}\left\langle\delta i^{\beta}\left|\left(I - P^{\beta}\right)P_c^{\alpha}\right|i^{\beta}\right\rangle. \tag{17}$$

In (17) we took equation (10) $P_c^{\alpha}|i^{\beta}\rangle = 0$, $i^{\beta} = q + 1, q + 2, \ldots, q + p$, into account.

By analogy, the second term in (15) gives the complex conjugate one

$$\sum_i^{q}\left\langle i^{\beta}\left|\left(I - P_c^{\alpha}\right)\right|\delta i^{\beta}\right\rangle = -\sum_i^{q+p}\left\langle i^{\beta}\left|P_c^{\alpha}\left(I - P^{\beta}\right)\right|\delta i^{\beta}\right\rangle. \tag{18}$$

Let us consider now the third term in equation (15). Using the properties of the orthoprojector, it is easy to show that

$$\delta P_c^\alpha = \sum_j^q \big[(I - P^\alpha) | \delta j^\alpha \rangle \langle j^\alpha | + | j^\alpha \rangle \langle \delta j^\alpha | (I - P^\alpha) \big]. \tag{19}$$

Here $P^\alpha = \sum_i^{q+p} | i^\alpha \rangle \langle i^\alpha |$.

Inserting equation (19) into the third term in (15), we obtain

$$\sum_i^q \langle i^\beta | \delta P_c^\alpha | i^\beta \rangle = \sum_i^{q+p} \langle \delta i^\alpha | (I - P^\alpha) P_c^\beta | i^\alpha \rangle + \text{complex conjugate}. \tag{20}$$

Finally, from equations (14), (17), (18) and (20) we find

$$\delta L = \sum_i^{q+p} \langle \delta i^\alpha | (I - P^\alpha) (\mathbf{F}^\alpha - \lambda P_c^\beta) | i^\alpha \rangle + \sum_i^{q+p} \langle \delta i^\beta | (I - P^\beta) (\mathbf{F}^\beta - \lambda P_c^\beta) | i^\beta \rangle$$
$$+ \text{complex conjugate}. \tag{21}$$

If the MOs are expanded in a finite basis set (LCAO approximation) then the identity in (21) should be substituted by the orthoprojector P defined by this basis set (dimension m). It leads to the amended UHF equations for MOs:

$$P \big(\mathbf{F}^\alpha - \lambda P_c^\beta - \varepsilon_i^\alpha \big) P | i^\alpha \rangle = 0, \quad i = 1, 2, \ldots, m, \tag{22}$$
$$P \big(\mathbf{F}^\beta - \lambda P_c^\alpha - \varepsilon_i^\beta \big) P | i^\beta \rangle = 0, \quad i = 1, 2, \ldots, m. \tag{23}$$

In these equations λ is still not determined and the condition (9) has not been satisfied.

As we mentioned, the basic moment of our TOCIA method is that the constraint vectors must be the eigenvectors of the modified operator. For example, for equation (22) the "core" MO^β are the constraint vectors and eigenvectors of the effective operator $P(\mathbf{F}^\alpha - \lambda P_c^\beta) P$, i.e.,

$$P \big(\mathbf{F}^\alpha - \lambda P_c^\beta - \varepsilon_{ci}^\beta \big) P | i^\beta \rangle = 0, \quad i^\beta = 1, 2, \ldots, q.$$

This can be so if and only if $\lambda \to \infty$ (the reader is referred to section 1).

The additional term in (22) means that the subspace defined by the limiting core orbitals of the β set and the corresponding core subspace of the α set are the same. By analogy, the term λP_c^α, $\lambda \to \infty$, in equation (23) means that the core subspace of the α orbitals coincides with the corresponding core subspace of the β set. Thus, equations (22) and (23) lead to the identical core subspaces for both sets, i.e., $P_c^\alpha X^{(1)} = P_c^\beta X^{(1)}$, where $X^{(1)}$ is the Hilbert space of one-particle states. Therefore,

$$P_c^\alpha | i^\beta \rangle = P_c^\beta | i^\beta \rangle = 0, \quad P_c^\beta | i^\alpha \rangle = P_c^\alpha | i^\alpha \rangle = 0, \quad i = q+1, q+2, \ldots, q+p,$$

i.e., in our formalism the condition (10) is fulfilled automatically (see also table 4). It is worth noting that the formalism of [10] does not lead automatically to equations (10) and some precautions should be taken to ensure the orthogonality of the open-shell MOs

to the closed-shell orbitals in the course of the iteration procedure. For example, instead of the Fockian for the open shell h^α the operator $(I - P_c)h^\alpha(I - P_c)$ has been used [10].

Each additional term in equations (22), (23) leads to the identical "core" subspace MOs, but only both terms simultaneously lead to a minimum in the total energy (see table 2). In practice, $\lambda \approx 50$–100 has provided the identical "core" subspaces for both sets (see table 4). After solving equations (22), (23) the "core" orbital energies ε_i^β and ε_i^α, $i = 1, 2, \ldots, q$, will be shifted. They should be redefined in the usual way:

$$\varepsilon_i^\alpha = \langle i^\alpha | \mathbf{F}^\alpha | i^\alpha \rangle \quad \text{and} \quad \varepsilon_i^\beta = \langle i^\beta | \mathbf{F}^\beta | i^\beta \rangle.$$

As one can see, the proposed method requires minimal extra calculations and can be easily attached to the standard UHF programs. From a practical point of view, the proposed intermediate scheme is flexible enough. On the one hand, the closed-shell RHF solution can be easily obtained if the orthoprojector P_c^γ is substituted by P^γ, $\gamma = \alpha, \beta$. On the other hand, the value of $\lambda = 0$ leads to the UHF function. It should be also emphasized that equations (22), (23) are cubic with respect to the LCAO coefficients whereas PRHF formalism of [10] leads to the fifth-degree equations (see [10, equations (17), (18)]).

Moreover, equations (22) and (23) allow us to use the well-established spin-projected MP-like PTs [7,8,22], where a zeroth-order Hamiltonian is built as a sum of Fockians:

$$H^{(0)} = \sum_i^{n^\alpha} \mathbf{F}^\alpha(i) + \sum_i^{n^\beta} \mathbf{F}^\beta(i)$$

with

$$\mathbf{F}^\alpha = \sum_k^M |k^\alpha\rangle \varepsilon_k^\alpha \langle k^\alpha|, \qquad \mathbf{F}^\beta = \sum_k^M |k^\beta\rangle \varepsilon_k^\beta \langle k^\beta|.$$

In particular, if we deal with one unrestricted broken orbital pair, then an UMP PT with a single annihilation [8] provides a spin eigenstate of $\mathbf{S}^2$.

4. Illustrative calculations

As mentioned above, the proposed method is general. It can be applied to any molecular system with any basis sets. Basis set truncation is often the dominant source of errors in contemporary molecular structure calculations. At present much progress has been achieved in developing the methods allowing basis set truncation errors to be controlled [26, and references therein]. Certainly, the extended basis sets (e.g., [27]) are preferred to clarify peculiar features of a new method. Nevertheless, comparisons of the different methods against each other in the same small basis set are instructive and can be considered as a preliminary test for the proposed method. Here the model calculations for CH^+ have been carried out to make clear some its features. We used a

Table 1
Non-linear basis parameters for CH^+. $E^{UHF} = -37.362399$ hartrees, $R = 5.0a_0$.

k[a]	α_k	X_k	Y_k	Z_k[c]
1	0.1623957E+03[b]	0	0	−0.4178851E−04
2	0.2439437E+02	0	0	0.1692488E−04
3	0.1817613E+01	0	0	0.4691178E+00
4	0.3843411E+00	0	0	−0.3063808E+00
5	0.2752028E+00	0	0	0.4867170E+01
6	0.3418764E+00	0	0	0.2276131E+00
7	0.5287032E+01	−0.1500000E−01	0	0
8	0.5287032E+01	0.1500000E−01	0	0
9	0.5287032E+01	0	−0.1500000E−01	0
10	0.5287032E+01	0	0.1500000E−01	0

[a] Number of a basis set function.
[b] $0.1623957E+03 = 0.1623957 \times 10^3$.
[c] The frame of reference is connected with the nucleus of C.

basis set consisting of six $1s$ Gaussians located along the molecular axis OZ and one p_x and p_y functions. Each p-function was presented by two $1s$ Gaussians. Non-linear basis parameters (the exponents and centers) were partly optimized by minimizing the UHF energy. The corresponding values are given in table 1. Thus, our results can be easily reproduced. The SCF iterations were continued until an absolute accuracy of 10^{-7} was achieved in the elements of the density matrix.

All calculations were performed at $R = 5a_0$, where the energies of $^1\Sigma^+$ and $^3\Pi$ states are close. The corresponding UHF function contains an approximately equal mixture of these states, $\langle S^2 \rangle = 0.934256$ (see table 3, $\lambda = 0$). In other words, at this geometry we deal with the singlet–triplet instability and the overlap integral $\langle 3^\alpha | 3^\beta \rangle = -0.256952$ (see table 4, $\lambda = 0$) is much smaller than one. In this case spin contaminated UHF solution ($E^{UHF} = -37.362399$ H) becomes variationally preferred to the closed-shell RHF solution ($E^{RHF} = -37.266021$ H).

Table 2 demonstrates the energy results as a function of λ. We examined different versions of obtaining a PRHF function. Version 1 corresponds to the value of $\lambda = 0$ in equation (22) while the value of $\lambda = 0$ in equation (23) leads to version 2. The results of version 3 were computed in accordance with equations (22) and (23) where $\lambda \neq 0$ simultaneously. All versions gave close energies. But as mentioned in section 2, only version 3 leads to a minimum in the total energy. For this version we observed that the greater the value of λ the worse the iterative convergence whereas versions 2 and 3 showed good convergence.

Annihilation of the triplet component in the WF (version 3) gives pure singlet states with the energies E_{proj} presented in column 4 of table 2 (e.g., for $\lambda = 1000$, $E_{proj} = -37.364552$ H). It is useful to note that the E_{proj} energies go below the RHF and UHF solutions. The quantity Δ in this table is the decrease in E_{proj} between successive entries. It allows us to observe the convergence of the proposed method as λ is increased.

Table 2
Energy results (in hartrees) for CH^+ as a function of λ at $R = 5$ a.u.

λ	1[a]	2	3	E_{proj}[b]	Δ[c] (mH)
0	−37.362399	−37.362399	−37.362399	−37.364958	–
10	−37.361585	−37.362124	−37.362149	−37.364611	0.347
50	−37.361390	−37.362012	−37.362106	−37.364566	0.045
100	−37.361356	−37.361989	−37.362099	−37.364558	0.008
500	−37.361325	−37.361968	−37.362093	−37.364553	0.005
1000	−37.361321	−37.361965	−37.362092	−37.364552	0.001

[a] Version 1 means that $\lambda = 0$ in equation (15), version 2: $\lambda = 0$ in equation (16), version 3: $\lambda \neq 0$ for both equations (15) and (16). The first row corresponds to the UHF function.
[b] The value E_{proj} corresponds to the energy of the singlet state $^1\Sigma^+$ with a wave function obtained by annihilation of the triplet component (version 3).
[c] Δ (in millihartrees) is the decrease in the energy E_{proj} between successive entries.

Table 3
Expectation value of $\langle S^2 \rangle$ as a function of λ (a.u.).

λ	1[a]	2	3	$\langle S^2 \rangle$[b]
0	0.934256	0.934256	0.934256	0.000606
10	0.932502	0.934385	0.933656	0.000005
50	0.932329	0.934382	0.933626	0.0
100	0.932305	0.934381	0.933622	0.0
500	0.932289	0.934379	0.933619	0.0
1000	0.932282	0.934379	0.933617	0.0

[a] The numbers 1, 2, 3 mean the same as in table 2.
[b] The value of $\langle S^2 \rangle$ after annihilation for version 3.

Table 4
Overlap matrix elements as a function of λ.

	$\lambda = 0$	$\lambda = 10$	$\lambda = 50$	$\lambda = 100$	$\lambda = 500$
$\langle 1^\alpha \vert 1^\beta \rangle$	0.999997	0.999998	0.999998	0.999998	0.999998
$\langle 2^\alpha \vert 2^\beta \rangle$	0.999529	0.999967	0.999998	0.999998	0.999998
$\langle 3^\alpha \vert 3^\beta \rangle$	−0.256982	−0.257579	−0.257630	−0.257630	−0.257643
$\langle 1^\alpha \vert 3^\beta \rangle$	−0.000052	−0.000011	−0.000003	−0.000002	0.0
$\langle 2^\alpha \vert 3^\beta \rangle$	−0.024679	−0.000800	−0.000164	−0.000082	−0.000016
$\langle 1^\beta \vert 3^\alpha \rangle$	0.000379	0.000122	0.000033	0.000017	0.000004
$\langle 2^\beta \vert 3^\alpha \rangle$	0.005741	0.000007	0.0	0.0	0.0

The expectation values of $\langle S^2 \rangle$ for different versions and $\langle S^2 \rangle$ after annihilating for version 3 are collected in table 3. As one can see, the value of $\lambda \approx 50$–100 and annihilation procedure provide the spin eigenstate. Table 4, where the overlap elements for the version 3 are given, shows that the proposed formalism leads to the same core

subspaces for the α and β sets (see rows 1, 2). The fulfillment of the condition (10) one can see by examining rows 4, 5, 6 and 7 of this table.

Thus, the proposed method involves relatively minor adaptation of existing UHF codes and preliminary calculation results show its performance. A more complete test will be carried out to estimate workability and accuracy of the method.

5. Conclusion

In this work the TOCIA method previously developed by us has been applied to determine the MOs of a single partially restricted Slater determinant. On the one hand, such a function has the freedom of being symmetry broken, on the other hand, it allows one to design a spin eigenfunction in a simple way.

The proposed formalism has some fascinating features:

 (i) There is not any problem connected with off-diagonal Lagrangian multipliers coupling the open and closed shell orbitals.

 (ii) Ambiguity problems in constructing Fock operators and, therefore, a zeroth-order Hamiltonian for a PT do not appear. This is important, because the choice of $H^{(0)}$ is crucial to the success of any PT.

 (iii) Unlike [10] our equations provide the conditions (10) automatically.

 (iv) Equations (22) and (23) are much simpler than the corresponding equations of [10] (cf. [10, equations (17), (18)]). We deal with the cubic equations with respect to LCAO coefficients, whereas PRHF formalism based on the Roothaan coupling method leads to the fifth-degree equations.

 (v) Unlike the known Roothaan-based methodology our UHF formalism is more suitable for use with the conventional PTs in incorporating the correlation effects.

 (vi) Preliminary test calculations show the performance of the method. It requires minimal extra calculations and can be easily attached to the existing standard UHF computer programs.

In conclusion, it is worth noting that the formalism developed here can be useful to construct a scheme for description of the singlet excited states based on a PRHF function.

References

[1] C. Møller and M.S. Plesset, Phys. Rev. 46 (1934) 618.
[2] J.A. Pople, J. Stephen and R. Seeger, Int. J. Quant. Chem. Symp. 10 (1976) 1.
[3] R.J. Bartlett and D.M. Silver, J. Chem. Phys. 62 (1975) 3258.
[4] P.O. Löwdin, Phys. Rev. 97 (1955) 1509.
[5] I. Mayer, Adv. Quant. Chem. 12 (1980) 189.
[6] T. Amos and G.G. Hall, Proc. Roy. Soc. London Ser. A 263 (1961) 483.
[7] P.J. Knowles and N.C. Handy, J. Phys. Chem. 92 (1988) 3097.

[8] H.B. Schlegel, J. Chem. Phys. 84 (1986) 4530.

[9] Y.G. Smeyers and L. Doreste-Suarez, Int. J. Quant. Chem. 7 (1973) 687.

[10] C. Kollmar, J. Chem. Phys. 100 (1994) 3683.

[11] C.C.J. Roothaan, Rev. Mod. Phys. 32 (1960) 179.

[12] S. Huzinaga, J. Chem. Phys. 51 (1961) 3971.

[13] R.D. Amos, J.S. Andrews, N.C. Handy and P.J. Knowles, Chem. Phys. Lett. 185 (1991) 256.

[14] C.W. Murray and N.C. Handy, J. Chem. Phys. 97 (1992) 6509.

[15] T.J. Lee, A.P. Rendel, K.G. Dyal and D. Jayatilaka, J. Chem. Phys. 100 (1994) 7400.

[16] P.M. Kozlowski and E.R. Davidson, J. Chem. Phys. 100 (1994) 3672.

[17] V.N. Glushkov, Chem. Phys. Lett. 273 (1997) 122.

[18] V.N. Glushkov, Chem. Phys. Lett. 287 (1998) 189.

[19] V.N. Glushkov and A.Ya. Tsaune, Opt. Spectrosc. 87 (1999) 249.

[20] V.N. Glushkov and A.Ya. Tsaune, Zh. Vychisl. Mat. Mat. Fiz. 25 (1985) 298.

[21] A.Ya. Tsaune, V.N. Glushkov and A.I. Aprasyukhin, J. Mol. Struct. (Theochem) 312 (1994) 289.

[22] H.B. Schlegel, J. Phys. Chem. 92 (1988) 3075.

[23] N. Gidopoulos, V.N. Glushkov and S. Wilson, Proc. Roy. Soc. London 457 (2001) 1657.

[24] P.E. Gill and W. Murrey, *Numerical Methods for Constrained Optimization* (Academic Press, London/New York/San Francisco, 1974).

[25] A.C. Hurley, *Introduction to the Electron Theory of Small Molecules* (Academic Press, London/New York/San Francisco, 1976).

[26] S. Wilson, Distributed Gaussian basis sets: Some recent results and prospects, in: eds. C.A. Tsipis et al., *New Methods in Quantum Theory* (Kluwer Academic Publishers, Dordrecht, 1996) pp. 437–461.

[27] T.H. Dunning, Jr., J. Chem. Phys. 90 (1989) 1007.