Simplified Non-Empirical Unrestricted Hartree-Fock Approximation (SUHF) for the Calculation of Electronic Ground State Properties of Molecules with Closed and Open Valence Shells. I. Method

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Focusing on relative stabilities of electronic states with different spin multiplicities of polyatomic molecules, a simplified unrestricted Hartree-Fock (SUHF) procedure is described. Using different orbitals for different spins (DODS), electron correlation effects of both closed-shell and open-shell systems are expected to be taken into account in the simplest way. While working within a symmetrically orthogonalized (Löwdin) basis we make use of the NDDO approximation (neglect of diatomic differential overlap) concerning the evaluation of electron repulsion and nuclear attraction integrals. Originally, a locally orthogonalized all-electron atomic orbital set of Slater type is considered. The approximation method is completely non-empirical. Rotational invariance is fully retained.

Key words: Unrestricted Hartree-Fock theory; Symmetrically orthogonalized (Löwdin-)basis; Neglect of diatomic differential overlap; Atomic orbitals of Slater type.

1. Introduction

In order to establish a useful and conceptionally simple approximation for the determination of electronic state energies of medium-size polyatomic molecules, we take the standard Pople-Nesbet formulation of *unrestricted Hartree-Fock* theory (UHF) [1] as starting point. Unrestricted Slater determinants in general do not represent pure spin states (i.e. singlets, doublets, triplets etc.) but contain contaminations from configurations of other symmetries. Nevertheless, UHF theory leads to a better description of electron correlation effects as compared to a corresponding Restricted Hartree-Fock (RHF) solution [2], since the use of *different orbitals for different spins* (DODS) enables the electrons to stay apart from one another in different regions of space [3].

Hence, there is one principal difficulty inherent in Hartree-Fock theory, sometimes called its *symmetry dilemma* [6]:

- Restricted determinants with well-defined spin symmetries lead to increased state energies.
- Use of different orbitals for different spins, on the other hand, yields a better description of the electronic correlation leading to lower state energies. The symmetry properties of the resulting determinants, however, get lost in this case.

Pople-Nesbet UHF theory will serve us as a testing method for some simplifying assumptions to be specified below – mainly for reasons of simplicity and generality [7]:

- It can be regarded as the easiest way of accounting for part of the electronic correlation.
- It allows to deal with open-shell systems.
- Moreover, whenever the number of unpaired electrons of a chemical system is small compared with its total number, electronic spin states tend to be representable by unrestricted determinants as well [8].

2. Basic Equations [4]

Expanding the space-dependent *unrestricted molecular orbitals* ${}^{\phi}\psi_j^{\alpha}(\boldsymbol{r})$ and ${}^{\phi}\psi_j^{\beta}(\boldsymbol{r})$ for α and β spin, respectively, as a linear combination of N_o real *atomic orbitals* $(\{\phi_j | j = 1, 2, \ldots, N_o\}$ localized at N_a atomic

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$$ {}^{\phi}\psi_j^{\alpha}(\boldsymbol{r}) = \sum_{M}^{N_a} \sum_{\mu\in M} {}^{\phi}C_{\mu j}^{\alpha}\,\phi_\mu(\boldsymbol{r}-\boldsymbol{R}_M), \quad j=1,2,\ldots,N_o \tag{1} $$

(where $\boldsymbol{r}=(x, y, z)$, and $\boldsymbol{R}_M$ is the position vector of atom M to which all orbitals with index μ belong (notation: $\mu\in M$); an equivalent formula holds for β spin) one finally obtains from the unrestricted integro differential Hartree-Fock equations [4] the *Pople-Nesbet matrix equations* of the form

$$ {}^{\phi}\mathbf{F}^{\alpha}\,{}^{\phi}\mathbf{C}^{\alpha} = {}^{\phi}\mathbf{S}\,{}^{\phi}\mathbf{C}^{\alpha}\,\mathbf{E}^{\alpha} \quad \text{and} \quad {}^{\phi}\mathbf{F}^{\beta}\,{}^{\phi}\mathbf{C}^{\beta} = {}^{\phi}\mathbf{S}\,{}^{\phi}\mathbf{C}^{\beta}\,\mathbf{E}^{\beta}. \tag{2} $$

The orbital basis will be indicated by a left-side superscript throughout in this paper. $\mathbf{E}^{\alpha}$ and $\mathbf{E}^{\beta}$ are diagonal matrices containing the molecular *orbital energies*, ${}^{\phi}\mathbf{C}^{\alpha}$ and ${}^{\phi}\mathbf{C}^{\beta}$ are the corresponding *coefficient matrices*. Considering real atomic orbitals, elements of the *overlap matrix* ${}^{\phi}\mathbf{S}$ have the form

$$ {}^{\phi}S_{\mu\nu} = \int \mathrm{d}\boldsymbol{r}\,\phi_\mu(\boldsymbol{r}-\boldsymbol{R}_M)\,\phi_\nu(\boldsymbol{r}-\boldsymbol{R}_N), \tag{3} $$
$$ M, N = 1, 2, \ldots, N_a, \quad \mu\in M, \quad \nu\in N. $$

The Fock matrices ${}^{\phi}\mathbf{F}^{\alpha}$ and ${}^{\phi}\mathbf{F}^{\beta}$ consist of one part ${}^{\phi}\mathbf{H}$ for the one-electron interactions and another part ${}^{\phi}\mathbf{G}^{\alpha}$ and ${}^{\phi}\mathbf{G}^{\beta}$, respectively, for the two-electron interactions. For α spin:

$$ {}^{\phi}\mathbf{F}^{\alpha} = {}^{\phi}\mathbf{H} + {}^{\phi}\mathbf{G}^{\alpha}. \tag{4} $$

Elements of the *core-Hamiltonian matrix* ${}^{\phi}\mathbf{H}$ are composed of one *kinetic energy* term ${}^{\phi}\mathbf{K}$ and N_a *nuclear attraction* terms ${}^{\phi}\mathbf{V}(A)$:

$$ {}^{\phi}\mathbf{H} = {}^{\phi}\mathbf{K} + \sum_{A}^{N_a} {}^{\phi}\mathbf{V}(A), \tag{5} $$

where (again for real atomic orbitals)

$$ {}^{\phi}K_{\mu\nu} = -\tfrac{1}{2}\int \mathrm{d}\boldsymbol{r}\,\phi_\mu(\boldsymbol{r}-\boldsymbol{R}_M)\,[\Delta(\boldsymbol{r})\,\phi_\nu(\boldsymbol{r}-\boldsymbol{R}_N)], \qquad M, N = 1, 2, \ldots, N_a, \quad \mu\in M; \quad \nu\in N, \tag{6} $$

$$ {}^{\phi}V_{\mu\nu}(A) = -Z_A\int \mathrm{d}\boldsymbol{r}\,\phi_\mu(\boldsymbol{r}-\boldsymbol{R}_M)\,|\boldsymbol{r}-\boldsymbol{R}_A|^{-1}\,\phi_\nu(\boldsymbol{r}-\boldsymbol{R}_N), \qquad M, N, A = 1, 2, \ldots, N_a, \quad \mu\in M; \quad \nu\in N, \tag{7} $$

with $\Delta(\boldsymbol{r}) = \dfrac{\partial^2}{\partial x^2} + \dfrac{\partial^2}{\partial y^2} + \dfrac{\partial^2}{\partial z^2}$, the Laplacian operator in cartesian coordinates, and Z_A, the atomic number of nucleus A.

The two-electron *repulsion matrix* elements for α spin read

$$ {}^{\phi}G_{\mu\nu}^{\alpha} = \sum_{R,S}^{N_a} \sum_{\substack{\varrho\in R\\ \sigma\in S}} {}^{\phi}P_{\varrho\sigma}^{t}(\phi_\mu\phi_\nu|\phi_\varrho\phi_\sigma) - {}^{\phi}P_{\varrho\sigma}^{\alpha}(\phi_\mu\phi_\varrho|\phi_\nu\phi_\sigma), \qquad M, N = 1, 2, \ldots, N_a, \quad \mu\in M; \quad \nu\in N, \tag{8} $$

where the two-electron *repulsion integrals* over real atomic orbitals are written using the chemists' (11|22) notation:

$$ (\phi_\mu\phi_\nu|\phi_\varrho\phi_\sigma) = \iint \mathrm{d}\boldsymbol{r}_1\,\mathrm{d}\boldsymbol{r}_2\,\phi_\mu(\boldsymbol{r}_1-\boldsymbol{R}_M)\,\phi_\nu(\boldsymbol{r}_1-\boldsymbol{R}_N)\,|\boldsymbol{r}_1-\boldsymbol{r}_2|^{-1}\,\phi_\varrho(\boldsymbol{r}_2-\boldsymbol{R}_R)\,\phi_\sigma(\boldsymbol{r}_2-\boldsymbol{R}_S), \tag{9} $$
$$ M, N, R, S = 1, 2, \ldots, N_a, \quad \mu\in M; \quad \nu\in N; \quad \varrho\in R; \sigma\in S. $$

Since we are interested in lowest Hartree-Fock states with different *spin multiplicities* $\mathcal{M}$ [9], the columns of the coefficient matrices have to be rearranged according to the corresponding orbital energies in ascending order. Then, the *density matrix* for spin α is defined through

$$ {}^{\phi}P_{\varrho\sigma}^{\alpha} = \sum_{a}^{N_\alpha} {}^{\phi}C_{\varrho a}^{\alpha}\,{}^{\phi}C_{\sigma a}^{\alpha}, \tag{10} $$

where N_α is the number of α electrons. If, for convenience, we chose $N_\alpha \geqq N_\beta$, then

$$ N_\alpha = \frac{N_e + \mathcal{M} - 1}{2} \quad \text{and} \quad N_\beta = \frac{N_e - \mathcal{M} + 1}{2}. \tag{11} $$

Here, N_e indicates the total number of electrons [10]. Again, equivalent formulas hold for β spin [11].

The *total density matrix* ${}^{\phi}\mathbf{P}^{t}$ and the *spin density matrix* ${}^{\phi}\mathbf{P}^{s}$ are defined as

$$ {}^{\phi}\mathbf{P}^{t} = {}^{\phi}\mathbf{P}^{\alpha} + {}^{\phi}\mathbf{P}^{\beta}, \tag{12} $$

$$ {}^{\phi}\mathbf{P}^{s} = {}^{\phi}\mathbf{P}^{\alpha} - {}^{\phi}\mathbf{P}^{\beta}. \tag{13} $$

Since both kinds of Fock matrices ${}^{\phi}\mathbf{F}^{\alpha}$ and ${}^{\phi}\mathbf{F}^{\beta}$ depend on both kinds of *coefficient matrices* ${}^{\phi}\mathbf{C}^{\alpha}$ and ${}^{\phi}\mathbf{C}^{\beta}$, the Pople-Nesbet matrix equations have to be solved iteratively by means of a *self-consistent-field* procedure (SCF), starting from two *initial guesses* at the two sets of coefficient matrices or, equivalently, at the corresponding two sets of density matrices (10) [12].

For each iteration of the SCF procedure the Pople-Nesbet equations have to be solved. This mainly involves three steps:

- The orthogonalization of both kinds of Fock matrices by means of a previously determined transformation matrix. Using, for instance, the symmetrical (Löwdin) orthogonalization [4] with the transformation matrix ${}^{\phi}\mathbf{S}^{-\frac{1}{2}}$ having the property

$${}^{\phi}\mathbf{S}^{-\frac{1}{2}}\,{}^{\phi}\mathbf{S}\,{}^{\phi}\mathbf{S}^{-\frac{1}{2}} = {}^{\phi}\mathbf{S}^{-\frac{1}{2}}\,{}^{\phi}\mathbf{S}^{+\frac{1}{2}} = \mathbf{1} = {}^{\lambda}\mathbf{S}, \tag{14}$$

we get for the α-spin Fock matrix of the symmetrically (Löwdin-)orthogonalized (λ-)basis:

$${}^{\lambda}\mathbf{F}^{\alpha} = {}^{\phi}\mathbf{S}^{-\frac{1}{2}}\,{}^{\phi}\mathbf{F}^{\alpha}\,{}^{\phi}\mathbf{S}^{-\frac{1}{2}}. \tag{15}$$

An equivalent formula holds for β spin.
- The diagonalization of both kinds of orthogonalized Fock matrices ${}^{\lambda}\mathbf{F}^{\alpha}$ and ${}^{\lambda}\mathbf{F}^{\beta}$ by means of standard numerical algorithms [13, 14]. For α spin:

$${}^{\lambda}\mathbf{C}^{\alpha\dagger}\,{}^{\lambda}\mathbf{F}^{\alpha}\,{}^{\lambda}\mathbf{C}^{\alpha} = \mathbf{E}^{\alpha}. \tag{16}$$

- The back-transformation of both kinds of orthonormal coefficient matrices ${}^{\lambda}\mathbf{C}^{\alpha}$ and ${}^{\lambda}\mathbf{C}^{\beta}$ obtained in this way into the original non-orthogonal basis. For α spin:

$${}^{\phi}\mathbf{C}^{\alpha} = {}^{\phi}\mathbf{S}^{-\frac{1}{2}}\,{}^{\lambda}\mathbf{C}^{\alpha}. \tag{17}$$

Once the iterative process has converged due to a previously defined criterion [15], all important quantities now can be calculated, namely the *electronic energy*

$$\mathcal{E}_{\mathrm{e}} = \frac{1}{2}\sum_{i,j}^{N_o} {}^{\phi}P^{t}_{ij}\,{}^{\phi}H_{ij} + {}^{\phi}P^{\alpha}_{ij}\,{}^{\phi}F^{\alpha}_{ij} + {}^{\phi}P^{\beta}_{ij}\,{}^{\phi}F^{\beta}_{ij} \tag{18}$$

and, by adding the classical nuclear repulsion $\mathcal{E}_{\mathrm{n}}$, the *total energy*

$$\mathcal{E}_{\mathrm{t}} = \mathcal{E}_{\mathrm{e}} + \mathcal{E}_{\mathrm{n}} = \mathcal{E}_{\mathrm{e}} + \frac{1}{2}\sum_{\substack{A,B\\ B\neq A}}^{N_a} \frac{Z_A Z_B}{|\boldsymbol{R}_A - \boldsymbol{R}_B|}. \tag{19}$$

Atomic populations ${}^{\phi}\varrho^{t}_{M}$ and *atomic charges* ${}^{\phi}q_{M}$ ($M = 1, 2, \ldots, N_{\mathrm{a}}$) can be obtained from a *Mulliken population analysis* through

$${}^{\phi}\varrho^{t}_{M} = \sum_{\mu\in M}\sum_{j}^{N_{\mathrm{o}}} {}^{\phi}P^{t}_{\mu j}\,{}^{\phi}S_{\mu j}, \tag{20}$$

$${}^{\phi}q_{M} = Z_{M} - {}^{\phi}\varrho^{t}_{M}, \quad M = 1, 2, \ldots, N_{\mathrm{a}}.$$

Finally, *atomic spin densities* ${}^{\phi}\varrho^{s}_{M}$ ($M = 1, 2, \ldots, N_{\mathrm{a}}$) can be obtained in an analogous way by substituting ${}^{\phi}P^{t}_{\mu j}$ in (20) by ${}^{\phi}P^{s}_{\mu j}$:

$${}^{\phi}\varrho^{s}_{M} = \sum_{\mu\in M}\sum_{j}^{N_{\mathrm{o}}} {}^{\phi}P^{s}_{\mu j}\,{}^{\phi}S_{\mu j}, \quad M = 1, 2, \ldots, N_{\mathrm{a}}. \tag{21}$$

From the definition (13) of the spin density matrices it is clear that ${}^{\phi}\varrho^{s}_{M}$ of an atom M is positive whenever the spin density for α spin exceeds the β-spin density. In the reversed case, ${}^{\phi}\varrho^{s}_{M}$ is negative.

3. Simplified Integral Evaluation

Constructions of the Fock matrices ${}^{\lambda}\mathbf{F}^{\alpha}$ and ${}^{\lambda}\mathbf{F}^{\beta}$ may be simplified considerably if one applies the following integral simplification scheme (indicated by a superscript s) investigated in a previous paper [16]:

$$(\lambda_{\mu}\lambda_{\nu}|\lambda_{\varrho}\lambda_{\sigma})^{s} := \delta_{MN}\,\delta_{RS}\,(\phi_{\mu}\phi_{\nu}|\phi_{\varrho}\phi_{\sigma}) \tag{22}$$
$$M, N, R, S = 1, 2, \ldots, N_{\mathrm{a}}, \quad \mu\in M;\ \nu\in N;\ \varrho\in R;\ \sigma\in S,$$

and

$${}^{\lambda}V^{s}_{\mu\nu}(A) := \delta_{MN}\,{}^{\phi}V_{\mu\nu}(A), \tag{23}$$
$$M, N, A = 1, 2, \ldots, N_{\mathrm{a}}, \quad \mu\in M;\ \nu\in N.$$

Thus, we make use of the NDDO approximation (*neglect of diatomic differential overlap*) [16] concerning the evaluation of electron repulsion and nuclear attraction integrals. Moreover, the surviving integrals of the symmetrically (Löwdin-)orthogonalized (λ-)basis are identified directly with those over *locally orthogonalized atomic orbitals* (ϕ-basis).

The most appealing features of the proposed simplifications are [16]:

- The number of atomic orbital integrals to be evaluated and to be stored is drastically reduced.
- Since all three-center and four-center integrals are neglected completely, the common use of Gaussian-type basis functions is not obligatory. Atomic orbitals of Slater-type, which are expected to stand for a favorable basis set in molecular orbital calculations, may be considered as well.

Furthermore, the simplification scheme

- is completely non-empirical,
- retains the rotational invariance property [16], and
- is appropriate for the UHF treatment of closed and open shell systems.

4. Simplified Unrestricted Hartree-Fock Procedure (SUHF)

Referring to the integral simplification scheme summarized above, we are now in a position to sketch a conceptionally simple approximate UHF procedure as follows:

We start with the Pople-Nesbet equations for a symmetrically (Löwdin-)orthogonalized basis set (cf. (16)):

$$ {}^{\lambda}\mathbf{F}^{\alpha}\,{}^{\lambda}\mathbf{C}^{\alpha} = {}^{\lambda}\mathbf{C}^{\alpha}\,\mathbf{E}^{\alpha} \quad \text{and} \quad {}^{\lambda}\mathbf{F}^{\beta}\,{}^{\lambda}\mathbf{C}\beta = {}^{\lambda}\mathbf{C}^{\beta}\,\mathbf{E}^{\beta}, \tag{24} $$

where

$$ {}^{\lambda}\mathbf{F}^{\alpha} = {}^{\lambda}\mathbf{H} + {}^{\lambda}\mathbf{G}^{\alpha} = {}^{\lambda}\mathbf{K} + \sum_{A}^{N_a} {}^{\lambda}\mathbf{V}(A) + {}^{\lambda}\mathbf{G}^{\alpha}. \tag{25} $$

Using (22), we obtain quite simple NDDO approximated expressions for the real two-electron repulsion matrix elements in the λ-basis. Distinguishing the two cases of one- and two-center interactions we get for α spin

$$ \begin{aligned} {}^{\lambda}G^{\alpha}_{\mu\nu} := {} & \sum_{R}^{N_a} \sum_{\varrho,\sigma\in R} {}^{\lambda}P^{t}_{\varrho\sigma}(\phi_\mu\phi_\nu|\phi_\varrho\phi_\sigma) \\ & - \sum_{\varrho,\sigma\in M} {}^{\lambda}P^{\alpha}_{\varrho\sigma}(\phi_\mu\phi_\varrho|\phi_\nu\phi_\sigma), \end{aligned} \tag{26} $$

$$ M = 1, 2, \ldots, N_a, \quad \mu, \nu \in M, $$

$$ {}^{\lambda}G^{\alpha}_{\mu\nu} := - \sum_{\substack{\varrho\in M\\ \sigma\in N}} {}^{\lambda}P^{\alpha}_{\varrho\sigma}(\phi_\mu\phi_\varrho|\phi_\nu\phi_\sigma) \tag{27} $$

$$ M, N, = 1, 2, \ldots, N_a;\; M \neq N, \quad \mu\in M; \quad \nu\in N. $$

According to (23), elements of the nuclear repulsion matrices ${}^{\lambda}\mathbf{V}(A)$ will be identified with the corresponding simplified integrals

$$ {}^{\lambda}\mathbf{V}(A) := {}^{\lambda}\mathbf{V}^{s}(A). \tag{28} $$

The kinetic matrix ${}^{\phi}\mathbf{K}$, on the other hand, has to be transformed accurately into the symmetrically orthogonalized basis

$$ {}^{\lambda}\mathbf{K} = {}^{\phi}\mathbf{S}^{-\frac{1}{2}}\,{}^{\phi}\mathbf{K}\,{}^{\phi}\mathbf{S}^{-\frac{1}{2}}. \tag{29} $$

Formulas equivalent to (10), (12), and (13) also hold for the λ-basis. Orthogonalizations of the Fock matrices (cf. (15)) and back-transformations of the coefficient matrices (according to (17)) are inapplicable, since from now on we will employ an orthogonal basis throughout.

Atomic populations ${}^{\lambda}\varrho^{t}_{M}$, atomic charges ${}^{\lambda}q_{M}$, and atomic spin densities ${}^{\lambda}\varrho^{s}_{M}$ $(M = 1, 2, \ldots, N_a)$ in the symmetrically orthogonal basis can be obtained from a *Löwdin population analysis* (cf. [4]) through

$$ {}^{\lambda}\varrho^{t}_{M} = \sum_{\mu\in M} {}^{\lambda}P^{t}_{\mu\mu}, \tag{30} $$

$$ {}^{\lambda}q_{M} = Z_{M} - {}^{\lambda}\varrho^{t}_{M}, \quad M = 1, 2, \ldots, N_a $$

$$ {}^{\lambda}\varrho^{s}_{M} = \sum_{\mu\in M} {}^{\lambda}P^{s}_{\mu\mu}, \qquad M = 1, 2, \ldots, N_a. \tag{31} $$

5. Practical Considerations

The computer implementation of the simplified procedure now can be outlined as follows: There are only few input data defining the chemical system under consideration:

- The number N_a of atoms,
- the electric charge of the molecule (in atomic units), and
- the spin multiplicity $\mathcal{M}$.

For each atom A we have to specify

- the atomic number Z_A,
- the cartesian coordinates x_A, y_A, and z_A (in atomic units), and
- the Slater orbital exponents $\{\zeta_i | j = 1, 2, \ldots, N_o\}$ [19, 20].

  Single-zeta exponents are available either from Slater's rules [19] or Burns' rules [21] for any atomic ground state configuration defining the basis set. We prefer the optimized single-zeta sets of Clementi and Roetti [22] for the atomic ground states of the elements with $2 \leqq Z \leqq 54$.

The total number N_o of orbitals, and the total number N_e of electrons, as well as the nuclear repulsion energy $\mathscr{E}_n$ now can be easily calculated. Furthermore, N_α and N_β are defined through (11).

Integral evaluation and orthogonalization procedures have been described elsewhere [16].

6. Estimation of Expense

Considering a homonuclear molecule where each atom contributes n_o orbitals to the basis set (i.e. $N_o = N_a n_o$), we can try to estimate the computational expense of our simplified approach as follows: Provided that the integral determination part is the *"computational bottleneck"* like in every Hartree-Fock calculation, for instance, we may simply count the number of integrals to be stored. Whenever symmetry considerations are not taken into account, we will have to evaluate

$N_a^2 n_o^2$	overlap integrals,
$N_a^2 n_o^2$	kinetic energy integrals,
$N_a^2 n_o^2$	non-vanishing nuclear attraction integrals, and
$N_a^2 n_o^2 \cdot n_o^2$	non-vanishing repulsion integrals.

All together we need storage capacity for about $N_a^2 n_o^2 [3 + n_o^2]$ integrals. The factor in brackets may be regarded as a measure for the computational expense compared to an equivalent all-electron molecular orbital calculation of Extended-Hückel type, where only $N_a^2 n_o^2$ overlap integrals have to be evaluated. For example, within a minimal basis set, n_o^2 equals 1, 25, or 225, for hydrogen, second period atoms, or first row transition metals, respectively.

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[11] However, assuming $N_\alpha \geqq N_\beta$, the case $N_\beta = 0$ with $\mathbf{P}^\beta = \mathbf{0}$ has to be taken into account (cf. (10)).

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$$\sigma(I) = \left[\frac{1}{N_o^2} \sum_{i,j}^{N_o} {}^{(I)}P_{ij}^t - {}^{(I-1)}P_{ij}^t)^2 \right]^{1/2}$$

is smaller than a predefined threshold value [4, 17], which was closen to be 10^{-6} atomic units (a.u.). Alternatively, the SCF procedure can be repeated until the electronic energy converges to 10^{-6} a.u. [18]. In order to accelerate the SCF convergence, it may be recommendable to average corresponding density matrix elements of subsequent iterations.

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