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Non Self-Consistent Field Theory — A New Approach in Quantum Mechanical Calculations

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An $\boldsymbol{R}^o$-independent electronic repulsion matrix is constructed, replacing the $\boldsymbol{R}^o$-dependent Hamiltonian matrix ($\boldsymbol{R}^o$ is the density matrix). A non-SCF theory is developed to solve the eigenequation without using an iterative procedure. Three methods are proposed to solve for the eigenvectors and eigenvalues. Illustrative calculations are reported comparing the non-SCF and SCF theories. The calculated results are as expected: the ground state energies are nearly unchanged while the orbital energies are nearer to the experimental results. Other physical properties and spectral quantities are also compared. It is found that the ZDO assumption is applicable in the non-SCF theory *if* it is applicable in SCF theory.

Eine $\boldsymbol{R}^o$-unabhängige Elektronenabstoßungsmatrix wird eingeführt, die die $\boldsymbol{R}^o$-abhängige Hamiltonmatrix ersetzt ($\boldsymbol{R}^o$ ist die Dichtematrix). Zur Lösung der Eigenwertgleichung ohne iterative Prozeduren wird eine sog. Nicht-SCF-Theorie aufgestellt. An Beispielen werden die Ergebnisse von SCF- und Nicht-SCF-Rechnungen verglichen; dabei erweisen sich die Energien des Grundzustandes als nahezu unverändert, während die Energien der Orbitale näher bei den experimentellen Werten liegen. Die „zero-differential-overlap"-Näherung ist immer dann in der neuen Theorie anwendbar, *wenn* sie in der SCF-Theorie anwendbar ist.

Une matrice de répulsion électronique indépendante de $\boldsymbol{R}^o$ est construite, remplaçant la matrice hamiltonienne dépendant de $\boldsymbol{R}^o$ ($\boldsymbol{R}^o$ matrice de densité). Une théorie non SCF est développée afin de résoudre l'équation aux valeurs propres sans itérations. Trois méthodes de résolution du problème aux valeurs propres sont proposées. Des calculs illustrent la comparaison entre les théories SCF et non SCF. Les résultats des calculs sont comme prévus: l'énergie de l'état fondamental varie peu alors que les énergies orbitales sont plus proches des résultats expérimentaux. D'autres propriétés physiques ainsi que des grandeurs spectrales sont comparées. On trouve que l'approximation du recouvrement différentiel nul est applicable dans la théorie non SCF *si* elle est applicable dans la théorie SCF.

I. Introduction

The eigenvalue problem has long been the most important topic in quantum mechanics. In molecular calculations, Roothaan's SCF–LCAO method [*1*] seems to be the best known method. However, since the Hamiltonian matrix itself is a function of density matrix $\boldsymbol{R}^o$ (or eigenvector $\boldsymbol{C}^o$), the successive iterations to improve the $\boldsymbol{R}^o$ and thus the Hamiltonian matrix are unavoidable in solving the eigenequation $\boldsymbol{F}\boldsymbol{C}^o = \boldsymbol{S}\boldsymbol{C}^o\boldsymbol{E}^o$. This situation can be improved. Since individual orbitals have no real significance, all physically relevant information being obtained by summation over all occupied orbitals, McWeeny was able to use the so-called density matrix method [*2*] without successively solving the eigenequation. In his method, the density matrix, which determines the behaviour of a system without depending on the form of the individual orbitals, is iterated by the steepest descent method, but successive iteration of the density matrix is still unavoidable. In the present paper, a new electronic repulsion matrix, which is $\boldsymbol{R}^o$-independent, is introduced to replace the $\boldsymbol{R}^o$-dependent Hamiltonian matrix $\boldsymbol{F}(\boldsymbol{R}^o)$, so that the successive solution of the eigenequation can be completely avoided. The construction of this new $\boldsymbol{R}^o$-independent matrix is based on the following arguments:

1. In the variation method, it is well known that, in the LCAO approximation, the more and more basis atomic orbitals used, the lower the energy can be obtained. In other words, the more dummy virtual molecular orbitals introduced, the greater the accuracy achieved. (Note that if there is a $2n$ electron system of n doubly occupied orbitals with m basis atomic orbitals, then the eigenequation always gives m eigenvectors and $(m-n)$ of them are unoccupied dummy orbitals.) Therefore, the dummy unoccupied MO's seem to be important in the variation method.

2. If we define $\boldsymbol{C}^o$ as those n molecular orbitals with lowest energies, and $\boldsymbol{C}^u$ as those $(m-n)$ orbitals of higher energies, then although the virtual MO's $\boldsymbol{C}^u$ do not contain an electron, every electron can arbitrarily be put into any MO, no matter whether it is a $\boldsymbol{C}^o$ or a $\boldsymbol{C}^u$. Consequently, all the energy levels could be minimized but not necessarily restricted to those of lowest energy levels only, provided that all $\boldsymbol{C}^u$ are regarded as dummy orbitals when physically relevant quantities are considered.

3. The introduction of these dummy orbitals $\boldsymbol{C}^u$ does not change the original occupied molecular state. Furthermore, the $\boldsymbol{R}^o$-independent matrix $\boldsymbol{K}$ is obtained from the minimization of $\varepsilon = \sum_{i=1}^{m} \varepsilon_i$, where the ε_i are orbital energies. Such a minimization is simply a procedure of optimization of all the orbitals $\boldsymbol{C}^o$ and $\boldsymbol{C}^u$ but *not* a minimization of a *new* molecular state with all its m orbitals being occupied. This point can easily be found from the difference between ε and the energy of such a new molecular state.

II. Theory

Let us express the n occupied one electron molecular orbitals by the row matrix $\boldsymbol{\phi} = (\phi_1 \phi_2 \ldots \phi_n)$, and the non-orthogonal basis atomic orbitals by the row matrix $\mathscr{S} = (\mathscr{S}_1 \mathscr{S}_2 \cdots \mathscr{S}_m)$, $m \geq n$. Then the LCAO expression of the MO's can be shown by

$$\boldsymbol{\phi} = \mathscr{S}\, \boldsymbol{C}^o \tag{1}$$

where $\boldsymbol{C}^o$ is the $m \times n$ coefficient matrix. Then ROOTHAAN's SCF method solves the eigenequation

$$\boldsymbol{F}\, \boldsymbol{C}^o = \boldsymbol{S}\, \boldsymbol{C}^o\, \boldsymbol{E}^o \tag{2}$$

where

$$\boldsymbol{S} = \mathscr{S}^\dagger\, \mathscr{S}, \; \boldsymbol{F} = \mathscr{S}^\dagger \boldsymbol{f}\, \mathscr{S} = \boldsymbol{H} + \boldsymbol{G}. \tag{3}$$

$\boldsymbol{H}$ is the nuclear field matrix while $\boldsymbol{G}$ is the electronic repulsion matrix; and $\boldsymbol{f}$ is the one electron Hamiltonian operator such that

$$F_{\mu\nu} = H_{\mu\nu} + \sum_{\lambda,\sigma} R^o_{\sigma\lambda} \left[2 \langle \mu\nu \mid \lambda\sigma \rangle - \langle \mu\sigma \mid \lambda\nu \rangle\right] \tag{4}$$

where

$$H_{\mu\nu} = \int \mathscr{S}_\mu^*(1)\left(-\tfrac{1}{2}\nabla_1^2 - \sum_{\varrho} \frac{Z_\varrho^*}{r_{1\varrho}}\right) \mathscr{S}_\nu(1)\, dv(1)$$

$$\langle \mu\nu \,|\, \lambda\sigma \rangle = \int \mathscr{S}_\mu^*(1)\, \mathscr{S}_\nu(1) \frac{1}{r_{12}}\, \mathscr{S}_\lambda^*(2)\, \mathscr{S}_\sigma(2)\, dv(1)\, dv(2)$$

and

$$R_{\lambda\sigma}^o = \sum_{i=1}^{n} C_{\lambda i}^o\, C_{\sigma i}^{o*}$$

is the matrix element of the density matrix

$$\boldsymbol{R}^o = \boldsymbol{C}^o\, \boldsymbol{C}^{o\dagger}\,. \tag{5}$$

Since $\boldsymbol{F}$ is a $\boldsymbol{R}^o$-dependent matrix, a self-consistent process as shown in the following diagram has to be used to solve the eigenequation (2):

$$\begin{tikzcd}\text{guess } \boldsymbol{C}^o \arrow[r] & \boldsymbol{R}^o \arrow[r] & \boldsymbol{F}(\boldsymbol{R}^o) \arrow[r] & \boldsymbol{C}^o\,. \arrow[lll, bend left]\end{tikzcd}$$

However, the $\boldsymbol{R}^o$ dependent matrix $\boldsymbol{F}$ can be replaced by a new $\boldsymbol{R}^o$-independent interelectronic repulsion matrix $\boldsymbol{K}$ so that the successive iterative process is avoided. In order to derive the $\boldsymbol{R}^o$-independent matrix $\boldsymbol{K}$, the row matrix $\boldsymbol{\phi}$ should be extended to have the same length as $\mathscr{S}$, i.e., besides the n occupied MO's, $\boldsymbol{\phi}$ should also consist of the $(m-n)$ virtual unoccupied MO's. In fact, ROOTHAAN's SCF method always produces $(m-n)$ dummy orbitals [*1*]. Consequently,

$$\phi = \mathscr{S}\boldsymbol{C} \tag{6}$$

with

$$\boldsymbol{C} = [\boldsymbol{C}^o \,\vdots\, \boldsymbol{C}^u] \tag{7}$$

where $\boldsymbol{C}^u$ is the $m \times (m-n)$ coefficient matrix for the $(m-n)$ virtual unoccupied MO's. And $\boldsymbol{C}$ is now a $m \times m$ square coefficient matrix. The eigenequation then becomes

$$\boldsymbol{F}\boldsymbol{C} = \boldsymbol{S}\boldsymbol{C}\boldsymbol{E} \tag{8}$$

where $\boldsymbol{F}$ and $\boldsymbol{S}$ have already been defined in Eq. (3), and

$$\boldsymbol{E} = \left[\begin{array}{c:c} \boldsymbol{E}^o & 0 \\ \hdashline 0 & \boldsymbol{E}^u \end{array}\right] \tag{9}$$

where the superscripts o and u designate "occupied" and "virtual unoccupied" respectively. These notations will be used throught this paper.

Now, the condition of orthonormalization requires that:

$$\mathscr{S}' = \mathscr{S}\boldsymbol{A},\ \boldsymbol{C}' = \boldsymbol{A}^{-1}\boldsymbol{C} \tag{10}$$

or

$$\mathscr{S} = \mathscr{S}'\boldsymbol{A}^{-1},\ \boldsymbol{C} = \boldsymbol{A}\,\boldsymbol{C}' \tag{11}$$

where $\boldsymbol{A}$ is a $m \times m$ non-singular matrix; it can be an upper triangular matrix [*3*] (Gram-Schmidt orthogonalization process), a $\boldsymbol{S}^{-1/2}$ matrix [*4*] (Symmetric orthogonalization process), or a matrix product $\boldsymbol{Y}\boldsymbol{D}^{-1/2}$ where $\boldsymbol{Y}$ and $\boldsymbol{D}$ are eigenvector matrix and eigenvalue matrix of $\boldsymbol{S}$ respectively [*5*] (Canonical orthogonalization process). Left multiplication of the eigenequation (8) by $\boldsymbol{A}^\dagger$ then gives

$$\boldsymbol{A}^\dagger\, \boldsymbol{F}\, \boldsymbol{A}\, \boldsymbol{A}^{-1}\, \boldsymbol{C} = \boldsymbol{A}^\dagger\, \boldsymbol{S}\, \boldsymbol{A}\, \boldsymbol{A}^{-1}\, \boldsymbol{C}\, \boldsymbol{E}$$

or

$$\boldsymbol{F}'\,\boldsymbol{C}' = \boldsymbol{S}'\,\boldsymbol{C}'\,\boldsymbol{E} \tag{12}$$

where

$$\boldsymbol{F}' = \boldsymbol{A}^\dagger\,\boldsymbol{F}\,\boldsymbol{A} = \mathcal{S}'^\dagger \boldsymbol{f}\,\mathcal{S}' \tag{13}$$

and

$$\boldsymbol{S}' = \boldsymbol{A}^\dagger\,\boldsymbol{S}\,\boldsymbol{A} = \mathcal{S}'^\dagger\,\mathcal{S}' = 1_m\,. \tag{14}$$

It should be noted that $\boldsymbol{C}'$ is a square coefficient matrix of the orthonormal basic set, and is a *unitary* matrix such that

$$\boldsymbol{C}'\,\boldsymbol{C}'^\dagger = \boldsymbol{C}'^\dagger\,\boldsymbol{C}' = \boldsymbol{l}_m \tag{15}$$

and matrix elements of $\boldsymbol{F}'$ are given by

$$\begin{aligned} F'_{rs} &= H'_{rs} + \sum_{\lambda,\sigma} R^o_{\sigma\lambda}\,[2\,\langle(\boldsymbol{A}_r^\dagger\,\mathcal{S}^\dagger)\,(\mathcal{S}\,\boldsymbol{A}_s)\,|\,\lambda\sigma\rangle - \langle(\boldsymbol{A}_r^\dagger\,\mathcal{S}^\dagger)\,\sigma\,|\,\lambda(\mathcal{S}\,\boldsymbol{A}_s)\rangle] \\ &= H'_{rs} + \sum_{\nu,\mu}\;\sum_{\lambda,\sigma} A_{\nu s}\,A^*_{\mu r}\,R^o_{\sigma\lambda}\,[2\,\langle\mu\nu\,|\,\lambda\sigma\rangle - \langle\mu\sigma\,|\,\lambda\nu\rangle] \end{aligned} \tag{16}$$

where $\boldsymbol{A}_r$ is the r^{th} column of $\boldsymbol{A}$ matrix; λ, σ, μ and ν denote non-orthonormal basis atomic orbitals whereas r, s, t and u denote orthonormal basis atomic orbitals, and $H'_{rs} = \boldsymbol{A}_r^\dagger\,\boldsymbol{H}\,\boldsymbol{A}_s$, where $\boldsymbol{H}$ is the nuclear field matrix of the non-orthonormal basis atomic orbitals.

It is equally valid if all the $\mathcal{S}_\lambda$ and $\mathcal{S}_\sigma$ involved are replaced by $\mathcal{S}'_t$ and $\mathcal{S}'_u$, and also $R^o_{\lambda\sigma}$ be replaced by R^o_{tu} which is defined in terms of the coefficients of the orthonormalized basis set instead of the coefficients of the non-orthonormal basis set.

Left multiplying Eq. (12) by $\boldsymbol{C}'^\dagger$ gives

$$\boldsymbol{C}'^\dagger\,\boldsymbol{F}'\,\boldsymbol{C}' = \boldsymbol{E}\,. \tag{17}$$

With the aid of Eq. (15), the energy sum of the individual one electron molecular orbitals can then be obtained directly from above equations:

$$\begin{aligned} \varepsilon &= \mathrm{Tr}\,\{\boldsymbol{E}\} = \mathrm{Tr}\,\{\boldsymbol{C}'^\dagger\,\boldsymbol{F}'\,\boldsymbol{C}'\} = \mathrm{Tr}\,\{\boldsymbol{F}'\,\boldsymbol{C}'\,\boldsymbol{C}'^\dagger\} = \mathrm{Tr}\,\{\boldsymbol{F}'\} \\ &= \mathrm{Tr}\,\{\boldsymbol{A}^\dagger\,\boldsymbol{H}\,\boldsymbol{A}\} + \sum_{r=1}^{m}\;\sum_{\mu,\nu}\;\sum_{\lambda,\sigma}\; A_{\nu r}\,A^*_{\mu r}\,R^o_{\sigma\lambda}\,[2\,\langle\mu\nu\,|\,\lambda\sigma\rangle - \langle\mu\sigma\,|\,\lambda\nu\rangle] \\ &= \mathrm{Tr}\,\{\boldsymbol{A}^\dagger\,\boldsymbol{H}\,\boldsymbol{A}\} + \mathrm{Tr}\,\{\boldsymbol{R}^o\,\boldsymbol{K}\}\,, \end{aligned} \tag{18}$$

where the matrix elements of $\boldsymbol{K}$ are defined by

$$\begin{aligned} K_{\lambda\sigma} &= \sum_{r} [2\,\langle(\boldsymbol{A}_r^\dagger\,\mathcal{S}^\dagger)\,(\mathcal{S}\,\boldsymbol{A}_r\rangle\,|\,\lambda\sigma\rangle - \langle(\boldsymbol{A}_r^\dagger\,\mathcal{S}^\dagger)\,\sigma\,|\,\lambda\,(\mathcal{S}\,\boldsymbol{A}_r\rangle] \\ &= \sum_{\mu,\nu} T_{\nu\mu}\,[2\,\langle\mu\nu\,|\,\lambda\sigma\rangle - \langle\mu\sigma\,|\,\lambda\nu\rangle] \end{aligned} \tag{19}$$

with

$$T_{\nu\mu} = \sum_{r=1}^{m} A_{\nu r}\,A^*_{\mu r}\,. \tag{20}$$

Since the introduction of the virtual molecular orbitals does not change the nuclear field matrix $\boldsymbol{H}$ and the electronic repulsion matrix $\boldsymbol{G}(\boldsymbol{R}^o)$, and since every electron can arbitrarily be put into any one molecular orbital, no matter whether it is $\boldsymbol{C}^o$ or $\boldsymbol{C}^u$, we could require that all the energy levels are to be minimized not only those of lowest energy levels. Therefore, the minimization of ε is equally valid as the minimization of the ground state energy $\mathrm{Tr}\,[\boldsymbol{R}^o(2\boldsymbol{H}+\boldsymbol{G})]$.

It should be emphasized that since the $\boldsymbol{C}^u$ are only dummy orbitals, their introduction does not change the original occupied molecular state. Furthermore, the minimization of ε is just a procedure for optimizing all the orbital energies of $\boldsymbol{C}^o$ and $\boldsymbol{C}^u$. This is not the minimization of a new molecular state with all its m orbitals occupied; such a molecular state would have the energy

$$2 \sum_{i=1}^{m} \sum_{r,s} C_{ri}^* C_{si} H_{sr} + \sum_{i,j=1}^{m} \sum_{r,s,p,q} C_{si}^* C_{qj}^* C_{ri} C_{pj} \left[2 \langle pq \mid rs\rangle - \langle ps \mid rq\rangle\right]$$

if all $\boldsymbol{C}^o$ and $\boldsymbol{C}^u$ are doubly occupied, or

$$\sum_{i=1}^{m} \sum_{r,s} C_{ri}^* C_{si} H_{sr} + \sum_{i,j=1}^{m} \sum_{r,s,p,q} C_{si}^* C_{qj}^* C_{ri} C_{pj} \left[\langle pq \mid rs\rangle - \langle ps \mid rq\rangle\right]$$

if all $\boldsymbol{C}^o$ and $\boldsymbol{C}^u$ are singly occupied and all the electrons have the same spin. It is obvious that above energies are different from ε, where ε can also be expressed as

$$\varepsilon = \sum_{i=1}^{n} \sum_{r,s} C_{ri}^* C_{si} H_{sr} + \sum_{i=1}^{m} \sum_{j=1}^{n} \sum_{r,s,p,q} C_{si}^* C_{qj}^* C_{ri} C_{pj} \left[2 \langle pq \mid rs\rangle - \langle ps \mid rq\rangle\right].$$

If the variation method in Lagrange multiplier form [6] is applied to minimize the energy sum ε subject to the orthonormality condition

$$\boldsymbol{C}^{o\dagger} \boldsymbol{S} \boldsymbol{C}^o = \boldsymbol{1}_n \tag{21}$$

then

$$\frac{\partial \varepsilon}{\partial C_{pi}^{o*}} - 2 \frac{\partial \operatorname{Tr}\left[(\boldsymbol{C}^{o\dagger} \boldsymbol{S} \boldsymbol{C}^o - \boldsymbol{1}_n)\, \boldsymbol{\varepsilon}_1^o\right]}{\partial C_{pi}^{o*}} = 0\,, \qquad \begin{pmatrix} i = 1, 2 \ldots n \\ p = 1, 2 \ldots m \end{pmatrix} \tag{22}$$

and it follows that

$$(\boldsymbol{K} \boldsymbol{C}^o)_{pi} - (\boldsymbol{S} \boldsymbol{C}^o \boldsymbol{\varepsilon}_2^0)_{pi} = 0$$

where $\boldsymbol{\varepsilon}_1^0$ is the Lagrange multiplier matrix and $\boldsymbol{\varepsilon}_2^0 = 2\boldsymbol{\varepsilon}_1^0$. Therefore, the following new eigenequation is derived:

$$\boldsymbol{K} \boldsymbol{C}^o = \boldsymbol{S} \boldsymbol{C}^o \boldsymbol{\varepsilon}_2^0\,. \tag{23}$$

Although $\boldsymbol{\varepsilon}_2^0$ is not diagonal, a unitary transformation

$$\boldsymbol{C}^o = \boldsymbol{V}^o \boldsymbol{B}^{o\dagger} \text{ or } \boldsymbol{V}^o = \boldsymbol{C}^o \boldsymbol{B}^o \tag{24}$$

where $\boldsymbol{B}^o$ is an $n \times n$ unitary matrix and $\boldsymbol{V}^o$ is the new $(m \times n)$ coefficient matrix after transformation, can always transform $\boldsymbol{\varepsilon}_2^0$ into a diagonal matrix $\boldsymbol{\varepsilon}^o$:
from Eq. (23) we have

$$\boldsymbol{K} \boldsymbol{V}^o \boldsymbol{B}^{o\dagger} = \boldsymbol{S} \boldsymbol{V}^o \boldsymbol{B}^{o\dagger} \boldsymbol{\varepsilon}_2^0$$

right multiplying by $\boldsymbol{B}^o$ gives

$$\boldsymbol{K} \boldsymbol{V}^o = \boldsymbol{S} \boldsymbol{V}^o \boldsymbol{\varepsilon}^o \tag{25}$$

where

$$\boldsymbol{\varepsilon}^o = \boldsymbol{B}^{o\dagger} \boldsymbol{\varepsilon}_2^0 \boldsymbol{B}^o\,.$$

The solution of eigenequation (25) is similar to the solution of eigenequation (2). i.e., first $\boldsymbol{V}^o$ is expanded into $\boldsymbol{V} = [\,\boldsymbol{V}^o \mid \boldsymbol{V}^u]$, and $\boldsymbol{\varepsilon}^o$ into $\boldsymbol{\varepsilon} = \left[\begin{array}{c|c} \boldsymbol{\varepsilon}^o & \boldsymbol{0} \\ \hline \boldsymbol{0} & \boldsymbol{\varepsilon}^u \end{array}\right]$, so that

$$\boldsymbol{K}\,\boldsymbol{V} = \boldsymbol{S}\,\boldsymbol{V}\,\varepsilon$$

and

$$\boldsymbol{K}'\,\boldsymbol{W} = \boldsymbol{S}'\,\boldsymbol{W}\,\varepsilon = \boldsymbol{W}\,\varepsilon \tag{26}$$

where

$$\boldsymbol{W} = \boldsymbol{A}^{-1}\,\boldsymbol{V} \text{ or } \boldsymbol{V} = \boldsymbol{A}\,\boldsymbol{W} \tag{27}$$

and

$$\boldsymbol{K}' = \boldsymbol{A}^{\dagger}\,\boldsymbol{K}\,\boldsymbol{A}\,. \tag{28}$$

Therefore $\boldsymbol{V}$ can be obtained from Eq. (27) after the eigenvector matrix $\boldsymbol{W}$ has been obtained from the diagonalization of $\boldsymbol{K}'$ according to Eq. (26). But since the eigenvalue matrix ε is not equal to the individual orbital energy matrix $\boldsymbol{E}$, the sorting of the energy levels and their corresponding orbitals must be carried out by means of a new sorting programme which is given in the following section. Assume that $\boldsymbol{V}$ can be partitioned into $\boldsymbol{V} = [\boldsymbol{V}^o \,\vdots\, \boldsymbol{V}^u]$ then the density matrix can be expressed in terms of $\boldsymbol{V}^o$ as below:

$$\boldsymbol{R}^o = \boldsymbol{C}^o\,\boldsymbol{C}^{o\dagger} = \boldsymbol{V}^o\,\boldsymbol{B}^{o\dagger}\,\boldsymbol{B}^o\,\boldsymbol{V}^{o\dagger} = \boldsymbol{V}^o\,\boldsymbol{V}^{o\dagger}\,. \tag{29}$$

Besides the invariant property of the density matrix under the unitary transformation (24), it is well known [7] that the single determinant is also invariant, i.e.,

$$\Phi' = \Phi\,\det{}^2(\boldsymbol{B}^o)$$

where Φ' is the single determinant constructed from $\boldsymbol{C}^o$ whereas Φ is constructed from $\boldsymbol{V}^o$.

However, although the $\boldsymbol{C}^o$ and $\boldsymbol{R}^o$ are initially exactly the same as those of ROOTHAAN's method, the minimization of ε causes the difference from the minimization of ground state energy. The differences will be examined in subsequent calculations.

After the density matrix has been obtained, the molecular orbitals and their corresponding eigenvalues can be calculated by one of the following methods:

Method I [8]

$$\boldsymbol{C} = [\boldsymbol{C}^o \,\vdots\, \boldsymbol{C}^u] = \boldsymbol{S}^{-1/2}\,\boldsymbol{Q} = \boldsymbol{S}^{-1/2}\,[\boldsymbol{Q}^o \,\vdots\, \boldsymbol{Q}^u]$$

and

$$\boldsymbol{E} = \boldsymbol{C}^{\dagger}\,\boldsymbol{F}\boldsymbol{C}$$

where $\boldsymbol{Q}$ is the eigenvector matrix of $\varrho = \boldsymbol{S}^{1/2}\,\boldsymbol{R}^o\,\boldsymbol{S}^{1/2}$ i.e.

$$\boldsymbol{Q}^{\dagger}\,\varrho\,\boldsymbol{Q} = \boldsymbol{P} = \left[\begin{array}{c:c} \boldsymbol{1}_n & \boldsymbol{0} \\ \hdashline \boldsymbol{0} & \boldsymbol{0}_{m-n} \end{array}\right]$$

where $\boldsymbol{Q}^o$ corresponds to eigenvalues $\boldsymbol{1}_n$, while $\boldsymbol{Q}^u$ corresponds to $\boldsymbol{0}_{m-n}$. $\boldsymbol{1}_n$ is a unit matrix of order n, $\boldsymbol{0}_{m-n}$ is a $(m-n)$ order null matrix, and $\boldsymbol{0}$ is a null matrix whose order is self evident.

Method II

From the density matrix $\boldsymbol{R}^o = \boldsymbol{V}^o\,\boldsymbol{V}^{o\dagger}$ which we obtained from the $\boldsymbol{K}$ matrix, a Hamiltonian matrix $\boldsymbol{F}$ which is defined by $\boldsymbol{R}^o$ can be constructed, and the molecular orbitals $\boldsymbol{C}$ and their corresponding eigenenergies $\boldsymbol{E}$ can be solved directly from the eigenequation $\boldsymbol{F}\boldsymbol{C} = \boldsymbol{S}\boldsymbol{C}\boldsymbol{E}$. The above eigenequation can be solved easily either by orthonormalization of the basis set such as Löwdin's method [4] following by a diagonalization of the real symmetric matrix or by the so-called Cholesky method [9].

Method III

While $\boldsymbol{C}^o = \boldsymbol{V}^o\boldsymbol{B}^{o\dagger}$ and $\boldsymbol{C}^u = \boldsymbol{V}^u\boldsymbol{B}^{u\dagger}$ are true, $\boldsymbol{B}^o$ and $\boldsymbol{B}^u$ cannot be calculated from

$$\boldsymbol{C}^{o\dagger}\,\boldsymbol{F}\boldsymbol{C}^o = \boldsymbol{E}^o \quad \text{or} \quad \boldsymbol{B}^o\,(\boldsymbol{V}^{o\dagger}\,\boldsymbol{F}\,\boldsymbol{V}^o)\,\boldsymbol{B}^{o\dagger} = \boldsymbol{E}^o$$

and

$$\boldsymbol{C}^{u\dagger}\,\boldsymbol{F}\boldsymbol{C}^u = \boldsymbol{E}^u \quad \text{or} \quad \boldsymbol{B}^u(\boldsymbol{V}^{u\dagger}\,\boldsymbol{F}\,\boldsymbol{V}^u)\,\boldsymbol{B}^{u\dagger} = \boldsymbol{E}^u$$

as demonstrated in the appendix.

However, the following approximation

$$\boldsymbol{C}'' = \boldsymbol{V}\boldsymbol{B} = [\boldsymbol{V}^o \,\vdots\, \boldsymbol{V}^u] \left[\begin{array}{c:c} \boldsymbol{B}^1 & \boldsymbol{B}^3 \\ \hdashline \boldsymbol{B}^2 & \boldsymbol{B}^4 \end{array}\right]$$

converged to the solution of method II.

Thus it appears that

$$\boldsymbol{B}^2, \boldsymbol{B}^3 \cong 0$$

so that

$$\begin{aligned} \boldsymbol{C}'' &= [\boldsymbol{V}^o\boldsymbol{B}^1 + \boldsymbol{V}^u\boldsymbol{B}^2 \,\vdots\, \boldsymbol{V}^o\boldsymbol{B}^3 + \boldsymbol{V}^u\boldsymbol{B}^4] = [\boldsymbol{V}^o\boldsymbol{B}^{o\dagger} \,\vdots\, \boldsymbol{V}^u\boldsymbol{B}^{o\dagger}] \\ &= [\boldsymbol{C}^o \,\vdots\, \boldsymbol{C}^u] = \boldsymbol{C}\,. \end{aligned}$$

Therefore after $\boldsymbol{R}^o = \boldsymbol{V}^o\boldsymbol{V}^{o\dagger}$ is calculated, the eigenvectors and eigenvalues can be solved from

$$\boldsymbol{F}\boldsymbol{C}'' = \boldsymbol{S}\boldsymbol{C}''\boldsymbol{E}$$

where

$$\boldsymbol{C}'' = [\boldsymbol{V}^o \,\vdots\, \boldsymbol{V}^u]\,\boldsymbol{B}$$

i.e., from

$$\boldsymbol{B}^\dagger(\boldsymbol{V}^\dagger\,\boldsymbol{F}\,\boldsymbol{V})\,\boldsymbol{B} = \boldsymbol{E}\,,$$

where $\boldsymbol{B}$ is a unitary matrix and is the eigenvector matrix of the diagonalization of $(\boldsymbol{V}^\dagger\,\boldsymbol{F}\,\boldsymbol{V})$.

III. Comparison of Previous and new Methods of the Eigenvalue Problem

(A) Previous Methods

The general Roothaan-Löwdin [1, 4] scheme is used as the typical example. In fact, all the other semiempirical or empirical methods such as the Pople-Pariser-Parr method or the Extended Hückel method are special cases of this general method. The procedure of calculation can be briefly summarized as below:

1. Guess $\boldsymbol{C}^o$, where $\boldsymbol{C}^o$ is the $m \times n$ coefficient matrix containing all the n occupied molecular orbitals as its columns. From $\boldsymbol{C}^o$ calculate $\boldsymbol{R}^o = \boldsymbol{C}^o\boldsymbol{C}^{o\dagger}$ and $\boldsymbol{F}(\boldsymbol{R}^o)$.
2. Orthonormalize $\mathscr{S}$ into $\mathscr{S}'$ to get the $\boldsymbol{A}$ matrix.

3. Calculate $\boldsymbol{F}'$ from Eq. (13) and diagonalize it to get the unitary eigenmatrix $\boldsymbol{C}'$ and diagonal $\boldsymbol{E}$. Then $\boldsymbol{C} = \boldsymbol{A}\,\boldsymbol{C}'$ can be obtained.

4. Sort the energy levels of $\boldsymbol{E}$ and their corresponding order of columns in $\boldsymbol{C}$. The n lowest energy levels are assigned as occupied molecular orbitals.

5. When $\boldsymbol{C}^o$ has been sorted out from $\boldsymbol{C}$, then the new $\boldsymbol{R}^o$ and thus the new $\boldsymbol{F}'$ can be calculated.

6. Diagonalize the new $\boldsymbol{F}'$. Repeat the iteration procedure until the self-consistency is reached.

(B) The New Method

The calculation procedure of the non-SCF theory can be summarized as below:

1. Orthonormalize $\mathscr{S}$ into $\mathscr{S}'$ to get the $\boldsymbol{A}$ matrix.

2. From $\boldsymbol{A}$ calculate $\boldsymbol{K}(\boldsymbol{A})$ and then $\boldsymbol{K}'$.

3. Diagonalize $\boldsymbol{K}'$ to get the unitary eigenmatrix $\boldsymbol{W}$ according to Eq. (26). Then $\boldsymbol{V} = \boldsymbol{A}\,\boldsymbol{W}$ can be obtained.

4. A sorting program as briefly described below is then used to sort the energy levels in $\boldsymbol{E}$ and their corresponding columns in $\boldsymbol{V}$ so that $\boldsymbol{V}$ can be partitioned into $\boldsymbol{V} = [\boldsymbol{V}^o \,\vdots\, \boldsymbol{V}^u]$.

5. The density matrix $\boldsymbol{R}^o$ and the energy sum of individual occupied molecular orbitals or the ground state energy $\mathrm{Tr}[\boldsymbol{R}^o(2\boldsymbol{H} + \boldsymbol{G})]$ are by products of the sorting programme.

6. After $\boldsymbol{R}^o$ is obtained, the eigenvectors and eigenvalues can be solved from either one of the three methods proposed above.

(C) Comparison of the Two Methods

1. In previous methods, one orthonormalization of the basic set, and one diagonalization of $\boldsymbol{F}'$ for empirical methods such as the extended Hückel method were required and additionally one diagonalization for diagonalizing the new $\boldsymbol{F}'$ from every additional iteration, for semiempirical methods such as the Pople-Pariser-Parr method [*8*] and theoretical methods such as ROOTHAAN's method [*1*]. The number of sortings of the energy levels, and their corresponding eigenvectors, is equal to the number of diagonalizations of $\boldsymbol{F}'$. In the new method, only one orthonormalization of the basic set, two diagonalizations and two sorting procedures to sort the occupied and unoccupied molecular orbitals are required no matter if it is applied to semiempirical, or theoretical methods. Much computer time is therefore saved. The difficulty in choosing the initial $\boldsymbol{C}^o$ is also avoided.

2. The new method is a direct solution of the eigenequation, whereas the earlier methods were iterative approximations, except the empirical method. The price of removing the iterative procedure in the empirical method is the necessity of guessing crude approximations to the Hamiltonian matrix. It is now possible to remove completely the iterative procedure without appeal to the use of empirical parameters to approximate the Hamiltonian matrix.

(D) Sorting Procedure

In the non-SCF theory, partitioning $\boldsymbol{V}$ into $[\boldsymbol{V}^o \,\vdots\, \boldsymbol{V}^u]$ is an important step in obtaining the correct $\boldsymbol{R}^o$, and thus the correct occupied molecular orbitals. It is therefore necessary to develop a sorting procedure so that the n occupied eigenvectors $\boldsymbol{C}^o$ can be constructed from a suitable choice of n columns of $\boldsymbol{V}$. The criterion of this sorting procedure is either to use the energy sum of individual occupied molecular orbitals $\mathrm{Tr}\,\boldsymbol{E}^o = \mathrm{Tr}(\boldsymbol{R}^o\boldsymbol{F})$, or the ground state energy $\varepsilon = \mathrm{Tr}\,\boldsymbol{R}^o\boldsymbol{f}$, where $\boldsymbol{f} = 2\boldsymbol{H} + \boldsymbol{G}$.

The sorting procedure can be summarized as below:

1. Consider $[V_1\, V_2 \cdots V_{n-1}]\, V_n \cdots V_m$, with the bracket containing the (n–1) columns initially assumed to be part of $\boldsymbol{V}^o$. Compare the energy values $\varepsilon = \mathrm{Tr}[\boldsymbol{V}^o\boldsymbol{V}^{o\dagger}\,(2\boldsymbol{H}+\boldsymbol{G})]$ of the $(m - n + 1)$ combinations which are constructed from the $(n - 1)$ columns in the bracket and one each of the columns from V_n to V_m in turn. If one of these combinations $V_i (n \leq i \leq m)$ has the lowest energy value ε, this V_i will be assigned to V_1, and V_1 exchanged into V_i.
2. Consider the *new* $[V_1\, V_2 \cdots V_{n-1}]\, V_n \cdots V_m$, and find another $V_i (n \leq i \leq m)$ whose combination possess the lowest ε among all the $(m - n + 1)$ combinations. This time V_i is assigned to be V_2, and V_2 is exchanged into V_i.
3. Repetition of the exchanging procedure, each time produces one column of $\boldsymbol{V}^o$. Therefore, after n times, the n columns of $\boldsymbol{V}^o$ can be assigned.
4. After $\boldsymbol{V}^o$ is obtained, $\boldsymbol{R}^o = \boldsymbol{V}^o\boldsymbol{V}^{o\dagger}$ is also obtained; and the final lowest ε value is the ground state energy of the system of method I.

IV. Illustrative Examples

One would expect that the minimization of ε instead of the minimization of ground state energy would produce different values of $\boldsymbol{R}^o$ despite that the ε and $\boldsymbol{R}^o$ are originally those in ROOTHAAN's SCF method. It is therefore necessary to examine the non-SCF theory by comparing the results of some practical calculations with the results of SCF theory. In this paper trans- and cis-butadiene are calculated by SCF method and the three non-SCF methods as reported in this text. In these test cases, only the π electrons are considered.

The cis- and trans-isomeric forms of 1,3-butadiene have been reported by ASTON et al. [*12*]. The geometry of the carbon skeletons $C_a - C_b - C_c - C_d$ according to SCHOMAKER and PAULING [*13*] is: skeleton planar, $C_a - C_b - C_c$ and $C_b - C_c - C_d$ angles 124°, $C_a - C_b$ and $C_c - C_d$ distances 1.35 Å, $C_b - C_c$ distance 1.46 Å.

The purpose of the calculation is to compare the results of the SCF theory and the non-SCF theory, therefore only the ground state and the lowest mono-excited states are considered, and no configuration interaction is considered. Furthermore, since the general atomic orbitals are used to construct the initial $\boldsymbol{C}^o$, no symmetric restriction has been used to construct the symmetric orbitals before the calculation, only a 4 × 4 secular equation is being solved rather than two 2 × 2 secular equations. The construction of the Hamiltonian is based on the GOEPPERT-MAYER and SKLAR approach [*14*] with the hydrogen atoms neglected:

$$F_{\mu\nu} = H_{\mu\nu} + \sum_{\lambda,\sigma} R^o_{\sigma\lambda}\,[2\,\langle\mu\nu \mid \lambda\sigma\rangle - \langle\mu\sigma \mid \lambda\nu\rangle]$$

where

$$H_{\mu\nu} = W_{2p} - \sum_{\substack{\lambda=1\\ \lambda\neq\nu}}^{4} [\langle\lambda : \mu\nu\rangle + \langle\mu\nu \mid \lambda\lambda\rangle]$$

and W_{2p} is the energy of a $2p$-electron in a carbon atom in its tetravalent valence state. All the required numerical values of the above integrals have been reported by PARR and MULLIKEN [*15*], using the formulas of CRAWFORD and PARR [*16*].

In the SCF calculation, Hückel's molecular orbitals are chosen as the initial $\boldsymbol{C}^o$. The quantity which is used for testing the self-consistency is due to MECKLER [*17*]:

$$\mathrm{Tr}(\boldsymbol{R}^{o\prime} - \boldsymbol{R}^o)^2$$

where $\boldsymbol{R}^o$ is the input density matrix and $\boldsymbol{R}^{o\prime}$ is the output density matrix.

In the non-SCF calculation, the $\boldsymbol{K}$ matrix is defined by

$$K_{\lambda\sigma} = \sum_{r=1}^{4} \sum_{\mu,\nu=1}^{4} A_{\nu r} A_{\mu r} \left[2 \langle \mu\nu \mid \lambda\sigma \rangle - \langle \mu\sigma \mid \lambda\nu \rangle\right]$$

where $A_{\nu r}$ is the matrix element of $\boldsymbol{S}^{-1/2}$.

In the calculation of excitation energies, configurations of mono-excited states belonging to the same symmetry have not been mixed. The energy differences between ground state and singlet or triplet mono-excited states are calculated from

$$E(N \to V_{ij}) = E(V_{ij}) - E_N = \varepsilon_j - \varepsilon_i - J_{ij} + K_{ij}$$

and

$$E(N \to T_{ij}) = E(T_{ij}) - E_N = \varepsilon_j - \varepsilon_i - J_{ij}$$

where ε_i is i-th orbital energy, and J_{ij}, K_{ij} are the "Coulomb" and "Exchange" integrals respectively.

The oscillator strength f and transition moment eQ of a specified excitation are defined by [*18*]

$$f = 8.75164 \times 10^{-2}\, \omega\, Q^2$$

where $\omega =$ transition frequency in unit of eV, while the transition moment is given by

$$Q^2 = Q_x^2 + Q_y^2 + Q_z^2$$

with

$$Q_i = \int \Phi_k^* \, \boldsymbol{i} \, \Phi_l \, d\tau, \; (i = x, y, z)$$

where $\boldsymbol{i}$ is the algebraic sum of the i's for the two electrons.

The ionization potential and the electron affinity are given by [*1, 19, 20*], respectively,

$$I = -\,\varepsilon_2 = -\int \phi_2 \boldsymbol{f} \phi_2 \, d\tau$$

and

$$A = -\,\varepsilon_3 = -\int \phi_3 \boldsymbol{f} \phi_3 \, d\tau \, .$$

The bond lengths R_{ab} are calculated according to COULSON'S formula [*21*]:

$$R_{ab} = S - \frac{s-d}{1 + 0.506\,(1 - P_{ab})/P_{ab}}$$

where s is the natural bond length of single bond, d is the natural bond length of double bond, and P_{ab} is the mobile bond order defined by

$$P_{ab} = 2 \sum_{i=1}^{2} C_{ai}\, C_{bi} \, .$$

Table 1. *Comparison of* NNDO *Results of Trans-butadiene*[a]

	Non-SCF Methods			SCF Method	Obs.
	I	II	III		
$E_N = E_e + E_n^b$	−70.1484	−85.3819	−85.3819	−85.5270	
ε_1	—	−11.7188	−11.7188	−10.3781	
$\varepsilon_2 = -I$	—	− 8.9301	− 8.9301	− 7.0342	−9.0[c]
$\varepsilon_3 = -A$	—	− 2.2953	− 2.2953	− 1.3951	
ε_4	—	0.1807	0.1807	2.0442	
R_{ab}	1.4538	1.3678	1.3678	1.3715	1.34[d]
R_{bc}	1.5251	1.5060	1.5060	1.4727	1.48[d]
$f(N \rightarrow V_{14})$	—	0.3725	0.3725	0.3194	
$f(N \rightarrow V_{23})$	—	1.1574	1.1574	1.3157	0.53[e]
$\Delta E(N \rightarrow V_{23})$	—	6.4001	6.4001	5.9375	6.0[f]
$\Delta E(N \rightarrow V_{24})$	—	6.8034	6.8043	6.3683	7.2[f]
$E_N(\text{cis}) - E_N(\text{trans})$	0.5101	0.3356	0.3356	0.1133	~0.1[g]

[a] Energies and lengths have units eV and Å respectively.

[b] E_e is electronic energy while E_n is the nuclear energy.

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Table 2. *Comparison* of NNDO *Results of Cis-butadiene*

	Non-SCF Methods			SCF Method
	I	II	III	
$E_N = E_e + E_n$	−69.6383	−85.0463	−85.0463	−85.4137
ε_1	—	−11.4986	−11.4986	−10.4318
ε_2	—	− 8.3723	− 8.3723	− 6.9379
ε_3	—	− 1.9210	− 1.9210	− 1.3176
ε_4	—	0.5446	0.5446	2.1211
R_{ab}	1.4416	1.3688	1.3688	1.3709
R_{bc}	1.5220	1.5169	1.5169	1.4757
$f(N \rightarrow V_{14})$	—	0.0080	0.0080	0.0020
$f(N \rightarrow V_{23})$	—	0.4816	0.4817	0.6259
$f(N \rightarrow V_{13})$	—	0.3751	0.3751	0.3876
$f(N \rightarrow V_{24})$	—	0.4006	0.4005	0.3491
$\Delta E(N \rightarrow V_{23})$	—	5.8583	5.8583	5.6689
$\Delta E(N \rightarrow V_{24})$	—	6.7509	6.7507	6.4393

The calculated NNDO (no neglect of differential overlap) results are summarized in Tabs. 1 and 2. All the non-SCF methods give nearly the same or better results than the SCF method, except method I.

V. Validity of Zero Differential Overlap in Non-SCF Theory

The assumption of zero differential overlap (ZDO) by Pople and Pariser and Parr can be expressed as

$$\begin{aligned}
&\langle \nu \mid \mu \rangle = \delta_{\mu\nu} \\
&\langle \nu \mid H^{core} \mid \mu \rangle \neq 0 \quad \text{if } \nu = \mu \pm 1 \\
&\langle \nu \mid H^{core} \mid \mu \rangle = 0 \quad \text{if } \nu = \mu \pm n,\, n > 1 \\
&\langle \nu\mu \mid \lambda\sigma \rangle = \langle \nu\nu \mid \lambda\lambda \rangle\, \delta_{\nu\mu}\, \delta_{\lambda\sigma}\,.
\end{aligned} \tag{30}$$

It has been shown that the above assumptions are reasonable if orthonormalized atomic orbitals (OAO) [*22*] are used, [*23*]; Then the ZDO assumption can be expressed as

$$\begin{aligned}
&\langle \nu' \mid \mu' \rangle = \sum_{\nu,\mu=1}^{m} A_{\nu\nu'}\, A_{\mu\mu'}\, \langle \nu \mid \mu \rangle = \delta_{\nu'\mu'} \\
&\langle \nu' \mid H^{core} \mid \mu' \rangle = \sum_{\nu,\mu=1}^{m} A_{\nu\nu'}\, A_{\mu\mu'}\, \langle \nu \mid H^{core} \mid \mu \rangle \neq 0 \quad \text{if } \nu' = \mu' \pm 1 \\
&\langle \nu' \mid H^{core} \mid \mu' \rangle = \sum_{\nu,\mu=1}^{m} A_{\nu\nu'}\, A_{\mu\mu'}\, \langle \nu \mid H^{core} \mid \mu \rangle = 0 \quad \text{if } \nu' = \mu' \pm n,\, n > 1 \\
&\langle \nu'\mu' \mid \lambda'\sigma' \rangle = \sum_{\mu,\nu,\lambda,\sigma=1}^{m} A_{\nu\nu'}\, A_{\mu\mu'}\, A_{\lambda\lambda'}\, A_{\sigma\sigma'}\, \langle \nu\mu \mid \lambda\sigma \rangle\, \delta_{\nu'\mu'}\, \delta_{\lambda'\sigma'}
\end{aligned} \tag{31}$$

where ν', μ', λ' and σ' are OAO's while ν, μ, λ and σ are ordinary AO's, and $\boldsymbol{A}$ is the matrix as defined in Eq. (10).

Since there is no point in using the ZDO assumption if all the $\langle \nu\mu \mid \lambda\sigma \rangle$ integrals are known, and since the purpose of this section is simply to compare the results of SCF theory and non-SCF theory, the assumption

$$\langle \nu\mu \mid \lambda\sigma \rangle = \langle \nu\nu \mid \lambda\lambda \rangle\, \delta_{\nu\mu}\, \delta_{\lambda\sigma} \tag{32}$$

will be used in which $\langle \nu\mu \mid \lambda\sigma \rangle$ is the only integral required in the $\boldsymbol{K}$ matrix, and the matrix elements of $\boldsymbol{K}$ then become

$$\begin{aligned}
K_{\lambda\sigma} &= -\, T_{\lambda\sigma}\, \langle \sigma\sigma \mid \lambda\lambda \rangle \\
K_{\lambda\lambda} &= T_{\lambda\lambda}\, \langle \lambda\lambda \mid \lambda\lambda \rangle + 2 \sum_{\substack{\sigma=1 \\ (\sigma\neq\lambda)}}^{m} T_{\sigma\sigma}\, \langle \lambda\lambda \mid \sigma\sigma \rangle\,.
\end{aligned} \tag{33}$$

In fact,

$$\langle \nu'\mu' \mid \lambda'\sigma' \rangle = \langle \nu'\nu' \mid \lambda'\lambda' \rangle \delta_{\nu'\mu'}\, \delta_{\lambda'\sigma'} \tag{34}$$

Table 3. *Comparison of* KNDO *Results of Trans-butadiene*

	Non-SCF Methods			SCF Method	Obs.
	I	II	III		
$E_N = E_e + E_n$	−50.5496	−104.0560	−104.0560	−104.0560	
ε_1	—	− 21.8561	− 21.8561	− 21.5472	
$\varepsilon_2 = -I$	—	− 14.9243	− 14.9243	− 14.5143	−9.0
$\varepsilon_3 = -A$	—	− 1.6351	− 1.6351	− 1.0317	
ε_4	—	9.2748	9.2748	10.0086	
R_{ab}	1.3777	1.3729	1.3729	1.3729	1.34
R_{bc}	1.4710	1.4650	1.4650	1.4651	1.48
$f(N \to V_{14})$	—	0.7545	0.7545	0.7652	
$f(N \to V_{23})$	—	3.1871	3.1870	3.2290	0.53
$\Delta E(N \to V_{23})$	—	13.6796	13.6795	13.8672	6.0
$\Delta E(N \to V_{24})$	—	21.4578	21.4578	21.7941	7.2
E_N(cis)−E_N(trans)	0.2037	− 0.1612	− 0.1612	− 0.1627	~0.1

Table 4. *Comparison of* KNDO *Results of Cis-butadiene*

	Non-SCF Methods			SCF Method
	I	II	III	
$E_N = E_e + E_n$	−50.3459	−104.2172	−104.2172	− 104.2187
ε_1	—	− 21.9826	− 21.9826	− 21.7349
ε_2	—	− 14.8367	− 14.8367	− 14.5799
ε_3	—	− 1.5588	− 1.5588	− 1.1915
ε_4	—	9.8271	9.8271	10.4103
R_{ab}	1.3756	1.3718	1.3718	1.3719
R_{bc}	1.4723	1.4696	1.4696	1.4693
$f(N \rightarrow V_{14})$	—	0.0130	0.0130	0.0133
$f(N \rightarrow V_{23})$	—	1.5444	1.5444	1.5605
$f(N \rightarrow V_{24})$	—	1.1517	1.1517	1.1593
$f(N \rightarrow V_{13})$	—	0.9316	0.9316	0.9455
$\Delta E(N \rightarrow V_{23})$	—	13.3312	13.3312	13.4600
$\nabla E(N \rightarrow V_{24})$	—	21.8927	21.8927	22.1704

should be used instead of Eq. (32) in the *actual calculation*, and all the λ and σ in Eq. (33) should be replaced by λ' and σ' respectively.

Similarly, in the test cases, only the assumption of Eq. (32) is used in the SCF calculation rather than using the whole set of ZDO assumptions of Eq. (31).

The calculated KNDO ($\boldsymbol{K}$ matrix neglect the differential overlap) results are summarized in Tabs. 3 and 4. Although the results are not good because (32) was used instead of (34), the results of non-SCF methods are nearly the same as those of SCF method except in method I, therefore it can be expected that if the ZDO assumption is applicable to the SCF method, it is also applicable to the non-SCF method, provided that orthonormalized basis orbitals are used.

VI. Discussion

From the calculated results it can be seen that the non-SCF methods II and III give nearly the same ground state energy as the SCF method, *and* produce *more* reasonable orbital energies. The other physical properties and spectral quantities are all in reasonable ranges as well as the SCF method. However, non-SCF method I gives worse results, possibly because the eigenvectors in method I should satisfy not only the orthonormality condition but also the eigenequation (2), but since $\boldsymbol{F}$ does not commute with $\boldsymbol{K}$, this is not true for $\boldsymbol{V}^o$. Method I is therefore applicable to SCF method (such as McWeeny's density method) only, and should not be used in the non-SCF theory unless we are sure that $\boldsymbol{V}^o$ is also an eigenvector of $\boldsymbol{F}$.

The advantage of using the non-SCF methods instead of SCF method is obvious, not only does it save computation time, but it also avoids the difficulty of guessing the initial input orbitals which may cause serious trouble of convergency.

A direct extention of the non-SCF theory to the open shell system seems quite difficult, because the coupled matrix in open shell Hamiltonian matrix cannot be resorted into a $\boldsymbol{C}$-independent matrix. However, approximate solution similar to the closed shell system seems possible. Since the non-SCF methods are based on the optimization of all orbitals including C^o and C^u, and produce better orbital energies, the results also agree well with the closed shell SCF theory which is based on the minimization of closed shell orbitals only, it is expected that the above non-SCF methods may also predict well the non-closed shell states by distributing all the electrons in suitable orbitals. In doing this, a more complicate sorting programme must be used to construct the required different density matrices of closed shell and non-closed shell from the $\boldsymbol{V}$ coefficient matrix.

Finally, a few words on the application of ZDO assumption should be noted. Since the purely theoretical evaluation of the three and four center integrals is a difficult and time consuming job, no matter if it is applied to Gaussian basis set [*25*] or Slater basis set [*26*], for an approximate but practical point of view the validity of ZDO assumption should be noted. Although the calculated results in using ZDO of non-orthogonal basis set for SCF and non-SCF methods are not good, they give nearly the same results. It is therefore clear that if ZDO assumption is applicable to SCF theory, it is also applicable to non-SCF theory under the same condition.

Appendix

Theorem 1

If $\boldsymbol{C}$ is a $m \times m$ square coefficient matrix which satisfies eigenequation (A1)

$$\boldsymbol{F}\boldsymbol{C} = \boldsymbol{S}\boldsymbol{C}\boldsymbol{E} \tag{A1}$$

where $\boldsymbol{S}$ is a non-singular positive definite overlap matrix, then the density matrix $\boldsymbol{R} = \boldsymbol{C}\boldsymbol{C}^\dagger$ is the inverse of $\boldsymbol{S}$.

[Proof]

Subjecting to the symmetry orthonormalization

$$\boldsymbol{C}' = \boldsymbol{S}^{1/2}\boldsymbol{C}$$

to transform Eq. (A1) into

$$(\boldsymbol{S}^{-1/2}\boldsymbol{F}\boldsymbol{S}^{-1/2})\boldsymbol{C}' = \boldsymbol{C}'\boldsymbol{E} \tag{A2}$$

we have

$$\boldsymbol{R} = \boldsymbol{C}\boldsymbol{C}^\dagger = \boldsymbol{S}^{-1/2}\boldsymbol{C}'\boldsymbol{C}'^\dagger\boldsymbol{S}^{-1/2} = \boldsymbol{S}^{-1/2}\boldsymbol{S}^{-1/2} = \boldsymbol{S}^{-1}.$$

Therefore the theorem is proved.

Theorem 2

If $\boldsymbol{C}$ is a $m \times m$ square coefficient matrix and satisfies Eq. (A1), then $\boldsymbol{C}$ also satisfies Eq. (A3); furthermore, the reverse is also true.

$$\boldsymbol{C}^\dagger\boldsymbol{F}\boldsymbol{C} = \boldsymbol{E}. \tag{A3}$$

[Proof]

Left multiply Eq. (A1) by $\boldsymbol{C}^\dagger$ and use the orthonormality condition $\boldsymbol{C}^\dagger\boldsymbol{S}\boldsymbol{C} = \boldsymbol{1}$, then we obtain Eq. (A3). Therefore the condition that $\boldsymbol{C}$ satisfies Eq. (A3) is proved. Now, let us left multiply Eq. (A3) by $\boldsymbol{S}\boldsymbol{C}$, we have

$$\boldsymbol{S}\boldsymbol{C}\boldsymbol{C}^\dagger\boldsymbol{F}\boldsymbol{C} = \boldsymbol{S}\boldsymbol{C}\boldsymbol{E}.$$

Since from theorem 1 we know $\boldsymbol{S}\boldsymbol{C}\boldsymbol{C}^\dagger = \boldsymbol{1}$ if $\boldsymbol{S}$ is non-singular, therefore we have also proved that if $\boldsymbol{C}$ satisfies Eq. (A3) then it also satisfies Eq. (A1).

Theorem 3

If $\boldsymbol{C}^o$ is a $m \times n$ rectangular coefficient matrix which represents the occupied MO's, then if $\boldsymbol{C}^o$ satisfies

$$\boldsymbol{F}\boldsymbol{C}^o = \boldsymbol{S}\boldsymbol{C}^o\boldsymbol{E}^o \tag{A4}$$

it will also satisfy Eq. (A5)

$$\boldsymbol{C}^{o\dagger}\boldsymbol{F}\boldsymbol{C}^o = \boldsymbol{E}^o\,. \tag{A5}$$

But the reverse is not true.

[Proof]

The proof of the first part is the same as theorem 2. Now let us prove that a coefficient matrix $\boldsymbol{C}^o$ which satisfies Eq. (A5) does not necessarily satisfy Eq. (A4). Left multiply Eq. (A5) by $\boldsymbol{S}\boldsymbol{C}^o$ then

$$\boldsymbol{S}\boldsymbol{C}^o\boldsymbol{C}^{o\dagger}\boldsymbol{F}\boldsymbol{C}^o = \boldsymbol{S}\boldsymbol{C}^o\boldsymbol{E}^o$$

or

$$\boldsymbol{S}\boldsymbol{R}^o\boldsymbol{F}\boldsymbol{C}^o = \boldsymbol{S}\boldsymbol{C}^o\boldsymbol{E}^o\,. \tag{A6}$$

Since from theorem 1, we know

$$\boldsymbol{S}\boldsymbol{R} = \boldsymbol{S}(\boldsymbol{R}^o + \boldsymbol{R}^u) = 1$$

hence

$$\boldsymbol{S}\boldsymbol{R}^o = 1 - \boldsymbol{S}\boldsymbol{R}^u \neq 1$$

where

$$\boldsymbol{R}^o = \boldsymbol{C}^o\boldsymbol{C}^{o\dagger} \text{ and } \boldsymbol{R}^u = \boldsymbol{C}^u\boldsymbol{C}^{u\dagger}\,.$$

Therefore Eq. (A6) is not the same as Eq. (A4). Consequently, we have proved that the $\boldsymbol{C}^o$ which satisfies Eq. (A5) will also satisfy Eq. (A6) but not (A4).

The important utility of this theorem is that if we know $\boldsymbol{C}^o = \boldsymbol{V}^o\boldsymbol{B}^o$, where $\boldsymbol{V}^o$ is of the same size as $\boldsymbol{C}^o$, and $\boldsymbol{B}^o$ is a $n \times n$ unitary matrix, then the $\boldsymbol{B}^o$ (and hence the $\boldsymbol{C}^o$) which is obtained from the diagonalization

$$\boldsymbol{B}^{o+}(\boldsymbol{V}^o\boldsymbol{F}\boldsymbol{V}^o)\boldsymbol{B}^o = \boldsymbol{E}^o$$

is not consistent with Eq. (A4).

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