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An Iterative Process to Calculate the SCF Open Shell Orbitals

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A method is described for calculating SCF open shell orbitals. In comparison with the coupling operator method, a greater velocity of convergency of the iterative process is obtained by taking into account not only the correct variational conditions, but also the best variations of orbitals step by step.

Key words: Open shells – Coupling operators

The problem of the determination of the SCF open shell orbitals arises in the calculation of many wavefunctions in relation to the ground state of several atoms, some molecules or radicals and also to many electronic excited states of atoms and molecules. Many authors [1–12] have reduced this problem to the determination of the eigenfunctions of an appropriate operator (coupling operator). Recently Hirao and Nakatsuji [2] (hereafter referred to as H.N.) have suggested two very general coupling operators, showing that they satisfy the correct variational conditions on the orbitals, unlike many others previously proposed. As the coupling operators are constructed from the same orbitals to be determined, the problem becomes iterative: one starts from some trial orbitals and improves them step by step. On analogy with the procedure for the closed-shell systems, the problem should be solved by successive diagonalizations of the representative matrix of the operator. We have tried using both the proposed operators and have found great difficulty in reaching the convergency, even in very simple cases like that of the first ^3S state of He. This fact has led us to analyse the iterative process in detail. We have noticed that the diagonalization of the matrices of the coupling operators does not give the best variations for the trial orbitals, although these operators satisfy the right variational conditions at convergency [13, 14]. So we propose an iterative process based on the diagonalization of the matrices relative to some combinations of fundamental operators.

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We refer to the general treatment of H.N., who have reexamined the coupling operators for the open shells; they have paid particular attention to the introduction of the correct variational conditions, thus pointing out the mistakes of much previous work. The authors write the wavefunction as the sum of many configurations,

$$\Phi_0 = \sum_k c_k \Psi_k \tag{1}$$

The Ψ_k's are antisymmetric many-electron wavefunctions, built up from n spin-orbitals $\{\phi_m\}$, where $\phi_m = \chi_i\alpha$ or $\phi_m = \chi_i\beta$. If the set $\{\chi\}$ of the spatial orbitals is orthonormal, then the energy can be written as

$$E = \sum_{i=1}^{n} f_i \langle\chi_i|h|\chi_i\rangle + \sum_{i,j=1}^{n} (a_{ij}J_{ij} - b_{ij}K_{ij}) \tag{2}$$

where the coefficients f_i, a_{ij}, b_{ij}, depend on c_k's in (1); J_{ij} and K_{ij} are defined as in Roothaan [15]. H.N. showed that the χ_i orbitals can be derived as the eigenfunctions of the $\mathscr{R}$ operator so defined:

$$\begin{aligned}\mathscr{R}|\chi_i\rangle = \{\mathscr{F}_i|\chi_i\rangle - \sum_j |\chi_j\rangle\langle\chi_j|\mathscr{F}_i|\chi_i\rangle\} + \\ + \sum_{j(\neq i)} (\lambda_{ji}-\lambda_{ij})|\chi_j\rangle\langle\chi_j|\mathscr{F}_i - \mathscr{F}_j|\chi_i\rangle + |\chi_i\rangle\langle\chi_i|\mathscr{F}_i|\chi_i\rangle\end{aligned} \tag{3}$$

$\mathscr{F}_i$ and $\mathscr{F}_j$ are the usual operators which one obtains by differentiating (2). They are given by:

$$\begin{aligned}&\mathscr{F}_i = f_i h + \sum_k (a_{ik}\mathscr{J}_k - b_{ik}\mathscr{K}_k) \\ & \qquad\qquad\qquad\qquad\qquad i,j \leqslant n \\ &\mathscr{F}_j = f_j h + \sum_k (a_{jk}\mathscr{J}_k - b_{jk}\mathscr{K}_k) \\ &\mathscr{F}_i = \mathscr{F}_j = 0 \quad i,j > n\end{aligned} \tag{4}$$

λ_{ij} and λ_{ji} are arbitrary parameters, with the conditions $\lambda_{ji} \neq \lambda_{ij}$, $\lambda_{ji} \neq 0$, $\lambda_{ij} \neq 0$. Adding to $\mathscr{R}$ the operator

$$\mathscr{V} = (1 - \sum_j |\chi_j\rangle\langle\chi_j|) \sum_i \mathscr{F}_i (1 - \sum_k |\chi_k\rangle\langle\chi_k|) \tag{5}$$

one obtains the new operator $\mathscr{R}' = \mathscr{R} + \mathscr{V}$, proposed for a correct treatment of the open shell problems. $\mathscr{R}$ and $\mathscr{R}'$ satisfy the right Hermiticity conditions and the symmetry properties of the Lagrange multipliers; they give the correct variational equations, unlike many other previously proposed operators. Going into the details of the iterative process, we observe that from a set $\{\chi^0\}$, we obtain the representative matrices of R and R', whose elements are

$$\begin{aligned}R_{pq} &= \langle\chi_p^0|\mathscr{R}|\chi_q^0\rangle \\ R'_{pq} &= \langle\chi_p^0|\mathscr{R}'|\chi_q^0\rangle\end{aligned}$$

The diagonalization process combines between them the χ^0 orbitals and gives the new χ orbitals which, in a first approximation, are related to the preceding ones, two by two, in the following way:

$$\begin{aligned} &\chi_p = \cos\theta\chi_p^0 + \sin\theta\chi_q^0 \\ &\chi_q = -\sin\theta\chi_p^0 + \cos\theta\chi_q^0 \\ &\theta \simeq \sin\theta = \frac{R_{pq}}{R_{pp}-R_{qq}} \quad \text{or} \quad \theta \simeq \sin\theta = \frac{R'_{pq}}{R'_{pp}-R'_{qq}} \end{aligned} \tag{6}$$

Among the combinations which lower the energy, let us consider the one between an occupied orbital χ_p^0 and a virtual one χ_q^0. Taking into account the expression of $\mathscr{R}$ and $\mathscr{R}'$, we have[1]:

$$\begin{aligned} &R_{pq} = R'_{pq} = \langle\chi_p^0|\mathscr{F}_p|\chi_q^0 \\ &R_{pp} = R'_{pp} = \langle\chi_p^0|\mathscr{F}_p|\chi_p^0\rangle \\ &R'_{qq} = \langle\chi_q^0|\sum_i \mathscr{F}_i|\chi_q^0\rangle \neq R_{qq} = 0 \end{aligned}$$

Thus it is clear that the coefficients of the combinations and hence the steps of the iterative process are very different, if one uses either of the operators, even though they give the correct variational equations at the convergency. Because of this arbitrariness, it seems that a reliable convergency of the process is not assured, as has in fact been remarked in many tests. We think therefore that while the work of H.N. has stated precisely the conditions at the convergency, it leaves many unresolved problems regarding the process needed to arrive at it. For this purpose we have reexamined the problem in the following way.

Let $\{\chi^0\}$ be an orthogonal set of trial orbitals; χ_p and χ_q are two orbitals obtained from χ_p^0 and χ_q^0 by the unitary transformation

$$\begin{aligned} &\chi_p = \cos\theta\chi_p^0 + \sin\theta\chi_q^0 \\ &\chi_q = -\sin\theta\chi_p^0 + \cos\theta\chi_q^0 \end{aligned}$$

Substituting the new orbitals in (2) and developing trigonometric functions up to second order in θ, we get

$$\begin{aligned} E(\theta) = E_0 + 4\theta F_{pq} + 2\theta^2\{F_{qq} - F_{pp} + (J_{pq}+K_{pq})(2b_{pq} - b_{pp} - b_{qq}) \\ + 2K_{pq}(a_{pp} + a_{qq} - 2_{pq})\} \end{aligned} \tag{7}$$

where

$$\begin{aligned} &F_{pq} = \langle\chi_p|\mathscr{F}_p - \mathscr{F}_q|\chi_q\rangle \\ &F_{pp} = \langle\chi_p|\mathscr{F}_p - \mathscr{F}_q|\chi_p\rangle \\ &F_{qq} = \langle\chi_q|\mathscr{F}_p - \mathscr{F}_q|\chi_q\rangle \end{aligned}$$

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[1] Using the operator $\mathscr{R}$ defined by (10) in Ref. [12], one obtains for this combination the same matrix elements as those of $\mathscr{R}'$, if operator $\mathscr{R}_0$ is that defined in (5) and not in (7) of that paper, otherwise the interaction terms between occupied and virtual orbitals are zero and the process would converge to a wrong limit.

From (7), by minimizing with respect to θ, we obtain the optimized angle expression

$$\theta \simeq \sin\theta = \frac{F_{pq}}{F_{pp} - F_{qq} + (J_{pq} + K_{pq})(b_{pp} + b_{qq} - 2b_{pq}) + 2K_{pq}(2a_{pq} - a_{pp} - a_{qq})} \tag{8}$$

The denominator of (8) can be simplified both because in some cases $(b_{pp} + b_{qq} - 2b_{pq}) = 0$ and $(a_{pp} + a_{qq} - 2a_{pq}) = 0$, and because J_{pq} and K_{pq} integrals are small as compared to the difference $F_{pp} - F_{qq}$. So it is possible to reduce Eq. (8) to the following form:

$$\theta \simeq \sin\theta = \frac{F_{pq}}{F_{pp} - F_{qq}} \tag{9}$$

Let us notice that Eq. (9), in the approximation order that we assumed, is the same formula which arises in the diagonalization of the matrix $\boldsymbol{F}$ by the method of Jacobi. Let us compare the expressions (9) and (6), obtained from the H.N. operators. We consider the case in which χ_p and χ_q are occupied orbitals with $\mathscr{F}_p \neq \mathscr{F}_q$ (the case $\mathscr{F}_p = \mathscr{F}_q$ gives $E(\theta) = E_0$). Taking into account the expression (3), the formulae (6) become

$$\theta \simeq \sin\theta = \frac{\langle\chi_p|\mathscr{F}_p - \mathscr{F}_q|\chi_q\rangle}{\langle\chi_p|\mathscr{F}_p|\chi_p\rangle - \langle\chi_q|\mathscr{F}_q|\chi_q\rangle} \tag{10}$$

while the (9) becomes

$$\theta \simeq \sin\theta = \frac{\langle\chi_p|\mathscr{F}_p - \mathscr{F}_q|\chi_q}{\langle\chi_p|\mathscr{F}_p - \mathscr{F}_q|\chi_p\rangle - \langle\chi_q|\mathscr{F}_p - \mathscr{F}_q|\chi_q\rangle} \tag{11}$$

From a comparison between (10) and (11), one can deduce that the H.N. formulae did not give, far from the convergency, the right linear combinations between the orbitals which minimize the energy. Analogous remarks can be made for the other combinations useful to lower the energy.

Going back to (9), we observe that to calculate its terms, we do not need to know so many operators as are the orbitals: all the doubly occupied orbitals have the same operator, while the virtual orbitals have null operator. Let us consider, as an example, the fairly frequent case in which there are, in the same irreducible representation, m doubly occupied orbitals, two non-degenerate singly occupied orbitals (χ_a, χ_b) and k virtual orbitals. The operators which arise are the following:

$$\mathscr{F}_d = h + \sum_{j=1}^{m} (2\mathscr{J}_j - \mathscr{K}_j) + \mathscr{J}_a + \mathscr{J}_b \pm \tfrac{1}{2}(\mathscr{K}_a + \mathscr{K}_b)$$

$$\mathscr{F}_a = h + \sum_{j=1}^{m} (2\mathscr{J}_j - \mathscr{K}_j) + \mathscr{J}_b \pm \mathscr{K}_b$$

$$\mathscr{F}_b = h + \sum_{j=1}^{m} (2\mathscr{J}_j - \mathscr{K}_j) + \mathscr{J}_a \pm \mathscr{K}_a$$

where the + sign holds for singlet states, the − for the triplet. Let $\boldsymbol{\chi}^0$ be the row vector of the trial orbitals, obtained from the basis row vector $\boldsymbol{\sigma}$ by the $\boldsymbol{C}^0$ matrix: $\boldsymbol{\chi}^0=\boldsymbol{\sigma}\boldsymbol{C}^0$. Firstly we build up the $\boldsymbol{d}$, $\boldsymbol{a}$, $\boldsymbol{b}$ matrices, whose elements are thus defined:

$$d_{ij}=\langle\sigma_i|\mathscr{F}_d|\sigma_j\rangle$$

$$a_{ij}=\langle\sigma_i|\mathscr{F}_a|\sigma_j\rangle$$

$$b_{ij}=\langle\sigma_i|\mathscr{F}_b|\sigma_j\rangle$$

Let $\boldsymbol{C}$ be the rectangular matrix obtained from $\boldsymbol{C}^0$ drawing the columns relative to the doubly occupied and virtual orbitals; we use it to construct

$$\boldsymbol{D}=\boldsymbol{C}^\dagger\boldsymbol{d}\boldsymbol{C}$$

If $\boldsymbol{U}$ is the matrix which diagonalizes $\boldsymbol{D}$, $\boldsymbol{C}_1=\boldsymbol{C}\boldsymbol{U}$ gives the new orbitals obtained by optimizing the linear combinations between doubly occupied and virtual orbitals. The diagonalization process involves the vanishing of all the elements $D_{ij}(i\neq j)$. To be rigorous, it is necessary to make only the combinations, in accord with (9), between doubly occupied and virtual orbitals ($i\leqslant m, j>m+2$). None of the combinations into the two subsets of doubly occupied and virtual orbitals contributes to improving the energy and they can be skipped. Normally, however, the time required to completely diagonalize the matrices is negligible in comparison with that necessary to construct $\boldsymbol{d}$, $\boldsymbol{a}$ and $\boldsymbol{b}$; so the advantage is not relevant. The $\boldsymbol{C}_1$ matrix will replace in $\boldsymbol{C}^0$ the columns corresponding to $\boldsymbol{C}$; so we obtain the $\boldsymbol{C}_1^0$ matrix. Now, we build up a new $\boldsymbol{C}$ matrix, drawing from $\boldsymbol{C}_1^0$ the columns corresponding to χ_a^0 and virtual orbitals, and we calculate $\boldsymbol{A}=\boldsymbol{C}^\dagger\boldsymbol{a}\boldsymbol{C}$. If $\boldsymbol{U}$ is the matrix which diagonalizes $\boldsymbol{A}$, then $\boldsymbol{C}_1=\boldsymbol{C}\boldsymbol{U}$ gives us the new singly occupied orbital, obtained from the optimized linear combination between χ_a^0 and virtual orbitals. The $\boldsymbol{C}_1$ matrix will replace in $\boldsymbol{C}_1^0$ the columns corresponding to $\boldsymbol{C}$, and we obtain the $\boldsymbol{C}_2^0$ matrix. In a similar way we shall act on the second singly occupied orbital, χ_b^0, to obtain $\boldsymbol{C}_3^0$. Now, we construct a new $\boldsymbol{C}$ matrix drawing from $\boldsymbol{C}_3^0$ the columns of the doubly occupied and the first singly occupied orbitals. If $\boldsymbol{U}$ diagonalizes $\boldsymbol{C}^\dagger(\boldsymbol{d}-\boldsymbol{a})\boldsymbol{C}$, then $\boldsymbol{C}_1=\boldsymbol{C}\boldsymbol{U}$ gives us the new optimized doubly occupied and first singly occupied orbitals. By substitution of $\boldsymbol{C}_1$ in $\boldsymbol{C}_3^0$ we obtain $\boldsymbol{C}_4^0$; we operate in a similar way between the doubly occupied orbitals and the second singly occupied to calculate $\boldsymbol{C}_5^0$. From this last matrix we shall construct a two column matrix $\boldsymbol{C}$, corresponding to the two singly occupied orbitals. Diagonalizing $\boldsymbol{C}^\dagger(\boldsymbol{a}-\boldsymbol{b})\boldsymbol{C}$ by $\boldsymbol{U}$ and replacing in $\boldsymbol{C}_5^0$ the two columns of $\boldsymbol{C}_1=\boldsymbol{C}\boldsymbol{U}$, we obtain the $\boldsymbol{C}^1$ matrix which gives us the new set of orbitals, $\{\chi^1\}$, for a successive iteration.

Every step of SCF process is worked out by the diagonalization of six different matrices, obtained from the matrices relative to the three different operators. As we have said above, most of the time is spent in constructing the fundamental matrices, rather than in the subsequent diagonalizations and reelaborations; this is true mostly when one employs a very large basis set. The configuration scheme we have analyzed is very frequent; for other configurations the only variation consists in the number of operators, and therefore of the matrices to be diagonalized step by step. A more detailed description seems quite superfluous; indeed the generalization of our method is obvious.

Going back to (9), we observe that the form of the diagonal elements F_{pp} and F_{qq}, which appear on the denominator, is

$$F_{pp} = \langle \chi_p | \mathscr{F}_p - \mathscr{F}_q | \chi_p \rangle$$
$$F_{qq} = \langle \chi_q | \mathscr{F}_p - \mathscr{F}_q | \chi_q \rangle$$

Therefore one cannot construct one operator only, whose representative matrix has the right elements for all pairs on the diagonal. An exception is the case of the closed shells, where the energy changes only by combinations between doubly occupied and virtual orbitals, and for the latter there is a null operator. For these reasons we do not think that in open shell calculations the coupling operator method is very suitable, even though it furnishes the right conditions at convergency.

The above described iterative method has been checked by calculations on many atomic states from He to Ne and for some excited states of formaldehyde [16] and ethylene [17]. We have always obtained a quick convergency to the right SCF limit, which has also been verified by the fulfilment of the correct variational conditions, as reported by H.N.

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