Theoret. Chim. Acta (Berl.) 47, 305–314 (1978)

THEORETICA CHIMICA ACTA

Role of Coupling Operators on Open Shell RHF Equations

Federico Moscardó and José Ignacio Fernández-Alonso

Departamento de Química Física y Química Cuántica, Centro Coordinado UAM-CSIC, Facultad de Ciencias, Universidad Autónoma de Madrid, Cantoblanco, Madrid, 34, Spain

We have derived the expressions for the extremum condition of $\langle E \rangle$, corresponding to any wave function. These expressions are given as a function of the spin orbitals. We have carried out the derivation considering the spin orbitals as vectors belonging to an orthonormal basis. The corresponding variational equations have been derived introducing the condition that the norm of the wave function is constant, as the only additional constraint.

From the expression obtained for the first variation of the matrix elements of H, as a function of the spin orbitals, we have derived the RHF equations for a simple case.

In the present procedure, the couplings between orbitals of different shells appear directly, being defined explicitly, and they may be taken as corresponding with the elements of a Hermitian matrix.

The calculations that we have carried out show that the coupling operators defined in the paper give results which are variationally correct.

Key words: Open-shell theory – RHF equations

1. Introduction

Much attention has been given to the Open Shell Restricted Hartree-Fock (OS-RHF) [1–17] theory, due to the fact that the couplings between different shells cannot be eliminated from the Euler equations except in the particular case where different symmetries exist.

In all the methods usually employed, the energy expression to be varied is obtained

0040–5744/78/0047/0305/$02.00

taking explicitly into account the orthonormality property of the orbitals

$$\langle \phi_i \mid \phi_j \rangle = \delta ij \tag{1}$$

and consequently, the constraint

$$\langle \delta\phi_i \mid \phi_j \rangle + \langle \phi_i \mid \delta\phi_i \rangle = 0 \tag{2}$$

must be introduced in the energy variation procedure via the Lagrange multipliers.

In this work the approach to the OS-RHF problem is different. We start from the general wave function ψ of the system and we define $\delta\psi$. We have

$$\langle \delta\psi \,|H-E|\, \psi \rangle + \langle \psi \,|H-E|\, \delta\psi \rangle = 0 \tag{3}$$

as the definition of the extremum condition in a general form. Subsequently this equation is developed in terms of the spin orbitals and finally the characteristic constraints defining the RHF method are introduced.

The Euler equations resulting from this development have all the couplings in a self-defined way. Therefore no subsidiary conditions such as the Hermiticity of the undetermined Lagrange multipliers (ULM) are necessary when this technique is used [6–9].

In the next section, starting from a wave function in the most general form, the contributions of the spin orbitals to the first variation of the energy are introduced.

In the following sections, the general form is not kept as we have restricted ourselves to the particular case of a Slater determinant.

In Sect. 3, the OS-RHF equations are deduced and compared with those obtained by other methods in the literature. Finally several calculations on Li and Na atoms have been performed in order to study the influence of the different coupling operator definitions on the convergency of the OS-RHF equations. In Sect. 4 the most significant results are given.

2. Variational Procedure

Let us consider a wave function ψ, approximated by a linear combination of Slater determinants:

$$\psi = \sum_{\mu} c_\mu \psi^\mu \tag{4}$$

where ψ^μ is the μth determinant of dimension N, equal to the number of electrons being considered:

$$\psi^\mu = \|\psi_1^\mu \psi_2^\mu \ldots \psi_N^\mu\| \tag{5}$$

where ψ_i^μ is one of the M spin orbitals of the basis set, with $M \geqslant N$. The expectation value of the energy associated with Eq. (4) is given by

$$\langle E \rangle = \langle \psi \,|H|\, \psi \rangle / \langle \psi \mid \psi \rangle \tag{6}$$

and consequently, the stationarity of $\langle E\rangle$ implies that

$$\langle\delta\psi\,|H-E|\,\psi\rangle+\langle\psi\,|H-E|\,\delta\psi\rangle=0 \tag{7}$$

where E represents the extreme value of the energy, and $\delta\psi$ is written as a function of the variation in the spin orbitals, $\delta\psi_i^\mu$.

Given the arbitrary character of $\delta\psi_i^\mu$, we may substitute $\delta\psi_i^\mu$ by $i\delta\psi_i^\mu$ and, consequently, $\delta\psi$ by $i\delta\psi$. With these substitutions, Eq. (7) becomes

$$\langle\delta\psi\,|H-E|\,\psi\rangle=0 \tag{8}$$

Substituting Eq. (4) in Eq. (8) and fixing the values of the c_μ while varying the Slater determinants, ψ^μ, we obtain

$$\sum_{\mu,\nu} c_\mu^* c_\nu \langle\delta\psi^\mu\,|H-E|\,\psi^\nu\rangle=0 \tag{9}$$

Let us consider any diagonal matrix element from Eq. (9); as the antisymmetrizing operator commutes with the Hamiltonian and is idempotent, it follows:

$$\begin{aligned}\langle\delta\psi^\mu\,|H-E|\,\psi^\mu\rangle&=(\langle\delta\psi_1^\mu\psi_2^\mu\ldots\psi_N^\mu|+\langle\psi_1^\mu\,\delta\psi_2^\mu\ldots\psi_N^\mu|+\cdots\\&+\langle\psi_1^\mu\psi_2^\mu\ldots\delta\psi_N^\mu|)(H-E)\sum_P(-1)^pP\,|\psi_1^\mu\psi_2^\mu\ldots\psi_N^\mu\rangle\end{aligned} \tag{10}$$

Let us take, for example, the term corresponding to the variation in the i'th spin orbital

$$\sum_P\langle\psi_1^\mu\psi_2^\mu\ldots\delta\psi_i^\mu\ldots\psi_N^\mu|\,(H-E)(-1)^pP|\,\psi_1^\mu\psi_2^\mu\ldots\psi_N^\mu\rangle \tag{11}$$

Assuming that the spin orbitals are orthonormal, and since in general, $\langle\delta\psi_i^\mu\,|\,\psi_j^\mu\rangle\neq0$, the expansion of Eq. (11) leads to a monoelectronic and a bielectronic part. In the former, the non-zero terms are associated with the identity and P_{ij} permutations, while in the latter the non-zero terms are associated with the identity, P_{ij}, P_{ik} and $P_{ij}P_{ik}$ permutations. With these considerations, Eq. (10) may be written as

$$\begin{aligned}\langle\delta\psi^\mu\,|H-E|\,\psi^\mu\rangle&=\sum_i[\langle\delta\psi_i^\mu\,|h+\sum_{j\neq i}L_j-E|\,\psi_i^\mu\rangle\\&+\langle\delta\psi_i^\mu\,|\psi_i^\mu\rangle\sum_{j\neq i}\langle\psi_j^\mu\,|h+\tfrac{1}{2}\sum_{K\neq i,j}L_K|\,\psi_j^\mu\rangle\\&-\sum_{j\neq i}\langle\delta\psi_i^\mu\,|\,\psi_j^\mu\rangle\langle\psi_j^\mu\,|h+\sum_{K\neq i,j}L_K|\,\psi_i^\mu\rangle],\end{aligned} \tag{12}$$

where L_j groups the Coulomb J_j and exchange K_j operators in the usual way, that is, $L_j=J_j-K_j$.

In a similar way it is easy to expand a general term, $\langle\delta\psi^\mu\,|H-E|\,\psi^\nu\rangle$, from Eq. (9). The possible cases giving a non-zero result are:

1) $\psi^\mu=\psi^\nu$; first variation given by Eq. (12),

2) ψ^μ and ψ^ν differ in one spin orbital $\psi_a^\mu \neq \psi_a^\nu$

$$\begin{aligned}\langle\delta\psi^\mu|H-E|\psi^\nu\rangle &= \langle\delta\psi_a^\mu|h+\sum_{i\neq a} L_i - E|\psi_a^\nu\rangle \\ &+\langle\delta\psi_a^\mu|\psi_a^\nu\rangle \sum_{i\neq a}\langle\psi_i^\mu|h+\tfrac{1}{2}\sum_{j\neq i,a} L_j|\psi_i^\nu\rangle + \sum_{i\neq a}(\langle\delta\psi_i^\mu|L_a|\psi_i^\nu\rangle \\ &+\langle\delta\psi_i^\mu|\psi_i^\nu\rangle\langle\psi_a^\mu|h+\sum_{j\neq i,a} L_j|\psi_a^\nu\rangle - \langle\delta\psi_a^\mu|\psi_i^\nu\rangle\langle\psi_i^\mu|h+ \\ &+\sum_{j\neq i,a} L_j|\psi_a^\nu\rangle - \langle\delta\psi_i^\mu|\psi_a^\nu\rangle\langle\psi_a^\mu|h+\sum_{j\neq i,a} L_j|\psi_i^\nu\rangle \\ &-\sum_{j\neq i,a}\langle\delta\psi_i^\mu|\psi_j^\nu\rangle\langle\psi_j^\mu|La|\psi_i^\nu\rangle)\end{aligned} \tag{13}$$

3) ψ^μ and ψ^ν differ in two spin orbitals $\psi_a^\mu \neq \psi_a^\nu$; $\psi_b^\mu \neq \psi_b^\nu$

$$\begin{aligned}\langle\delta\psi^\mu|H-E|\psi^\nu\rangle &= \sum_p^2 \sum_{q\neq p}^2 [\langle\delta\psi_p^\mu|L_q|\psi_p^\nu\rangle \\ &+\sum_{i\neq p,q}(\langle\delta\psi_p^\mu|\psi_p^\nu\rangle\langle\psi_q^\mu|h+L_i|\psi_q^\nu\rangle + \tfrac{1}{2}\langle\delta\psi_i^\mu|\psi_i^\nu\rangle\langle\psi_p^\mu|L_q|\psi_p^\nu\rangle \\ &-\langle\delta\psi_p^\mu|\psi_q^\nu\rangle\langle\psi_q^\mu|h+L_i|\psi_p^\nu\rangle - \langle\delta\psi_p^\mu|\psi_i^\nu\rangle\langle\psi_i^\mu|L_q|\psi_p^\nu\rangle \\ &-\langle\delta\psi_i^\mu|\psi_p^\nu\rangle\langle\psi_p^\mu|L_q|\psi_i^\nu\rangle)]\end{aligned} \tag{14}$$

4) ψ^μ and ψ^ν differ in three spin orbitals $\psi_a^\mu \neq \psi_a^\nu$; $\psi_b^\mu \neq \psi_b^\nu$; $\psi_c^\mu \neq \psi_c^\nu$

$$\begin{aligned}\langle\delta\psi^\mu|H-E|\psi^\nu\rangle &= \sum_p^3 \sum_{q\neq p}^3 \sum_{r\neq p,q}(\tfrac{1}{2}\langle\delta\psi_p^\mu|\psi_p^\nu\rangle\langle\psi_q^\mu|L_r|\psi_q^\nu\rangle \\ &-\langle\delta\psi_p^\mu|\psi_q^\nu\rangle\langle\psi_q^\mu|L_r|\psi_p^\nu\rangle)\end{aligned} \tag{15}$$

All the terms in Eqs. (12–15) with factors of the type $\langle\delta\psi_i|\psi_j\rangle$, appear only because we did not proceed in the usual way. That is, if the energy expression had been obtained following the Slater rules as a previous step to the variational procedure, all these terms (which follow directly from the products $\langle\psi_i|\psi_j\rangle$) would not be present in Eqs. (12–15) due to the orthogonality property of the orbitals.

Eqs. (12–15) are the general Euler equations for an orthonormal basis of spin orbitals.

Any restricted equation may be obtained as a particular case of Eqs. (12–15) by introduction of the appropriate relation between the spin orbitals (i.e. closed subshell, degenerate open subshell, etc.).

In this work we limit our analysis to the OS-RHF with a single Slater determinant. In the next section the form taken by Eqs. (12–15) in this case will be deduced and a comparative analysis of our formalism with that of other authors will also be given.

3. Case of a Slater Determinant, RHF Equations

Let us assume that the wave function is approximated by a Slater determinant: $\psi = \|\psi_1 \ldots \psi_N\|$.

The stationarity condition of $\langle E\rangle$ implies the nullity of Eq. (12) and, given the non-zero character of $\delta\psi_i$, we must have:

$$\begin{aligned}&\{h+\sum_{j\neq i} L_j-E+\sum_{j\neq i}\langle\psi_j|h+\tfrac{1}{2}\sum_{k\neq i,j}L_k|\psi_j\rangle\\&-\sum_{j\neq i}|\psi_j\rangle\langle\psi_j|(h+\sum_{k\neq i,j}L_k)\}\,|\psi_i\rangle=0\end{aligned}\tag{16}$$

Let us consider for example that the Slater determinant has $2M$ spin orbitals associated with a closed subshell, and that the remaining N—$2M$ correspond to orbitals that are singly occupied and have a common spin factor (α or β). Let us also write $\psi_i=\phi_i\eta_i$ where ϕ_i and η_i are spatial and spin functions respectively. These considerations imply $\phi_1=\phi_e;\ldots;\ \phi_{2M-}{}^1=\phi_{2M};\ \phi_{2M+1}\neq\cdots\neq\phi_N$. The introduction of these conditions in Eq. (16) and the integration over the spin coordinates lead to the RHF equations:

$$\begin{aligned}&[F^c-\sum_{l}|\phi_l\rangle\langle\phi_l|F^o]\,|\phi_i\rangle=\theta_{ii}\,|\phi_i\rangle+\sum_{j\neq i}|\phi_j\rangle\langle\phi_j|F^c|\phi_i\rangle\\&[F^o-\sum_{j}|\phi_j\rangle\langle\phi_j|F^o]\,|\phi_k\rangle=\theta_{kk}\,|\phi_k\rangle+\sum_{l\neq k}|\phi_l\rangle\langle\phi_l|F^o|\phi_k\rangle\end{aligned}\tag{17}$$

where i and j refer to a closed shell orbital and k and l refer to an open one. F^c and F^o are Fock operators for closed shell and open shell orbitals respectively:

$$\begin{aligned}&F^c=h+\sum_j(2J_j-K_j)+\sum_k(J_k-\tfrac{1}{2}K_k)\\&F^o=\tfrac{1}{2}\{h+\sum_j(J_j-K_j)+\sum_k(J_k-K_k)\}\end{aligned}\tag{18}$$

θ_{ii} and θ_{kk} bear explicit expressions given by:

$$\begin{aligned}&\theta_{ii}=\langle\phi_i|F^c|\phi_i\rangle\\&\theta_{kk}=\langle\phi_k|F^o|\phi_k\rangle\end{aligned}\tag{19}$$

and can be interpreted as the ionization potentials with sign changed of the i and k levels respectively in the frozen orbital approximation (really, θ_{kk} is $-\mathrm{IP}/2$).

From the expressions (19) it can be easily seen that the *occupied orbitals* form an orthogonal set.

Using a unitary transformation of the type

$$\begin{aligned}&\Phi'_c=\Phi_c\mathrm{U}_c\\&\Phi'_o=\Phi_o\mathrm{U}_o\end{aligned}\tag{20}$$

it is possible to eliminate the off-diagonal terms corresponding to the orbitals of the same shell, and Eq. (17) may be reduced to:

$$\begin{aligned}&[F^c-\sum_l|\phi_l\rangle\langle\phi_l|F^o]\,|\phi_i\rangle=0_{ii}\,|\phi_i\rangle\\&[1-\sum_j|\phi_j\rangle\langle\phi_j|]F^o\,|\phi_k\rangle=\theta_{kk}\,|\phi_k\rangle\end{aligned}\tag{21}$$

By defining

$$\theta_{ik}=\theta_{ki}^{*}=\langle\phi_i|F^o|\phi_k\rangle \tag{22}$$

Eq. (21) takes the usual form for the Euler equations in the ULM technique, and the θ_{ik} elements may be directly compared with the Hermitian off-diagonal elements of the ULM matrix.

By premultiplying the first of the Eqs. (21) by a bra of the open shell, and having in mind the orthonormality of the orbitals, it holds that

$$\langle\phi_k|F^c-F^o|\phi_i\rangle=0 \tag{23}$$

It is well known that in most of the approaches related to the OS-RHF theory the main condition for a well defined coupling, is the Hermiticity of the ULM, introduced via the Eq. (23) [6–14].

In the present procedure, the Hermiticity of the couplings given by Eq. (22) and Eq. (23) both hold automatically, and as a consequence the integral from Eq. (23) can be considered as a test integral, so that, when the orbitals are those which extremalize the energy, the integral value must be zero.

Because Eqs. (21) lead to the Eqs. (22) and (23), the former can be considered as the natural OS-RHF equations related to the example chosen in this section.

Let us write

$$\begin{aligned} H^c|\phi_i\rangle&=\lambda_{ii}|\phi_i\rangle\\ H^o|\phi_k\rangle&=\lambda_{kk}|\phi_k\rangle \end{aligned} \tag{24}$$

where

$$\begin{aligned} H^c&=F^c-P^o[\mu_{oc}F^c+(1-\mu_{oc})F^o]\\ H^o&=F^o-P^c[\mu_{co}F^c+(1-\mu_{co})F^o] \end{aligned} \tag{25}$$

with F^c and F^o defined by Eq. (18), and where P^c and P^o are the projectors for the closed and open subshells respectively.

By taking the appropriate values for the μ_{oc} and μ_{co} parameters, we can classify the theories of the literature in which we are interested [6–15]. Table 1 gives the μ_{oc} and μ_{co} parameters related to the different equations.

The Eq. (25) seems to be an unnecessary complication of Eq. (21) since the couplings implied in Eq. (25) are formally those defined by Eq. (19) because of the

Table 1. Theories considered and corresponding parameters in Eqs. (25)

Theory	Huzinaga [8]	Birss and Fraga [4]	Goddard *et al.* [15]	Morikawa [13, 14]	Levy [7]	Present work
μ_{oc}	variable	1	0	1/2	variable	0
μ_{co}	variable	0	1	1/2	μ_{oc}	0

requirement of Eq. (23). However Eqs. (25) are useful for the calculations of the later section.

In order to perform test calculations with the operators defined by Eq. (25), it is useful to define an operator in the way

$$H = H^c(1-P^o) + H^o(1-P^c) \tag{26}$$

which leads to the same eigenvalue equations as Eq. (25).

The operator defined by Eq. (26) guarantees the couplings, and because their matrix representation is not symmetrical, their eigenvectors may be not orthonormal, and for this reason no additional loss of freedom is added to the proper restrictions of the problem, a very important fact when a theory is tested.

In order to obtain the eigenvalues and eigenvectors of Eq. (26) the following procedure has been adopted:

To calculate the eigenvalues we have:

1) to previously condition the matrix by equilibrating it through diagonal similarities [18],
2) to reduce it to the Hessenberg form by orthogonal similarities [19], and
3) to compute the Hessenberg matrix eigenvalues [19].

To calculate the eigenvectors we have applied the recurrence relations

$$c_{il} = -\sum_{j>i} \frac{a^i_{ij}}{a^i_{ii}} c_{jl} \tag{27}$$

$$a^i_{ij} = a^i_{ij} - \frac{a^n_{ij} - a^n_{nj}}{a_{nn}}, \; n = i-1 \tag{28}$$

where c_{il} represents the i'th expansion coefficient of the l'th orbital, and a^1_{ij} is given by

$$a^1_{ij} = H_{ij} - \varepsilon_l s_{ij} \tag{29}$$

where H_{ij} is an element of the matrix associated with the H operator from Eq. (26); ε_l is the l'th eigenvalue, and S_{ij} is an element of the overlap matrix. By using Eqs. (27–29) the first $N-1$ coefficients of an orbital can be computed; to compute the remaining coefficient we can use the norm condition of the orbital.

As has been shown [6, 21], convergence in the energy or in the orbital's coefficients is not a sufficient criterion to guarantee that the solutions obtained in a SCF calculation are Hartree-Fock solutions. In the calculations of the next section, we adopt the zero value of the integral from Eq. (23) as a criterion for the convergency.

4. Results

Some calculations have been carried out in order to show the influence the coupling operators have on the convergence of the variational equations.

First, we have carried out the calculations for the $1s^2 2s^1$ and $1s^2 2s^2 2p^6 3s^1$ configurations of the Li and Na atoms respectively. The STO basis set used is that given by Clementi [20].

Figs. 1 and 2 show the convergence for different values of $\mu = \mu_{oc} = \mu_{co}$ and for $\mu_{oc} = 1$, $\mu_{co} = 0$, the latter corresponding to Birss and Fraga's equations [4].

Both atoms show a similar behaviour, with the rate of convergence decreasing as μ increases; anyhow, for $0 \leqslant \mu < 1$, they both converge to the same value, -7.43272707 and -161.84972989 a.u. for the Li and Na atoms respectively; the values of the integral from Eq. (23) being zero in both cases.

Although convergence is achieved for $\mu = 1$ and for $\mu_{oc} = 1$, $\mu_{co} = 0$, they give higher energy values than those obtained when $\mu < 1$. The values corresponding to $\mu = 1$ are -7.43257584 a.u. for the Li atom and -161.84413466 a.u. for the Na atom, and the integral from Eq. (23) takes values sensibly different from zero; for the Li atom $\langle \phi_{2s} | F^c - F^o | \phi_{1s} \rangle = -0.00911408$ and for Na $\langle \phi_{3s} | F^c - F^o | \phi_{1s} \rangle = 0.0401580$ and $\langle \phi_{3s} | F^c - F^o | \phi_{2s} \rangle = 0.0586906$. Our calculations with $\mu > 1$ show no convergence.

Many calculations have been carried out using different values for the two parameters appearing in Eq. (25). The μ_{oc} parameter, which is the one related to the closed-shell operator, is the dominant one since, if we fix μ_{oc} while varying μ_{co}, the point of convergence is not affected significantly. For $\mu_{oc} = 0$, the energy value corresponding to $\mu = 0$ in Figs. 1 and 2, is achieved independently of that given to μ_{co}. If $\mu_{oc} = 1$, we are always led to convergences which are dependent on the values of μ_{co}; however, the result does not vary significantly as we change μ_{co}

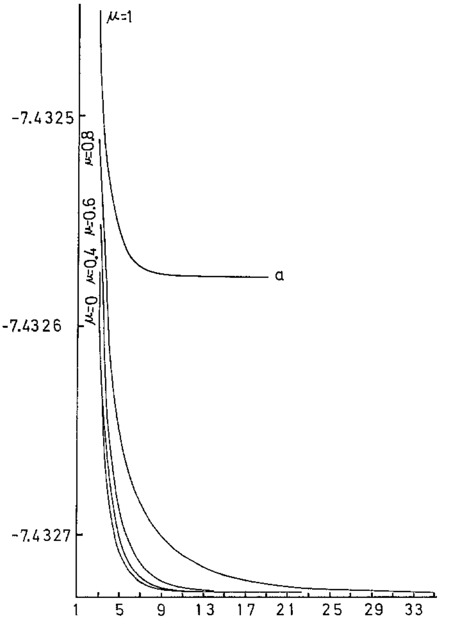

Fig. 1. Li atom. Rate of convergence for different values of μ in Eqs. (26). (a) Results for Birss and Fraga formalism

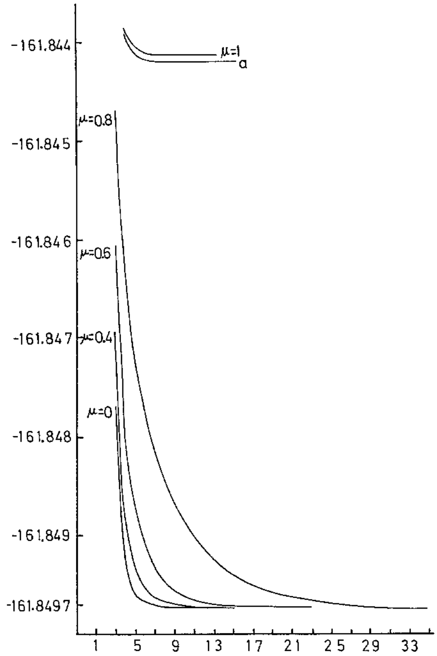

Fig. 2. Na atom. Rate of convergence for different value of μ in Eqs. (26). (a) Results for Birss and Fraga formalism

and, in any case, the point of convergence has a lower bound corresponding to Birss' and Fraga's equations [4], and in such cases the value of the test integral of the Eq. (23) is sensibly different from zero.

For $\mu_{oc} > 1$, convergence is not achieved, regardless of the value given to μ_{co}.

All these results show that the condition given in Eq. (23) may be relaxed except for the closed-shell operator defined by Eq. (25). This can explain the fact that the equations corresponding to $\mu_{oc} = 0$, and $\mu_{co} = 1$ give good convergence although, in the intermediate steps of the SCF calculation, they do not satisfy the Hermiticity of the ULM matrix.

For the lowest value, the greatest rate of convergence is achieved with $\mu_{oc} = \mu_{co} = 0$; these values are related to the Eqs. (21) obtained in the present paper.

Defining H^c and H^o as in Eq. (25), the results obtained clearly show the influence that the choice of parameters may have upon the results. Hence, it is hard to predict the best set of parameters for a more complicated system and whether a particular choice will yield correct results.

We have carried out calculations without any coupling operators. As expected, these calculations do not give good results (-7.43257120 and -161.84327423 a.u. for the Li and Na atoms respectively). Elimination of the couplings results in an inappropriate mixing of both orbitals. The corresponding values of the integral in Eq. (23) are significantly different from zero, -0.0782816 for the Li atom and -0.037750 and 0.01640 for the Na atom. This gives a further proof of the fact that the orbitals obtained in this case do not extremalize the energy and the usefulness of the integral of Eq. (23) as a good tool in analyzing the variational character of the SCF results.

The diagonalization of the matrix associated to operator of Eq. (26) gives orbitals which, for $\mu_{oc} = \mu_{co} = 0$, are variationally correct solutions since the integral in Eq. (23), defined by the orbitals of both shells, is zero.

References

1. Roothaan, C. C.: Rev. Mod. Phys. **32**, 179 (1960)
2. Huzinaga, S.: Phys. Rev. **120**, 866 (1960)
3. Huzinaga, S.: Phys. Rev. **122**, 131 (1961)
4. Birss, F. W., Fraga, S.: J. Chem. Phys. **38**, 2552 (1963)
5. Hunt, W. J., Dunning Jr., T. H., Goddard III, W. A.: Chem. Phys. Letters **3**, 606 (1969)
6. Albat, R., Gruen, N.: Chem. Phys. Letters **18**, 572 (1973)
7. Levy, B.: J. Chem. Phys. **48**, 1994 (1968)
8. Huzinaga, S.: J. Chem. Phys. **51**, 3971 (1969)
9. Hirao, K., Nakatsuji, H.: J. Chem. Phys. **59**, 1457 (1973); Hirao, K.: J. Chem. Phys. **60**, 3215 (1974)
10. Dahl, J. P., Joansen, H., Truax, D. R., Zeigler, T.: Chem. Phys. Letters **6**, 64 (1970)
11. Dahl, J. P.: Atlas International Symposium (1974)
12. Peters, D.: J. Chem. **57**, 4351 (1972)
13. Morikawa, T.: Chem. Phys. Letters **17**, 297 (1972)
14. Morikawa, T.: Chem. Phys. Letters **32**, 521 (1975)
15. Goddard III, W. A., Dunning Jr., T. H., Hunt, W. J.: Chem. Phys. Letters **6**, 231 (1969)
16. Caballol, R., Gallifa, R., Riera, J. M., Carbó, R.: Intern. J. Quantum Chem. **8**, 373 (1974)
17. Kobe, D. H.: J. Chem. Phys. **56**, 5990 (1972)
18. Osborne, E. E.: J. of the Association for Computing Machinery **7**, 338 (1960)
19. Wilkinson, J. H.: The algebraic eigenvalue problem. Oxford, London: Clarendon Press 1965
20. Clementi, E.: Atomic function tables. IBM Corporation (1965)
21. Sleeman, D. H.: Theoret. Chim. Acta (Berl.) **11**, 135 (1968)

Received April 6, 1977/August 17, 1977/October 24, 1977