

## Comment on “Combined open shell Hartree–Fock theory of atomic-molecular and nuclear systems” [J. Math. Chem. 42 (2007) 177]

Boris N. Plakhutin · Ernest R. Davidson

Received: 10 March 2008 / Accepted: 4 April 2008 / Published online: 8 July 2008  
© Springer Science+Business Media, LLC 2008

A starting point of the commented work [1] is the three assumptions concerning the present state of the art of the ROHF method and the background of this method, which is the classic Roothaan’s one-open-shell SCF theory [2]. These assumptions are presented in [1] as though they were well-accepted results, however, these assumptions are, in fact, *in sharp contrast* to all of the previous well-substantiated results, and because of this, need a detailed discussion. These assumptions are as follows:

- (i) The expression for the total electronic energy in the one-open-shell ROHF method introduced by Roothaan [2] is orbital-dependent, and therefore, is not invariant under unitary transformation of the orbitals within the respective electronic shells, i.e., within the open or/and closed shells (for details, see the paragraph involving Eq. 27 and Conclusion in [1]).
- (ii) The Fock operators of Roothaan’s approach cannot be diagonalized—see Eq. 27 and the respective text in [1].
- (iii) The Roothaan’s approach [2] does not seem to have been extended to arbitrary open shells (see Introduction in [1]).

Based on these assumptions, Guseinov tries [1] to eliminate the respective “drawbacks” of the ROHF method in his “combined” theory. In the present Letter we show that the first two of the three assumptions above are *undisputedly wrong*, while the

---

Dedicated to Professor C. C. J. Roothaan on the occasion of his 90th anniversary.

---

B. N. Plakhutin (✉)  
Laboratory of Quantum Chemistry, Boreskov Institute of Catalysis, Russian Academy of Sciences,  
prospekt Lavrentieva 5, Novosibirsk 630090, Russia  
e-mail: plakhutin@catalysis.ru

E. R. Davidson  
Department of Chemistry, University of Washington, Seattle, WA 98195-1700, USA  
e-mail: erdavid@earthlink.net

third one fails to acknowledge the many previous works in which the Roothaan's one-open-shell SCF theory [2] has been extended to many-open-shell systems.

## 1 Total electronic energy in the ROHF method

The foundation of the ROHF method has been laid out by Roothaan in his classic work [2]. Generalizations of Roothaan's approach to systems not covered by the theory [2], and several implementations and reformulations of the method [2] have been developed (for a review and bibliography, see monographs [3–5] and review [6]). The present-day formulation of the ROHF method is based on the familiar representation for the total electronic energy:

$$E_{ROHF} = 2 \sum_i f_i H_{ii} + \sum_i \sum_j f_i f_j (2a_{ij} J_{ij} - b_{ij} K_{ij}), \quad (1)$$

that involves only the Coulomb  $J_{ij}$  and exchange  $K_{ij}$  integrals and does not involve the 3- and 4-indexed electron repulsion integrals  $\langle ij | kl \rangle$ . In Eq. 1 and below, the indices  $i, j$  numerate the occupied orbitals;  $f_i$  is the occupation number for the orbital  $\phi_i$  ( $f_i = 1$  for the closed-shell orbitals, and  $0 < f_i < 1$  for the open-shell orbitals);  $a_{ij}$  and  $b_{ij}$  are non-variable coefficients specific for the system under consideration. For the particular case of closed-shell systems, coupling coefficients  $a_{ij}$  and  $b_{ij}$  are equal to:

$$a_{ij} = b_{ij} = 1. \quad (2)$$

For the open-shell systems having the degenerate electronic configuration  $\gamma^N$  ( $\gamma = s, p, d, \dots$  for atoms, and  $\gamma = e, t, g, h$  for nonlinear molecules, and  $N$  is the number of open-shell electrons), Eq. 1 takes the form:

$$E_{ROHF} = E_{rest} + f^2 \sum_m \sum_n (2a_{mn} J_{mn} - b_{mn} K_{mn}), \quad (3)$$

where the indices  $m, n$  run over degenerate open-shell orbitals ( $m, n \in \gamma$ );  $f = N / (2 \dim \gamma)$ ;  $\dim \gamma$  is the dimension of the irreducible representation  $\gamma$ ; and the term  $E_{rest}$  is the same for all states of the configuration  $\gamma^N$ :

$$E_{rest} = 2 \sum_k H_{kk} + \sum_k \sum_l (2J_{kl} - K_{kl}) + 2f \left[ \sum_m H_{mm} + \sum_k \sum_m (2J_{km} - K_{km}) \right], \quad (4)$$

where  $k, l$  are indices for the closed-shell orbitals.

For the  $\gamma^N$  states described by Roothaan’s one-open-shell SCF theory [2], coupling coefficients  $a_{mn}$  and  $b_{mn}$  of Eq. 3 take the form:

$$a_{mn} = a, \quad b_{mn} = b. \tag{5}$$

Taken together, Eqs. 3–5 represent the familiar Roothaan’s expression for the ROHF energy,

$$E_{ROHF} = E_{rest} + f^2 \sum_m \sum_n (2a J_{mn} - b K_{mn}). \tag{6}$$

It is this expression that has been claimed by Guseinov [1] to be both orbital-dependent and non-invariant under unitary transformation of the orbitals.

Both these claims are undisputedly wrong. It is easy to see that each of the sums of integrals in Eqs. 4 and 6 is a trace of a matrix of a totally symmetric operator, for example,

$$\begin{aligned} \sum_k \sum_m J_{km} &= \sum_k \sum_m (\hat{J}_k)_{mm} = \sum_m (\hat{J}_c)_{mm} \\ &= \sum_k \sum_m (\hat{J}_m)_{kk} = \sum_k (\hat{J}_o)_{kk}, \end{aligned} \tag{7}$$

where  $\hat{J}_c$  and  $\hat{J}_o$  are totally symmetric Coulomb operators for the closed and open shells, respectively [2], and hence, all the sums of integrals in Eqs. 4 and 6 are invariant under unitary transforms of orbitals within the closed or open shells. In whole, the expression for the energy (6) is orbital-independent, i.e., all the orbitals having the same occupation number enter Eq. 6 in an equivalent form.

To clarify the source of the wrong claims [1] we here recall that, according to Roothaan, the energy is “the average expectation value for all the degenerate total wave functions of the state under consideration” [2, p. 183]. For the particular case of a  $2^{S+1}L$  atom discussed in [1], the Roothaan’s definition of the energy [2, p. 183] can be presented in the form:

$$\begin{aligned} E_{ROHF}(2^{S+1}L) &= \frac{1}{(2S + 1)(2L + 1)} \sum_{M_S} \sum_{M_L} \langle \Psi(S, M_S, L, M_L) | \hat{H} | \Psi(S, M_S, L, M_L) \rangle, \end{aligned} \tag{8}$$

where  $\Psi(S, M_S, L, M_L)$  represents the family of the total degenerate ROHF wave functions of the true spin and spatial symmetry. Each of these wavefunctions is a combination of Slater determinants, the coefficients of which are fully defined by symmetry, and the sum (8) is invariant under unitary transforms of the orbitals.

The definition of the energy by a formula of the kind (8) is the fundamental idea of Roothaan that enabled him to overcome the problems arising in ROHF calculations of degenerate electronic states. Although all the matrix elements in Eq. 8 representing the energy of the respective  $(S, M_S, L, M_L)$  states,

$$\langle \Psi(S, M_S, L, M_L) | \hat{H} | \Psi(S, M_S, L, M_L) \rangle = E(S, M_S, L, M_L), \quad (9)$$

are equivalent (and are equal to the left-hand side of Eq. 8), a direct evaluation of the energy by Eq. 9 for the case  $L > 0$  gives an orbital-dependent expression, i.e., an expression of the kind (1) in which the degenerate open-shell orbitals having the same occupation number appear in a non-equivalent form. Application of the variational principle to the so derived energy functional (1) gives orbitals that do not possess the true spatial symmetry (for details, see [2] and references therein).

As compared to this, the representation of the energy (8) in terms of integrals  $H_{ii}$ ,  $J_{ij}$  and  $K_{ij}$  gives the constrained form for the energy functional possessing all the desired transformation properties. For the particular case of one-open-shell systems discussed by Roothaan, i.e., for an atom having the open-shell configuration  $s^1$  or  $p^N$  ( $N = 1, 2, \dots, 5$ ) and a linear molecule with configurations  $\pi^N$  or  $\delta^N$  ( $N = 1, 2, 3$ ), the representation of the energy (8) in the form (1) immediately yields the formula (6) with the coefficients  $f$ ,  $a$ , and  $b$  presented in Roothaan's paper [2].

The further analysis of the wrong claims [1] has revealed an unexpected issue. A comparison between the "new" expression for the energy of atom C ( $^3P, 1s^2 2s^2 2p^2$ ), presented in Guseinov's paper as an example (see Table 3 in [1]), and the respective Roothaan's energy (6) where  $f = 1/3$ ,  $a = 3/4$ ,  $b = 3/2$  [2] shows that both expressions for the energy are *identical*. A similar identity has been found between the expression (6) and Guseinov's expressions for the energy of atom N ( $^4S, 1s^2 2s^2 2p^3$ ) and of high-spin excited states of atoms C ( $^5S, 1s^2 2s^1 2p^3$ ) and N ( $^6S, 1s^2 2s^1 2p^3 3s^1$ ) presented in the recent paper [7].

There is nothing surprising in the identity of the energies (6) and [1, 7] for one-open-shell systems, as Guseinov's approach [1, 7] to deriving the expression for the ROHF energy is identical to the classic Roothaan's approach [2] based on a direct evaluation of the expression (8). It should be emphasized here that Roothaan's definition (8) is presented in the paper [1] but in the form of *Guseinov's original equation* (see Eq. 7 and the respective text in [1]) without a reference to the classic work [2].

## 2 Fock operators and total one-electron Hamiltonian

Application of the variational principle to the energy functional (1) gives the familiar Euler equations [2, 8]:

$$\hat{F}_i |\phi_i\rangle = \sum_j |\phi_j\rangle \theta_{ji}, \quad (10a)$$

$$\theta_{ji} = \theta_{ij}^*, \quad (10b)$$

where  $\theta_{ji} = \langle \phi_j | \hat{F}_i | \phi_i \rangle$  are the Lagrangian multipliers, and  $\hat{F}_i$  is the Fock operator

$$\hat{F}_i = f_i \left( \hat{h} + \sum_j f_j (2a_{ij} \hat{J}_j - b_{ij} \hat{K}_j) \right), \quad (11)$$

expressed in terms of the Hermitian one-electron  $\hat{h}$ , Coulomb  $\hat{J}_j$  and exchange  $\hat{K}_j$  operators. Within the ROHF method the Eqs. 10–11 were first derived by Fock [8]. The set of coupled equations (10) can be solved using Hinze and Yutsever's technique [9] implemented, for example, in program Monstergauss [10].

An alternative but equivalent approach to minimizing the energy (1) lies in combining the Euler equations (10a), (10b) into the generalized Hartree–Fock equation:

$$\hat{R}|\phi_i\rangle = \varepsilon_i|\phi_i\rangle, \quad (12)$$

where  $\hat{R}$  is the total one-electron Hamiltonian usually called a unified coupling operator (UCO). The sought-for definition of  $\hat{R}$  was originally derived by Roothaan for states characterized by two coupling coefficients (5), (see Eq. 36 in [2]).

The idea of reducing the Euler equations (10) to the Hartree–Fock equation (12) and his novel approach to constructing an orbital-independent ROHF Hamiltonian (12) represent the second fundamental contribution of Roothaan to a development of the ROHF method.

Based on the well-known equations 10–12 we can revert to a discussion of the assumption (ii) above. For completeness, we also present here another Guseinov's assumption presented in his previous paper [11]: “*a single Fock operator does not exist*”. According to the terminology [1, 11], the phrase “*a single Fock operator*” means a total ROHF Hamiltonian (12), while the phrase “*the Fock operators of Roothaan's approach*” means the two operators of Roothaan's two-Hamiltonian approach [2]. It follows from Eqs. 10–12 that both assumptions [11] and (ii) are wrong. The assumption [11] merely shows that Guseinov is unaware of the definition of the ROHF Hamiltonian given by Roothaan. The assumption (ii) is wrong because each of the two-Hamiltonian approach operators (see Eqs. 31–32 in [2]) is Hermitian and totally symmetric, and hence, can be diagonalized.

### 3 Generalizations of the Roothaan's approach

The most general definition for the UCO (12) valid for an arbitrary (non-repeated) state arising from an arbitrary many-open-shell electronic configuration was first derived by Dyadyusha and Kuprievich [12], and, later and independently, by Hirao and Nakatsuji [13]. Both derivations [12, 13] are essentially based on the commutation relationships of McWeeny [5]. We here present the definitions [12, 13] in the same (slightly simplified) form:

$$\begin{aligned} \hat{R} &= \hat{R}_{(1)} + \hat{R}_{(2)} + \hat{R}_{(3)} \\ &= \sum_i \rho^i \hat{Q} \rho^i \\ &\quad + \sum_i [(I - \rho) \hat{F}_i \rho^i + \rho^i \hat{F}_i (I - \rho)] \\ &\quad + \sum_i \sum_j \lambda_{ij} \rho^j (\hat{F}_i - \hat{F}_j) \rho^i, \end{aligned} \quad (13)$$

where  $\rho^i = |\phi_i\rangle\langle\phi_i|$  and  $\rho = \sum_{(i)} \rho^i$  are the projection operators;  $\hat{F}_i$  is the Fock operator (11);  $I$  stands for identity operator;  $\lambda_{ij} = -\lambda_{ji}$  are arbitrary nonzero numbers; and  $\hat{Q}$  is an arbitrary (nonzero) totally symmetric operator.

As shown in [12, 13], the general definition (13) is reduced to the one given by Roothaan [2] by appropriate choice of arbitrary operator  $\hat{Q}$  and coefficients  $\lambda_{ij}$  (and of other arbitrary coefficients that appear in the original definitions [12, 13]). Of particular interest is the case of high-spin half-filled open-shell systems characterized by Roothaan coefficients  $f = 1/2$ ,  $a = 1$ ,  $b = 2$  [2]. For this case, various ROHF treatments based on the one-, two-, and three-Hamiltonian approaches [2, 14–18] as well as the atomic Roothaan–Hartree–Fock theory [19] and the Euler equations (10) can be presented in the same form of a one-Hamiltonian approach (12), in which the UCO takes the form (13) with different forms for the operator  $\hat{Q}$ . The respective forms of operator  $\hat{Q}$  are summarized in [20].

This shows that Guseinov’s assumption (iii) above is wrong. Below we also demonstrate that calculations by Guseinov et al. [7] based on the “new” approach [1, 11] have already been derived many years ago and that the real problems arising in ROHF calculations of certain (“non-Roothaan”) states [6] have not been even mentioned in [1, 7, 11].

#### 4 Two-open-shell systems

The general definition of the ROHF Hamiltonian (13) provides a solution of the problem of calculations of arbitrary open-shell systems by the Hartree–Fock method. The only remaining problem is a definition of coupling coefficients  $a_{ij}$  and  $b_{ij}$  of Eq. 1 specific for the state and configuration under study.

In order to perform a ROHF calculation of a state arising from the two-open-shell configuration  $\gamma_1^{N_1} \gamma_2^{N_2}$  such as  $s^1 p^N$  by Eqs. 12–13, one should define the two matrices of open-shell coupling coefficients of Eq. 1 having the form

$$\begin{array}{|c|c|} \hline a_{mn} & a_{mn'} \\ \hline a_{m'n} & a_{m'n'} \\ \hline \end{array} \quad (14)$$

where  $m, n \in \gamma_1$ , and  $m', n' \in \gamma_2$ . A derivation of coefficients (14) is trivial in the case of high-spin states of configurations  $s^1 p^N$  and  $s^1 d^N$  if the respective parent states of the one-open-shell configurations  $p^N$  and  $d^N$  are “Roothaan states”, i.e., are described by two coupling coefficients (5). For this case, coefficients (14) may be easily derived by direct representation of the expression (8) in the form (1). The so derived coefficients (14) for all the high-spin states of  $s^1 p^N$  configurations ( $N = 1–5$ ) and for a number of  $s^1 d^N$  states are summarized, for example, in the manuals to programs MELD [21], Monstergauss [10] and Turbomole [22].

In the recent paper [7], Guseinov et al. describe in detail a trivial procedure of deriving “coupling-projection” coefficients for the high-spin states of configuration  $s^1 p^N$ . (The so called “coupling-projection” coefficients [1, 7, 11] are nothing but coefficients (14) multiplied by  $f_m^2$ ,  $f_{m'}^2$ , and  $f_m f_{m'}$  in the diagonal and off-diagonal blocks, respectively. It should be noted here that the form [1, 7] for coefficients (14) has been

suggested several decades ago—see, for example, [3]). Needless to say that Guseinov's coefficients [7] are identical to those directly derived by Roothaan's equation (8) and summarized in [10,21,22].

## 5 “Non-Roothaan” states

More complex problems arise in ROHF calculations of so called “non-Roothaan”  $\gamma^N$  states [6] which cannot be described by two coupling coefficients (5) and are characterized by matrices  $a_{mn}$  and  $b_{mn}$  (3) of a general (real) form. Such states appear in the atomic configurations  $l^N$  ( $l = d, f, \dots$ ) [23,24] and in molecular configurations  $e^2$  ( $D_{4h}, C_{4v}, D_{2d}$ ) [25,26],  $t^N$  ( $T_d, O, O_h$ ) [26,27], and  $g^N$  ( $I, I_h$ ) [6], as well as in two-open-shell systems such as  $\pi_u^3\pi_g^1$  ( $D_{\infty h}$ ) [28] and  $p^{N_p}d^{N_d}$  [29].

A discussion of the problems arising in calculations of “non-Roothaan” states goes beyond the scope of this Comment, as these problems have not been even mentioned by Guseinov in his theory [1,7,11] claimed to be more general than all the previously developed ROHF treatments. We just refer the reader to a discussion of these problems in reviews [6,24].

## 6 Concluding remarks

We have shown that all the Guseinov's assumptions [1,7,11] concerning both the classic Roothaan's one-open-shell SCF theory [2] and the present state of the art of the ROHF method are *undisputedly wrong*. The main results and conclusions presented in the papers [1,7,11] are either trivial or contradictive. The examples presented above show that the expression for the ROHF energy of atomic  $p^N$  and high-spin  $s^1p^3$  states derived by Guseinov [1,7] is identical to Roothaan's expression (6). Disregarding this fact, Guseinov claims [1] that the famous Roothaan's formula (6) is wrong and that the same formula derived by Guseinov is correct [1]. The fundamental definition of the energy given by Roothaan [2] (this definition is presented by Eq. 8 above) has been presented in papers [1,7] in the form of *Guseinov's original equation*.

**Acknowledgments** This work was partially supported by the Russian Foundation for Basic Research (grant RFBR 06-03-32587) and by the grant for Fundamental Researches of the Chemistry and Material Science Section of the Russian Academy of Sciences.

## References

1. I.I. Guseinov, J. Math. Chem. **42**, 177 (2007)
2. C.C.J. Roothaan, Rev. Mod. Phys. **32**, 179 (1960)
3. R. Carbó, J.M. Riera, Lecture notes in chemistry, vol. 5. A general SCF theory (Springer, Berlin, 1978)
4. S. Huzinaga, *Method of Molecular Orbitals* (Mir, Moscow, 1983) (Translated from Japanese to Russian)
5. R. McWeeny, *Methods of Molecular Quantum Mechanics*, 2nd edn. (Academic Press, New York, 1992).
6. B.N. Plakhtin, in *Reviews of Modern Quantum Chemistry*, vol. I, ed. by K.D. Sen (World Scientific, Singapore, 2002), pp. 16–42
7. I.I. Guseinov, B.A. Mamedov, M. Erturk, H. Aksu, E. Sahin, Few-Body Syst. **41**, 211 (2007)
8. (a) V.A. Fock, Zs. f. Phys. **61**, 126 (1930); (b) V.A. Fock, Proc. State Opt. Inst. (USSR) **5**(51), 1–28 (1931)

9. J. Hinze, E. Yutsever, *J. Chem. Phys.* **70**, 3188 (1979)
10. M. Peterson, R. Pourier, Monstergauss-92, Department of Chemistry, University of Toronto and Memorial University of Newfoundland, St. John's, Newfoundland, Canada (1992)
11. I.I. Guseinov, *J. Mol. Struct. (Theochem)* **422**, 69 (1998)
12. G.G. Dyadyusha, V.A. Kuprievich, *Theor. Exp. Chem. (in Russian)* **1**, 406 (1965)
13. K. Hirao, H. Nakatsuji, *J. Chem. Phys.* **59**, 1457 (1973)
14. R. McWeeny, G. Diercksen, *J. Chem. Phys.* **49**, 4852 (1968)
15. E.R. Davidson, *Chem. Phys. Lett.* **21**, 565 (1973)
16. M.F. Guest, V.R. Saunders, *Mol. Phys.* **28**, 819 (1974)
17. J.S. Binkley, J.A. Pople, P.A. Dobosh, *Mol. Phys.* **28**, 1423 (1974)
18. K. Faegri, R. Manne, *Mol. Phys.* **31**, 1037 (1976)
19. C.C.J. Roothaan, P.S. Bagus, *Methods Comput. Phys.* **2**, 47 (1963)
20. B.N. Plakhutin, E.V. Gorelik, N.N. Breslavskaya, *J. Chem. Phys.* **125**, 204110 (2006)
21. L.E. McMurchie, S.T. Elbert, S.R. Langhoff, D. Feller, D.C. Rawlings, E.R. Davidson, *The MELD Series of Electronic Structure Codes* (Indiana University, Bloomington, IN, 2002)
22. <http://www.turbomole.com>
23. B.N. Plakhutin, G.M. Zhidomirov, A.V. Arbuznikov, *Int. J. Quantum Chem.* **41**, 311 (1992)
24. B.N. Plakhutin, *J. Math. Chem.* **22**, 203 (1997)
25. B.N. Plakhutin, G.M. Zhidomirov, *J. Struct. Chem. (in Russian)* **27**(2), 3 (1986)
26. G.T. Klimko, M.M. Mestechkin, B.N. Plakhutin, G.M. Zhidomirov, R.A. Evarestov, *Int. J. Quantum Chem.* **37**, 35 (1990)
27. B.N. Plakhutin, A.V. Arbuznikov, *Chem. Phys. Lett.* **232**, 247 (1995)
28. J.B. Rose, V. McKoy, *J. Chem. Phys.* **55**, 5435 (1971)
29. B.N. Plakhutin, A.V. Arbuznikov, A.B. Trofimov, *Int. J. Quantum Chem.* **45**, 363 (1993)