

## MULTIPLY STRUCTURE OF UHF WAVE FUNCTION

J. TIŇO and V. KLIMO

*Institute of Polymers, Slovak Academy of Sciences,  
809 34 Bratislava*

Received May 15th, 1975

Energy calculations were carried out for a selected system of radicals after a complete projection, annihilation and single annihilation. The relationship between the values of these energies and those obtained without the projection is discussed.

In spite of certain shortcomings the unrestricted Hartree-Fock method has become a powerful tool in quantum chemistry, namely when open-shell molecules are solved. Since the wave function does not represent a pure spin state a great attention is focused on the projection methods and on consequences of their use. In many cases the application of an annihilation operator gives satisfactory results<sup>1</sup>. If the mean value of operator  $S^2 \sim 0.75$  then the coefficients of the multiplet structure of the wave function<sup>2</sup>

$$\psi_U = \sum_S C_S \psi_S \quad (1)$$

are very small for higher multiplicities<sup>3</sup>. The annihilation operator is, however, not idempotent so that the average values of operators cannot be calculated by the simple annihilation technique (*asa*). It is, however, a common practice to do so since the relationship enabling to calculate  $E_{aa}$  (energy after annihilation) has not been derived. We shall calculate both  $E_{asa}$  and  $E_{aa}$  to show the consequences of the annihilator not being idempotent. The symbols used throughout this paper are identical with those used by Amos and Snyder<sup>4</sup>.

A series of papers due to Philips and Schug has shown certain interesting properties of the UHF wave function, namely its multiplet structure<sup>5-7</sup>. The Harriman method<sup>8</sup> used in their paper<sup>5</sup> was employed to calculate the energy of individual multiplets. Also some new aspects have been shown concerning the application of natural orbitals. Although the procedure is interesting and facilitates the use of the extended Hartree-Fock method<sup>11</sup> we shall use the method due to Mestechkin<sup>9</sup>. The latter method is an elegant culmination of the author's endeavour to formulate simply the Hartree-Fock problem by means of charge and spin-density matrices. The values of energies in the projected state will be calculated for a selected system of radicals.

*Relationship between Energies*

On the basis of expansion (1) it holds that

$$E_U = \sum_S \omega_S E_S \quad \omega_S = C_S^2$$

$$E_{PU} = E_{1/2},$$

$$E_{aa}^S = \frac{\sum_{S'} \omega_{S'} (B_{S'}^S)^2 E_{S'}}{\sum_{S'} \omega_{S'} (B_{S'}^S)^2} \quad \text{where} \quad B_{S'}^S = S'(S' + 1) - S(S + 1), \quad (2)$$

$$E_{asa}^S = \frac{\sum_{S'} \omega_{S'} B_{S'}^S E_{S'}}{\sum_{S'} \omega_{S'} B_{S'}^S}.$$

The basic inequalities for non-projected and projected energy and for the energy after annihilation of quartet component can be derived from equation (2). Inequalities (3)–(5) follow from the requirement  $E_{PU} \leq E_U$ ,  $E_{aa} \leq E_U$  and  $E_{PU} \leq E_{aa}$  while equation (6) holds for  $\Delta E_{asa}^{PU}$ .

$$\Delta E_{PU} = E_{PU} - E_U = \sum_{S'} \omega_{S'} (E_{1/2} - E_{S'}) \leq 0, \quad (3)$$

$$\Delta E_{aa}^{3/2} = E_{aa}^{3/2} - E_U \rightarrow \sum_{S'} \omega_{S'} (B_{S'}^{3/2})^2 (E_{S'} - E_U) \leq 0, \quad (4)$$

$$\Delta E_{aa}^{PU} = E_{PU} - E_{aa}^{3/2} \rightarrow \sum_{S'} \omega_{S'} (B_{S'}^{3/2})^2 (E_{1/2} - E_{S'}) \leq 0, \quad (5)$$

$$\Delta E_{asa}^{PU} = E_{PU} - E_{asa}^{3/2} = \frac{\sum_{S'} \omega_{S'} B_{S'}^{3/2} (E_{1/2} - E_{S'})}{\sum_{S'} \omega_{S'} B_{S'}^{3/2}}. \quad (6)$$

*Method of Calculation and Parameters*

The energy after a complete projection  $E_{PU}$  and other multiplet energies  $E_S$  corresponding to individual components of the expansion (1) were calculated according to Mestechkin and Whyman<sup>9</sup>. The system of free radicals (allyl, pentadienyl, benzyl, and cation and anion naphthalene radical) selected for the calculation was solved using the  $\pi$ -electron approximation (PPP method), the following parameters being employed: ionisation potential in the valence state 11.16 eV,  $\gamma_{ii} = 11.13$  eV,  $\beta_{ij} = -2.395$  eV (for neighbouring atoms, otherwise zero),  $r_{ij} = 1.4$  Å, gamma integrals being calculated by the Nishimoto–Mataga<sup>10</sup> approximation.

## RESULTS AND DISCUSSION

Besides calculations using the above mentioned parameters for given radicals we also employed parameters given by Phillips and Schug<sup>5</sup> for the case of allyl calculation:

$$\beta_{12} = -2.39 \text{ eV}, \quad \gamma_{11} = 11 \text{ eV}, \quad \gamma_{12} = 7.10 \text{ eV} \quad \text{and} \quad \gamma_{13} = 5.428 \text{ eV}.$$

TABLE I

Allyl Radical

Energy (in eV), expansion coefficients ( $\omega$ ) and spin densities ( $\rho$ ).

Parameter	Sando Harriman <sup>11</sup>	Schug Phillips <sup>5</sup>	Our results
$E_0$	-24.3455	-23.9608	-23.9608098
$E_{1/2}$	-24.4822	-24.0964	-24.0961479
$E_{3/2}$	<sup>a</sup>	-19.6280	-19.628000
$\omega_{1/2}$	<sup>a</sup>	0.96966	0.9697105
$\omega_{3/2}$	<sup>a</sup>	0.03034	0.0302895
$(\rho_1)_u$	0.651	<sup>a</sup>	0.6507
$(\rho_2)_u$	-0.302	<sup>a</sup>	-0.3014
$(\rho_1)_{1/2}$	0.547	0.5466	0.5466
$(\rho_2)_{1/2}$	-0.093	-0.0933	-0.0932

<sup>a</sup> Values not given.

TABLE II

Energy (in eV) and  $\omega$  Coefficients for a Selected System of Radicals

Parameter	Allyl	Pentadienyl	Benzyl	Naphthalene <sup>+</sup>	Naphthalene <sup>-</sup>
$E_U$	-51.51470	-103.70608	-176.88824	-291.34934	-302.53994
$E_{1/2}$	-51.80482	-104.20611	-177.32221	-291.46854	-302.65854
$E_{3/2}$	-48.04320	-101.30823	-174.25365	-286.70723	-297.90723
$E_{5/2}$	—	-96.95807	-170.59834	-281.88592	-293.07592
$E_{7/2}$	—	—	-165.45114	-276.98344	-288.17318
$E_{aa}$	-51.80482	-104.07784	-177.19663	-291.46357	-302.65357
$E_{asa}$	-51.80482	-104.28531	-177.39542	-291.47149	-302.66149
$\omega_{1/2}$	0.922874	0.835586	0.865114	0.975220	0.975220
$\omega_{3/2}$	0.077126	0.158995	0.129475	0.024601	0.024601
$\omega_{5/2}$	—	0.005419	0.005355	0.000178	0.000178
$\omega_{7/2}$	—	—	0.000056	0.000000	0.000000
$\omega_{9/2}$	—	—	—	0.000000	0.000000

The results of these authors are not in agreement with those published by Sando and Harriman<sup>11</sup>. Table I presents our values which are identical with those calculated by Phillips and Schug. The small differences may be due to both inconsistencies in accuracy of diagonalization procedure and number of iteration steps during the SCF procedure (our results correspond to 13th iteration step in which there is the closest agreement with values of Phillips and Schug<sup>5</sup>).

Löwdin has shown<sup>12</sup> that in the case of an orthonormal set of molecular orbitals,  $M$  being equal to zero, the higher multiplicity states (expansion (1)) possess lower energy ( $E_S \geq E_{S+1}$  for  $S = 0, \dots, q$ ). This conclusion is correct also when  $M \neq 0$ . Therefore for the doublet state ( $S = 1/2$ ) the expression  $E_S - E_{S'} \geq 0$  in inequality (3). Since the value of  $\omega_S$  is not negative this inequality is never fulfilled. The projection in the orthonormal base always increases the energy. On the other hand, as it follows from Table II and Fig. 1 presented in paper<sup>13</sup>, the sequence of multiplet energies is in reversed order in the MO base which is orthonormal only within  $\alpha$  or  $\beta$  electrons. In such a base the projection will always decrease the energy.

On the other hand, the multiplet energy corresponding to  $S = 3/2$  is higher than  $E_U$ . The coefficients  $\omega_S$  for  $S = 5/2$  and higher are small (Table II). Similarly as in (3) it is possible to write  $E_{3/2} - E_U = \sum_S \omega_S (E_{3/2} - E_S)$ ; the main contribution in this sum is due to the first term and assuming that  $E_{3/2} - E_{1/2} > 0$  one obtains  $E_{3/2} > E_U$ . The scheme of energetic levels in a molecule, which meets the requirements for the application of an annihilator<sup>1</sup> (see also Table II), looks as follows:

$$E_{1/2} < E_U < E_{7/2} < E_{5/2} < E_{7/2}.$$

Assuming this and taking into account the fact that  $B_{3/2}^{3/2} = 0$  the inequality (4) is always fulfilled. It follows from the latter inequality that the annihilation lowers the energy. According to inequality (5) however, the projected energy is lower than  $E_{aa}$ . This enables to arrange the following sequence:  $E_U \geq E_{aa} \geq E_{PU}$ .

It should be noted, however, that  $E_{aa}$  is not interchangeable for  $E_{asa}$  which can be lower than the energy after projection (Table II). This follows also from equation (6) when one takes into account that  $B_{1/2}^{3/2} = -3$  and  $B_{3/2}^{3/2} = 0$ . When assuming that the value of  $\omega_S$  is low for higher states, neglecting octet and higher states, it is possible to obtain  $E_{PU} \geq E_{asa}$  from equation (6).

#### REFERENCES

1. Amos A. T., Hall G. G.: Proc. Roy Soc. Ser A, 263, 483 (1961).
2. Sasaki F., Ohno K.: Mat. Phys. 4, 1140 (1963).
3. Tiño J., Klimo V.: This Journal 41, 960 (1976).
4. Amos A. T., Snyder L. C.: J. Chem. Phys. 41, 1773 (1964).
5. Phillips D. H., Schug J. C.: J. Chem. Phys. 61, 1031 (1974).
6. Phillips D. H., Schug J. C.: J. Chem. Phys. 57, 3498 (1972).

7. Schug J. C., Phillips D. H.: *J. Chem. Phys.* *59*, 1616 (1973).
8. Harriman J. E.: *J. Chem. Phys.* *40*, 2827 (1964).
9. Mestechkin M. M., Whyman C. E.: *Int. J. Quantum Chem.* *8*, 45 (1974).
10. Nishimoto K., Mataga N.: *Z. Phys. Chem. (Frankfurt am Main)* *12*, 335 (1957).
11. Sando K. M., Harriman J. E.: *J. Chem. Phys.* *47*, 180 (1967).
12. Löwdin P. O.: *Phys. Rev.* *97*, 1474 (1955).
13. Pauncz R. in the book: *Molecular Orbitals in Chemistry Physics and Biology* (P. O. Löwdin, B. Pullman, Eds), p. 440. Acad. Press, New York and London 1964.

Translated by J. Pác.