

## SOME REMARKS ON THE FOUNDATIONS OF THE IMPROVED LCAO THEORY

BY K. JANKOWSKI

Physics Department, Nicholas Copernicus University, Toruń\*

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Basing on the properties of really effective correlation factors a critical review of the foundations of Julg's improved LCAO method is presented.

A serious defect of the majority of existing semiempirical methods for treating pi-electronic systems is the lack of compact theoretical foundations. Therefore the "Improved LCAO Theory" of Julg [1]–[2] which seemed to possess strong theoretical justification is worthy of noticing. By means of this theory Julg and his school obtained a lot of interesting results. But in some cases *e. g.* for the benzene molecule [3], there exist serious discrepancies between theoretical and experimental positions of excited states.

The aim of the present note is a critical review of theoretical foundations of the Improved LCAO Theory, especially of the new, more complete, version presented by Julg in 1964 [4].

The essential point of Julg's theory is a statement that it is possible to introduce a great part of electron correlation into the theory, retaining the formalism of the independent-particle scheme, only by the modification of the potential part of the Hamiltonian, which gets the form

$$H = \sum_i (T(i) + U(i)) + \sum_{i < j} \frac{\Phi^2(r_{ij})}{r_{ij}}. \quad (1)$$

The electron-electron repulsion terms  $1/r_{ij}$  are replaced by terms of the form  $\varphi(r_{ij})/r_{ij}$ , where  $\varphi(r_{ij})$  is a correlation factor which will be discussed later.

Before we present our objections to the justification of the formalism based on expression (1) and its consequences, we will discuss briefly some general problems connected with the correlation factor method [5]. It seems to be useful because in the literature there is

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\* Address: Katedra Fizyki Doświadczalnej Uniwersytetu im. Mikołaja Kopernika, Toruń 1, Grudziądzka 5, Polska.

some arbitrariness in the interpretation of the role of correlation factors in the description of correlation effects. For reasons of convenience we confine us to the two-electron case.

In the independent-particle scheme the spatial part of the wavefunction for closed-shell systems may be written as

$$\Psi_0 = N_0 \varphi_1(\mathbf{x}_1) \varphi_1(\mathbf{x}_2) \quad (2)$$

where  $\varphi_1(\mathbf{x}_1)$  designates the one-electron wavefunction.

Julg and some other authors find it absurd that the probability density  $|\Psi_0(\mathbf{x}_1, \mathbf{x}_2)|^2$  for finding the electrons in the neighborhood of the points 1 and 2 respectively has a nonzero value when  $\mathbf{x}_1 = \mathbf{x}_2$ , because as they conclude, this has as a consequence the possibility of finding two electrons at the same point. To remove this difficulty Julg postulated to use functions of the form

$$\Psi = N \varphi_1(\mathbf{x}_1) \varphi_1(\mathbf{x}_2) \Phi(r_{12}) \quad (3)$$

with a correlation factor  $\varphi(r_{12})$ , being a function of the interelectronic distance  $r_{12}$ , fulfilling the condition

$$\Phi(0) = 0 \quad (4)$$

It should be emphasized that we have no information concerning the value of the exact wavefunction at the point  $r_{12} = 0$  as obtained from general analysis. Therefore we have no mathematical proof of the condition

$$\Psi(\mathbf{x}_1, \mathbf{x}_1) = 0, \quad (5)$$

as well as for the correctness of (4).

What concerns the physical arguments mentioned above it seems that they are also not so convincing because in the Schrödinger equation electrons are considered as point particles for which the probability to be at the same points is of course zero. Therefore there are no reasons to force the approximate wavefunction to fulfill condition (5). This seems also to be confirmed by the result of Fock [6] from which it follows that the two-electron wavefunction for the ground state have in the region near the nucleus a behaviour of

$$\Psi \sim 1 - Z(r_1 + r_2) + \frac{1}{2} r_{12} + \dots \quad (6)$$

where  $Z$  is the nuclear charge.

Therefore it seems that the only cogent arguments for the introduction of correlation factors in order to describe correlation effects may be obtained on the ground of the energy criterion.

From this point of view functions of the form (3) are much better suitable than functions (2) when certain class of  $\Phi(r_{12})$  functions is used. Let us now recall the most important properties of that class of functions which really describe correlation effects, and compare them with the properties postulated by Julg in the foundation of his theory.

The results of numerous calculations showed that correlation effects may be introduced

into the wavefunction (2) only by these factors which in the region of small  $r_{12}$  values up to 2 a. u. behave approximately like the functions

$$\Phi(r_{12}) = 1 + \alpha r_{12} \quad (7)$$

where  $\alpha$  fulfills the condition  $0.2 < \alpha < 0.6$ . This property of the effective correlation factors is of course incompatible with (4).

It has also been shown [7], [8] that in the case of the helium ground state the region in which the correlation factors are important extends over a wide vicinity of the point  $r_{12} = 0$ , which has the dimensions comparable to that of the system under consideration (about 2 a. u.).

It should be mentioned that calculations for systems more directly connected with pi-electronic systems than the helium atom in its ground state disclosed the same features *e. g.* Dewar and Chung [9] used the correlation factor method for the  $(2p_0)^2$  state of helium, which may be considered as a model for an atom in the pi-electronic system.

These in one sense "empirical" results may be better understood on the ground of more fundamental considerations. It has been shown [10]–[12] that there exists a great class of really effective correlation factors which allow to eliminate the singularities from the Schrödinger equation and, therefore reproduce the correct behaviour of the wavefunctions in the region of small  $r_{12}$  values what is impossible by means of products of one-electron functions only. All other, really effective, correlation factors mentioned above are related to that class [12].

Bearing in mind all previous remarks let us proceed to the justification of Julg's procedure [4]. The considerations of Julg base on two assumptions which are difficult to justify from our point of view.

(a) The function  $\Phi(r_{12})$  is essentially different from unity only in a little sphere around the point  $r_{12} = 0$ . A radius of this sphere was adopted which is nearly two orders of magnitude inferior with respect to the radius of effectiveness of correlation factors mentioned above (2 a. u.).

(b) In the interior of this sphere it adopts the form

$$\Phi(r_{12}) = Ar_{12}^n \quad (8)$$

where  $n$  is a great number. This assumption is in evident contradiction with Fock's result [6] and with equation (7) fulfilled by all really effective factors. Functions with correlation factors of that form also do not allow to fulfill the well known correlation cusp condition

$$\left( \frac{1}{\Psi} \frac{\partial \Psi}{\partial r_{12}} \right)_{r_{12}=0} = \frac{1}{2}. \quad (9)$$

Only on the ground of these two assumptions it is possible to obtain the fundamental normalization condition

$$\int \int \varphi_1^2(\mathbf{x}_1) \varphi_1^2(\mathbf{x}_2) \Phi^2(r_{12}) dV_1 dV_2 = 1 \quad (10)$$

in the case of normalized one-electron functions  $\varphi_1(\mathbf{x})$ . Without equation (10) it is impossible to justify the correctness of the modified Hamiltonian and, therefore of the whole Improved LCAO Theory.

At the end, in order to get some insight into the situation obtained when correlation factors similar to the form postulated by Julg were used, we present results of a calculation for the helium ground state with the factor  $\Phi(r_{12}) = \alpha r_{12}$  admitted by Julg [2]. The values (in a.u.) of the energy and matrix element  $\langle r_{12}^{-1} \rangle$  for the function  $\Psi = N \exp[-\eta(r_1+r_2)]r_{12} - E = -2.60453$ ,  $\langle r_{12}^{-1} \rangle = 0.7206$  are much inferior to its counterparts  $-2.84766$  and  $1.0547$  when the uncorrelated function  $\exp[-\eta(r_1+r_2)]$  is used the "exact" Pekeris results are  $-2.90372$ ,  $0.9458$ ). It is thus evident that the factor  $\alpha r_{12}$  is useless in the description of correlation effects from the point of view of the energy criterion. That factor also reduces much too strongly the value of the matrix element  $\langle r_{12}^{-1} \rangle$  which is sensitive to correlation effects. This element is also frequently considered as the analog of the one-center Coulomb repulsion integral of the pi-electron theory. It is noteworthy that the value of this integral obtained for the carbon atom with Slater atomic orbitals was reduced some years ago by introduction of the correlation factor  $\alpha r_{12}$  from the value  $17.3$  eV to  $10.29$  eV, which is in good agreement with the values used in the semiempirical theory. This reduction is also possible for the really effective correlation factors. When the factor  $1 + 0.5r_{12}$  was used we obtained the value  $12.94$  eV which is quite near to its counterpart obtained by Orloff and Sinanoglu [13] in their advanced analysis ( $12.72$  eV).

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