

CONTRIBUTIONS TO THE GENERAL THEORY OF LCAO-MO METHOD

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The coefficients of the AO's in different MO's belonging to degenerate energy states and the physical quantities dependent on these coefficients, as well, are not unequally determined, but are dependent on diophantic parameters of uncertainty. It will be proved that: (i) the diophantic parameters of uncertainty refer to rotations in the eigenspace of MO's belonging to degenerate energy states; (ii) in the case of closed shells of MO's the physical quantities are independent of the diophantic parameters of uncertainty; (iii) the physical quantities in the case of non-closed electron shells of MO's are only independent of the diophantic parameters of uncertainty if the "number of electrons" is the same on the different MO's corresponding to the same energy.

§ 1. Introduction

Owing to the great success of the molecular orbital (MO) method — particularly if one considers the MO's as linear combinations of atomic orbitals (LCAO-MO method) — in dealing with the practical problem of quantum chemistry, the general theory of the LCAO-MO method has been investigated in detail by several authors [1]—[5]. Nevertheless, in order to solve an actual problem of quantum chemistry by the LCAO-MO method, one of us (M. I. B.) has suggested a practical problem which may also be of interest from the point of view of the general theory, especially in the case of non-closed electron shells (in terms of ROOTHAAN [5]). It is well-known on the one hand that the coefficients of atomic orbitals (AO) in different MO's belonging to degenerate energy states are not unequally determined and on the other hand that such important quantities as the electron densities and the bond orders, respectively, are dependent on these coefficients of the AO's. As a matter of fact, it should be of interest in which cases these quantities are not influenced by the uncertainty of the coefficients of AO's in MO's. It will be proved below that (i) the uncertainty of the electron density as well as that of the bond order due to the uncertainty of the coefficients of AO's in MO's for closed shells are automatically eliminated; (ii) in the case of

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non-closed shells in order to remove the same difficulty the equalization of the "number" of electrons among the MO's belonging to the same energy will be proposed.

§ 2. Reinvestigation of benzene as a model

To prepare the general treatment let us briefly investigate the well-known problem of benzene. Taking only the π electrons of the C atoms of benzene into account, the MO's of the π electrons will be denoted by

$$\psi = \sum_{r=1}^6 c_r \Phi_r, \quad (2, 1)$$

where the index r of the AO's refers to atom r ($r=1, 2, \dots, 6$). The energy of the MO's as well as the coefficients of the AO's in these MO's can be obtained by solution of the system of linear equations:

$$\sum_{r=1}^6 c_r (\mathcal{H}_{sr} - E \mathcal{S}_{sr}) = 0, \quad (s=1, 2, \dots, 6) \quad (2, 2)$$

with

$$\mathcal{H}_{sr} = \int \Phi_s^* H \Phi_r d\tau, \quad \mathcal{S}_{sr} = \int \Phi_s^* \Phi_r d\tau, \quad (2, 3)$$

where H denotes the Hamiltonian of the system. Without any essential specialization of the problem suggested, one can only deal with the well-known approximation of the LCAO-MO method:

$$\mathcal{S}_{sr} = \delta_{sr}, \quad \mathcal{H}_{sr} = \begin{cases} \alpha & \text{for } s=r, \\ \beta & \text{for } s=r \pm 1, \\ 0 & \text{otherwise.} \end{cases} \quad (2, 4)$$

The solution of equation (2, 2) leads to four energy values, two of which belong to doubly degenerated energy states. For sake of perspicuity of the following paragraphs the energy values as well as the MO's, *i.e.* electron shells, will be denoted as follows:

$$E_{i,\varrho}: \quad \begin{aligned} E_{1,1} &= \alpha + 2\beta, & E_{2,1} &= E_{2,2} = \alpha + \beta, \\ E_{3,1} &= E_{3,2} = \alpha - \beta, & E_{4,1} &= \alpha - 2\beta, \end{aligned} \quad (2, 5)$$

$$\psi_{i,\varrho} = \sum_{r=1}^6 c_{ri,\varrho} \Phi_r. \quad (i=1, \dots, 4; \varrho=1, 2) \quad (2, 6)$$

Note that the first index of $c_{ri,\varrho}$ (as well as in the following s, t, u) refers to the AO's, the second one (as in the following j, k, l) to the MO's; by the third one (as in the following by σ, τ) the different MO's are denoted belonging to the degenerated energy $E_{i,\varrho}$ and $\varrho=1, 2, \dots, f_i$, where f_i refers to the order of degeneracy of energy $E_{i,\varrho}$.



Owing to the orthonormality of the MO's belonging to different electron shells:

$$\int \psi_{i,\sigma}^* \psi_{j,\sigma} d\tau = \delta_{ij} \quad (2, 7)$$

and (2, 4), we have

$$\sum_{r=1}^6 c_{ri,\sigma}^* c_{rj,\sigma} = \delta_{ij}. \quad (2, 8)$$

In order to determine the MO's *i. e.* the coefficients of the AO's in the MO's explicitly, one can proceed by the following two methods:

2.1. Taking the equations (2, 2) and (2, 8) into account in the cases $i=1$ and $i=4$ the coefficients $c_{ri,\sigma}$ can be immediately obtained. However, in the case of the degenerated energy states $i=2$ and $i=3$ our equations (2, 2) and (2, 8) do not provide equations enough for the determination of $c_{ri,\sigma}$'s. As matters stand, one can use [6], *e. g.*, for $i=2$ the following method:

Due to (2, 2) for the $c_{r2,\sigma}$ the relations

$$c_{12,\sigma} = -c_{42,\sigma}; \quad c_{22,\sigma} = -c_{52,\sigma}; \quad c_{32,\sigma} = -c_{62,\sigma} = -c_{12,\sigma} + c_{22,\sigma} \quad (2, 9)$$

can be obtained. Considering also the equations (2, 8) we have 10 equations for the 12 unknown coefficients ($\sigma=1, 2$). Let the uncertainty be expressed by the diophantic parameters λ_2 and μ_2 :

$$\begin{aligned} c_{12,1} &= -c_{42,1}, & c_{12,2} &= -c_{42,2} = (1-\mu_2)c_{22,2}, \\ c_{22,1} &= -c_{52,1} = \lambda_2 c_{12,1}, & c_{22,2} &= -c_{52,2}, \\ c_{32,1} &= -c_{62,1} = (\lambda_2 - 1)c_{12,1}; & c_{32,2} &= -c_{62,2} = \mu_2 c_{22,2}. \end{aligned} \quad (2, 10)$$

Table I*

r	$i=1$	$i=2$		$i=3$		$i=4$
		$\sigma=1$	$\sigma=2$	$\sigma=1$	$\sigma=2$	
1	$6^{-1/2}$	k	$3^{-1/2}(2\lambda_2 - 1)k$	$-3^{-1/2}(2\lambda_3 + 1)k'$	k'	$6^{-1/2}$
2	$6^{-1/2}$	$\lambda_2 k$	$3^{-1/2}(\lambda_2 - 2)k$	$3^{-1/2}(\lambda_3 + 2)k'$	$\lambda_3 k'$	$-6^{-1/2}$
3	$6^{-1/2}$	$(\lambda_2 - 1)k$	$-3^{-1/2}(\lambda_2 + 1)k$	$3^{-1/2}(\lambda_3 - 1)k'$	$-(1 + \lambda_3)k'$	$6^{-1/2}$
4	$6^{-1/2}$	$-k$	$-3^{-1/2}(2\lambda_2 - 1)k$	$-3^{-1/2}(2\lambda_3 + 1)k'$	k'	$-6^{-1/2}$
5	$6^{-1/2}$	$-\lambda_2 k$	$-3^{-1/2}(\lambda_2 - 2)k$	$3^{-1/2}(\lambda_3 + 2)k'$	$\lambda_3 k'$	$6^{-1/2}$
6	$6^{-1/2}$	$-(\lambda_2 - 1)k$	$3^{-1/2}(\lambda_2 + 1)k$	$3^{-1/2}(\lambda_3 - 1)k'$	$-(1 + \lambda_3)k'$	$-6^{-1/2}$

* In Table I $k = (4\lambda_2^2 - 4\lambda_2 + 4)^{-1/2}$ and $k' = (4\lambda_3^2 - 4\lambda_3 + 4)^{-1/2}$

Since, the different MO's belonging to the same electron shell can be orthonormalized one can replace (2, 8) by

$$\sum_{r=1}^6 c_{ri,\sigma}^* c_{rj,\sigma} = \delta_{ij} \delta_{\sigma\sigma}, \quad (2, 11)$$

therefore, our system of equations is completed by

$$c_{12,1} c_{22,2} [1 - \mu_2 + \lambda_2 + \mu_2(\lambda_2 - 1)] = 0 \quad (c_{12,1} c_{22,2} \neq 0) \quad (2, 12)$$

and, finally, we have

$$\mu_2 = -\frac{\lambda_2 + 1}{\lambda_2 - 2}. \quad (2, 13)$$

This means that the coefficients of the AO's in the MO's are only dependent on λ_i . (Table I.)

2.2. For sake of simplicity one can use the method of group theory. Taking, e. g., the C_{3v} symmetry of benzene into consideration, then the 6-dimensional representation Γ in the linear space of AO's is splitting into

$$\Gamma = 2A_1 + 2E. \quad (2, 14)$$

(Concerning the notation cf. e. g. [7]). The corresponding new basic vectors are

$$\begin{aligned} \varphi^{(A_1)} &= 1/\sqrt{3}(\Phi_1 + \Phi_2 + \Phi_3); & \varphi^{(A_1')} &= 1/\sqrt{3}(\Phi_2 + \Phi_4 + \Phi_5); \\ \varphi_1^{(E)} &= 1/\sqrt{2}(\Phi_2 - \Phi_6), & \varphi_2^{(E)} &= 1/\sqrt{6}(2\Phi_4 - \Phi_3 - \Phi_6); \\ \varphi_1^{(E')} &= 1/\sqrt{2}(\Phi_2 - \Phi_5), & \varphi_2^{(E')} &= 1/\sqrt{6}(\Phi_3 + \Phi_5 - 2\Phi_1). \end{aligned} \quad (2, 15)$$

Naturally, the energy values are the same ones as in (2.5). As to the determination of $c_{ri,\sigma}$ one can use our equation (2, 2) and (2, 8) again, but, of

Table II

r	$i=1$	$i=2$		$i=3$		$i=4$
		$e=1$	$e=2$	$e=1$	$e=2$	
1	$6^{-1/2}$	$3^{-1/2}$	0	0	$3^{-1/2}$	$6^{-1/2}$
2	$6^{-1/2}$	$12^{-1/2}$	-2^{-1}	2^{-1}	$-12^{-1/2}$	$-6^{-1/2}$
3	$6^{-1/2}$	$-12^{-1/2}$	-2^{-1}	-2^{-1}	$-12^{-1/2}$	$6^{-1/2}$
4	$6^{-1/2}$	$-3^{-1/2}$	0	0	$3^{-1/2}$	$-6^{-1/2}$
5	$6^{-1/2}$	$-12^{-1/2}$	2^{-1}	2^{-1}	$-12^{-1/2}$	$6^{-1/2}$
6	$6^{-1/2}$	$12^{-1/2}$	2^{-1}	-2^{-1}	$-12^{-1/2}$	$-6^{-1/2}$

course, the AO's have to be replaced by the basic vectors (2, 15). The $c_{ri, \varrho}$ are in this case unambiguous (Table II), and the relations of orthonormality (2, 11) are automatically fulfilled.

Taking other symmetry groups of benzene into account (e. g. C_{2v} , D_{6h} [8]) for $c_{ri, \varrho}$ exactly the same table as Table II can be obtained.

One observes immediately that Table II with $\lambda_2 = 1/2$ and $\lambda_3 = -1/2$ can be derived from Table I.

§ 3. Electron density and bond order

As is well-known based on the LCAO-MO method several quantities characterizing the physical and chemical properties of molecules (in the following *physical quantities*) can be dealt with. Owing to a previous investigation of C. A. COULSON and H. C. LONGUET-HIGGINS [4] all of these physical quantities can be derived from the *electron density at the atom r*

$$q_r = \sum_i \sum_{\varrho=1}^{f_i} n_{i, \varrho} c_{ri, \varrho}^* c_{ri, \varrho} \quad (3, 1)$$

and from the *bond order between the atoms r and s*

$$p_{rs} = \sum_i \sum_{\varrho=1}^{f_i} n_{i, \varrho} c_{ri, \varrho}^* c_{si, \varrho}, \quad (3, 2)$$

where $n_{i, \varrho}$ refers to the number of electrons in MO $\psi_{i, \varrho}$ and the sum has to be extended over all electron shells of the MO's.

Owing to the fact that the coefficients of AO's in MO's with $f_i > 1$ are depending on λ_i , i. e.

$$c_{ri, \varrho} = c_{ri, \varrho}(\lambda_i), \quad (3, 3)$$

one may generally expect that the electron density as well as the bond order are also dependent on λ_i 's:

$$q_r = q_r(\lambda_1, \lambda_2, \dots) \quad \text{and} \quad p_{rs} = p_{rs}(\lambda_1, \lambda_2, \dots), \quad (3, 4)$$

respectively.

In spite of this one can observe that, e. g., for benzene

$$q_r = 1 \quad \text{and} \quad p_{rs} = \frac{2}{3} \quad (s = r + 1, r = 1, 2, \dots, 6). \quad (3, 5)$$

This means that the electron density and the bond order do not depend on the diophantic parameter of uncertainty introduced.

However, for the positive molecule-ion of benzene having a π -electron system of only five electrons on suggesting the occupation of the energy states by electrons as

$$n_{1,1} = 2, \quad n_{2,1} = 2, \quad n_{2,2} = 1, \quad n_{3,1} = n_{3,2} = n_{4,1} = 0, \quad (3, 6a)$$

and as

$$\tilde{n}_{1,1} = 2, \quad \tilde{n}_{2,1} = 1, \quad \tilde{n}_{2,2} = 2, \quad \tilde{n}_{3,1} = \tilde{n}_{3,2} = \tilde{n}_{4,1} = 0, \quad (3, 6b)$$

respectively, the electron densities at the different atoms

$$q_1 = q_4 = \frac{1}{12} \frac{8\lambda_2^2 - 8\lambda_2 + 11}{\lambda_2^2 - \lambda_2 + 1}, \quad q_2 = q_3 = q_5 = q_6 = \frac{1}{12} \frac{11\lambda_2^2 - 8\lambda_2 + 8}{\lambda_2^2 - \lambda_2 + 1}, \quad (3, 7a)$$

and

$$\tilde{q}_1 = \tilde{q}_4 = \frac{1}{4} \frac{4\lambda_2^2 - 4\lambda_2 + 3}{\lambda_2^2 - \lambda_2 + 1}, \quad \tilde{q}_2 = \tilde{q}_3 = \tilde{q}_5 = \tilde{q}_6 = \frac{1}{4} \frac{3\lambda_2^2 - 4\lambda_2 + 4}{\lambda_2^2 - \lambda_2 + 1}, \quad (3, 7b)$$

respectively, can be obtained, without having any physical reason to dis-

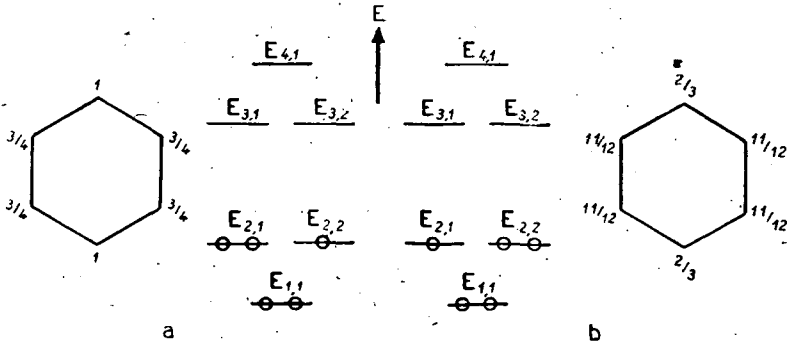


Fig. 1

tinguish among the two distributions proposed. Fig. 1 refers to both models (3, 6a) and (3, 6b), respectively, for $\lambda = 1/2$.

Concerning the bond orders one can obtain similar results for benzene as well as for the molecule-ion of benzene too.

It seems as if in the case of the electron shells of MO's filled up by electrons and in that of electron shells of MO's without electrons (benzene), respectively, the electron density as well as the bond order are independent of the diophantic parameters of uncertainty introduced; however, in the case of electron shells of MO's which are not filled up by electrons (molecule-ion of benzene) both quantities are dependent on the diophantic parameters of uncertainty without any physical reason. Whether these conclusions can be generally suggested will be discussed in the next paragraph.

§ 4. Investigation and removal of the uncertainty

In order to really understand the meaning of the uncertainty mentioned in the previous two paragraphs let us consider the functional space of MO's. First, it seems suitable to formulate the problem in the case of benzene for $i = 2$ again.

4.1. The functional space of the corresponding MO's — being the eigenspace of energy $E_{2,\varrho}$ — is in this case a two-dimensional subspace of all the MO's. One can use arbitrary pairs of functions of this eigenspace as basic vectors fulfilling (2, 11). Let us consider the MO's

$$\begin{aligned}\psi_{2,1} &= 1/\sqrt{3} \left(\Phi_1 + \frac{1}{2} \Phi_2 - \frac{1}{2} \Phi_3 - \Phi_4 - \frac{1}{2} \Phi_5 + \Phi_6 \right), \\ \psi_{2,2} &= 1/2 (-\Phi_2 - \Phi_3 + \Phi_5 + \Phi_6),\end{aligned}\quad (4, 1)$$

which can be obtained by the method mentioned in 2.1. In view of fact that the basic vectors (4, 1) are real, by a rotation with angle α another arbitrary basis system

$$\begin{aligned}\psi'_{2,1} &= \psi_{2,1} \cos \alpha + \psi_{2,2} \sin \alpha \\ \psi'_{2,2} &= -\psi_{2,1} \sin \alpha + \psi_{2,2} \cos \alpha\end{aligned}\quad (4, 2)$$

can be derived from the basis system (4, 1).

One may observe, of course, a correspondence between the diophantic parameter of uncertainty λ_2 and the angle α of rotation and it can be proved that

$$\lambda_2 = \frac{1}{2} (1 \pm \sqrt{3} \operatorname{tg} \alpha) \quad (4, 3)$$

is valid for all values of α . By the usual limiting process one can easily see that the coefficients of the AO's in MO's are finite also for the case $\alpha = \pi/2, 3\pi/2$.

Due to these considerations the diophantic parameter of uncertainty gets an immediate geometrical meaning.

4.2. Now, the question has to be investigated in which cases the diophantic parameters of uncertainty occur? Taking the considerations of 4.1. into account it looks as *if and only if the quantum mechanical problem has degenerated energy states*. Namely, on the one hand, only the eigenspace of degenerated energy states are multi-dimensional and on the other hand, only in this case can different orthonormal basis systems in the eigenspace of MO's — connected by orthogonal transformations — be introduced. Finally, these orthogonal transformations may be characterized by diophantic parameters of uncertainty.

In the course of our above considerations we have only explicitly considered the double-degenerated energy state $E_{2,\varrho}$ ($\varrho = 1, 2$) of benzene. One can readily see that in the case of a f_i -dimensional eigenspace of energy $E_{i,\varrho}$ ($\varrho = 1, 2, \dots, f_i$) the number of diophantic parameters of uncertainty is the same as the number of parameters of the f_i -dimensional rotational group.

Let us consider the f_i -dimensional eigenstate of the f_i -fold-degenerated energy state $E_{i,\varrho}$ ($\varrho = 1, 2, \dots, f_i$) as well as two different basis systems $\{\psi_{i,\varrho}\}$ and $\{\psi'_{i,\varrho}\}$, respectively. They are connected by orthogonal transformations $S = (S_{\varrho\sigma})$:

$$\psi'_{i,\varrho} = \sum_{\sigma=1}^{f_i} S_{\varrho\sigma} \psi_{i,\sigma} \quad (4, 4)$$

with

$$\sum_{\varrho=1}^{f_i} S_{\varrho\sigma} S_{\varrho\tau} = \delta_{\sigma\tau}. \quad (4, 5)$$

Considering that on the one hand due to (2, 6) and (3, 3) one can generally write

$$\begin{aligned} \psi_{i,\sigma} &= \sum_{r=1}^N c_{ri,\sigma}(\lambda_i) \Phi_r, \\ \psi'_{i,\varrho} &= \sum_{r=1}^N c_{ri,\varrho}(\lambda_i) \Phi_r \end{aligned} \quad (4, 6)$$

and on the other hand taking (4, 4) into account one has

$$\psi'_{i,\varrho} = \sum_{\sigma=1}^{f_i} S_{\varrho\sigma} \sum_{r=1}^N c_{ri,\sigma}(\lambda_i) \Phi_r = \sum_{r=1}^N \sum_{\sigma=1}^{f_i} S_{\varrho\sigma} c_{ri,\sigma}(\lambda_i) \Phi_r. \quad (4, 7)$$

Thus one can immediately obtain:

$$c_{ri,\varrho}(\lambda_i) = \sum_{\sigma=1}^{f_i} S_{\varrho\sigma} c_{ri,\sigma}(\lambda_i), \quad (4, 8)$$

where N refers to the number of the AO's of the problem considered, furthermore λ_i and λ'_i denote the set of diophantic parameters of uncertainty. It may be observed in this way in what manner the uncertainty can be represented by the matrix instead of the diophantic parameters.

4. 3. Owing to the definitions of the electron density (3, 1) and that of bond order (3, 2), for investigation of the dependence of physical quantities on the diophantic parameters of uncertainty it will be enough to deal with the bond order:

$$\begin{aligned} p'_{rs} &= \sum_i^{f_i} \sum_{\varrho=1}^{f_i} n_{i,\varrho} c_{ri,\varrho}^*(\lambda_i) c_{si,\varrho}(\lambda_i) = \\ &= \sum_i^{f_i} \sum_{\sigma=1}^{f_i} \sum_{\tau=1}^{f_i} c_{ri,\sigma}^*(\lambda_i) c_{si,\tau}(\lambda_i) \sum_{\varrho=1}^{f_i} n_{i,\varrho} S_{\varrho\sigma} S_{\varrho\tau}. \end{aligned} \quad (4, 9)$$

It can be proved that *the bond order and the physical quantities are only independent of the diophantic parameters of uncertainty if the number of electrons $n_{i,\varrho}$ does not depend on ϱ , i. e. if the "number" of electrons is the same on the different MO's corresponding to the same energy E_i .*

Namely, for

$$n_{i,\varrho} = n_i = \text{const (dependent on } i) \quad (4, 10)$$

due to (4, 9) and (4, 5)

$$\begin{aligned} p'_{rs} &= \sum_i \sum_{\sigma=1}^{f_i} \sum_{\tau=1}^{f_i} c_{ri, \sigma}^* (\lambda_i) c_{si, \tau} (\lambda_i) n_i \delta_{\sigma\tau} = \\ &= \sum_i \sum_{\sigma=1}^{f_i} n_i c_{ri, \sigma}^* (\lambda_i) c_{si, \sigma} (\lambda_i) = p_{rs} \end{aligned} \quad (4, 11)$$

can be obtained.

4.4. In order to summarize the physical conclusions of the above results it looks as if the guess suggested at the end of § 3. would be generally proved:

(i) *in the case of closed electron shells of MO's the physical quantities are independent of the diophantic parameters of uncertainty, i. e. of the choice of the basis systems in the different subspaces of MO's.*

Namely, in this case the $n_{i, q}$'s are either 2 or 0 and, of course, the condition (4, 10) is fulfilled.

Owing to this result, a remark of Appendix 2 of COULSON and LONGUET-HIGGINS's paper [4] seems to be unnecessary, since, that paper refers only to closed shells.

(ii) *in the case of non-closed electron shells of MO's to render possible the independence of physical quantities from the diophantic parameters of uncertainty the "number" of electrons must be the same on the different MO's corresponding to the same energy.*

Consider the example of benzene again. In spite of (3, 6a) and (3, 6b) we have

$$n_{1,1} = 2, \quad n_{2,1} = n_{2,2} = 1,5, \quad n_{3,1} = n_{3,2} = n_{4,1} = 0. \quad (4, 12)$$

One can immediately see that in this case

$$q_i = 5/6 \quad (i = 1, 2, \dots, 6). \quad (4, 13)$$

It looks as if the suggested solution of the problem might be accepted also from the physical point of view, namely, in the case of unperturbed systems one has not any argument to expect some asymmetry in the electron density of the molecules *etc.*, except if the asymmetry mentioned would be based on any physical reason.

Furthermore, it is well known that — according to MCCONNEL's theory of paramagnetic resonance for aromatic systems — the distances of hyperfine structure lines of protons are dependent on the electronic densities at the C atoms. However, in such cases it was not observed so far that any difference between the hyperfine structure lines would have occurred. As a matter of fact, our proposal based on quite other arguments is supported by these experimental evidences too.

4.5. Finally, we have to consider the generalizations of the version of the LCAO-MO method mentioned. The generalization means, *e. g.*, that at the approximation of higher orders some of our suppositions (2, 4) have to be

changed. Due to WIGNER's results [9] — although the energy values and the coefficients of AO's in MO's as well can be modified — the degeneration induced by the symmetry of the molecules, the so-called *normal degeneration*, cannot be eliminated. This means, however, that the problem treated above occurs in general cases too and it can immediately be proved that our above considerations can be repeated without any difficulty.

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ЗАМЕЧАНИЯ ОБ ОБЩЕЙ ТЕОРИИ МЕТОДА МО-ЛКАО

М. И. Бан, Ф. И. Гилде и Я. И. Хорват

Коэффициенты атомных орбит в различных молекулярных орбитах, относящихся к вырожденному значению энергии, и физические величины, зависящие от этих коэффициентов, неоднозначны, а они зависят от параметров неопределенности Диофанта. Было показано: что (I) эти параметры Диофанта связаны с поворотами собственного поля, относящегося к вырожденному значению энергии; и что (II) физические величины, в случае занятых МО, не зависят от параметров Диофанта; и что (III) физические величины, в случае не совсем занятых МО, только тогда независимы от параметров Диофанта, когда число электронов является тождественным для различных МО, относящихся к вырожденному значению энергии.