Quantum-mechanical analysis of the MO method and VB method from the position of PQS.

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Abstract: The MO method and the VB method are analyzed using the principle of quantum superposition (PQS) and the method of describing a quantum system consisting of several parts. It is shown that the main assumption of the molecular orbitals method (namely, that the molecular orbital can be represented like a linear combination of overlapping atomic orbitals) enters into an insurmountable contradiction with the principle of quantum superposition. It is also shown that the description of a quantum system consisting of several parts (adopted in quantum mechanics) actually prohibits ascribe in VB method to members of equation corresponding canonical structures.

Keywords: The method of molecular orbitals, linear combination of atomic orbitals, valence bonds method, the principle of quantum superposition, quantum mechanics, the superposition of "wave functions".

INTRODUCTION.

The basis of mathematical apparatus of quantum mechanics constitutes assertion that the state of a quantum system can be described by a certain function of the coordinates ψ (q) called a wave function (the square of the modulus of this function determines the probability distribution of coordinate values) [1]. The MO method, like the VB method [2, 3], uses the wave function ψ to describe the behavior of electrons in atoms and molecules. Therefore, both the MO method and the VB method can be analyzed using the PQS. To do this, let us recall the principle of quantum superposition (PQS) [4, p. 1]: “For example, consider two quantum states (actually existing) are described by wave functions ψ1 and ψ2. From the principle of superposition [1, p. 21] it should be clearly, that their linear combination ($\psi 3 = C_1\psi 1 + C_2\psi 2$) will be the third quantum state (as actually existing), which will be described by a wave function $\psi 3$. What does it mean? The fact that the measurement of a certain physical value d in the state $|\psi 1>$ will result d_1, and for measure a value for of d in the state $|\psi 2>$ will result d_2. When the third quantum state $|\psi 3>$ is realized, then when measuring a physical quantity, the quantum system will take the values d_1 and d_2 with probabilities, respectively, $|C_1|$^2 and $|C_2|$^2. That is, in a quantum state $|\psi 3>$ when we will have many dimensions sometimes d_1 value and sometimes d_2 (with certain known frequency).”.

It should also be noted that since L. Pauling's resonance theory is a particular case of the VB theory, the conclusion made about the insuperable conflict of resonance theory with the quantum superposition principle [4] can be transferred to the VB theory. In the VB method, the wave equations as well as in the theory of resonance are written for each of the possible electronic structures of the molecule [3] (each of them is called the canonical structure) and the total function ψ is obtained by summing all conceivable functions with the corresponding weight coefficients:

$$\psi = C_1\psi 1 + C_2\psi 2 + C_3\psi 3 + \dots$$

where $\psi 1$, $\psi 2$, $\psi 3$ — are wave functions of canonical structures.

In calculations using the MO method, the wave function is represented by a linear combination of overlapping atomic orbitals [3] (called linear combination of atomic orbitals):

$$\psi = C_1\psi 1 + C_2\psi 2$$

where $\psi 1$, $\psi 2$ — wave functions of atomic orbitals, and C_1, C_2 — represent their weight coefficients.

But then it is obvious that both the MO method and the VB method contradict the principle of quantum superposition. Since the real molecule in the VB method will be described by a discrete set of canonical structures, which does not correspond to the existence of a single real molecule.

Similarly, in the MO method, the molecular orbital will be described by a discrete set of AO, which also does not correspond to the provisions of the MO theory. Next, we will carry out a more detailed analysis of the theory of the VB and the theory of MO.

RESULTS AND DISCUSSION.

For a more detailed analysis, it is necessary to take into account one nuance. To this end, consider a quantum system consisting of two parts. Suppose that the state of this system is given in such a way that each of the parts is described in its entirety. Then we can assert [1, p. 21], that the probabilities of the coordinates q_1 of the first part are independent of the probabilities of the coordinates q_2 of the second part, and therefore the probability distribution for the system as a whole must be equal to the product of the probabilities for its parts. This means that the wave function $\psi 12\ (q_1, q_2)$ of the system can be represented as the multiplication of the wave functions $\psi 1\ (q_1)$ and $\psi 2\ (q_2)$ of its parts:

$$\psi 12\ (q_1,\ q_2) = \psi 1\ (q_1) * \psi 2\ (q_2)$$

It should be noted that if both parts do not interact with each other, then this relationship between the wave functions of the system and its parts will continue at future times:

$$\psi 12\ (q_1,\ q_2, t) = \psi 1\ (q1, t) * \psi 2\ (q_2, t)$$

Therefore, in quantum chemistry, when considering molecules in the approximation of independent particles, the many-electron wave function must have the form of a multiplication of one-electron wave functions [2, p. 212]. But there are two ways to construct such a molecular wave function:

1. In the MO method, we choose the multiplication of members that are themselves linear combinations of one-electron wave functions:

$$\psi MO = \psi MO_1 * \psi MO_2$$

$$\psi MO_1 = C_1\psi AO\ A(1) + C_2\psi AO\ B(1)$$

$$\psi MO_2 = C_1\psi AO\ A(2) + C_2\psi AO\ B(2)$$

2. In the VB method choose a linear combination of members, each of which is a multiplication of one-electron wave functions:

$$\psi VB = C_1\psi AO\ A(1) * \psi AO\ B(2) + C_2\psi AO\ A(2) * \psi AO\ B(1)$$

Let us analyze these equations in more detail. We begin with the MO method.

$$\psi MO = \psi MO_1 * \psi MO_2$$

$$\psi MO_1 = C_1\psi AO\ A(1) + C_2\psi AO\ B(1)$$

$$\psi MO_2 = C_1\psi AO\ A(2) + C_2\psi AO\ B(2)$$

In the MO theory one basic assumption is made [3] that the wave function of the one-electron molecular orbitals is a linear combination of single-electron atomic orbitals of individual atoms (for a diatomic molecule AB, ψA (AO) and ψB (AO)):

$$\psi MO = C_1\psi A\ (AO) + C_2\psi B\ (AO)$$

for example, consider the first quantum state of an electron that represents this electron located on the atomic orbital of atom A and which is described by the wave function $\psi AO\ A\ (1)$. The second quantum state of the same electron will be a given electron located on the atomic orbital of atom B and described by the wave function $\psi AO\ B\ (1)$. From the principle of quantum superposition it follows that their linear combination

$$\psi 3 = C_1\psi AO\ A(1) + C_2\psi AO\ B(1)$$

will be the third quantum state, which will be described by the wave function $\psi 3$. According to the MO method, their linear combination will be a molecular orbital. But this directly contradicts the principle of quantum superposition. Proceeding from this equation

$$\psi 3 = C_1\psi AO\ A(1) + C_2\psi AO\ B(1)$$

and according to the principle of quantum superposition, when the third quantum state is realized $|\psi 3>$ (which is described by the wave function $\psi 3$), then when measuring a physical quantity, for example, the orbital energy, the quantum system will take the values of E_1 (the energy of the atomic orbital of atom A) and E_2 (the energy of the atomic orbital of atom B) with frequency respectively $|C1|^2$ and $|C2|^2$, that is, it will have a discrete description. When measuring the energy of a given orbital, we sometimes register the value of E_1, and sometimes the value of E_2. But this directly contradicts the idea of the MO method, since one-electron MO should be formed with an energy lower (if it is a bonding MO) than the energies of individual AO (according to the idea of linear combination of atomic orbitals, two MOs are formed from two AO, one MO with reduced energy and the other MO with increased energy). But the principle of quantum superposition prohibits this. With a linear combination of one-electron atomic orbitals, we will not be able to obtain a "new quality", that is, a one-electron molecular orbital, but we will have the spectrum of AO.

Analysis of the second equation

$$\psi MO_2 = C_1\psi AO\ A(2) + C_2\psi AO\ B(2)$$

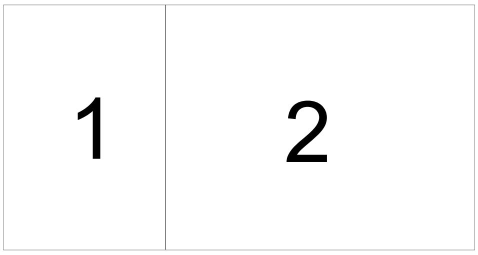
In which a linear combination of one-electron atomic orbitals of atoms A and B is considered, it is completely analogous to the foregoing. Therefore, the MO theory, like the VB theory, is insuperably contradictory to the principle of quantum superposition.

Now we will analyze the VB method.

As already mentioned above, in the VB method, choose a linear combination of members, each of which is a multiplication of one-electron wave functions. So for a diatomic molecule A-B (for example, hydrogen molecules), we get the following equation:

$$\psi VB = C_1\psi AO\ A(1) * \psi AO\ B(2) + C_2\psi AO\ A(2) * \psi AO\ B(1)$$

On the right-hand side of this equation, the first part ($C_1\psi AO\ A(1) * \psi AO\ B(2)$) describes the quantum system that consists of two parts. The first part of this system represents the atom A with the first (1) electron on the atomic orbital (atom A), the second part represents the atom B with the second (2) electron on the atomic orbital (atom B). The second part ($C_2\psi AO\ A(2) * \psi AO\ B(1)$) describes a quantum system when electrons 1 and 2 are reversed. And further in quantum chemistry is told occurrence due to these exchanges between electrons exchange interaction which leads to the formation of an appropriate molecule (in our case, hydrogen molecules). Moreover, these members are associated with canonical structures. For further consideration, it is necessary to remember how the wave function of a quantum system consisting of two parts is expressed. Consider the quantum system depicted in the figure and consisting of two parts 1 and 2.



$\psi 1\ (q_1)$ $\psi 2\ (q_2)$

In quantum mechanics [1, p. 21] it is shown that the wave function $\psi 12\ (q_1,\ q_2)$ of the system can be represented as a multiplication of the wave functions $\psi 1\ (q_1)$ and $\psi 2\ (q_2)$ and it's parts:

$$\psi 12\ (q_1,\ q_2) = \psi 1\ (q_1) * \psi 2\ (q_2)$$

And now look at the parts of the equation (from VB method):

$$\psi VB = C_1\psi AO\ A(1) * \psi AO\ B(2)\ +\ C_2\psi AO\ A(2) * \psi AO\ B(1)$$

Consider, for example, the first part:

$$C_1\psi AO\ A(1) * \psi AO\ B(2)$$

We see the multiplication of one wave function that describes the one-electron atomic orbital of atom A to another wave function that describes the one-electron atomic orbital of atom B. That is, this multiplication of two wave functions $\psi AO\ A(1) * \psi AO\ B(2)$ describes a system of two atoms A and B with the first (1) and second (2) electrons in the corresponding atomic orbitals. Especially note that it is the system of two isolated atoms, but not a molecule.

Similarly, the second part:

$$C_2\psi AO\ A(2) * \psi AO\ B(1)$$

Describes a system of two atoms A and B with the second (2) and first (1) electrons in the corresponding atomic orbitals (the electrons are reversed). Therefore, it is not entirely correct to ascribe to any member (or the sum of members) the canonical structure, since the description of two isolated atoms is not a description of the molecule that was formed from these two atoms. Permutations of electrons also do not significantly change anything, since two atoms remain two atoms in which the electrons are reversed. Two atoms are just two isolated atoms, but not a molecule. So if we mentally "place next" two hydrogen atoms, then the distance between the nuclei will be 1.06 Å (two Bohr radius), and the bond length in the hydrogen molecule is 0.74 Å, which confirms (for chemists it is obvious) that a system of two isolated atoms (the number of atoms doesn't matter) is not a canonical structure.

Therefore, when describing the molecule in the VB method, using the corresponding equations (and as a consequence of canonical structures), the chemical bond is simply "lost". Moreover, attributing to the members of the corresponding equation of canonical structures contradicts quantum mechanics, or more precisely, the description of a quantum system consisting of several parts.

The chemical bond was also "lost" in the MO description. This is easy to understand if we reduce the brackets to the corresponding equations in the corresponding equations:

$$\psi MO = \psi MO_1 * \psi MO_2$$

$$\psi MO_1 = C_1\psi AO\ A(1) + C_2\psi AO\ B(1)$$

$$\psi MO_2 = C_1\psi AO\ A(2) + C_2\psi AO\ B(2)$$

That is, we have:

$$\psi MO = \psi MO_1 * \psi MO_2 = (C_1\psi AO\ A(1) + C_2\psi AO\ B(1)) * (C_1\psi AO\ A(2) + C_2\psi AO\ B(2))$$

If we open the parentheses, we get members similar to the members of the equation from the VB method. Therefore, in order to "restore" the chemical bond in the corresponding equations and to exclude the inconsistency with the quantum superposition principle, it is necessary to not express MO in members of a linear combination of AO, but postulate the existence of MO as a new fundamental quality that describes a specific chemical bond and is not derived from simpler structural elements. Then we will "return" the chemical bond to the calculation methods and possibly significantly simplify the quantum chemical calculations. This is due to the fact that the energy of the chemical bonds is well known, and since the MO will describe the chemical bond (and the chemical bond energy is known), it will be easy to calculate the MO energy simply by substraction the chemical bond energy from the AO energy.

Since the chemical bond is the result of the interaction of fermions and they interact [5] according to the Hückel rule (4n + 2) (or 2n, n - unpaired), we can schematically depict molecular orbitals similarly to atomic orbitals. The number of electrons according to Hückel's rule will be: 2, 6, 10, 14, 18, …

Accordingly, the molecular orbitals of the chemical bond are denoted as follows:

MO (s) is a molecular s-orbital, 1 cell, can contain up to 2 electrons.

MO (p) is a molecular p-orbital, 3 cells, can contain up to 6 electrons.

MO (d) - molecular d-orbital, 5 cells, can contain 10 electrons.

MO (f) is a molecular f-orbital, 7 cells, can contain up to 14 electrons.

MO (g) is a molecular g-orbital, 9 cells, can contain up to 18 electrons.

Then the usual single bond will be described by the molecular s-orbitale (MO(s)).

To describe the double bond, we need to assume that it is formed from two equivalent single bonds (as pointed out by L. Pauling [6]), and is then described by two molecular s-orbitals (2 MO(s)).

The triple bond will be described by a molecular p-orbital (MO (p)), then all six electrons of the triple bond will occupy one molecular p-orbit, which very well explains the difference between acetylene and ethylene (meaning C-H acidity).

In benzene 18 - electronic cyclic system can occupy one molecular g-orbital (MO(g)).

To describe the molecules, it is still necessary to introduce the concept of the molecular orbitals of an undivided pair, we shall designate it as MO(uns), on which the electrons of an undivided pair of atoms, unpaired electrons, and so on.

Then to describe the molecule it will be necessary to calculate the wave function which will be equal to the multiplication of all the wave functions of the chemical bonds and all the wave functions of the undivided pairs: $\psi MO = \psi MO(s1) * \psi MO(p) * \psi MO(s2) * \psi MO(uns) * \psi MO(uns2)$ ...

Wave functions that describe chemical bonds and undivided pairs are selected using mathematical expediency.

CONCLUSION.

Using the quantum superposition principle, the MO method and the VB method were analyzed and it is shown that they are in contradiction with quantum mechanics. Also, using the quantum-mechanical description of a system consisting of several parts, it is shown that the attribution of canonical structures to the members of the equation is incorrect. Therefore, both the MO method and the VB method did not describe molecules with chemical bonds but actually, a lot of independent atoms (of which the described molecules consisted). That is, in the quantum chemical calculations, the chemical bond was "lost". Therefore, in order to "introduce" a chemical bond into calculations and avoid conflict with quantum mechanics, it is suggested to postulate the existence of MO as a new fundamental quality that describes a specific chemical bond and is not derived from simpler structural elements.

REFERENCES.

1. L. D. Landau, E. M. Lifshitz, Theoretical physics in 10 volumes. Volume 3. Quantum mechanics. Fourth Edition. Moscow .: Science, 1989, pages 19 - 21. ISBN 5-02-014421-5 (Volume 3).

2. R. Flurry. Quantum Chemistry. Introduction. Translated from English. Moscow .: Mir, 1985, pages 202, 212 - 217.

3. J. March. Organic Chemistry. Reactions, mechanisms, and structure. Advanced course for universities and chemical universities. In four volumes. Volume 1. Translated from English. Moscow .: Mir, 1987, pages 17 — 18.

4. Bezverkhniy V. D., Bezverkhniy V. V. Quantum-mechanical aspects of the L. Pauling's resonance theory. p. 1. http://vixra.org/pdf/1702.0333v2.pdf

5. Bezverkhniy V. D. Review. Benzene on the basis of the three-electron bond. p. 75 http://vixra.org/pdf/1612.0018v5.pdf

6. Pauling L. Kekule and chemical bonding. Theoretical Organic Chemistry. Translation from English edition of 1959 year, Edited by R.H. Freidlin. Moscow. Foreign Literature Publishing House, 1963, p. 8.