Hybridization theory of L. Pauling, chemical bond and quantum mechanics.

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Abstract: The theory of hybridization of atomic orbitals of L. Pauling is analyzed using the principle of quantum superposition. It is shown that the principle of quantum superposition, and therefore quantum mechanics as a whole, is in insurmountable contradiction with the theory of hybridization of atomic orbitals. Since the concept of σ- and π-bonds automatically follows from the theory of hybridization, the classical chemical description of single, double and triple bonds (based on σ- and π-bonds) is also in insurmountable contradiction with the principle of quantum superposition.

Keywords: The theory of hybridization of atomic orbitals of L. Pauling, principle of quantum superposition, chemical bond, σ-bond, π-bond, MO method.

INTRODUCTION.

Hypothesis of hybridization, that is, the mixing of atomic orbitals, was proposed by L. Pauling in 1931 to explain the tetrahedral environment of methane-type compounds [1]. The carbon atom at the external energy level has 2s- and 2p-orbitals, and therefore the methane molecule must form chemical bonds of different energy and direction: three identical bonds directed at a right angle (2p-orbitals are used), and the fourth weaker bonding directed in some arbitrary direction (2s-orbital is used). But, in fact, all four bonds of methane have the same energy and are spatially equivalent (directed to the vertices of the tetrahedron). To explain this fact, L. Pauling proposed the hypothesis of AO hybridization: in the presence of four hydrogen atoms, the 2s- and 2p-orbitals of the carbon atom form four equivalent hybrid orbitals in energy and direction (sp^3 orbitals), which are directed along four bonds C-H [2].

This approach (hybridization theory) has been widely applied in chemistry and today it gives a simple orbital picture equivalent to Lewis structures. The theory of hybridization is an integral part of organic chemistry, since the concept of σ- and π-bonds, and hence the concept of single and multiple chemical bonds, is a consequence of the hybridization of carbon atoms. In fact, the classical concept of a localized chemical bond is based on the hybridization hypothesis. Therefore, the theory of hybridization explains the bonding in alkanes, alkenes, alkynes and other organic and inorganic compounds, and also makes it possible to draw various mechanisms of organic reactions (electrophilic addition, nucleophilic substitution, etc.).

RESULTS AND DISCUSSION.

In the MO method, the molecular orbital in the classical canonical description is a delocalized orbital, while the concept of a localized chemical bond (that is, a bond between two atoms) loses meaning [3]. Let us quote from the book "Theory of the Structure of Molecules" (see the link), which conveys well the meaning of what was said (a description is given of MO typical for university textbooks on quantum chemistry) [3]:

"In the qualitative theory of MO, the molecular orbitals of polyatomic molecules obtained as a result of approximate solutions of the Schrödinger equation are, in the general case, multicenter functions — linear combinations of the AO of several atomic centers. Such a description is not directly related to the concept of chemical bonding in structural theory, where a bond is a local property that relates to two neighboring atoms. Atomic orbitals can be transformed in such a way as to give them the direction characteristic of the configuration of chemical bonds formed by a given atom, and based on these new (hybrid) AO, approach description and prediction geometry of molecules.

The concept of hybridization of atomic orbitals were introduced in the 1930s by L. Pauling. The concept of hybridization of orbitals is closely related to the concept of localized MO.

...The MO molecules delocalized over many centers, obtained by solving the Roothaan equations (4.62), called canonical MO, can be converted to another kind of MO localized on specific bonds (or fragments) of the molecule. Such MO are called localized and denoted as LMO".

If you look at the wave functions of the canonical delocalized MO of methane [3, p. 386]:

$$\Psi 1 = A(2S) + B(Ha + Hb + Hc + Hd)$$

$$\Psi 2 = A(2px) + B(Ha + Hb - Hc - Hd)$$

$$\Psi 3 = A(2py) + B(Ha - Hb - Hc + Hd)$$

$$\Psi 4 = A(2pz) + B(Ha - Hb + Hc - Hd)$$

It is obvious that canonical MO are completely delocalized over all hydrogen atoms in a molecule, and are not localized on individual C–H bonds. Since each canonical MO includes 1s-orbitals of all four hydrogen atoms, that is, each MO is delocalized over all four C–H bonds, and therefore the concept of a localized chemical bond does not make sense (in this description). Moreover, the reduced system of equations is confirmed by experimental data of photoelectron spectroscopy, which clearly show the presence of two energy levels in the methane molecule:

the first ionization potential of methane (13.2 eV) corresponds to the separation of an electron from one of $\Psi(2, 3, 4)$-orbitals;

the second ionization potential of methane (22.1 eV) corresponds to the separation of an electron from $\Psi 1$-orbital [3, p. 386].

The presence of the methane molecule of the two "first" ionization potentials cannot be explained using equivalent hybridized MO, since with this description all bonds in the methane molecule are absolutely equivalent, and therefore all 8 electrons are also equivalent (and therefore the first ionization potential must be one). But the data of photoelectron spectroscopy show that such a description does not correspond to reality. But it must be remembered that if the MO method is analyzed from the point of view of quantum mechanics, then it is also not true, since it contradicts the principle of quantum superposition [4].

It can be shown that the theory of hybridization also contradicts the principle of quantum superposition. This is evident already from the fact that hybridization AO are obtained in hybridization theory by mixing the corresponding AO (s-, p-, d-) of a particular atom, that is, they are obtained by a linear combination of AO [3, p. 387]. But, from the principle of quantum superposition it strictly follows that with a linear combination of AO it is impossible to obtain a "new quality", that is, a hybrid AO (or MO) [4, pp. 3 - 5]. It does not matter to whom the original AO belong: to one atom (hybridization theory) or to various atoms (MO theory).

Recall that in the theory of MO, one fundamental assumption is made, namely, that the wave function of the one-electron molecular orbital Ψ_{MO} is a linear combination of one-electron AO of different atoms. So for the diatomic molecule A-B, we get the equation [5]:

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

In hybridization, we also have a linear combination of one-electrons AO, but already one atom, for example, a carbon atom. For sp-hybridized orbitals, this can be written as:

$$\Psi\ (sp\text{-}AO) = C_1\ \Psi\ (s\text{-}AO) + C_2\ \Psi\ (p(x)\text{-}AO)$$

L. Pauling for the methane molecule gave an equivalent series of tetrahedral (hybrid) orbitals, see picture [6]:

$$t_{111} = \frac{1}{2}(s + p_x + p_y + p_z);$$

$$t_{1\bar{1}\bar{1}} = \frac{1}{2}(s + p_x - p_y - p_z);$$

$$t_{\bar{1}1\bar{1}} = \frac{1}{2}(s - p_x + p_y - p_z);$$

$$t_{\bar{1}\bar{1}1} = \frac{1}{2}(s - p_x - p_y - p_z).$$

As can be seen from the Pauling equations, they essentially do not different from the corresponding equation for the MO: in both cases we have a linear combination of AO, but for hybridization, these one-electron orbitals belong to the same atom.

Thus, both the MO theory and the hybridization theory are based on one fundamental assumption:

the resulting wave function of a single-electron orbital (or MO, or hybrid AO) is a linear combination of single-electron atomic orbitals (or different atoms, or one atom).

Let us demonstrate this by the general equation of the wave function of the one-electron orbital for MO of a diatomic molecule (A-B), and an sp-hybrid AO:

$$\Psi(\text{MO or sp-AO}) = C_1\, \Psi(\text{AO(A) or s-AO}) + C_2\, \Psi(\text{AO(B) or p(x)-AO})$$

Therefore, the proof given about the contradiction of MO theory to the principle of quantum superposition is also correct for the theory of hybridization, since the principle of quantum superposition in any linear combination of AO prohibits obtaining a “new quality” (or MO, or hybridized AO) [4]. This strictly follows from the very principle of quantum superposition [7]. Let's turn to the proof.

To do this, we recall the principle of quantum superposition [8]: “For example, consider two quantum states (actually existing) are described by wave functions $\psi1$ and $\psi2$. From the principle of superposition [1, p. 21] it should be clearly, that their linear combination ($\psi3 = C_1\psi1 + C_2\psi2$) will be the third quantum state (as actually existing), which will be described by a wave function $\psi3$. What does it mean? The fact that the measurement of a certain physical value d in the state $|\psi1>$ will result d_1, and for measure a value for of d in the state $|\psi2>$ will result d_2. When the third quantum state $|\psi3>$ 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 $|\psi3>$ when we will have many dimensions sometimes d_1 value and sometimes d_2 (with certain known frequency)”.

And we take into account the fact that in quantum chemistry, when considering molecules in the approximation of independent particles, the many-electron wave function should have the form of a product of one-electron wave functions [9, 7]. Therefore, for the theory of hybridization, we construct such a hybrid wave function like the product of terms that are themselves linear combinations of one-electron wave functions:

$$\Psi(sp(x)\text{-}AO) = \Psi(sp(x)\text{-}AO)(1) * \Psi(sp(x)\text{-}AO)(2)$$

$$\Psi(sp(x)\text{-}AO)(1) = \Psi(s\text{-}AO)(1) + \Psi(p(x)\text{-}AO)(1)$$

$$\Psi(sp(x)\text{-}AO)(2) = \Psi(s\text{-}AO)(2) + \Psi(p(x)\text{-}AO)(2)$$

Here the numbers 1 and 2 are numbered electrons 1 and 2, which are located on the corresponding orbitals.

We will carry out a quantum mechanical analysis for the simplest case, namely for sp-hybridization, since it is obvious that the results of such an analysis will be correct for all other types of hybridization. To do this, consider a carbon atom (in the excited state), which has one electron per 2s-orbital and three electrons in three corresponding 2p-orbitals (2p(x)-, 2p(y)-, 2p(z)-). Analyze the sp(x)-hybridization. That is, we will consider only 2s-one-electron and 2p(x)-one-electron atomic orbitals. Then the main assumption of the theory of hybridization can be formulated as [6, pp. 87 - 104]: when hypothetically mixing one-electron 2s-orbital and one-electron 2p(x)-orbital, we obtain two energy-equivalent sp(x)-orbitals (directed to opposite ends of the x axis from the beginning of coordinates).

This assumption can be expressed by the corresponding equations:

$$\Psi(sp(x)\text{-}AO)(1) = \Psi(s\text{-}AO)(1) + \Psi(p(x)\text{-}AO)(1)$$

$$\Psi(sp(x)\text{-}AO)(2) = \Psi(s\text{-}AO)(2) + \Psi(p(x)\text{-}AO)(2)$$

Let's analyze the first equation:

$$\Psi(sp(x)\text{-}AO)(1) = C_1\,\Psi(s\text{-}AO)(1) + C_2\,\Psi(p(x)\text{-}AO)(1)$$

Consider the first quantum state of electron 1, which is this electron located on s-AO(1) and which is described by the wave function $\Psi(s\text{-}AO)(1)$. The second quantum state of the same electron will be a given electron located on p(x)-AO(1) and which is described by the wave function

Ψ(p(x)-AO)(1). From the principle of quantum superposition it clearly follows that their linear combination

$$\Psi(\mathrm{sp(x)\text{-}AO})(1) = C_1\,\Psi(\mathrm{s\text{-}AO})(1) + C_2\,\Psi(\mathrm{p(x)\text{-}AO})(1)$$

will be the third quantum state, which will be described by the wave function Ψ(sp(x)-AO)(1). From the fundamental assumption of the theory of hybridization, it clearly follows that their linear combination will be a hybrid orbital with a certain energy. But this directly contradicts the principle of quantum superposition.

Based on this equation

$$\Psi(\mathrm{sp(x)\text{-}AO})(1) = C_1\,\Psi(\mathrm{s\text{-}AO})(1) + C_2\,\Psi(\mathrm{p(x)\text{-}AO})(1)$$

and according to the principle of quantum superposition, when the third quantum state is realized |ψ3> (which is described by the wave function Ψ(sp(x)-AO)(1)), then, when measuring a physical quantity, for example, the energy of the orbitals, the quantum system will take the values E1 (energy s-AO) and E2 (energy p(x)-AO) with a frequency of |C1|^2 и |C2|^2, that is, it will have a discrete description. When measuring the energy of the hybrid orbitals, we will sometimes record the value of E1, and sometimes the value of E2. But this directly contradicts the idea of the theory of hybridization, since an sp(x)-hybrid one-electron orbital with a certain energy (Ei) different from the energies of individual (s-AO, p(x)-AO) should be formed. But the principle of quantum superposition forbids this. With a linear combination of one-electron atomic orbitals, we cannot get a “new quality”, that is, a sp(x)-hybrid one-electron orbital, but we will always have the corresponding AO spectrum. And this contradiction is fundamental and insurmountable.

Analysis of the second equation

$$\Psi(\mathrm{sp(x)\text{-}AO})(2) = C_1\,\Psi(\mathrm{s\text{-}AO})(2) + C_2\,\Psi(\mathrm{p(x)\text{-}AO})(2)$$

in which the linear combination of one-electron AO (s-AO, p(x)-AO) with the second electron (2) is completely similar to the above. Therefore, we can conclude that the theory of hybridization is in an insurmountable contradiction with the principle of quantum superposition and quantum mechanics in general.

CONCLUSION.

Using the principle of quantum superposition, the theory of hybridization L. Pauling is analyzed, and it is shown that it enters an irresistible contradiction with the principle of the quantum superposition. Moreover, this is a conceptual contradiction. Since proceeding from the hypothesis of atomic hybridization, a logical transition to the concept of σ- and π-bonds is carried out in chemistry, it is obvious that modern ideas about localized chemical bonds (single, multiple) contradict quantum mechanics as a whole. The reason is simple: the principle of quantum superposition prohibits to receive from the linear combination AO “new quality” (hybrid orbital, MO, σ-bond, π-bond, etc.), since according to this principle we only get a discrete description. Therefore, for a localized chemical bond, it is necessary to postulate the existence of MO as a new fundamental quality, which is not derived from simpler structural elements [4, pp. 7 - 8].

Using the Heisenberg uncertainty principle, a physically grounded theoretical model of chemical bonding can be obtained, by developing which, in the future, a complete theoretically rigorous description of a chemical bond can be obtained [10]. Modern concepts of chemical bonds (the concept of σ-bonds, π-bonds, single bonds, multiple bonds, etc.) should be considered as qualitative, which very clearly and simply explained the reasons for the formation of a chemical bond, and also made it possible to depict the mechanisms various reactions in organic chemistry.

It should be noted that it is reasonable to assume that a rigorous quantitative calculation of chemical bonding will undoubtedly have an “explosive” effect on quantum mechanics itself, or rather on its understanding, interpretation and development of its fundamental fundamentals, which will be determined by three basic principles:

1) the principle of uncertainty of Heisenberg;

2) wave-particle duality;

3) the oscillation hypothesis of Louis de Broglie [11].

It can also be hoped that the development of the theory of chemical bonding will clarify some questions of cosmology. Therefore, it is obvious that the theory of chemical bonding is important both for chemistry as a whole, and for quantum mechanics and cosmology.

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