Pauli principle, chemical bonding and atomic orbitals.

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According to the Pauli principle, two or more identical electrons cannot reside in the same orbital. But, it is necessary to clarify which orbitals are meant - atomic or molecular, and to consider the Pauli principle in more detail.

If we consider atomic orbitals, then everything is correct. But if we consider molecular orbitals, then some explanations are needed.

Firstly, the Pauli principle applies only to weakly interacting particles, when we can talk about the states of individual particles. Here is the corresponding quote [1]:

"...Of course, in this formulation, the Pauli principle can only be applied to systems of weakly interacting particles, when we can talk (at least approximately) about the states of individual particles...".

That is, if the particles interact strongly, then the Pauli principle does not apply.

Secondly, the Pauli principle applies to all fermions, including compound fermions, and not just to electrons.

Wolfgang Pauli initially formulated the exclusion principle for electrons (1925), but later generalized it to all fermions (Pauli's theorem, 1940). Therefore, if, under certain conditions, three electrons form a compound fermion, then the Pauli principle will apply specifically to the compound fermion. The proton and neutron are typical examples of compound fermions to which the Pauli exclusion principle applies (composed of three quarks).

Thirdly, the Pauli principle may be violated, for example, during the gravitational collapse of stars.

It is precisely because of the Pauli principle that atoms occupy volume and cannot be strongly compressed, since electrons of the same spin (↑↑) are spatially separated by repulsive exchange interaction. This is the reason why we can safely walk on a solid surface - two solid bodies cannot be in the same place. But, if the compression forces are much greater, for example, during the gravitational collapse of a star, then the exchange repulsion between electrons is overcome.

Thus, if we consider an atom, then indeed, according to the Pauli principle, only two electrons can be in one orbital. Moreover, electrons are weakly interacting particles.

But, if we consider a chemical bond (and, accordingly, a molecular orbital), then electrons can no longer be considered weakly interacting particles, and strictly speaking, the Pauli principle is not applicable in this case.

The fact that the electrons of a chemical bond are strongly interacting particles follows from the very fact of the existence of a chemical bond. Because the presence of exchange energy, which is 80 % of the energy of a chemical bond, means that the bond electrons are delocalized. That is, we can assume that all electrons in a chemical bond are absolutely equivalent. Next, consider a chemical bond that consists of 4 or 6 electrons. Such a bond also contains electrons of the same spin (↑↑), which should be spatially separated due to the repulsive short-range exchange interaction (in addition, there is also long-range Coulomb repulsion between electrons). But, since the electrons of a chemical bond are delocalized, localization and spatial separation of electrons cannot by definition exist. This means that bond electrons are strongly interacting particles and therefore the Pauli principle is not applicable to chemical bonds. This also means that a three-electron bond (for example, in a benzene molecule [2]) will be an ordinary fermion with spin 1/2.

Here is a quote from Louis de Broglie [3]:

“Wave mechanics allows... to understand the nature of homeopolar bonds by introducing the concept of exchange energy... if you carefully study the behavior of a system containing identical particles using wave mechanics, it turns out that in the expression for the energy of the system... terms of a new type appear, associated with the fact that identical particles can change places. These terms describe what we called exchange energy. They correspond to forces of a completely new type... which are enormous in magnitude...

The following remark is very instructive: exchange energy exists only when... two identical particles... are not localized... and only in the case when the probability density distributions for two particles of the same type overlap. This remark sheds light on the relationship between exchange energy and the inability to localize a particle in space...”.

The quote is very eloquent - a chemical bond exists only because the bond electrons are delocalized.

It is also very important that all electrons in a chemical bond are absolutely equivalent.

1. Davydov A. S. Quantum mechanics. Second edition. Publishing house “Science”. Moscow, 1973, p. 334.

2. Bezverkhniy V. D. Structure of the Benzene Molecule on the Basis of the Three-Electron Bond. SSRN Electronic Journal, 31 Dec 2018. https://dx.doi.org/10.2139/ssrn.3065241

3. Louis de Broglie “Revolution in Physics”. P. 125. Atomizdat; Moscow; 1965, 134 pages.