Symmetry properties of the electron density and following from it limits on the DFT applications

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At present the DFT approach elaborated by Kohn with co-authors more than 50 years ago became the most widely used method for study molecules and solids. Using modern computation facilities it can be applied to systems with million atoms [1]. In the atmosphere of such great popularity, it is particularly important to know the limits of the applicability of DFT methods. In this report I will discuss two cases when the conventional DFT approaches, using only electron density ρ and its gradients, cannot be applied (I will not consider the Ψ-versions of DFT). The first case is quite evident. In the degenerated states the electron density may not be defined, since electronic and nuclear motions cannot be separated, the vibronic interaction mixed them.

The second case is related to the spin of the state. As it was rigorously proved by group-theoretical methods at the theorem level [2], the electron density does not depend on the total spin S of the arbitrary N-electron state. It means that the Kohn-Sham equations have the same form for states with different S. From the critical survey [2] of elaborated DFT procedures, taking into account spin, follows that they modified only exchange functionals, the correlation functionals do not correspond to the spin of the state.

The conception of spin cannot be defined in the frame of the electron density formalism, which corresponds to the first-order reduced density matrix. This is the main reason of the problems arising in the study by DFT of magnetic properties of the transition metals [3]; although this reason was not discussed by the authors [3]. The possible way of resolving these problems can be found in the two-electron reduced density matrix formulation of DFT. Many years there were not practical achievements on this way. The recently elaborated by Staroverov with collaborators [4] original approach for finding exchange-correlations functionals using second-order reduced density matrices looks rather promising.

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