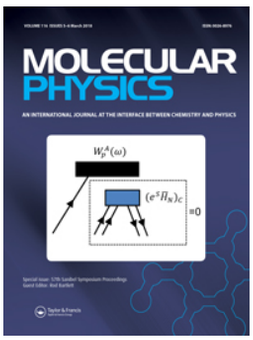

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Symmetry properties of the electron density and following from it limits on the KS-DFT applications

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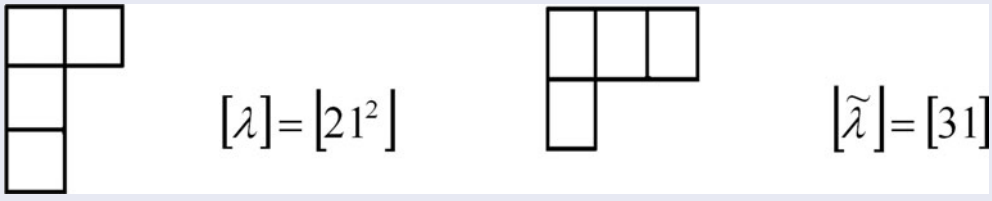
ABSTRACT

At present, the Density Functional Theory (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. 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, 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. The critical survey of elaborated DFT procedures, taking into account spin, shows that they modified only exchange functionals, the correlation functionals do not correspond to the spin of the state. The point is that the conception of spin cannot be defined in the framework of the electron density formalism, which corresponds to the one-particle reduced density matrix. This is the main reason of the problems arising in the study by DFT of magnetic properties of the transition metals. The possible way of resolving these problems can be found in the two-particle reduced density matrix formulation of DFT.



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1. Introduction and motivation

At present, the DFT method developed by Walter Kohn more than 50 years ago in his two historical papers with Hohenberg and Sham [1,2] became the most widely used method for calculations and modelling molecular systems and solids. It is impossible to review even recent achievements publishing in thousand papers and reports. According to Web of Science, see Ref. [3], Kohn's papers [1, 2] were cited 11,000 times in 2010 and 14,000 times in 2012; the number of citations is increasing every year.

In recent Energy Materials Nanotechnology Meeting on Computation and Theory in Las Vegas in October 2016, many reports were connected with the DFT approach. In one of the reports, Miyazaki claimed that using the modern computational facilities they are able to apply the DFT molecular dynamic simulation to systems with million atoms [4]. Certainly, it can be done only if one uses the traditional Kohn-Sham (KS) formalism based only on the electron density $\rho(r)$ and its gradients.

The electron density is the diagonal element of the spinless one-particle reduced density matrix,

$$\rho(\mathrm{r}_1) = N \sum_{\sigma_1,\ldots,\sigma_N} \int |\Psi(\mathrm{r}_1\sigma_1, \ldots \mathrm{r}_N\sigma_N)|^2 dV^{(1)}, \quad (1)$$

where sum is taken over the whole spin space and integration is performed over the configuration space of all electrons except the first. Ψ in Equation (1) is defined in N-particle 4N-dimensional Gilbert space, while $\rho(\boldsymbol{r})$ is defined in one-particle three-dimensional space. It is natural that all calculations, in which only $\rho(\boldsymbol{r})$ is used, must be considerably faster than in Ψ-formalism and can

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be applied to larger systems. Let us discuss what we lose going from Ψ-formalism to the electron density $\rho(\boldsymbol{r})$-formalism.

(1) First consider the transition from the wave function Ψ to its probability density $|\Psi|^2$. It is easy to see that in this transition we lose the phase of wave function, including very important in the case of degenerate states the Berry phase [5, 6]. But due to the insensitivity of the probability density to the symmetry of the state, we lose also the symmetry characteristic of the wave function and cannot determine the Pauli permitted states, on which molecular spectroscopy is based.
(2) The diagonal element of the full and all reduced density matrices, as we show further, does not depend on the symmetry of the state and its dimensionality; it is the same for the space degenerate and non-degenerate states, see Section 4. This does not allow to use the Levy–Lieb constrained search procedure [7, 8] in the case of degenerate states. We must also take into account that in this case the electron and nuclear densities cannot be defined since they are mixed by the vibronic interactions [9]. For these reasons, the DFT methods cannot be applied to study the degenerate states.
(3) It can be expected that after integration we lose some information. Thus, it is evident that the transition to the one-particle density leads to loss of information connected with the two-particle correlations, which are described by the two-particle reduced density matrix.
(4) What is not such evident, we also lose the information connected with the *total spin* S of the system. The point is that spin can be introduced in the reduced density matrix approach, but not in the one-particle approximation. This can be done at the two-particle reduced density matrix level.
(5) It should be noted that even in the framework of the two-particle reduced density matrix formalism one cannot study the non-additive many-body effects, for instance, the three-body dispersion forces, see chapter 4 in Ref. [10]. These well-known Axilrod–Teller–Mutto forces should be taken into account for study the rare-gas clusters. The many-body forces play also a decisive role in the stability of clusters built from close-shell atoms (atoms without valence electrons). A typical example is the alkaline-earth clusters: Be_n, Mg_n, Ca_n and etc., which are stabilised by the three-body forces, while the four-body forces are repulsive [11, 12].

After initial euphoria of successful application of DFT computational methods to large systems, which could not be studied before, it became clear that some results require an improvement or are simply incorrect. First, it was recognised in application of DFT to intermolecular interactions. Many early created functionals did not take into account the dispersion energy; as a result, the DFT potential curves for rare gas dimers were repulsive.

Then it became clear that DFT methods meet serious difficulties in studies of transition metals with *nd* electrons. These problems were analyzed by Cramer and Truhlar [13], although they did not stress that most of described difficulties are connected with spin and in principle cannot be resolved in the framework of $\rho(r)$ formalism; further I will discuss this in detail.

Last year, many comparative studies of the relative precision of exchange-correlation (XC) functionals are published. I will shortly discuss several papers published on this topic in 2016 and in the beginning of 2017 [14–18]. Gillan et al. [14] analyzed different kind of XC functionals for liquid and ice water and water clusters. The conclusion was that many functionals are not satisfactory because do not describe correctly the dispersion. However, as mentioned authors, even after including in XC functionals the non-local dispersion they are still cannot be admitted as completely satisfactory.

Taylor et al. [15] in a comprehensive review comprising 17 (!) authors analyze the precision of the DFT calculations of intermolecular interactions with respect to highly accurate benchmarks for 10 dimers. Among authors are the creators of XC functionals, analyzed in this study, Angyán, Hirao, Scuseria, Truhlar and others.

In the review by Yu et al. [16], the different aspects and perspective of DFT theory are discussed. They also summarised the results of applications of the latest Minnesota functionals. While in the paper by Mardirossian and Head-Gordon [17] the 14 Minnesota functionals benchmarked on a very comprehensive database. They estimated the main strength of analyzed functionals, although came to conclusion that none of them are state-of-the-art for full spectrum of non-covalent interactions and isomerisation energy.

The latest available publication on this topic is published online in January 2017. Medvedev et al. [18] analyzed 128 XC functionals created in period 1974–2015. They compared the DFT calculations of $\rho(r)$ for atoms and its ions with the *ab initio* density distribution calculated at the CCSD level, which was accepted as reference level. They demonstrated that if the average normalised error of $\rho(r)$ is decreasing up to early 2000 then it is increasing due to the modern many parameter semiempirical functionals, see Figure 1. Their general conclusion:

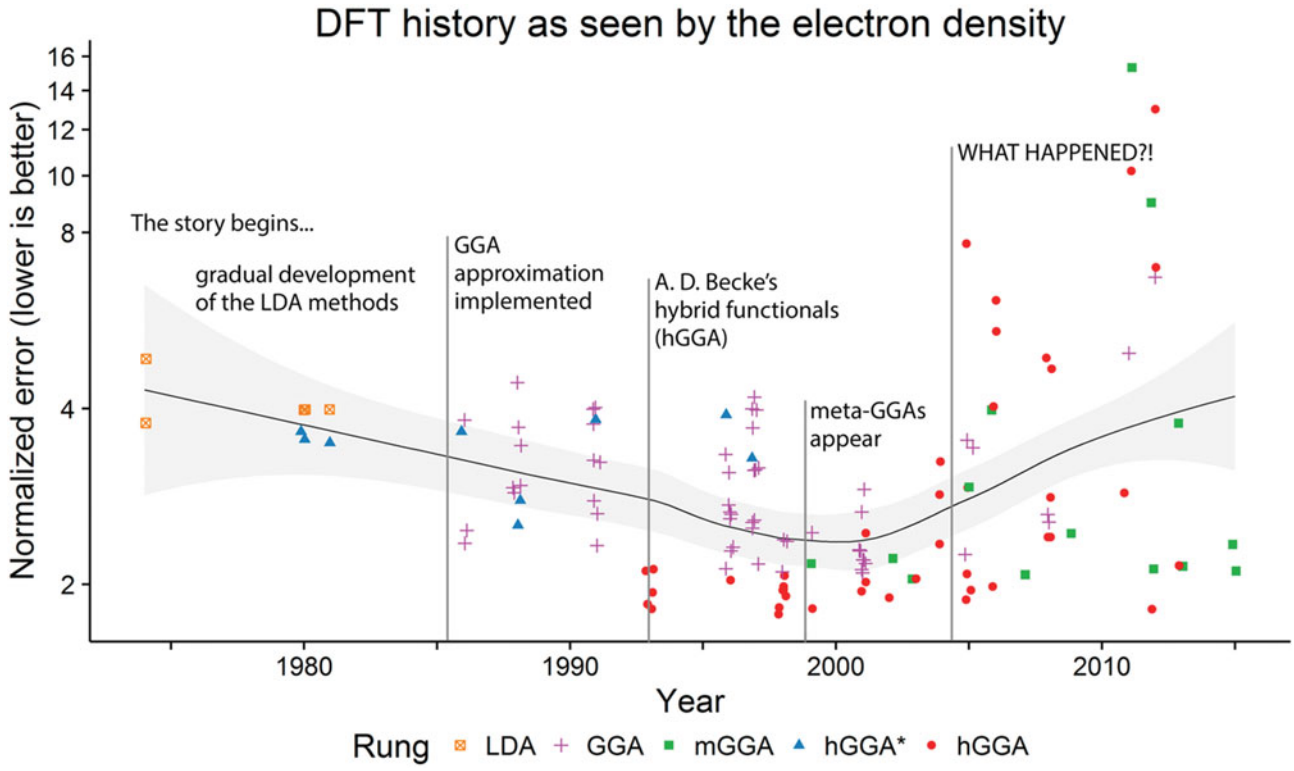


Figure 1. The precision of calculating ρ using diffrent functionals. .

'functionals constructed with little o no empiricism tend to produce more accurate electron densities than highly empirical ones'. However, it is worthwhile to note that this problem beside the electron density aspect can be considered from the energy aspect. Many parameter functionals give quite precise energy characteristics of the studied systems. Thus, all depend upon the problem studied. For some problems to obtain sufficiently exact energy is more important than an exact reproduction of the electronic density.

Thus, at present the DFT community is seriously concerned by the problems arising in the applications of the DFT methods to intermolecular interactions, transition metals and some other systems, even to water. As we noted above, most of discussions are focused on the comparative studies of different kind of XC-functionals. On the other hand, in such tremendous every-year increase of DFT applications, it is important to discuss the general *limits* on the applicability of DFT methods.

In the beginning of my presentation, I discussed evident benefits of using DFT approach and then very shortly enumerated what we lose by limited himself to the probability density description. Furthermore, I will discuss in detail two cases when the conventional DFT approach, based on electron density $\rho(r)$ and its gradients, cannot be applied:

(1) The problem of the total spin S in KS-DFT.
(2) The problem of degenerate states in DFT.

I will not consider Ψ-versions of DFT, which allows solving many of mentioned problems but losing the KS-DFT simplicity. Gőrling, Gross, Savin, Trickey, and other investigators have successfully combined Ψ-formalism with DFT approach. However, as estimated by Martirossyan and Head-Gordon [17], the old BLYP, B3LYP, PBE and PBEO functionals continue to be in use more often than the modern sophisticated functionals. Therefore the limitations, which I will discuss, are still remaining actual.

My discussion below is based on two theorems that I proved in 2007, see Ref. [19]. I will discuss them from the modern viewpoint taking into account last achievements.

2. Electron density ρ and the total spin S

The problems with spin in KS-DFT were recognised long ago. On the example of the two-electron system in the singlet and triplet spin states, McWeeny [20] showed that knowing only the electron density, one cannot identify the spin state (although it should be mentioned that for two electrons this problem was recognised even

earlier). Basing on it, McWeeny formulated the following statement:

electron spin is in a certain sense extraneous to the DFT.

Later Weiner and Trickey [21] in their analysis of the DFT foundations came to conclusion that

…the way that the ρ-based XC potential takes account of spin is very obscure except in the simplest configurations.

This statement is more exact than that by McWeeny, since it stresses ρ-based XC potentials, but not DFT as a whole. However, we should admit that both formulations are very cautious. I would like to stress that the problem with spin in DFT can be formulated more definite:

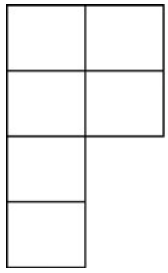
at the level of the first reduced density matrix, the conception of spin cannot be introduced in DFT .

Below I will consider the general case of the N-electron system in a state with an arbitrary total spin S and will present a theorem, which proves that the electron density does not depend upon the total spin of the state. This can be done by applying the permutation group apparatus, see chapter 2 in Ref. [22], while the application of the wave function as a linear combination of determinants corresponding to a given value of the total spin S does not allow to obtain general conclusions. Before the discussion of the group-theoretical proof, it is useful to present some necessary information on the irreducible representations of the permutation group and its connection with spin.

The irreducible representations of the permutation group with N elements are labelled by the Young diagrams $[\lambda]$ with N cells:

$$[\lambda] = [\lambda_1 \lambda_2 \cdots \lambda_k], \quad \lambda_1 \geq \lambda_2 \geq \cdots \geq \lambda_k, \qquad \sum_{i=1}^{k} \lambda_i = N \tag{2}$$

λ_i is represented by a row of λ_i cells. The presence of several rows with equal length λ_i is indicated by a power of λ_i. For example, $[\lambda] = [2^2 1^2]$ is depicted graphically as

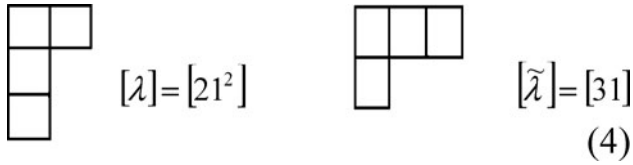


$[\lambda] = [2^2\,1^2]$

Though the concept of spin has enabled to explain the nature of chemical bond, electron spins are not involved directly in the formation of the latter. The interactions responsible for chemical bonding have a purely electrostatic nature. If we do not take into account the spin interactions, the total spin S is a good quantum number, and the wave functions should be eigenfunctions of $\hat{S}^2$. In the central field (atoms), this approximation is known as the Russell–Saunders, or LS-coupling. The spatial coordinates and spin variables in the total electron wave function can be separated, and the latter can be presented as a product of a spatial wave function Φ and a spin wave function Ω. Namely: the wave function anti-symmetric in respect to the electron permutations (obeying the Pauli principle) and describing the state with the total spin S can be constructed as linear combinations of products of spatial and spin wave functions, symmetrised according to the irreducible representations $\Gamma^{[\lambda]}$ of the permutation group [22]

$$\Psi^{[1^N]} = \frac{1}{\sqrt{f_\lambda}} \sum_r \Phi_r^{[\lambda]} \Omega_{\tilde{r}}^{[\tilde{\lambda}]}. \tag{3}$$

In Equation (3), $[\lambda]$ is the Young diagram and $\Gamma^{[\tilde{\lambda}]}$ denotes the representation conjugate to $\Gamma^{[\lambda]}$. Its matrix elements are $\Gamma^{[\tilde{\lambda}]}_{\tilde{r}\tilde{t}}(P) = (-1)^p \Gamma^{[\lambda]}_{rt}(P)$, where p is the parity of permutation P. The spin Young diagram $[\tilde{\lambda}]$ is dual to $[\lambda]$, i.e. it is obtained from the latter by replacing rows by columns. For example,



$[\lambda] = [21^2]$ $\qquad$ $[\tilde{\lambda}] = [31]$ (4)

The sum in Equation (3) is taken over all the basis functions of the representation. The factor $1/\sqrt{f_\lambda}$ provides the normalisation of the total wave function.

Since the electron spin $s = ½$ has only two projections $s_z = \pm ½$, the spin Young diagrams $[\tilde{\lambda}]$ cannot have more than two boxes in a column, i.e. each diagram has no more than two rows. Consequently, the coordinate Young diagrams $[\lambda]$ dual to it cannot have more than two columns. If in one box of a column in a spin Young diagram the electron spin projection is ½, then in the other box of this column the electron spin projection is $-½$, i.e. the spins of these two electrons should be coupled. It is evident that the contribution to the total spin of the system will come only from uncoupled electron spins; their number equals to the difference between the lengths of the rows in the

corresponding Young diagram, $(\tilde{\lambda}^{(1)} - \tilde{\lambda}^{(2)})$, and

$$S = \frac{1}{2}(\tilde{\lambda}^{(1)} - \tilde{\lambda}^{(2)}). \quad (5)$$

Equation (5) enables one to find easily the values of the spin S for each spin Young diagram. For example, for the spin Young diagram in Equation (4), S = 1. Such a one-to-one correspondence between a Young diagram and the total spin exists only for particles with spin ½.

Thus, the spatial Young diagram is uniquely connected with the total spin *S*, its permutation symmetry has a 'memory' of spin; as we already mentioned, the spatial wave function with the permutation symmetry $[\lambda] = [21^2]$ corresponds to S = 1. In the wave function formalism each value of S corresponds to a definite expectation value of energy due to the definite permutation symmetry of the corresponding spatial wave function. The situation is completely changed in the electron density formalism. The following theorem was proved by author in Ref. 19,

Theorem 1 (Kaplan [19]) *The electron density of an arbitrary N-electron system, characterised by the N-electron wave function corresponding to the total spin S and constructed on some orthonormal orbital set, does not depend upon the total spin S and always preserves the same form as it is for a single-determinantal wave function.*

The proof for the single-occupied orbital configuration is given in Ref. [19]. For any symmetry $[\lambda]$ of the spatial wave function, corresponding to a definite value of spin S, the electron density is equal

$$\rho_t^{[\lambda]}(\mathbf{r}) = \sum_{n=1}^{N} |\varphi_n|^2. \quad (6)$$

It is the well-known expression of the electron density for the state described by the one-determinantal function with single-occupied orbitals. It is easy to show that in the case of orbital configuration with arbitrary occupation numbers, the final expression (6) will also correspond to the electron density for the one-determinantal function. Due to the independence of the electron density on the total spin S, the density functionals, and, consequently, the conventional KS equations will be the same for all multi-determinantal wave functions corresponding to different S.

This means that the expression for the electron density is invariant in respect to the permutation symmetry of the wave function. It is also worthwhile to see on this problem from another side. The electron density is a one-electron quantity. As it was precisely established, see chapter 7 in book [22], the diagonal matrix elements of one-particle operators do not depend on the symmetry of the state. The same is correct for the diagonal matrix elements with operators equal to 1, as it is in the expression for the electron density.

Thus, the electron density for all S, describing by different multideterminantal wave functions, has the same form as for a single Slater determinant. This result is rather surprising, although it should be noted that the study of the ambiguity of the electron density description has a long history. I will mention only two publications.

In 1981, Harriman [23] has shown that for any given electron density ρ an arbitrary number of orthonormal orbitals (or built from them Slater's determinants) can be constructed. After 20 years, Cappelle and Vignale [24] have shown that in the standard LSDA approach distinct sets of potentials with the same ground-state density can be constructed.

It should be also noted that recently Jacob and Reiher [25] published rather comprehensive review on the spin problems in open-shell systems, in which they discussed the problems with spin in DFT, including spin-unrestricted and spin-restricted KS-DFT approaches. However, authors [25] did not discuss the limits on the applicability of the KS-DFT approach; the important paper [19], where Theorems 1 and 2 were proved and drawbacks of the spin-restricted KS-DFT procedure were discussed, was not cited.

We demonstrated that the KS equations cannot distinguish the states with different S. Meanwhile different methods allowing taking into account the spin multiplet structure were developed, they discussed in detail in Ref. [19]. In next section, I discuss two of these methods.

3. Methods allowing taking into account the spin multiplet structure within the DFT approach

All these methods are going beyond the KS formalism using the Ψ formalism. I will shortly consider two widely used approaches.

(1) The approach [26–30] starts from the procedure suggested by Ziegler et al. [26] and called in applications, see Refs. [31, 32], as multiplet-sum method (MSM). In MSM, the energies of multiplets are constructed as weighted sums of single-determinantal DFT energies in correspondence (indirect) with the appropriate linear combinations of the Slater determinants corresponding to the definite value of the total spin S. The multiplet splitting is expressed via the linear combinations of the single-determinant exchange energies, E_X. The correlation energy E_C is not touched by the MSM procedure and therefore does not correspond to the spin S.

Hence, the MSM procedure allows calculating approximately the multiplet structure, although it modifies only the exchange energy and does not take into account

the correlations energy. This was quite clear stressed in the modification of the MSM method by Daul [29] and Mineva et al. [30].

(2) The second group of methods [33–37] is designated as restricted open-shell Kohn–Sham (ROKS) method. In the first publication by Russo et al. [33], the ROKS Hamiltonian was constructed similar to the ROHF Hamiltonian [38] with an exception of the exchange part, which was replaced by the exchange-correlation functional. Since the exchange-correlation functional was presented as a sum

$$E_{XC} = E_X + E_C, \tag{7}$$

both functionals in the method [33] were multiplied by the same factor depending on the spin value and found for the exchange energy. Evidently, this procedure leads to errors, since the exchange and correlations functionals should have a different dependence on S.

In Refs. [34–37], the ROKS method, based on the Roothaan approach [38], was combined with the MSM procedure and applied to different classes of molecules. In these computational schemes, the correlation functional was treated inside E_{XC} in the same manner as the exchange one. Hence, in addition to some specific approximations limiting methods [34–37], they contain the same drawback as the initial ROKS method developed by Russo et al. [33]: the correlation functional does not correspond to the correct spin value.

Thus, in both discussed approaches, MSM and ROKS, the correlation functionals do not correspond to the total spin S. It should be mentioned that in spite of an incorrect form of the correlation functionals, in some cases the MSM and ROKS methods can produce quite reasonable multiplet energies due to the error compensation or not essential dependence of calculated multiplet structure on the correlation energy.

Illas et al. [39] analyzing magnetic systems came to conclusion that the DFT calculations exaggerate the ferromagnetic coupling. This conclusion is confirmed by our analysis [40] of the DFT calculations of Mn_2. It revealed that in the most of the DFT calculations, the ferromagnetic ground state with $S = 5$ is predicted, while in the precise MRCI approach [40] the anti-ferromagnetic ground state with $S = 0$ is obtained. Moreira et al. [41] tried to improve their results applying the Filatov–Shaik ROKS method [35 36], but they failed to improve the agreement with experiment. This can be expected, since, as we just discussed, the ROKS procedure uses correlation functionals not corresponding to a proper spin value.

The main problem with the correlation energy is the absence of analytical expression for it in the Ψ quantum mechanics due to its definition [42]:

$$E_{\text{corr}} = E_{\text{exact}} - E_{\text{HF}}. \tag{8}$$

'Exact' energy depends upon the method used for its calculation. Therefore, the correlation energy is method dependent and what is important, it cannot be expressed analytically.

As we noted in Introduction, a way to introduce spin in DFT can be found in the two-particle reduced density matrix formulation of DFT. There are a rather large number of publications on this topic, see, e.g. Refs. [43–53]. Unfortunately, in any of cited papers the possibility of solution of the spin problem has not been discussed, as if for authors this problem did not exist at all.

Nevertheless, irrelevant of the spin problem, the two-electron reduced density matrix formalism allows taking into account the two-electron correlations and finding more exact XC functionals. In this connection, the approaches developed by Staroverov with collaborators [51–53] look rather promising, although in their published studies only states with $S = 0$ were considered.

4. Symmetry properties of the density matrix; degenerate states

In DFT community, it has been accepted that the limitations on the degenerate states, which were introduced by the Hohenberg–Kohn theorem, were removed by the Levy–Lieb constraint search procedure [7,8]. In this procedure, one searches a set of anti-symmetric wave functions, which leads to the same electron density and then construct a linear combination of electron densities that minimises the expectation value of the energy. It is important to mention that in the case of *f-fold* degenerate state, all *f* one-electron densities can be really constructed but, as follows from the presented in this section Theorem 2, proved in Ref. [19], the appropriate linear combination of electron densities does not depend on the symmetry of the state and its degeneracy.

When we discussed the spin problem, we used the permutation group apparatus. The degenerate state problem is related to the spatial wave functions. In this case, we should use the point group apparatus. Let us consider some degenerate quantum state with symmetry of a point group **G**. The basis functions of it, in general case belonging to multidimensional irreducible representations $\Gamma^{(\alpha)}$, can be constructed as [22]

$$\Psi_{ik}^{(\alpha)} = \frac{f_\alpha}{g} \sum_R \Gamma_{ik}^{(\alpha)}(R)^* R\Psi_0, \tag{9}$$

where $\Gamma^{(\alpha)}_{ik}(R)$ are the matrix elements of the representation $\Gamma^{(\alpha)}$, f_α is its dimension, R runs over all g elements of the group **G**, and Ψ_0 is some non-symmetrised product of one-electron orbitals. The set of f_α functions with fixed second index k forms a basis for the representation $\Gamma^{(\alpha)}$, index k enumerates different bases. In a degenerate state, the system can be described with equal probability by any one of the f_α basis functions. As a result, we can no longer select a pure state (the one that is described by a wave function) and should regard the degenerate state as a mixed one, where each of the basis functions belonging to the degenerate state enters in the density with the same probability. Thus, in the case of degenerate state, the diagonal element of the density matrix must be written as

$$D^{(\alpha)}_k = \frac{1}{f_\alpha}\sum_{i=1}^{f_\alpha}\left|\Psi^{(\alpha)}_{ik}\right|^2. \tag{10}$$

For expression (10), the following theorem is valid :

Theorem 2 (Kaplan [19]) *The diagonal element of the full density matrix is invariant respecting all operations of the group symmetry of the state, that is, it is a group invariant.*

As was proved in Ref. [19], for every operation R of group **G** and all its irreducible representations $\Gamma^{(\alpha)}$.

$$RD^{\alpha}_k \equiv D^{\alpha}_k. \tag{11}$$

This means that the diagonal element of the full density matrix (and all reduced density matrices as well) transforms according to the totally symmetric one-dimensional representation A_1 of **G** regardless of the dimension of representation $\Gamma^{(\alpha)}$. In Ref. [19], this was proved for the arbitrary point group, but it is correct for any finite group. For the permutation group, this result was used in Refs. [54,55] in analysis of the foundations of the Pauli exclusion principle. To the best of our knowledge, it was not discussed in literature. Even in the specialised monograph by Davidson [56], the symmetry of the reduced density matrices is discussed only for non-degenerate states, but the latter is evident.

Thus, the symmetry properties of the diagonal element of the full and all reduced density matrices in the degenerate states are the same as in the non-degenerate states. From the possibility of construction by the Levy–Lieb constrained search procedure, linear combinations of electron densities does not follow that DFT can be applied to degenerate states.

On the other hand, the non-applicability of the DFT approach to the degenerate states can be based by very simple arguments. As is well known in quantum mechanics, in the case of degenerate states the Born–Oppenheimer approximation fails and the electronic and nuclear motions cannot be separated, they are mixed by the so-called vibronic interactions. As a result, the total wave function cannot be represented as a simple product of the electron and nuclear wave functions and appropriate densities cannot be constructed.

The applicability of the DFT approaches to degenerate states was analyzed in detail by Bersuker [57] who showed on the example of the widely-studied Jahn–Teller e-E problem that the DFT methods cannot, in principle, describe degenerate and pseudodegenerate states. On one hand, because of the already mentioned non-separability of electronic and nuclear functions; on the other hand, the Berry phase, from which the energy spectrum and wave functions of degenerate state are depend, cannot in principle be introduced in the pure density formulation of DFT.

There are publications in which the authors claimed that they developed the non-Born–Oppenheimer DFT in the frame of the electron density DFT. A simple analysis shows that their formalisms must be attributed to the Born–Oppenheimer approximation. Let us consider two examples.

(1) In the non-Born–Oppenheimer DFT approach developed by Capitani et al. [58], the authors used the Levy constraint search procedure and then constructed the total wave functions as a product of electronic and nuclear wave functions:

$$\Psi_{m\upsilon}(r,R) = \Psi_m(r,R_0)\Phi_{m\upsilon}(R), \tag{12}$$

where R_0 is the equilibrium distance (parameter), so the electronic wave function does not depend on the nuclear coordinates. However, the expression (12) is the definition of the Born–Oppenheimer approximation in its crude form (the so-called Condon adiabatic approximation).

(2) In the approach by Kryachko et al. [59], the electronic density contains the nuclear coordinates, nevertheless it also corresponds to the Born–Oppenheimer approximation, since the authors used the multiplicative form of electronic and nuclear wave functions,

$$\Psi_{m\upsilon}(r,R) = \Psi_m(r,R)\Phi_{m\upsilon}(R). \tag{13}$$

This presentation corresponds to the *full* or the Born adiabatic approximation, certainly, it is not valid for the degenerate states, see section A3.1 in Ref. [10].

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Disclosure statement

No potential conflict of interest was reported by the author.

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